

École polytechnique de Louvain

Integrated CO₂ capture and methanation

Author: **Charles BAIJOT**

Supervisor: **Juray DE WILDE**

Readers: **Patricia LUIS ALCONERO, Reza MONJEZI**

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Abstract

This thesis investigates integrated CO₂ capture and methanation (ICCM), a process concept in which CO₂ adsorption and catalytic hydrogenation are carried out sequentially on the same dual-function material (DFM), eliminating the intermediate steps that burden conventional Power-to-Methane chains. Both constituent functions are characterised independently on a Ni/Al₂O₃–MgO DFM before drawing the implications for the integrated process.

The methanation kinetics are studied in a micro-fixed bed reactor under steady-state conditions. Four Langmuir–Hinshelwood–Hougen–Watson mechanisms are derived and discriminated against the experimental dataset. A hybrid associative–dissociative route, in which CO₂ undergoes molecular pre-adsorption on basic surface sites followed by hydrogen-assisted C–O bond cleavage at the Ni surface, is selected as the reference kinetic model. The estimated parameters are consistent with the surface chemistry expected from the MgO-rich support and provide a quantitative rationalisation of the strong temperature dependence of CH₄/CO selectivity.

The CO₂ adsorption behaviour of the same material is characterised by pulse injection experiments. The measured capacity decreases monotonically with temperature, consistent with the exothermic character of CO₂ chemisorption on MgO basic sites. A one-dimensional transient fixed-bed model reproduces the outlet pulse sequences and reveals that the catalyst bed remains only partially saturated under the experimental conditions, a result of direct relevance for the sizing of the adsorption step in an ICCM cycle.

Both campaigns reveal a fundamental thermal mismatch between the adsorption and catalytic functions of the material: significant CO₂ uptake is confined to temperatures well below the range required for catalytic activity, confirming that capture and conversion must operate in distinct, sequential half-cycles. This constraint constitutes the primary design variable for ICCM systems based on this class of DFM, and the kinetic descriptions developed in this work provide the quantitative foundation needed to inform the rational design of such cycles.

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Chapter 1

Introduction

The global energy system is at a crossroads. Two centuries of fossil fuel combustion have driven extraordinary economic growth, but they have also released vast quantities of carbon dioxide into the atmosphere. CO₂ concentrations have now passed 420 ppm (a level not seen on Earth for at least three million years) and the consequences are increasingly difficult to ignore. Temperatures are rising, extreme weather events are becoming more frequent, and sea levels keep climbing [23]. Limiting global warming to 1.5 °C above pre-industrial levels, as called for by the Paris Agreement, demands nothing short of a structural transformation of the way the world produces and consumes energy.

Decarbonising that system is, however, far from straightforward. Renewable electricity from wind and solar has expanded rapidly and now competes on cost with fossil fuels in many markets, yet a significant share of global CO₂ emissions still comes from sectors where electrification alone is not enough. Cement kilns, steel furnaces, chemical plants and gas-fired power stations all produce concentrated CO₂ streams that cannot be eliminated simply by switching to a cleaner electricity source [22]. For these hard-to-abate sectors, carbon capture, utilisation and storage (CCUS) has emerged as one of the few credible pathways to deep decarbonisation, and international energy roadmaps increasingly treat it not as an option but as a necessity.

Capturing CO₂ is, of course, only half of the problem. Once captured, the gas must go somewhere. Permanent underground storage is technically feasible, but it raises questions of long-term safety, public acceptance and geographic availability. An alternative, and arguably more elegant approach is to use the captured CO₂ as a feedstock: rather than burying it, one can convert it into something useful. Among the available conversion routes, the catalytic hydrogenation of CO₂ to methane (known as the Sabatier reaction) occupies a special place, because the product is synthetic natural gas (SNG), a fuel that is already fully compatible with existing pipelines, storage facilities and end-use technologies [40, 38]. The overall reaction is deceptively simple:



A suitable catalyst is required. Nickel-based formulations are by far the most widely studied and industrially deployed, because they offer a good balance between activity, selectivity and cost [7, 29]. Operating temperatures typically lie between 200 and 400 °C, a window in which the reaction is kinetically accessible while remaining thermodynamically favourable. Its strongly exothermic character is both an asset and a challenge: the heat released can be recovered, but it must also be carefully managed to avoid catalyst overheating and sintering [14].

Industrially, methanation has so far been deployed almost exclusively in a very different context from CO₂ valorisation. Its main commercial use is the selective hydrogenation of residual carbon oxides in syngas clean-up units upstream of ammonia synthesis, where CO and CO₂ are present only as trace contaminants and the reaction operates far from any equilibrium constraint [40]. The hydrogenation of concentrated CO₂ streams to synthetic natural gas is another story. It remains at the pilot and demonstration stage, with landmark facilities such as the 6 MW Audi e-gas plant in Werlte or the Jupiter 1000 demonstrator showing that the chemistry can be operated reliably at the multi-megawatt scale [15]. Even so, a fully mature, large-scale deployment of Sabatier-based CO₂ valorisation is still ahead rather than behind us, which is why understanding and improving this chemistry retains both scientific and industrial relevance.

This chemistry is, in turn, the cornerstone of a broader concept: Power-to-Gas (PtG), and more specifically Power-to-Methane (PtM). The aim is to operate methane as a renewable energy carrier within a closed cycle, and the logic of that cycle is best understood by following the molecule through two alternating operating modes. When renewable electricity generation falls short of demand, methane is burned in a conventional gas-fired power plant to deliver dispatchable electricity; rather than venting the resulting CO₂ to the atmosphere, it is captured on site and stored on a suitable sorbent. When renewable generation subsequently exceeds demand, the situation reverses: the surplus electricity is sent to a water electrolyser to produce green hydrogen, which is then fed to the sorbent to trigger CO₂ desorption and its immediate catalytic hydrogenation back to methane through the Sabatier reaction. The synthetic natural gas thus produced can be injected into the existing gas grid, stored over long durations at low marginal cost, and burned again when needed, closing the loop. PtM therefore addresses two of the most pressing challenges of a high-renewables energy system in a single scheme: it valorises a greenhouse gas as a storable fuel, and it provides a large-scale, long-duration buffer for intermittent electricity generation [15, 38]. As renewable penetration increases and periods of excess generation become more frequent, the economic and strategic case for this approach

continues to grow.

Compelling as the underlying idea may be, conventional implementations of the cycle remain costly and energy-intensive. The reason is structural. In current designs, CO₂ capture and catalytic methanation are treated as entirely separate operations, linked by a chain of intermediate steps: sorbent regeneration, CO₂ desorption, compression, purification and transport. Each of these steps consumes energy and adds capital cost [30, 43]. The overall efficiency of the chain is then governed less by the performance of each unit in isolation than by the cumulative penalties incurred at their interfaces, and in particular by the heat that is repeatedly supplied to regenerate sorbents only to be rejected when the CO₂ is then cooled and compressed.

This is the motivation behind integrated CO₂ capture and methanation (ICCM). Rather than keeping capture and conversion in separate units, ICCM merges both functions within a single cyclic process, carried out on a so-called dual-function material (DFM). A DFM combines basic adsorption sites and metallic catalytic sites within one and the same particle. During the first half-cycle, a CO₂-containing gas stream (for instance a diluted flue gas) contacts the DFM, and CO₂ is adsorbed as surface carbonates or bicarbonates on its basic sites. The feed is then switched to hydrogen: this initiates the endothermic desorption of the stored CO₂ species, which are immediately hydrogenated over the neighbouring metallic sites through the exothermic Sabatier reaction, producing methane and regenerating the sorbent in a single step [17, 20, 36].

The arrangement does more than spare the CO₂ compression and transport stages. Because desorption and methanation take place on the same particle and within the same temperature window, the heat released by the exothermic methanation can be transferred directly through the solid to sustain the endothermic CO₂ desorption occurring alongside it, rather than being dissipated to the surroundings through external heat exchangers. In practice, a modest supply of external heat is required to initiate the first desorption; once methanation is underway, it provides the thermal driving force for further CO₂ release, and the process becomes, in principle, largely thermally self-sustaining. Taken together, these features give ICCM the potential to substantially reduce both the energy consumption and the capital footprint of PtM systems relative to conventional two-unit designs.

The scientific challenge, however, is considerable. A DFM must perform two demanding tasks within the same temperature window, and these requirements pull in opposite directions. Low temperatures favour CO₂ adsorption but slow down catalytic hydrogenation, while high temperatures accelerate the reaction but reduce uptake capacity and shift the methanation equilibrium away from methane. The thermal constraint is not the only one: the spatial proximity between adsorption and catalytic sites, the transport of reactive intermediates between them, and the inhibiting effect of the water produced during

methanation all shape the outcome of each cycle in ways that remain incompletely understood [9, 30]. Recent work on Ru/CeO₂–MgO dual-function materials has shown that morphology and metal–support interactions are decisive factors for methane yield and cycle stability [37], but a general design framework for ICCM systems is still lacking.

This thesis is a step in that direction. Integrated CO₂ capture and methanation cannot be understood without a solid grasp of its constituent sub-systems, so the work begins by characterising each function independently before bringing them together. The methanation kinetics of CO₂ are studied experimentally on a Ni/Al₂O₃–MgO catalyst through fixed-bed measurements, while CO₂ adsorption is characterised on the same dual-function material using pulse-response experiments. The insights drawn from both sub-systems are then used to identify the key constraints and design levers that govern ICCM performance, with the broader aim of informing the development of more efficient and integrated carbon capture and utilisation technologies.

Chapter 2

CO₂ Methanation

2.1 Introduction and Research Objectives

2.1.1 Context: Power-to-Methane and CO₂ Valorisation

CO₂ methanation, also called the Sabatier reaction, is a key reaction in Power-to-Gas (PtG) and more specifically Power-to-Methane (PtM) schemes. In such processes, renewable electricity is first converted into hydrogen by water electrolysis; the produced H₂ is then reacted with CO₂ to form synthetic methane (SNG), which can be injected into the natural gas grid. This approach simultaneously enables large-scale chemical energy storage and the valorisation of CO₂ from biogenic or industrial sources, contributing to a circular, low-carbon energy system [32, 31].

2.1.2 Global Reaction and Thermodynamic Features

The overall stoichiometry of the Sabatier reaction is



with a standard reaction enthalpy at 298 K of approximately

$$\Delta H_{298\text{K}}^0 \approx -165 \text{ kJ mol}^{-1}.$$

Reaction (2.1) is highly exothermic and equilibrium-limited. Low temperatures and high total pressures thermodynamically favor CH₄ formation, but the high kinetic stability of the CO₂ molecule requires the presence of an active catalyst to obtain appreciable conversion rates. In practice, operating temperatures typically lie between 200 and 400 °C, with pressures ranging from a few bar up to a few dozen bars depending on the targeted

application and reactor configuration [14].

Table 2.1 reports the equilibrium CO_2 conversion for the Sabatier reaction at 2 bar and a H_2/CO_2 feed ratio of 4, computed from the thermodynamic equilibrium constant correlation reported by Aparicio [2]. These values confirm that the reaction is strongly thermodynamically limited above 300 °C, and that the operating window 250–325 °C investigated experimentally in Chapter 2 corresponds to a regime where equilibrium conversion is high but kinetic activation remains the primary challenge.

Table 2.1: Equilibrium CO_2 conversion X_{eq} for the Sabatier reaction at 2 bar and $\text{H}_2/\text{CO}_2 = 4$, computed from the correlation of Aparicio [2].

Temperature (°C)	X_{eq} (%)
250	>99
275	>99
300	95
325	80
350	58

Note that at $\text{H}_2/\text{CO}_2 = 8$, a ratio commonly used in experimental studies to maximise CH_4 selectivity, the equilibrium conversion exceeds the values reported here at all temperatures below 325 °C, indicating that operation in this window remains kinetically controlled.

It is also worth pointing out that the equilibrium constraint shown in Table 2.1 is, to a non-negligible extent, an artefact of the modest operating pressure of 3 bar chosen for the experimental campaign of Chapter 2. The Sabatier reaction converts five moles of reactants into three moles of products, so raising the total pressure shifts the equilibrium toward CH_4 (Le Chatelier). This is precisely the rationale behind the pressures of 5–10 bar used in the Audi e-gas plant in Werlte [15] and, more generally, in industrial PtM demonstrators. Higher operating pressures nevertheless come at a cost: additional compression work upstream of the reactor, more demanding mechanical design and sealing, and a smaller margin against the onset of carbon deposition at the inlet. The 2 bar window adopted here therefore represents a deliberate trade-off between thermodynamic favourability and experimental simplicity, with the explicit consequence that the equilibrium ceiling becomes restrictive above 300 °C, which is exactly the regime where the LHHW analysis of Chapter 2 needs to incorporate the driving-force term explicitly to remain accurate.

2.1.3 Reaction Network: CO₂ Methanation, RWGS and CO Methanation

The overall conversion of CO₂ to CH₄ does not occur as a single elementary step. Instead, it is embedded in a network of elementary and pseudo-global reactions. A convenient decomposition is



CO can thus appear as an intermediate through the RWGS reaction (2.3), or be present in the feed gas, and, in turn, be consumed via CO methanation (2.4). Modern kinetic models therefore often describe separately the rates of reactions (2.2)–(2.4), or at least acknowledge that CO-containing species play an important role in the overall mechanism [14, 32].

The H₂/CO₂ feed ratio has a strong influence on both conversion and selectivity: suprastoechiometric ratios (above 4) thermodynamically favour CH₄ formation and kinetically accelerate the hydrogenation of surface intermediates, including the removal of inhibiting OH* and H₂O species from active Ni sites [35]. This effect is well documented in the literature: ratios of H₂/CO₂ = 8 are commonly employed in experimental studies to ensure near-complete CH₄ selectivity over the 250–350 °C range [35].

2.1.4 Ni-Based Catalysts: Support Effects and Reference Systems

A wide range of metals (Ni, Co, Ru, Rh, Pt, Pd) supported on oxides such as Al₂O₃, CeO₂, SiO₂, ZrO₂ or TiO₂ has been investigated. Nickel-based catalysts are by far the most studied and are already implemented at industrial scale due to their good compromise between activity, selectivity and cost [14].

The choice of support plays a critical role in determining the dispersion of Ni particles, the strength of metal–support interactions, and the mechanism of CO₂ activation. Supports with basic character (MgO, CeO₂) favour the adsorption of CO₂ as carbonate and bicarbonate species and enhance oxygen mobility, leading to higher activity and improved resistance to coking compared with neutral supports such as SiO₂ [29, 7]. Among these, MgO is of particular interest as both a support and a promoter: when incorporated into Ni/Al₂O₃ formulations, MgO increases the surface basicity, stabilises Ni particles against sintering through strong Ni–MgO interactions, and provides additional CO₂ adsorption

sites that can serve as a local CO₂ reservoir during reaction [29]. This dual role (catalytic support and CO₂ sorbent) is precisely what makes Ni/Al₂O₃–MgO materials relevant for integrated CO₂ capture and methanation, as discussed in Section 3.3.5.

Ni/Al₂O₃ is a representative commercial formulation. Quindimil et al. studied a low-loaded Ni/Al₂O₃ catalyst (9.5 wt. % Ni) and proposed a mechanism in which an H-assisted CO formation step from surface formate is rate determining [32]. Conversely, Ni/CeO₂ catalysts are known for their high activity, attributed to the ability of CeO₂ to provide oxygen vacancies and to develop strong metal–support interactions. Onrubia-Calvo et al. demonstrated that CO₂ methanation on an 8.5 wt. % Ni/CeO₂ catalyst is best described by an associative formate pathway involving two types of active sites (Ni⁰ and CeO₂ vacancies) [31].

2.2 Experimental Set-up

2.2.1 Steady state experiments with a micro-fixed bed reactor set-up

An overview of the micro-fixed bed reactor setup is shown in Fig. 2.1. The unit combines a fixed-bed reactor inside a tubular furnace, a gas feed panel with mass flow controllers, and an online mass spectrometer for effluent analysis. A complete piping and instrumentation diagram (P&ID) of the micro-fixed bed reactor setup, showing all gas lines, pressure regulators, mass flow controllers, the reactor, the condenser and the mass spectrometer, is provided in Appendix D.

reactor

The first part of experiments were carried out in a fixed-bed reactor made of stainless steel, consisting of two main components. The outer part is a straight tube, 30 cm in length, with an inlet diameter of 9.91 mm and an outlet diameter of 11.95 mm, sealed at each end using a bolt fastening system. Running through the center of this tube is a cylindrical rod, 35.5 cm long and 5.97 mm in diameter, designed to house the furnace thermocouple, which monitors the temperature within the bed and regulates the furnace accordingly. As a result of this concentric arrangement, the reactor’s cross-section takes on an annular shape. We can see the reactor dimension in Figure : 2.2

Gases feed

Five gas cylinders, each with a 50 L capacity and loaded at 200 bar, supply the experimental setup. Argon is by far the most consumed gas in this work, which is why two cylinders are connected in parallel and a simple manual valve is all it takes to switch



Figure 2.1: Picture view of the micro-fixed bed reactor set-up used to study the methanation of CO_2 .

from one to the other once the first runs out. The other gases include CO_2 , H_2 , and a calibration mixture of 0.5% CO , 1% CO_2 , 2% CH_4 , 15% H_2 and 81.5% Ar . Since 200 bar is far too high to feed directly into the mass flow controllers, a pressure regulator is placed right after each cylinder to bring the pressure down to a more manageable 50 bar, from where each gas line can be accurately and independently controlled throughout the experiments.

Mass flow controllers

To precisely control the gas flow, three mass flow controllers are used, one for each gas H_2 , Ar , CO_2 . The inlet pressure is 10 barg for all of them. However, before the feed enters the reactor, a pressure regulator allows the inlet pressure to be precisely adjusted. For the vast majority of experiments, this pressure is 3 barg. The gas mass flow controllers (MFCs)

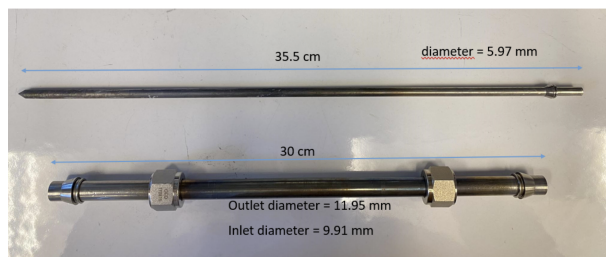


Figure 2.2: Dimensions of the reactor

were supplied by *Brooks Instrument*. Each MFC was calibrated in situ against a bubble flowmeter before the experimental campaign; the calibration data, the corresponding linear regressions and the resulting correction factors are reported in Appendix C.

Furnace

Since the methanation reaction requires relatively high operating temperatures, a furnace is used to bring the catalyst bed to the desired setpoint. A thermocouple is inserted directly into the reactor, with its tip positioned at the center of the bed, giving a representative measurement of the actual bed temperature. This reading is then used to fine-tune the temperature through the control interface. To minimize heat losses at the point where the thermocouple enters the reactor, insulation material has been added around the entry point.

Mass Spectrometer

To analyze the exhaust gases, a mass spectrometer from *Hidden* is used, specifically the *Hidden HPR-20 OEMS*. It is a gas analysis system designed for the continuous, real-time analysis of gases and vapours evolved during electrochemical processes. This MS is equipped with a quartz-lined ultra-low-flow sampling inlet operating at temperatures up to 200°C, providing response times of less than 3 s for most common gases and vapours. During the tests, the MS transmitted data every 5 seconds.

2.2.2 Catalyst Used

The dual-function material (DFM) studied in this work was provided as a scaled-up batch (internal reference: CO2MBS063) from the project consortium. It consists of a nickel-based mixed oxide dispersed within a magnesium–aluminium matrix, characterised by a nominal Mg:Al molar ratio of 5:1 and a nickel content of 20 mol% relative to the total metal loading. On the basis of these proportions, the overall composition can be approximated by the empirical formula $\text{Mg}_4\text{NiAlO}_x$, where x accounts for the oxygen stoichiometry required to satisfy charge neutrality, and is expected to vary with the oxidation state of each metal centre as well as the thermal history of the sample.



Figure 2.3: Gas cylinders feeding the micro-fixed bed reactor set-up.

The synthesis route was not disclosed as part of this study. No information was therefore available regarding the choice of precursors, precipitation conditions, ageing time, or calcination temperature. As a result, no assumption is made here about the phase composition, degree of crystallinity, or surface termination of the as-received powder. It is nonetheless worth noting that materials sharing this general Ni/Mg/Al stoichiometry are frequently synthesised via co-precipitation of hydrotalcite-like precursors [17, 3], a route known to yield well-dispersed nickel sites and a basic MgO-rich surface well-suited to CO₂ adsorption. Whether or not the present material follows the same preparation strategy, its composition is consistent with this broader family of DFMs reported in the literature.

It should be emphasised that Mg₄NiAlO_x is a nominal stoichiometric formula derived from the declared elemental composition of the batch, and should not be interpreted as a well-defined crystallographic phase. In practice, the material likely consists of a mixture of oxide phases (including periclase-type MgO, spinel-type MgAl₂O₄, and dispersed NiO) whose relative proportions and structural arrangement depend on conditions that remain unknown in this study.



Figure 2.4: Mass flow controllers (Brooks Instrument) of the micro-fixed bed reactor set-up.

2.2.3 micro-fixed bed reactor Loading

Prior to any experimental campaign, the micro-fixed bed reactor is packed in a specific sequence to ensure reproducible hydrodynamic conditions and to protect the active bed from thermal and mechanical stress. The packing is carried out from the bottom upwards, with each layer consolidated before the next is introduced.

The loading begins with a 2 cm layer of inert material (*alpha-alumina*, particle size $> 1180\text{ }\mu\text{m}$) at the bottom of the reactor tube. This coarse layer acts as a support and pre-distributes the gas flow before it reaches the active zone. A 0.5 cm layer of quartz wool is then placed on top, acting as a mechanical separator between the coarse inert material and the catalyst zone while keeping the bed permeable to gas.

The catalyst bed is loaded directly above this separator. It consists of a binary mixture of $\text{Ni}/\text{Al}_2\text{O}_3\text{--MgO}$ catalyst and an inert diluent (particle size $150\text{--}450\text{ }\mu\text{m}$), both sieved in the same range to ensure uniform packing density and avoid segregation. Using a finer inert in this zone improves thermal homogeneity and limits hot-spot formation under reaction conditions. The total catalyst mass and the dilution ratio are specified in the protocol of each individual run. A second 0.5 cm layer of quartz wool is then placed on



Figure 2.5: Early temperature controller used to regulate the micro-fixed bed reactor set-up furnace.



Figure 2.6: Hidden HPR-20 OEMS mass spectrometer used for online analysis of the micro-fixed bed reactor set-up effluent.

top of the bed.

Above this upper separator, a 2 cm layer of the same coarse inert material as at the bottom is added, mirroring the lower support and helping to retain the catalyst bed. Finally, quartz wool is packed at the very top to fill the remaining void space and to secure the bed against axial movement when the reactor is closed.

After each layer, the bed surface is checked visually for planarity and the reactor body is gently tapped to allow natural settling. Poor levelling can generate channelling and non-uniform radial flow, which would compromise the reliability of the conversion data.

Table 2.2: Nominal composition of the dual-function material used in this study.

Parameter	Value
Batch reference	CO2MBS063
Batch type	Upscaled production batch
Active metal	Nickel (Ni)
Support matrix	MgO–Al ₂ O ₃
Mg:Al molar ratio	5:1
Ni loading	20 mol% (of total metal content)
Nominal bulk formula	Mg ₄ NiAlO _x
Synthesis route	Not disclosed

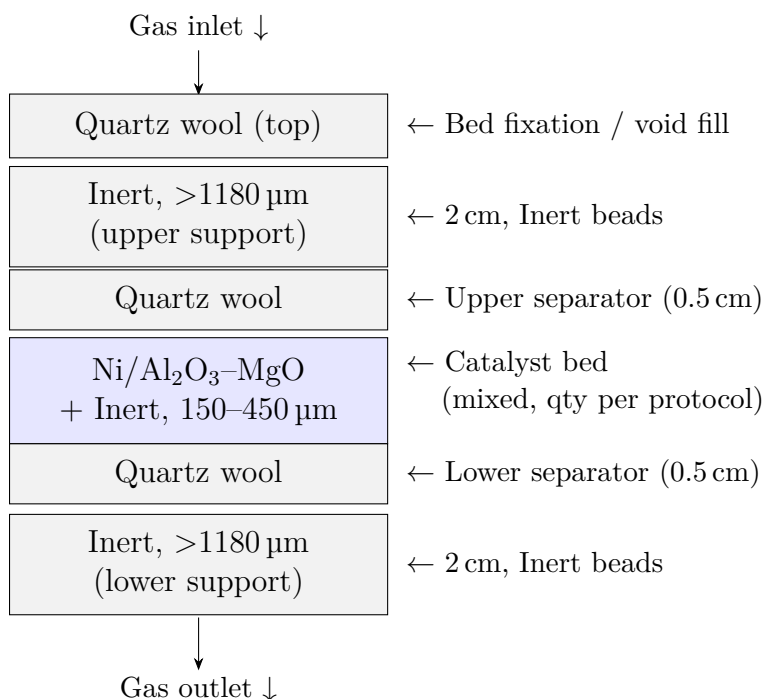


Figure 2.7: Diluted catalyst bed configuration.

2.2.4 Gas flow circuit and PID overview

The lab’s P&ID diagram can be found in Appendix A. As shown there, all gas streams are mixed, brought to the same pressure, and then fed into the reactor inlet. Inside the reactor, the gases are heated and the reaction takes place. The exhaust gases first pass through a condenser cooled by a *VWR RC 10* digital chiller, which removes water vapour before analysis. Part of the dried stream is then directed to the mass spectrometer, while the rest is vented to the hood. A bypass line allows the feed to skip the reactor entirely, which is used to calibrate the mass spectrometer without any reaction occurring.



Figure 2.8: VWR RC-10 digital chiller used to condense water vapour at the micro-fixed bed reactor outlet.

2.2.5 Mass spectrometer calibration and reference test

Calibration of micro-fixed bed reactor's mass spectrometer

To calibrate the mass spectrometer at the micro-fixed bed reactor outlet, the calibration mixture (0.5% CO, 1% CO₂, 2% CH₄, 15% H₂, balance Ar) is sent through the bypass at room temperature, so that no reaction takes place. The recorded signal is then compared to the known cylinder composition, and the response factors of the mass spectrometer are adjusted if necessary.

Reference Test

Every day, after calibrating the mass spectrometer, a test is performed using the same parameters (temperature, flow rate, pressure) as the last test. This test does not go through the bypass but rather through the reactor. If the results are similar, this indicates that the catalyst has not changed during the testing hiatus.

Tests

Tests were carried out at different temperatures and total flow rates to probe the reaction kinetics and the behaviour of the catalyst. The inlet composition is known from the MFC set-points, while the mass spectrometer provides the outlet mole fractions of H₂, CO₂, CH₄, CO and H₂O. From these quantities, the CO₂ conversion and the CH₄ yield are

computed for each operating point.

2.3 Kinetic Modelling Methodology

2.3.1 Reaction Mechanisms of CO₂ Methanation

General Picture and Surface Intermediates

Mechanistic studies on Ni-based catalysts typically combine kinetic modelling with in situ and operando spectroscopic techniques (DRIFTS, FTIR) to identify surface intermediates. On Ni/Al₂O₃ and Ni/CeO₂, one commonly observes surface carbonates and bicarbonates, formate species, formyl species, carbonyls chemisorbed on Ni, hydroxyls and adsorbed water. For the 9.5 wt. % Ni/Al₂O₃ catalyst, bicarbonates and carbonates dominate at low temperature and progressively evolve into formate species as temperature increases; carbonyl bands are weak but kinetically relevant. On Ni/CeO₂, bicarbonate and formate bands are strong, while carbonyl signatures are essentially absent, which strongly supports an associative formate mechanism [32, 31].

Based on this evidence, five main mechanistic families are generally distinguished: (i) a dissociative carbon route in which CO₂ is reduced to C; (ii) an associative formate route on a single site in which molecularly adsorbed CO₂ is stepwise hydrogenated; (iii) an associative formate route on two active site types in which molecularly adsorbed CO₂ is stepwise hydrogenated ; (iv) an H-assisted CO formation route where formate decomposes to CO and OH ; and (v) a hybrid route combining direct CO₂ dissociation to CO with a subsequent H-assisted C–O bond cleavage through oxygenated intermediates such as COH or COH₂ [32, 31, 21]. For Ni/CeO₂, the associative formate mechanism is further refined into a two-site mechanism, reflecting the specific roles of Ni and CeO₂, whereas on Ni/Al₂O₃ hybrid pathways have also been proposed to reconcile direct CO₂ dissociation with hydrogen-assisted surface transformations [21].

This mechanistic diversity is further supported by DFT calculations on Ni surfaces, which indicate that the relative energy barriers for dissociative and associative pathways depend sensitively on surface coverage, temperature and the specific facet exposed, with no single route being universally dominant; a comprehensive overview integrating experimental and computational evidence is provided by Vogt et al. [40].

In the following, the elementary steps of the most relevant mechanisms are presented in a compact tabular form similar to the format used in [31, 32, 21].

Dissociative Carbon Route

In the dissociative carbon route, CO_2 undergoes dissociative chemisorption on metallic Ni sites, yielding adsorbed CO^* and adsorbed atomic oxygen O^* . The carbonyl species CO^* can then undergo a second C–O bond scission to form adsorbed carbon C^* and a further O^* . Methane is produced through the stepwise hydrogenation of C^* into CH^* , CH_2^* and CH_3^* , before CH_4 desorbs into the gas phase. Throughout this section, asterisks denote species chemisorbed on active Ni sites, while the corresponding gas-phase species are written without an asterisk (for instance $\text{CO}(\text{g})$ and $\text{O}_2(\text{g})$). The elementary steps of this mechanism are listed in Table 2.3.

Table 2.3: Representative elementary steps for a dissociative carbon route on Ni-based catalysts (single-site description).

Step	Reaction
1	$\text{H}_2 + 2* \rightleftharpoons 2\text{H}^*$ (quasi-equilibrium)
2	$\text{CO}_2 + 2* \rightleftharpoons \text{CO}^* + \text{O}^*$ (quasi-equilibrium)
3	$\text{CO}^* \rightleftharpoons \text{CO}(\text{g}) + *$
4	$\text{CO}^* \rightleftharpoons \text{C}^* + \text{O}^*$ (RDS in some models)
5	$\text{C}^* + \text{H}^* \rightleftharpoons \text{CH}^* + *$
6	$\text{CH}^* + \text{H}^* \rightleftharpoons \text{CH}_2^* + *$
7	$\text{CH}_2^* + \text{H}^* \rightleftharpoons \text{CH}_3^* + *$
8	$\text{CH}_3^* + \text{H}^* \rightleftharpoons \text{CH}_4^* + *$
9	$\text{CH}_4^* \rightleftharpoons \text{CH}_4(\text{g}) + *$
10	$\text{O}^* + \text{H}^* \rightleftharpoons \text{OH}^* + *$
11	$\text{OH}^* + \text{H}^* \rightleftharpoons \text{H}_2\text{O}^* + *$
12	$\text{H}_2\text{O}^* \rightleftharpoons \text{H}_2\text{O}(\text{g}) + *$

From Table 2.3, a Langmuir–Hinshelwood–Hougen–Watson (LHHW) rate expression can be derived by assuming that step 4 is rate determining and that all other steps are either at quasi-equilibrium or fast. The derived rate typically presents positive reaction orders in H_2 and CO_2 , together with strong inhibition by adsorbed water and, when present, adsorbed CO. Nevertheless, for low-loaded Ni/ Al_2O_3 the carbon route poorly reproduces the experimental kinetics, which suggests that deep CO dissociation to C is not dominant [32].

Assuming that step 4 in Table 2.3



is rate determining, its elementary rate can be written in terms of surface coverages as

$$r_4 = k_4 \theta_{\text{CO}} \theta_* - k_{-4} \theta_{\text{C}} \theta_{\text{O}}, \quad (2.6)$$

where θ_i denotes the fractional coverage of species i and θ_* the fraction of free sites. Using

quasi-equilibrium relations for the adsorption steps and the site balance, the overall CO_2 consumption rate can be expressed in Langmuir–Hinshelwood–Hougen–Watson form as

$$-r_{\text{CO}_2} = \frac{k_4 K_{\text{CO}_2}^{1/2} K_{\text{H}_2}^{1/2} p_{\text{CO}_2}^{1/2} p_{\text{H}_2}^{1/2} \left(1 - \frac{p_{\text{CH}_4} p_{\text{H}_2\text{O}}^2}{p_{\text{CO}_2} p_{\text{H}_2}^4 K_{\text{eq}}^{\text{meth}}}\right)}{\left(1 + \sqrt{K_{\text{H}_2} p_{\text{H}_2}} + \sqrt{K_{\text{CO}_2} p_{\text{CO}_2}} + K_{\text{CO}} p_{\text{CO}} + K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}}\right)^2}, \quad (2.7)$$

where $K_{\text{eq}}^{\text{meth}}$ is the equilibrium constant of Reaction (2.2). Equation (2.7) reflects the positive apparent reaction orders in H_2 and CO_2 arising from the numerator and the strong inhibitory effects of CO and H_2O through the adsorption terms in the denominator.

Associative Formate Route on a Single Site Type

In associative mechanisms, CO_2 adsorbs molecularly, forming surface carbonates and bicarbonates that are then hydrogenated to formate. Methane is subsequently produced through further hydrogenation of the C_1 moiety. A representative mechanism assuming a single type of active site is given in Table 2.4. This type of route has been successfully applied to various Ni-based catalysts and is particularly relevant for Ni/CeO₂ [31].

Table 2.4: Associative formate mechanism on a single type of active site.

Step	Reaction
1	$\text{H}_2 + 2* \rightleftharpoons 2\text{H}* \quad (\text{quasi-equilibrium})$
2	$\text{CO}_2 + * \rightleftharpoons \text{CO}_2* \quad (\text{quasi-equilibrium})$
3	$\text{CO}_2* + \text{H}* \rightleftharpoons \text{HCOO}* + * \quad (\text{RDS in many models})$
4	$\text{HCOO}* + \text{H}* \rightleftharpoons \text{CHO}* + \text{OH}*$
5	$\text{CHO}* + \text{H}* \rightleftharpoons \text{CH}* + \text{OH}*$
6	$\text{CH}* + 3\text{H}* \rightleftharpoons \text{CH}_4* + 3*$
7	$\text{CH}_4* \rightleftharpoons \text{CH}_4(\text{g}) + *$
8	$\text{OH}* + \text{H}* \rightleftharpoons \text{H}_2\text{O}* + *$
9	$\text{H}_2\text{O}* \rightleftharpoons \text{H}_2\text{O}(\text{g}) + *$

When step 3 is taken as rate determining, the resulting LHHW expression for Reaction (2.2) exhibits an apparent first-order dependence on CO_2 at low coverage and a fractional positive order in H_2 , while water and hydroxyl species introduce strong inhibition through the site balance. This behaviour is consistent with experimental observations on highly active Ni/CeO₂ catalysts [31].

Within the one-site formate mechanism (Table 2.4), the elementary step



is usually taken as rate determining. Its elementary rate is then

$$r_3 = k_3 \theta_{\text{CO}_2} \theta_{\text{H}} - k_{-3} \theta_{\text{HCOO}} \theta_*. \quad (2.9)$$

By expressing the coverages in terms of gas-phase partial pressures and adsorption constants, and imposing thermodynamic consistency for Reaction (2.2), one obtains an LHHW-type rate expression of the form

$$-r_{\text{CO}_2} = \frac{k_3 K_{\text{CO}_2} K_{\text{H}_2}^{1/2} p_{\text{CO}_2} p_{\text{H}_2}^{1/2} \left(1 - \frac{p_{\text{CH}_4} p_{\text{H}_2\text{O}}}{p_{\text{CO}_2} p_{\text{H}_2}^2 K_{\text{eq}}^{\text{meth}}} \right)}{\left(1 + \sqrt{K_{\text{H}_2} p_{\text{H}_2}} + K_{\text{CO}_2} p_{\text{CO}_2} + K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}} \right)^2}. \quad (2.10)$$

The numerator in Equation (2.10) accounts for the positive dependence on CO_2 and H_2 partial pressures and for the approach to equilibrium of Reaction (2.2), whereas the denominator describes the competition for surface sites between adsorbed hydrogen, CO_2 and water, in line with the strong water inhibition observed experimentally on Ni/CeO_2 [31].

Associative Formate Route on Two Active Site Types (Ni/CeO_2)

Ni/CeO_2 catalysts require a refinement of the one-site formate mechanism because H_2 and CO_2 adsorb on different entities. The Ni particles are responsible for H_2 activation, whereas CO_2 is primarily adsorbed on oxygen vacancies at the Ni-CeO_2 interface. To account for this, Onrubia-Calvo et al. proposed a two-site mechanism, in which asterisks denote Ni sites and the symbol $\wedge$ denotes CeO_2 vacancy sites [31]. The corresponding elementary steps are listed in Table 2.5.

Table 2.5: Two-site associative formate mechanism for CO_2 methanation on Ni/CeO_2 (adapted from [31]). Asterisks (*) denote metallic Ni^0 sites responsible for H_2 dissociation; carets ($\wedge$) denote oxygen vacancy sites at the Ni-CeO_2 interface, responsible for CO_2 chemisorption.

Step	Reaction
1	$\text{H}_2 + 2* \rightleftharpoons 2\text{H}^*$ (quasi-equilibrium, on Ni)
2	$\text{CO}_2 + \wedge \rightleftharpoons \text{CO}_2^\wedge$ (quasi-equilibrium, on CeO_2 vacancy)
3	$\text{CO}_2^\wedge + \text{H}^* \rightleftharpoons \text{HCOO}^\wedge + *$ (RDS)
4	$\text{HCOO}^\wedge + \text{H}^* \rightleftharpoons \text{CHO}^\wedge + \text{OH}^*$
5	$\text{CHO}^\wedge + \text{H}^* \rightleftharpoons \text{CH}^\wedge + \text{OH}^*$
6	$\text{CH}^\wedge + 3\text{H}^* \rightleftharpoons \text{CH}_4^\wedge + 3*$
7	$\text{CH}_4^\wedge \rightleftharpoons \text{CH}_4(\text{g}) + \wedge$
8	$\text{OH}^* + \text{H}^* \rightleftharpoons \text{H}_2\text{O}^* + *$ (quasi-equilibrium, on Ni)
9	$\text{H}_2\text{O}^* \rightleftharpoons \text{H}_2\text{O}(\text{g}) + *$

The two-site formulation yields a rate expression similar in structure to the one-site model but with distinct adsorption terms for H_2 and CO_2 on their respective sites. It provides an excellent fit to a large experimental dataset while producing physically meaningful adsorption enthalpies and entropies, in particular a strong and favourable adsorption of CO_2 on CeO_2 vacancies [31].

For the two-site mechanism on Ni/CeO₂, step 3 in Table 2.5



is taken as the rate-determining surface reaction. The corresponding elementary rate can be written as

$$r_3 = k_3 \theta_{\text{CO}_2}^\wedge \theta_{\text{H}} - k_{-3} \theta_{\text{HCOO}}^\wedge \theta_*,$$
 (2.12)

After elimination of the surface coverages using the adsorption equilibria on both kinds of sites and the two independent site balances, Onrubia-Calvo et al. obtained a rate expression of the general form

$$-r_{\text{CO}_2} = \frac{k_3 K_{\text{CO}_2}^\wedge K_{\text{H}_2}^{1/2} p_{\text{CO}_2} p_{\text{H}_2}^{1/2} \left(1 - \frac{p_{\text{CH}_4} p_{\text{H}_2\text{O}}}{p_{\text{CO}_2} p_{\text{H}_2}^2 K_{\text{eq}}^{\text{meth}}} \right)}{\left(1 + \sqrt{K_{\text{H}_2} p_{\text{H}_2} + K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}}} \right)^2 \left(1 + K_{\text{CO}_2}^\wedge p_{\text{CO}_2} \right)^2}. \quad (2.13)$$

Compared with Equation (2.10), the two-site expression introduces a separate adsorption term $K_{\text{CO}_2}^\wedge$ for CO₂ on CeO₂ vacancies. This distinction allows the model to capture both the strong affinity of CO₂ for CeO₂ and the weaker adsorption of water on Ni sites, leading to physically meaningful adsorption enthalpies and entropies [31].

H-Assisted CO Formation Route on Low-Loaded Ni/Al₂O₃

For the 9.5 wt.% Ni/Al₂O₃ catalyst investigated by Quindimil et al., DRIFTS spectra show that carbonates and bicarbonates dominate at low temperature, while formates appear at higher temperature. CO selectivity reaches appreciable values at low contact times, but CO bands remain weak. Based on this, the authors proposed an H-assisted CO formation route in which formate decomposes into CO and OH, and this decomposition is rate determining [32]. A simplified set of steps is given in Table 2.6.

Assuming step 4 is rate determining and applying the usual LHHW procedure, Quindimil et al. derived a rate expression for CO₂ consumption of the form

$$-r_{\text{CO}_2} = \frac{k p_{\text{CO}_2} p_{\text{H}_2}^{1/2} \left(1 - \frac{p_{\text{CO}} p_{\text{H}_2\text{O}}}{p_{\text{CO}_2} p_{\text{H}_2} K_{\text{RWGS}}} \right)}{\left(1 + \sqrt{K_{\text{H}_2} p_{\text{H}_2} + K_{\text{CO}_2} p_{\text{CO}_2} + K_{\text{OH}} \frac{p_{\text{H}_2\text{O}}}{\sqrt{p_{\text{H}_2}}} + K_{\text{CO}} p_{\text{CO}}} \right)^2}, \quad (2.14)$$

where K_{RWGS} is the equilibrium constant of Reaction (2.3). Equation (2.14) reproduces a large set of kinetic data with a mean deviation of about 7 %, significantly outperforming simpler dissociative carbonyl models [32]. The numerator explicitly includes the driving force of the RWGS reaction, highlighting the strong coupling between CO formation and overall CO₂ methanation on this catalyst.

Table 2.6: H-assisted CO formation mechanism for low-loaded Ni/Al₂O₃ (adapted from [32]).

Step	Reaction
1	$\text{H}_2 + 2* \rightleftharpoons 2\text{H}* \quad (\text{quasi-equilibrium})$
2	$\text{CO}_2 + * \rightleftharpoons \text{CO}_2* \quad (\text{quasi-equilibrium; carbonate/bicarbonate pool})$
3	$\text{CO}_2* + \text{H}* \rightleftharpoons \text{HCOO}* + *$
4	$\text{HCOO}* + * \rightleftharpoons \text{CO}* + \text{OH}* \quad (\text{RDS, H-assisted CO formation})$
5	$\text{CO}* + \text{H}* \rightleftharpoons \text{CHO}* + *$
6	$\text{CHO}* + \text{H}* \rightleftharpoons \text{CH}* + \text{OH}*$
7	$\text{CH}* + 3\text{H}* \rightleftharpoons \text{CH}_4* + 3*$
8	$\text{CH}_4* \rightleftharpoons \text{CH}_4(\text{g}) + *$
9	$\text{CO}* \rightleftharpoons \text{CO}(\text{g}) + *$
10	$\text{OH}* + \text{H}* \rightleftharpoons \text{H}_2\text{O}* + *$
11	$\text{H}_2\text{O}* \rightleftharpoons \text{H}_2\text{O}(\text{g}) + *$

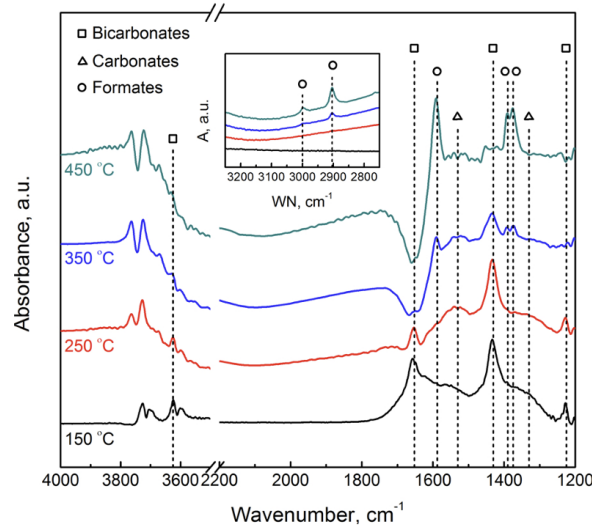


Figure 2.9: In situ DRIFTS spectra recorded over the 9.5 wt. % Ni/Al₂O₃ catalyst under CO₂/H₂/He at different temperatures, showing the gradual transformation of carbonates and bicarbonates into formate species with increasing temperature (reproduced from [32]).

The mechanistic interpretation proposed for the low-loaded Ni/Al₂O₃ catalyst is strongly supported by in situ DRIFTS measurements. Figure 2.9 shows the evolution of the surface species as the temperature is increased under a CO₂/H₂/He mixture. At low temperature, bands associated with carbonates and bicarbonates dominate the spectra, whereas at higher temperature these features gradually disappear in favour of intense formate bands. Carbonyl bands are comparatively weak. This behaviour is fully consistent with the H-assisted CO formation route discussed above, in which CO₂ is first stored in a carbonate/bicarbonate pool and then converted into formate species prior to their decomposition into CO* and OH* [32].

Hybrid Route Combining Direct CO₂ Dissociation and H-Assisted C–O Bond Cleavage on Ni/Al₂O₃

Beyond the purely dissociative carbon route and the H-assisted CO formation route, Lalande et al. also proposed a hybrid mechanism for Ni/Al₂O₃ in which CO₂ first dissociates to adsorbed CO* and O*, after which the second C–O bond cleavage is facilitated by hydrogen through COH* or COH₂* intermediates. The underlying idea is that the first C–O bond scission is energetically easier and faster, whereas the second one benefits from hydrogen assistance. The remaining elementary steps then follow the usual hydrogenation sequence toward CH₄ and H₂O. A representative set of elementary steps is reported in Table 2.7 [21].

Table 2.7: Hybrid mechanism combining direct CO₂ dissociation and H-assisted C–O bond cleavage on Ni/Al₂O₃ (adapted from [21]).

Step	Reaction
AB1	$\text{H}_2 + 2* \rightleftharpoons 2\text{H}^*$
AB2	$\text{CO}_2 + * \rightleftharpoons \text{CO}_2^*$
AB3	$\text{CO}_2^* + * \rightleftharpoons \text{CO}^* + \text{O}^*$
AB4	$\text{CO}^* + \text{H}^* \rightleftharpoons \text{COH}^* + *$
AB5	$\text{CO}^* + 2\text{H}^* \rightleftharpoons \text{COH}_2^* + 2*$
AB6	$\text{COH}^* + * \rightleftharpoons \text{CH}^* + \text{O}^*$
AB7	$\text{COH}^* + \text{H}^* \rightleftharpoons \text{CH}^* + \text{OH}^*$
AB8	$\text{COH}_2^* + * \rightleftharpoons \text{CH}^* + \text{OH}^*$
AB9	$\text{CH}^* + \text{H}^* \rightleftharpoons \text{CH}_2^* + *$
AB10	$\text{CH}_2^* + \text{H}^* \rightleftharpoons \text{CH}_3^* + *$
AB11	$\text{CH}_3^* + \text{H}^* \rightleftharpoons \text{CH}_4^* + *$
AB12	$\text{CH}_4^* \rightleftharpoons \text{CH}_4(g) + *$
AB13	$\text{O}^* + \text{H}^* \rightleftharpoons \text{OH}^* + *$
AB14	$\text{OH}^* + \text{H}^* \rightleftharpoons \text{H}_2\text{O}^* + *$
AB15	$\text{H}_2\text{O}^* \rightleftharpoons \text{H}_2\text{O}(g) + *$
AB16	$\text{CO}^* \rightleftharpoons \text{CO}(g) + *$

As for the previous mechanisms, a family of Langmuir–Hinshelwood–Hougen–Watson (LHHW) expressions can be derived from Table 2.7 by assuming one rate-determining surface reaction and quasi-equilibrated adsorption and desorption for the remaining steps. In the framework proposed by Lalande et al., the hybrid route corresponds to models in which either the formation of COH* or COH₂*, or the dissociation of these oxygenated intermediates, is rate determining. The resulting generalized methanation rate expression can be written as

$$r_{\text{CH}_4} = \frac{k_1 K_{Cx} p_{\text{CO}_2}^a K_{\text{H}_2}^b p_{\text{H}_2}^c p_{\text{H}_2\text{O}}^d \left(1 - \frac{p_{\text{CH}_4} p_{\text{H}_2\text{O}}^2}{p_{\text{CO}_2} p_{\text{H}_2}^4 K_{\text{eq}}^{\text{meth}}}\right)}{\left(1 + K_{Cx} p_{\text{CO}_2}^e K_{\text{H}_2}^f p_{\text{H}_2}^g p_{\text{H}_2\text{O}}^h + K_{\text{H}} p_{\text{H}_2}^{1/2} + K_{\text{OH}} \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}^{1/2}}\right)^i} \quad (2.15)$$

In Equation 2.15, K_{Cx} denotes the adsorption constant of the carbon-containing surface intermediate involved in the rate-determining step, whereas the exponents a – i depend on the particular mechanistic hypothesis. Lalinde et al. summarized these coefficients for the full family of tested models; within that framework, the hybrid mechanism corresponds specifically to models 8–14 in Table 2.8 [21].

Table 2.8: Parameters and exponents appearing in the generalized rate expression proposed by Lalinde et al. for the different mechanistic hypotheses. Models 8–14 correspond to the hybrid mechanism (adapted from [21]).

Model	Mechanism	K_{Cx}	a	b	c	d	e	f	g	h	i
1	A, AB, B	–	1.0	–	–	–	–	–	–	–	1.0
2	A, AB, B	–	1.0	–	–	–	–	–	–	–	2.0
3	A3, AB3	K_{CO_2}	1.0	–	–	–	1.0	–	–	–	2.0
4	A4	K_{CO}	0.5	–	–	–	0.5	–	–	–	2.0
5	A5	K_{C}	0.33	0.5	0.5	–	0.33	–	–	–	2.0
6	A6	K_{CH}	0.33	1.0	1.0	–	0.33	0.5	0.5	–	2.0
7	A7	K_{CH_2}	0.33	1.5	1.5	–	0.33	1.0	1.0	–	2.0
8	AB4	K_{CO}	0.5	0.5	0.5	–	0.5	–	–	–	2.0
9	AB5	K_{CO}	0.5	1.0	1.0	–	0.5	–	–	–	3.0
10	AB6	K_{COH}	0.5	0.5	0.5	–	0.5	0.5	0.5	–	2.0
11	AB7	K_{COH}	0.5	1.0	1.0	–	0.5	0.5	0.5	–	2.0
12	AB8	K_{COH_2}	0.5	1.0	1.0	–	0.5	1.0	1.0	–	2.0
13	AB9	K_{CH}	0.25	1.0	1.0	–	0.25	0.5	0.5	–	2.0
14	AB10	K_{CH_2}	0.25	1.5	1.5	–	0.25	1.0	1.0	–	2.0
15	B4	K_{HCOO}	1.0	0.5	0.5	–	1.0	0.5	0.5	–	2.0
16	B5	K_{HCOO}	1.0	1.0	1.0	–	1.0	0.5	0.5	–	2.0
17	B6	K_{COH}	1.0	1.5	2.0	-1.0	1.0	1.0	1.5	-1.0	2.0
18	B7	K_{COH}	1.0	1.0	1.5	-1.0	1.0	1.0	1.5	-1.0	2.0
19	B8	K_{CH}	1.0	2.0	3.0	-2.0	1.0	1.5	2.5	-2.0	2.0
20	B9	K_{CH_2}	1.0	2.5	3.5	-2.0	1.0	2.0	3.0	-2.0	2.0

Role of Water and CO in the Rate Expression

Irrespective of the detailed mechanism, two features of the rate expression deserve a specific comment. The first concerns water, and a precise terminology is in order. H_2O is a stoichiometric product of Reaction (2.2) and not a foreign species, so calling it an “inhibitor” (as is sometimes done in the methanation literature) is, strictly speaking, a mis-

nomer. What is actually observed is the standard behaviour of a Langmuir–Hinshelwood–Hougen–Watson rate law in the presence of an adsorbing product, namely two coupled effects that both go in the direction of slowing the net forward rate as H_2O accumulates. On the one hand, the partial pressure of H_2O enters the numerator through the driving-force term $\left(1 - p_{\text{CH}_4}p_{\text{H}_2\text{O}}^2/(p_{\text{CO}_2}p_{\text{H}_2}^4K_{\text{eq}}^{\text{meth}})\right)$, which pulls the system toward equilibrium. On the other hand, H_2O and the OH^* species derived from it adsorb on the active Ni sites and contribute to the denominator through the terms $K_{\text{H}_2\text{O}}p_{\text{H}_2\text{O}}$ or $K_{\text{OH}}p_{\text{H}_2\text{O}}/\sqrt{p_{\text{H}_2}}$ in expressions such as Equation (2.14). Competitive adsorption of an adsorbing species (whether reactant, intermediate or product) on the surface is, however, a perfectly normal feature of heterogeneous catalysis and is the very thing that LHHW kinetics are designed to describe; it is not, on its own, sufficient to qualify H_2O as an inhibitor.

The case of CO is different, and here the word inhibitor applies in its proper sense. CO is not a stoichiometric product of CO_2 methanation but a by-product of the parasitic reverse water–gas shift Reaction (2.3), and its strong chemisorption on metallic Ni occupies sites that would otherwise be available for the productive hydrogenation pathway. Even small CO partial pressures noticeably reduce the rate through the $K_{\text{CO}}p_{\text{CO}}$ term, particularly in mechanisms where CO^* appears explicitly as an intermediate. Accurate accounting for both effects (the thermodynamic feedback of H_2O through the driving force, the surface-coverage contribution of H_2O , OH^* and CO through the denominator) is essential when extrapolating intrinsic kinetics to reactor-scale simulations, where high water and CO mole fractions can be reached over part of the catalyst bed [14, 32].

2.3.2 Intrinsic kinetic data and modelling framework

Experimental design and intrinsic character of the kinetic datasets

The reference studies considered in this work were explicitly designed to obtain intrinsic kinetic data, that is, free from external and internal heat and mass transfer limitations. Three dimensionless criteria are routinely used to verify that the measured rates are not biased by transport phenomena. The Mears criterion bounds the external (interphase) mass transfer resistance, the Anderson criterion bounds the corresponding heat transfer resistance, and the Weisz–Prater criterion bounds the internal (intraparticle) mass transfer resistance. Each of these numbers must lie below its critical threshold for the measurement to qualify as intrinsic [25]. A concise compilation of these criteria and their thresholds, in a form directly usable for fixed-bed methanation and reforming experiments, is given by Minette et al. [27] in the context of intrinsic SMR kinetics on a thin Ni coating.

Champon et al. investigated CO_2 methanation over a commercial 14–17 wt. % Ni/ Al_2O_3 catalyst in a fixed-bed reactor operated at atmospheric pressure and temperatures between 623 and 723 K [14]. Catalyst particles were sieved to sizes between 125 and 250 μm

and diluted with inert material in order to minimise temperature gradients. All three transport criteria were satisfied, with dimensionless numbers well below their respective critical thresholds [14].

Quindimil et al. followed a similar philosophy for the low-loaded 9.5 wt. % Ni/Al₂O₃ catalyst [32]. After a 72 h stability test at 400 °C and 1 bar, the kinetic experiments were carried out by systematically varying the operating conditions in the following ranges: temperature 315–430 °C, total volumetric flow rate 200–1100 cm³ min⁻¹ (corresponding to a gas hourly space velocity, GHSV, of 12 000–66 000 h⁻¹ or a mass-to-flow ratio $W/F_{\text{CO}_2} = 1.6\text{--}24.9 \text{ g}_{\text{cat}} \text{ h mol}^{-1}$), H₂/CO₂ feed ratio between 2 and 10, and total pressure between 2 and 6 bar [32]. The reaction rates obtained in the differential regime ($X_{\text{CO}_2} \lesssim 10\%$) were then used for parameter estimation, while data at higher conversions served to validate the model under near-equilibrium conditions. The reliability of the apparent activation energies deduced from Arrhenius plots was confirmed a posteriori using the Mears and Anderson criteria for external and internal heat transfer, which were both satisfied despite the high reaction enthalpy of CO₂ methanation [32].

Onrubia-Calvo et al. extended this systematic approach to a highly active 8.5 wt. % Ni/CeO₂ catalyst [31]. Once the catalyst had been stabilised far from equilibrium, a large kinetic dataset was generated by varying the reaction temperature between 250 and 500 °C, the total flowrate between 200 and 1100 cm³ min⁻¹ (GHSV 12 000–66 000 h⁻¹), the H₂/CO₂ ratio in the feed between 1 and 16, and the total pressure between 1.4 and 6 bar, using N₂ as diluent [31]. As in the Ni/Al₂O₃ study, intrinsic conditions were ensured by checking standard transport criteria and by operating predominantly in the differential regime, while a subset of experiments at higher conversions was used to test the model under integral reactor conditions.

What makes these datasets a robust basis for reactor-scale simulations and process design is therefore not the absolute number of experimental points, which would be a misleading metric on its own (a hundred points clustered in a narrow window of conditions, or contaminated by transport limitations, would not be informative). It is rather the combination of three features. First, the operating window is wide and systematically explored: temperature, total pressure, space velocity and H₂/CO₂ ratio are each varied independently across a meaningful range. Secondly, both differential and integral regimes are sampled, so that the dataset contains information on the kinetic regime (where the rate is far from equilibrium and parameter estimation is well-conditioned) as well as on the approach to equilibrium (which constrains the thermodynamic consistency of the model). Thirdly, intrinsic conditions are explicitly verified through the transport criteria recalled above, rather than assumed. Datasets meeting these three conditions, even with a comparatively modest number of points, are well suited to discriminate between candidate mechanisms and to extrapolate the resulting rate expressions to operating conditions

outside the experimental window.

Experimental observations in the reference studies

Before turning to the kinetic modelling itself, it is worth pausing on the experimental observations these models are meant to describe. Three families of measurements recur across the reference studies and contain, taken together, most of the qualitative information needed to guide the choice of a rate expression: the light-off curve (X_{CO_2} versus T at fixed space time), the conversion profiles versus space time at several temperatures, and the partial pressure dependences of the rate. Each of them reveals one specific feature of the underlying kinetics.

Light-off curve and approach to equilibrium. Figure 2.10 reproduces the light-off curve and selectivity profiles reported by Quindimil et al. for the 9.5 wt. % Ni/Al₂O₃ catalyst at 1 bar, $\text{H}_2/\text{CO}_2 = 4$ and $W/F_{\text{CO}_2}^{\text{in}} = 4.7 \text{ g h mol}^{-1}$, together with the equilibrium curve for the Sabatier reaction. The shape of the conversion curve (panel a) is qualitatively the same on all Ni-based catalysts: a sigmoidal rise from negligible activity below 275 °C to a steep climb between 350 and 450 °C, followed by a flattening that progressively asymptotes to the equilibrium ceiling. The catalyst studied here is a low-loaded formulation, which is why the temperature of 50 % conversion (T_{50}) reaches 455 °C; on more active Ni/CeO₂ catalysts, T_{50} is shifted to around 300 °C [31]. The important point is that the experimental curve and the equilibrium curve converge at high temperature, which provides a clean visual diagnostic of the regime in which one is working: below the inflection point, the rate is essentially kinetically controlled and parameter estimation is well-conditioned; above it, the approach to equilibrium becomes the dominant feature and any rate expression that fails to include a driving-force term will give unphysical predictions.

The selectivity panel of Figure 2.10 contains a second piece of mechanistic information. At low temperature, S_{CH_4} is close to 90 % and S_{CO} is below 10 %, which indicates that virtually all converted CO₂ proceeds along the methanation pathway. As temperature increases, S_{CH_4} passes through a minimum around 350–400 °C while S_{CO} goes through a corresponding maximum. This non-monotonic behaviour reflects the growing thermodynamic favourability of the reverse water–gas shift Reaction (2.3), which is endothermic and therefore accelerated by temperature, in competition with the exothermic methanation step. The recovery of S_{CH_4} above 450 °C is the kinetic signature of the CO methanation Reaction (2.4) becoming fast enough to consume the CO produced by RWGS before it leaves the bed. Any kinetic description that aims to cover the full temperature window must therefore account for at least two coupled reactions (CO₂ methanation and RWGS, with CO methanation either lumped into the methanation rate or treated explicitly as in

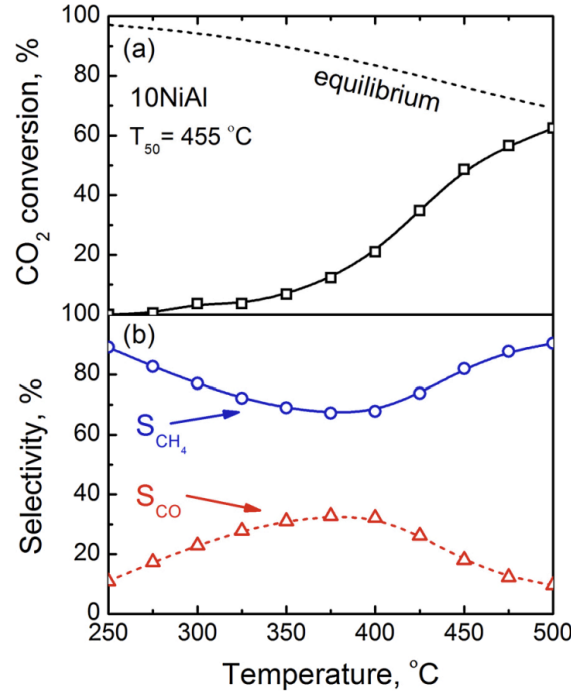


Fig. 2. (a) Light-off curve and (b) selectivity towards CH₄ (S_{CH₄}) and CO (S_{CO}) of Ni/Al₂O₃ catalyst recorded prior to the stability test. Reaction conditions: $P = 1$ bar, $H_2/CO_2 = 4$ and $W/F_{A0} = 4.7$ g h mol⁻¹.

Figure 2.10: Light-off curve (panel a) and selectivities towards CH₄ and CO (panel b) for the 10 wt. % Ni/Al₂O₃ catalyst reported by Quindimil et al. [32]. Operating conditions: $P = 1$ bar, $H_2/CO_2 = 4$, $W/F_{CO_2}^{in} = 4.7$ g h mol⁻¹. The dashed line in panel (a) is the equilibrium conversion of the Sabatier reaction at the same conditions. The selectivity panel shows the parasitic contribution of the RWGS reaction at intermediate temperatures.

[14]).

Conversion versus space time at fixed temperature. The second canonical measurement is the conversion profile as a function of space time at several fixed temperatures, illustrated in Figure 2.11 for the 8.5 wt. % Ni/CeO₂ catalyst of Onrubia-Calvo et al. at 2 bar and H₂/CO₂ = 4 [31]. Two features of this figure deserve attention. The first is that the conversions remain low (below 30 %) over the entire range of space times and temperatures, which is a deliberate experimental choice: operating in the differential regime ensures that the rate measured locally is close to the rate at the inlet partial pressures, so that the reaction quotient stays far from $K_{\text{eq}}^{\text{meth}}$ and the kinetic parameters are not absorbed into a residual driving-force term during regression. The second feature is the clean vertical separation of the five isotherms: at each space time, going from 255 to 295 °C multiplies the conversion by roughly a factor of three, which is the visual signature of an Arrhenius-type temperature dependence with an apparent activation energy of the order of 100 kJ mol⁻¹.

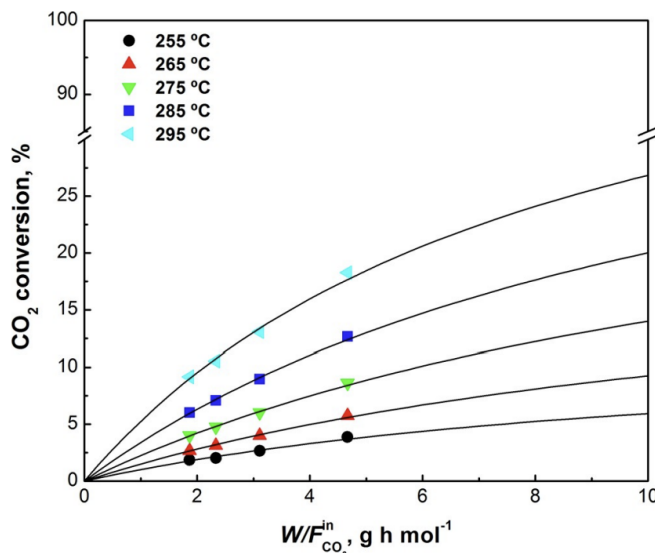


Figure 4. Effect of temperature on CO₂ conversion at increasing space times ($W/F_{\text{CO}_2}^{\text{in}}$). Symbols refer to experimental data and black lines to the obtained fits. Total pressure of 2 bar and H₂/CO₂ ratio of 4 in the feedstream.

Figure 2.11: CO₂ conversion as a function of space time $W/F_{\text{CO}_2}^{\text{in}}$ at five temperatures for the 8.5 wt. % Ni/CeO₂ catalyst studied by Onrubia-Calvo et al. [31]. Symbols are experimental data, lines are model fits. Operating conditions: $P = 2$ bar, H₂/CO₂ = 4. The measurements are deliberately confined to the differential regime ($X_{\text{CO}_2} < 30\%$) so that the apparent reaction orders and the activation energy can be estimated without interference from the approach to equilibrium.

The mild curvature of each isotherm at the highest space times is also informative. It is the first visible manifestation of the approach toward equilibrium, even at conversions well below X_{eq} , and confirms that the driving-force term $(1 - Q/K_{\text{eq}}^{\text{meth}})$ already contributes

significantly to slowing the net rate before equilibrium itself is reached. This is one of the practical reasons why a rate expression without an equilibrium factor cannot be fit to integral data, even when the absolute conversions are modest.

Partial pressure dependences. The third type of measurement systematically reported across the reference studies is the dependence of the rate on the partial pressure of each individual species, typically obtained by varying one feed composition at a time while keeping the others constant. Figure 2.12 reproduces such measurements for the 9.5 wt. % Ni/Al₂O₃ catalyst at 325 °C and 6 bar.

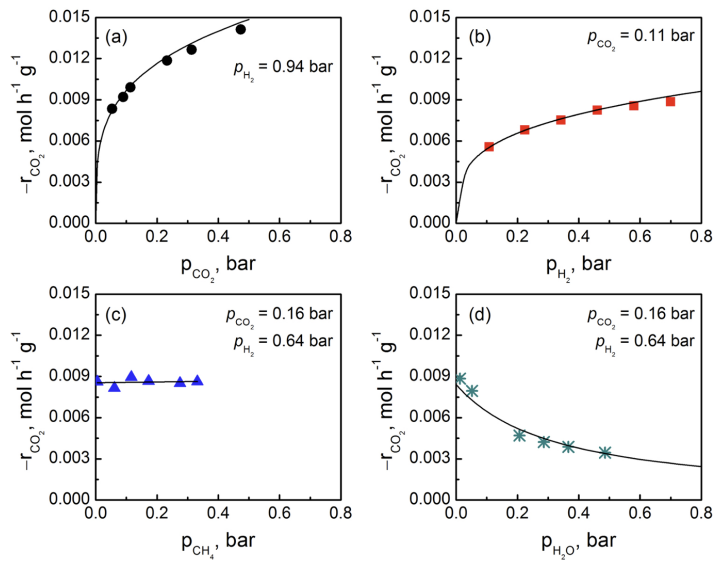


Figure 2.12: Influence of CO₂, H₂, CH₄ and H₂O partial pressures on the CO₂ methanation rate over the 9.5 wt. % Ni/Al₂O₃ catalyst at 325 °C and 6 bar (reproduced from [32]).

Four trends emerge from this figure and recur in most studies of CO₂ methanation on Ni-based catalysts. The rate depends positively on both p_{CO_2} and p_{H_2} , with apparent orders that are fractional (typically 0.2–0.4 in CO₂ and 0.2–0.5 in H₂). This fractional positive dependence is characteristic of a Langmuir–Hinshelwood mechanism in which both reactants compete with other species for surface sites, so that the surface coverage grows sub-linearly with the partial pressure. The rate is essentially independent of p_{CH_4} , which means that the methane product does not adsorb significantly under reaction conditions and doesn’t need to appear in the rate denominator. Finally, the rate decreases strongly with increasing $p_{\text{H}_2\text{O}}$, a feature already discussed in Section 2.3 and that motivates the inclusion of a water term in the denominator of the LHHW expression. Taken together, the three families of measurements illustrated in Figures 2.10, 2.11 and 2.12 contain all the qualitative information that the kinetic model is then required to reproduce: fractional positive orders in the reactants, weak dependence on methane, strong negative dependence on water, Arrhenius-type temperature dependence with an activation energy

in the range 80–110 kJ mol⁻¹, and an asymptotic approach to the Sabatier equilibrium at high temperature or long space time.

Apparent kinetic parameters: isothermal and non-isothermal treatment

The first quantitative step in any kinetic study consists in extracting apparent reaction orders and an apparent activation energy from the differential-regime data. This is done in two steps. The isothermal treatment, performed at fixed temperature, identifies the apparent orders in the partial pressures and the contribution of water to the rate. The non-isothermal treatment, performed at varying temperature, extracts the apparent activation energy through an Arrhenius analysis. This sequencing matters in practice: the apparent orders obtained isothermally are subsequently held fixed (or used as initial guesses) during the Arrhenius regression, so that the temperature dependence is not absorbed into a spurious variation of the orders.

Isothermal treatment: apparent reaction orders. For each catalyst, initial reaction rates obtained at fixed temperature in the differential regime are correlated with a power-law expression. Two features must be preserved at this stage. The dependence on each partial pressure is left as an adjustable apparent order, and a water term is kept in the denominator to account for the reduction of the rate by adsorbed H₂O and OH* species. More importantly, even at the power-law level, the expression must reflect the reversible nature of Reaction (2.2): without a thermodynamic driving force, the fitted expression would in principle predict a non-zero forward rate at equilibrium, and conversions above X_{eq} at finite space time, which is physically impossible. The power-law expression used in the reference studies therefore takes the form

$$-r_{\text{CO}_2} = \frac{k p_{\text{CO}_2}^\alpha p_{\text{H}_2}^\beta}{1 + K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}}} \left(1 - \frac{p_{\text{CH}_4} p_{\text{H}_2\text{O}}^2}{p_{\text{CO}_2} p_{\text{H}_2}^4 K_{\text{eq}}^{\text{meth}}} \right), \quad (2.16)$$

where k is an apparent rate constant, α and β are apparent reaction orders, $K_{\text{H}_2\text{O}}$ describes the contribution of water to the site balance, and $K_{\text{eq}}^{\text{meth}}$ is the equilibrium constant of the Sabatier reaction taken from the correlation of Aparicio [2]. The bracketed driving-force term is identical in structure to the one used in the LHHW expressions of Section 2.3, and ensures that $-r_{\text{CO}_2} \rightarrow 0$ as the reaction quotient approaches $K_{\text{eq}}^{\text{meth}}$.

Applied to the 9.5 wt. % Ni/Al₂O₃ catalyst, this isothermal treatment yields apparent reaction orders of 0.27 in CO₂ and 0.24 in H₂, and a water adsorption constant of approximately 3.1 atm⁻¹ [32]. The fractional positive orders confirm that both reactants contribute to the rate through competitive adsorption on Ni sites, with neither approaching a saturation regime under the explored conditions. The magnitude of $K_{\text{H}_2\text{O}}$ indicates that water already occupies a significant fraction of the active surface at the H₂O partial

pressures generated by the reaction itself. A similar analysis on the 8.5 wt. % Ni/CeO₂ catalyst returns apparent reaction orders of comparable magnitude and confirms the same qualitative picture [31].

Non-isothermal treatment: apparent activation energy. With the apparent orders fixed, the temperature dependence of the rate constant is extracted from an Arrhenius analysis of the differential-regime data acquired at several temperatures. For the 9.5 wt. % Ni/Al₂O₃ catalyst, this yields an apparent activation energy of 80.1 kJ mol⁻¹ [32]. For the 8.5 wt. % Ni/CeO₂ catalyst, the corresponding value is 103.9 kJ mol⁻¹ [31]. For the commercial 14–17 wt. % Ni/Al₂O₃ catalyst of Champon et al., the same procedure returns 110 kJ mol⁻¹ for CO₂ methanation, together with 97.1 kJ mol⁻¹ for the RWGS reaction and 97.3 kJ mol⁻¹ for CO methanation [14]. A broader survey of the literature places the apparent activation energies for NiAl-type catalysts in the range 75–118.7 kJ mol⁻¹ [32], with for instance 75–89 kJ mol⁻¹ for various 10–20 wt. % Ni/Al₂O₃ formulations, 99 kJ mol⁻¹ for Ni/MgO and 118.7 kJ mol⁻¹ for Ni supported on Ca-modified alumina. The value of 99 kJ mol⁻¹ for Ni/MgO is worth highlighting, as MgO incorporation into Ni-based catalysts enhances CO₂ adsorption and may modify the effective activation barrier relative to conventional Ni/Al₂O₃ formulations [29].

Two general observations close this paragraph. Ni/Al₂O₃ and Ni/CeO₂ catalysts exhibit comparable apparent activation energies in the range 80–110 kJ mol⁻¹, which places them within the expected window for Ni-based methanation and confirms that the underlying mechanisms are chemically reasonable. The differences between catalysts lie less in the value of E_a than in the nature of the dominant intermediates (CO*, formate, bicarbonate) and in the role of the support in CO₂ activation, as discussed in Section 2.2. The adsorption enthalpies reported by Champon et al. for CO, H₂, CO₂ and H₂O (40.6, 52.0, 9.7 and 14.5 kJ mol⁻¹ respectively) provide a complementary picture: CO and H₂ bind significantly more strongly to the Ni surface than CO₂ or H₂O, which is consistent with the strong effect of CO on the rate (genuine inhibition) and with the more moderate effect of water at low partial pressures.

Table 2.9 summarises the key quantitative parameters from the reference studies, providing a unified basis for comparison with the kinetic results obtained in Section 2.3.

What the apparent picture does, and does not. The preliminary apparent-parameter analysis serves three purposes. It confirms the intrinsic character of the data through consistent Arrhenius behaviour and reasonable apparent orders. It provides order-of-magnitude initial guesses for the rate constants and adsorption constants of the LHHW expressions derived later. And it identifies which gas-phase variables exert the strongest influence on the rate, guiding the choice of which intermediates to include in the mechanis-

Table 2.9: Key kinetic parameters for CO₂ methanation on Ni-based catalysts from the reference studies reviewed in this work. E_a : apparent activation energy from power-law fit; α , β : apparent reaction orders in CO₂ and H₂; mechanism: best-performing LHHW model; D : mean absolute deviation of the best model.

Catalyst	E_a (kJ mol ⁻¹)	α	β	Best mechanism	D (%)
Ni/Al ₂ O ₃ 14–17 wt % [14]	110	—	—	Indirect (RWGS + CO meth.)	—
Ni/Al ₂ O ₃ 9.5 wt % [32]	80.1	0.27	0.24	H-assisted CO formation	7
Ni/CeO ₂ 8.5 wt % [31]	103.9	—	—	Formate, two active sites	11.3

tic models. What it does not do is allow a mechanistic interpretation in its own right. The apparent orders and the apparent activation energy are convolutions of the elementary kinetic parameters and of the surface coverages, and as such are not directly comparable to the energy barriers obtained from DFT or microkinetic modelling. Mechanistic interpretation requires the LHHW analysis discussed next.

Mechanistic LHHW modelling and discrimination

Because several mechanistic hypotheses can reproduce CO₂ methanation data with comparable accuracy, a systematic model discrimination procedure is required. Formal statistical criteria such as the F-test, the Akaike Information Criterion (AIC) and the Bayesian Information Criterion (BIC) provide quantitative tools for model selection that penalise over-parameterisation [12]. In the kinetic studies reviewed here, model discrimination is based primarily on the mean relative deviation D combined with physical plausibility checks on the estimated parameters, an approach that is equivalent in spirit to information-theoretic criteria when the number of parameters is similar across candidate models.

Derivation of mechanistic LHHW models. Candidate mechanisms are formulated on the basis of literature data and in situ DRIFTS experiments. For Ni/Al₂O₃ and Ni/CeO₂, the mechanisms considered include (i) a carbon route involving CO* dissociation to C*, (ii) a formyl route in which CO* is hydrogenated to CHO*, and (iii) an associative formate route in which molecularly adsorbed CO₂ (as carbonate or bicarbonate) is hydrogenated to formate and then to methane [32, 31, 14]. For the low-loaded Ni/Al₂O₃ catalyst, DRIFTS data suggest a hybrid H-assisted CO formation route in which formate decomposes into CO* and OH*, followed by rapid CO hydrogenation [32]. For Ni/CeO₂, DRIFTS clearly indicates that CO₂ is adsorbed predominantly as bicarbonate and formate on CeO₂ vacancies, while H₂ is dissociated on metallic Ni, which motivates a two-site formate mechanism [31].

Each mechanism is translated into a set of elementary steps (adsorption, surface reactions and desorption). Under the usual assumptions of quasi-equilibrated adsorption and a single rate-determining surface reaction, an LHHW expression is derived for the net rate of CO₂ consumption. Thermodynamic consistency is enforced by including an explicit driving-force term of the type

$$\left(1 - \frac{Q}{K_{\text{eq}}}\right),$$

where Q is the reaction quotient and K_{eq} the equilibrium constant of the corresponding global reaction (CO₂ methanation or RWGS) [14, 33]. Adsorption and rate constants are expressed in Arrhenius–van ’t Hoff form, which allows a straightforward interpretation in terms of apparent activation energies and adsorption enthalpies.

Nonlinear parameter estimation and statistical criteria. The kinetic parameters in each LHHW expression are estimated by nonlinear regression, typically using a weighted least-squares objective function that minimises the difference between experimental and calculated reaction rates for all data points:

$$\Phi = \sum_{i=1}^N w_i (r_{\text{exp},i} - r_{\text{calc},i}(\boldsymbol{\theta}))^2, \quad (2.17)$$

where w_i are statistical weights and $\boldsymbol{\theta}$ is the vector of kinetic parameters. Quindimil et al. fit their models to 153 kinetic points, while Onrubia-Calvo et al. use 124 points for Ni/CeO₂, covering wide ranges of temperature, pressure, space velocity and gas composition [32, 31]. Champon et al. combine CO₂ methanation, RWGS and CO methanation data for a commercial Ni/Al₂O₃ catalyst to estimate three coupled rate expressions [14].

The quality of each model is assessed through several complementary indicators: the mean relative deviation D between experimental and calculated rates, the standard deviation of residuals, the coefficient of determination, and visual inspection of parity plots and residual plots. For the 9.5 wt. % Ni/Al₂O₃ catalyst, the H-assisted CO formation mechanism yields a mean deviation of approximately 7 %, while the conventional carbonyl route leads to $D \approx 20$ %, despite having a similar number of parameters [32]. For Ni/CeO₂, the one-site formate route gives $D \approx 10.4$ %, and the two-site formate model maintains a comparable deviation ($D \approx 11.3$ %) while providing adsorption enthalpies and entropies that are more consistent with independent physicochemical characterisation [31]. In all cases, the selected models are able to reproduce not only differential data but also conversion profiles up to thermodynamic equilibrium. The impact of the mechanistic hypothesis on model predictive capability is illustrated in Figures 2.13 and 2.14.

Panel (b) shows the parity plot obtained with a conventional carbonyl route, in which CO* is hydrogenated to CHO*, whereas panel (c) corresponds to the H-assisted CO formation

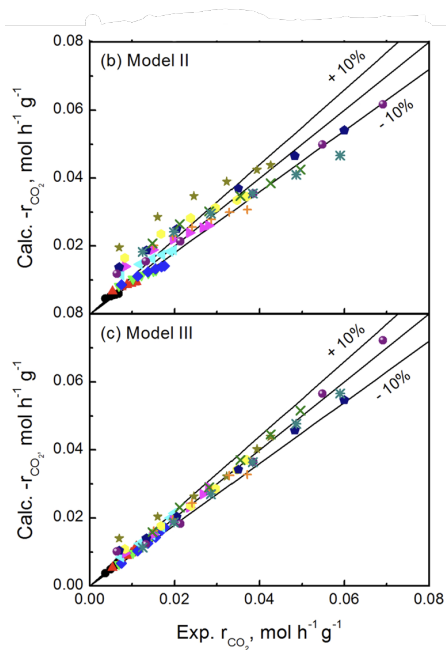


Figure 2.13: Parity plots comparing experimental and calculated CO_2 consumption rates for different kinetic models over the 9.5 wt. % $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst: (b) conventional carbonyl route and (c) H-assisted CO formation route (from [32]).

mechanism. Although both models reproduce the data reasonably well near the diagonal, the carbonyl route systematically underestimates the rate at low conversion and overestimates it close to equilibrium, yielding a mean deviation of about 20 %. The H-assisted CO formation mechanism, on the other hand, provides a much more homogeneous distribution of points around the diagonal and reduces the mean deviation to approximately 7 %, which justifies its selection as the reference model for low-loaded $\text{Ni}/\text{Al}_2\text{O}_3$ [32].

A similar analysis was performed by Onrubia-Calvo et al. for the Ni/CeO_2 catalyst. Figure 2.14 compares the parity plots obtained for carbon, formyl and two-site formate mechanisms. The carbon and formyl routes lead to significant systematic deviations, particularly at high rates, and yield thermodynamically inconsistent adsorption parameters. In contrast, the two-site formate model produces a narrow scatter of points around the diagonal and provides adsorption enthalpies and entropies that are compatible with independent characterisation of CO_2 and H_2 adsorption on Ni and CeO_2 [31]. This combination of statistical and physical arguments strongly supports the associative formate mechanism on two types of active sites.

Physical consistency and external validation. Statistical goodness-of-fit alone is not sufficient to discriminate between models. Parameters must also be physically meaningful. In practice, activation energies are required to lie within typical ranges for surface reactions on Ni -based catalysts (75–120 kJ mol^{-1} for standard Ni -based formulations, though lower values have been reported for highly active or promoted systems [31, 29]);

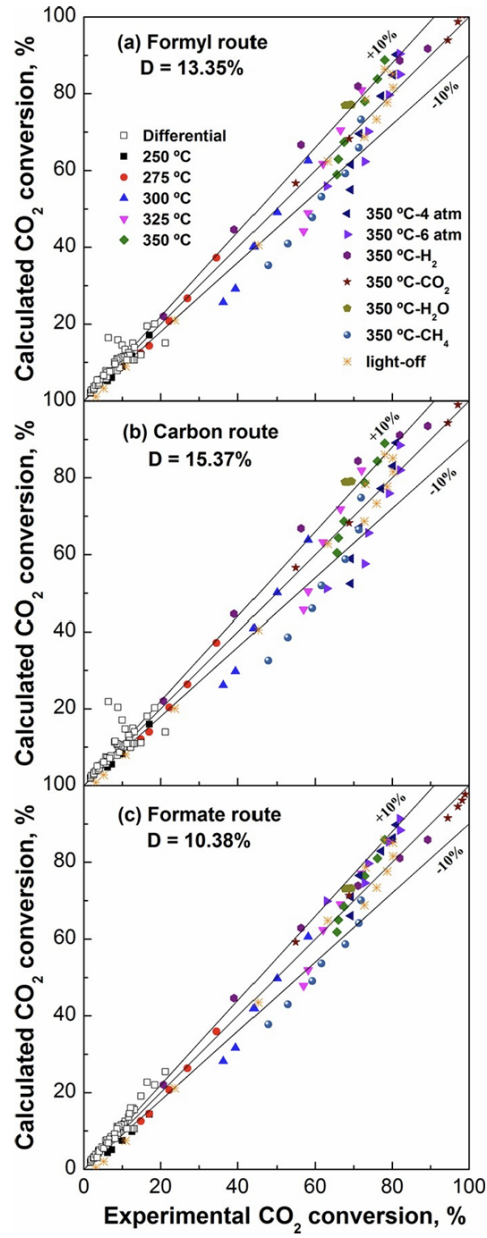


Figure 2.14: Model discrimination for CO_2 methanation on Ni/CeO_2 : parity plots for (a) carbon route, (b) formyl route and (c) formate route on two active sites (adapted from [31]).

adsorption enthalpies must have reasonable magnitudes and signs; and adsorption entropies should remain between gas-phase and condensed-phase limits [26, 33]. Models that yield unrealistically strong adsorption (e.g. very large negative enthalpies or positive entropies) are rejected even if the numerical fit is acceptable.

A final level of discrimination involves external validation. The best-performing LHHW models are tested against datasets that were not used in parameter estimation, for example experiments at higher conversions, different H_2/CO_2 ratios or additional total pressures. Both Quindimil et al. and Onrubia-Calvo et al. show that their preferred mechanisms (H-assisted CO formation for low-loaded Ni/ Al_2O_3 , two-site formate route for Ni/ CeO_2) accurately predict CO_2 conversion, CH_4/CO selectivities and the influence of water over a wide range of operating conditions [32, 31]. This multi-criteria approach, combining statistical quality, thermodynamic consistency and physical plausibility, is in line with recent microkinetic work on Ni-based methanation catalysts [33, 26].

2.3.3 Catalyst deactivation and stability under cyclic operation

The long-term performance of Ni-based methanation catalysts is governed not only by their intrinsic activity but also by their resistance to deactivation. Three main deactivation mechanisms are relevant for CO_2 methanation, and their importance is amplified in the context of cyclic ICCM operation [4].

Sintering. Thermal sintering of Ni particles leads to a progressive loss of metallic surface area and a decrease in the number of active sites. Sintering is accelerated at high temperature (above 400–450 °C) and in the presence of steam, which promotes Ostwald ripening of Ni crystallites [4]. The incorporation of MgO into the support has been shown to mitigate sintering by stabilising Ni particles through strong Ni–MgO interactions and by maintaining a high surface area under reaction conditions [29].

Carbon deposition (coking). Carbon deposition on the Ni surface occurs via the Boudouard reaction ($2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$) or via methane decomposition ($\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$) under hydrogen-lean or high-temperature conditions. Coking leads to physical blockage of active sites and, in severe cases, to mechanical disruption of the catalyst pellet [4]. Under the H_2 -rich conditions typical of methanation ($\text{H}_2/\text{CO}_2 \geq 4$), carbon deposition is thermodynamically suppressed, but may become relevant during transient periods or at the inlet of the catalyst bed where the local H_2/CO_2 ratio is lowest.

Re-oxidation under ICCM cycling. In integrated capture and methanation cycles, the catalyst is alternately exposed to CO_2 -containing streams (adsorption step) and H_2 streams (methanation/regeneration step). The CO_2 step can partially re-oxidise surface Ni^0 to NiO, reducing the number of metallic sites available for H_2 dissociation during the subsequent methanation step [9]. The extent of re-oxidation depends on the CO_2

partial pressure, the temperature, and the cycle duration, and constitutes a key stability concern specific to ICCM operation that does not arise under continuous steady-state methanation.

Understanding and mitigating these three deactivation pathways is therefore essential for the rational design of stable ICCM cycles based on Ni/Al₂O₃–MgO materials.

2.4 Experimental Data and Discussion

2.4.1 Overview

This chapter presents and interprets the experimental results obtained for CO₂ methanation over a Ni/Al₂O₃–MgO catalyst. A dataset of 162 experimental points was collected by systematically varying the space time $W/F_{\text{CO}_2}^0$ across nine values ranging from 0.168 kg s mol^{−1} to 4.03 kg s mol^{−1}, while the H₂/CO₂ ratio in the feed was additionally varied between 1 and 32 to enable partial-pressure analysis.

2.4.2 Experimental results of methanation

CO₂ conversion versus temperature

The catalytic performance of the Ni-based catalyst was characterised through a series of experiments conducted at fixed space time ($W/F_{\text{CO}_2}^0 \approx 1.34 \text{ kg} \cdot \text{s} \cdot \text{mol}^{-1}$) over a temperature range spanning from 250 to 325 °C, with an H₂/CO₂ feed ratio of 8. The CO₂ conversion profile as a function of temperature is reported in Figure 2.15, and the corresponding CH₄ and CO selectivities are shown in Figure 2.16.

Examination of Figure 2.15 reveals a sigmoidal evolution of CO₂ conversion with increasing temperature, a shape that is characteristic of a kinetically controlled system transitioning progressively toward a thermodynamically limited regime. At 250 °C, the conversion is comparatively modest, reflecting the strong kinetic barrier associated with CO₂ activation on the catalyst surface under these conditions. As temperature increases, the conversion rises steeply, indicating that the intrinsic reaction rate increases faster than equilibrium limitations begin to constrain the system. This behaviour is fully consistent with the Arrhenius dependence of the surface rate constant and with the apparent activation energies reported in the range of 80–110 kJ mol^{−1} for Ni-based methanation catalysts [31, 32]. Importantly, the measured CO₂ conversions remain substantially below the thermodynamic equilibrium values at all temperatures investigated, confirming that the system operates in a kinetically controlled regime throughout the explored window. At the operating conditions of Figure 2.15 ($W/F_{\text{CO}_2}^0 = 1.34 \text{ kg s mol}^{-1}$, $P = 3 \text{ bar}$, H₂/CO₂ = 8), the equilibrium conversions computed from the thermodynamic correla-

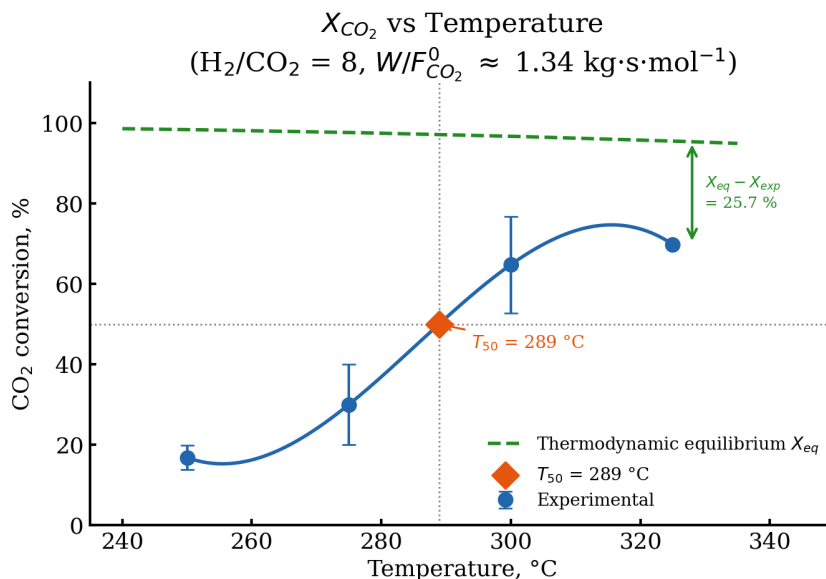


Figure 2.15: CO₂ conversion as a function of temperature at fixed space time ($W/F_{\text{CO}_2}^0 \approx 1.34 \text{ kg} \cdot \text{s} \cdot \text{mol}^{-1}$, $\text{H}_2/\text{CO}_2 = 8$). The orange diamond indicates the temperature at which 50% conversion is achieved ($T_{50} = 288^\circ\text{C}$). The solid line represents a smooth fit to the experimental data.

tion of Aparicio [2] are 97.6 % at 275°C , 96.7 % at 300°C and 95.5 % at 325°C , whereas the corresponding experimental values are 18.5 %, 66.6 % and 69.8 %, respectively gaps of 79, 30 and 26 percentage points. This significant deviation from equilibrium, also visible through the equilibrium curve overlaid on Figure 2.15, unambiguously confirms that the observed conversion profile reflects the intrinsic reaction kinetics rather than thermodynamic limitations. The absence of mass- and heat-transfer artefacts is further confirmed by the criteria presented in Section 2.4.2. A temperature of 50% CO₂ conversion (T_{50}) of approximately 288°C can be identified from the fitted curve, which provides a convenient benchmark for comparing intrinsic catalyst activity.

It is worth noting that the relatively low T_{50} value observed here is at least partly attributable to the high H_2/CO_2 ratio of 8 used in these experiments; a stoichiometric feed ratio of 4 did not allow 50% conversion to be reached within the explored temperature window, which highlights how the large hydrogen excess both thermodynamically shifts the equilibrium and kinetically accelerates the hydrogenation of surface intermediates, including the removal of inhibiting OH and H₂O species from active sites. The comparison with Onrubia-Calvo et al. [31], who report $T_{50} = 303^\circ\text{C}$ for an 8.5 wt.% Ni/CeO₂ catalyst at a stoichiometric H_2/CO_2 ratio of 4, should therefore be interpreted with this difference in operating conditions in mind.

Beyond the kinetic regime, a maximum in CO₂ conversion is observed near 300°C , beyond which the conversion increases modestly from 66.6 % at 300°C to 69.8 % at 325°C (a modest but reproducible decline). This rollover is a direct consequence of the thermody-

namic equilibrium constraint inherent to the Sabatier reaction. Since CO_2 methanation is highly exothermic ($\Delta H_{298\text{ K}}^0 \approx -165\text{ kJ mol}^{-1}$), the equilibrium conversion X_{eq} decreases with increasing temperature: from 96.7% at 300 °C to 95.5% at 325 °C at $P = 3\text{ bar}$ and $\text{H}_2/\text{CO}_2 = 8$ (Figure 2.15). While X_{eq} itself decreases only modestly over this interval, the intrinsic reaction rate accelerates with temperature, driving the system progressively closer to equilibrium and reducing the net forward driving force ($1 - X/X_{\text{eq}}$) that enters the LHHW rate expressions of Section 2.5.1. The apparent decrease in conversion above 300 °C is therefore not indicative of catalyst deactivation, but rather of the equilibrium ceiling being progressively approached, as confirmed by the quantitative gap $X_{\text{eq}} - X_{\text{exp}} = 25.7\%$ that persists even at 325 °C [31, 32]. The additional contribution of the reverse water-gas shift reaction ($\Delta H_{298\text{ K}}^0 \approx +41\text{ kJ mol}^{-1}$), which is endothermic and therefore increasingly at elevated temperatures, diverts part of the converted CO_2 toward CO rather than CH_4 and further reinforces this thermodynamic rationalisation. No replicate measurements were performed at identical operating conditions in the present dataset; the error bars shown in Figure 2.15 therefore represent an estimated measurement uncertainty of $\pm 2\%$ in absolute CO_2 conversion, accounting for the combined contributions of mass flow controller accuracy (1% of full scale), mass spectrometer signal stability, and carbon balance closure, the latter being within 1% for all experimental points reported.

CH_4 and CO selectivity versus temperature

The evolution of CH_4 and CO selectivities with temperature, presented in Figure 2.16 for the same fixed space time ($W/F_{\text{CO}_2}^0 \approx 1.34\text{ kg} \cdot \text{s} \cdot \text{mol}^{-1}$), provides complementary mechanistic insight into the reaction network.

At low temperatures, near 250 °C, CH_4 selectivity is close to 100% and CO selectivity is essentially negligible, confirming that virtually all converted CO_2 is directed toward methane formation. This experimental observation is consistent with the thermodynamic equilibrium, which at $P = 3\text{ bar}$ and $\text{H}_2/\text{CO}_2 = 8$ imposes $S_{\text{CH}_4}^{\text{eq}} \approx 99.6\%$ to 99.9% over the entire temperature range explored a value computed from the coupled methanation and RWGS equilibrium constants and shown as a green dashed line in Figure 2.16. Crucially, however, the experimental S_{CH_4} values lie substantially *below* this thermodynamic ceiling at intermediate and high temperatures, demonstrating that the observed selectivity trend is governed by kinetics rather than thermodynamics. Two concurring kinetic factors explain the high selectivity at low temperature: (i) the RWGS reaction is intrinsically slower than methanation in a hydrogen-rich environment, so that CO intermediates formed on the surface are rapidly hydrogenated before desorbing [32]; and (ii) the large hydrogen excess ($\text{H}_2/\text{CO}_2 = 8$) kinetically accelerates the removal of surface OH^* and H_2O species that would otherwise inhibit the active Ni sites. Symmetrically, the equilibrium

CO selectivity $S_{\text{CO}}^{\text{eq}}$ is virtually zero (0.1 % to 0.4 % over 250 °C to 325 °C), whereas the experimental values reach 10 % to 32 % depending on space time, confirming that CO production is an exclusively kinetic phenomenon driven by the RWGS reaction operating far from its thermodynamic equilibrium.

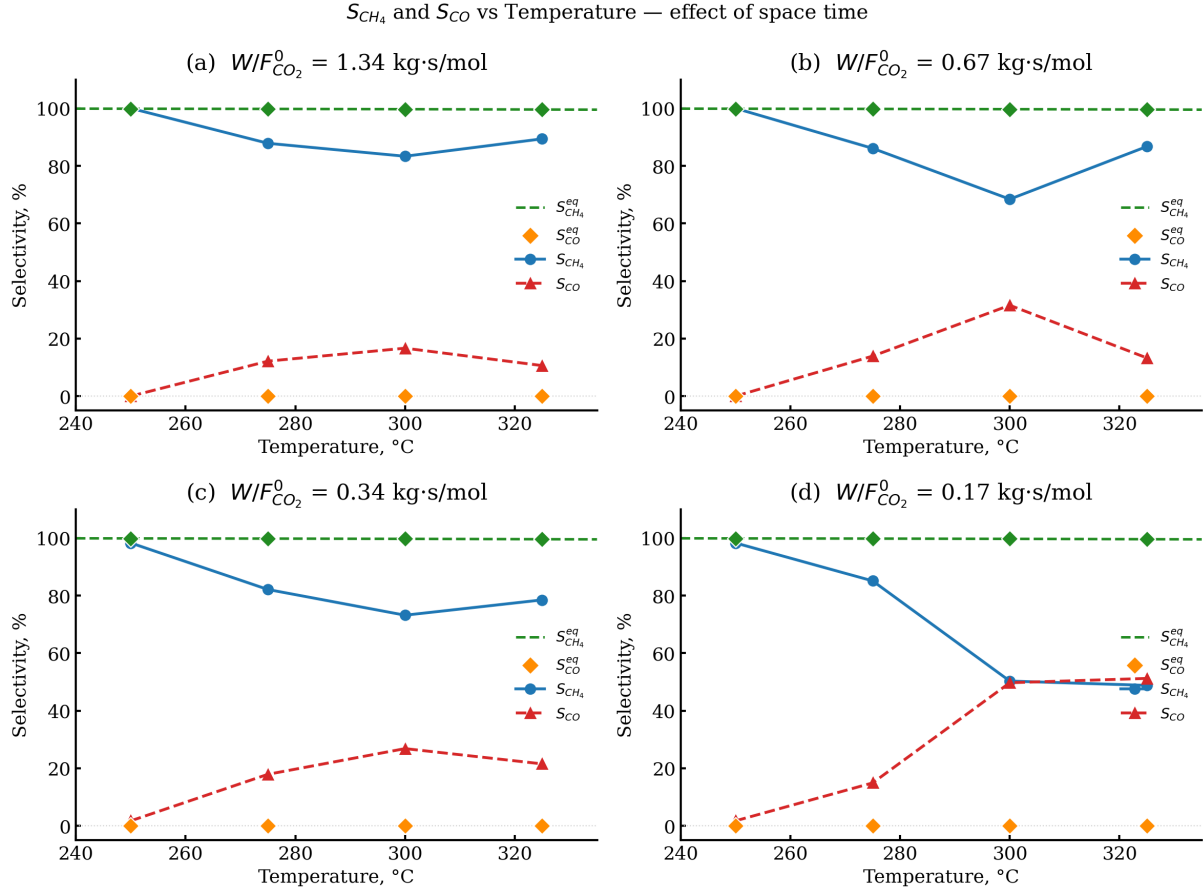


Figure 2.16: CH_4 selectivity (S_{CH_4}) and CO selectivity (S_{CO}) as a function of temperature for four different space times ($W/F_{\text{CO}_2}^0 = 1.34, 0.67, 0.34$ and $0.17 \text{ kg}\cdot\text{s}\cdot\text{mol}^{-1}$). $\text{H}_2/\text{CO}_2 = 8$, $P = 3 \text{ bar}$. The green dashed line indicates the thermodynamic equilibrium selectivity toward CH_4 ($S_{\text{CH}_4}^{\text{eq}} \approx 99.6\% \text{ to } 99.9\%$), computed from the coupled methanation and RWGS equilibrium constants at $P = 3 \text{ bar}$ and $\text{H}_2/\text{CO}_2 = 8$. The large gap between the experimental S_{CH_4} curves and the equilibrium line confirms that selectivity is controlled by kinetics rather than thermodynamics over the entire temperature range investigated.

At low temperatures, near 250 °C, CH_4 selectivity is close to 100% and CO selectivity is essentially negligible, confirming that virtually all converted CO_2 is directed toward methane formation. This high selectivity is consistent with two concurring factors: (i) the thermodynamic equilibrium strongly favours CH_4 over CO at low temperatures; and (ii) the RWGS reaction is intrinsically slower than methanation in a hydrogen-rich environment, so that CO intermediates formed on the surface are rapidly hydrogenated before desorbing [32].

As temperature increases toward 300 °C, CH_4 selectivity deteriorates progressively while

CO selectivity rises. This crossover is physically meaningful: the RWGS reaction ($\Delta H_{298\text{ K}}^0 \approx +41\text{ kJ mol}^{-1}$) is endothermic and therefore increasingly favoured at elevated temperatures, while the exothermic methanation pathway becomes progressively penalised. The transition between the two regimes occurs in the 275 °C to 300 °C range, consistent with literature observations for similar Ni-based catalysts [32, 14].

A partial recovery of CH₄ selectivity is observed at the highest temperatures explored (around 325 °C). This non-monotonic behaviour is most naturally interpreted through the sequential nature of the reaction network: CO produced via RWGS can itself serve as a substrate for CO methanation ($\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$), partially restoring the CH₄ yield. This secondary hydrogenation of CO is discussed further in Section 2.4.2, where the space-time dependence of CO selectivity provides direct experimental support for this interpretation. An alternative contribution may arise from the differential temperature sensitivity of the two rate constants: if the methanation rate constant increases faster than the RWGS rate constant over the 300 °C to 325 °C interval, the net selectivity toward CH₄ could transiently recover even in the absence of CO re-methanation. These two effects are not mutually exclusive and their relative importance could be resolved by targeted experiments at varying H₂/CO₂ ratios, which are planned as part of the next experimental campaign.

From a process perspective, the optimal operating temperature for SNG production under the present conditions lies in the 250 °C to 275 °C range, where the combination of acceptable CO₂ conversion and near-complete CH₄ selectivity is achieved.

Influence of space time on selectivity

The effect of space time on CH₄ and CO selectivities, shown in Figure 2.16 for four values of $W/F_{\text{CO}_2}^0$, provides additional mechanistic insight. At the highest space time ($W/F_{\text{CO}_2}^0 = 1.34\text{ kg s mol}^{-1}$), CH₄ selectivity remains close to 100% over the entire temperature range, indicating that the catalyst bed length is sufficient to allow secondary hydrogenation of CO intermediates before they exit. It should be noted, however, that this operating regime is not well-suited for measuring the intrinsic kinetics of reactions involving CO as a primary species, namely the RWGS reaction and CO methanation. At high space times, CO intermediates formed via RWGS are almost entirely re-hydrogenated to CH₄ within the catalyst bed before reaching the reactor outlet, so that the measured CO outlet flow is too small to provide reliable kinetic information on these secondary pathways. The partial pressure experiments reported in Section 2.4.2 were therefore conducted under differential conditions at lower space times ($W/F_{\text{CO}_2}^0 = 0.17\text{ kg s mol}^{-1}$), where CO selectivity reaches 15 % to 50 % depending on temperature (panels (c) and (d) of Figure 2.16), providing a measurable and meaningful signal for CO formation kinetics. The LHHW model selected in Section 2.5.1 explicitly accounts for the coupled methanation and RWGS pathways,

and its kinetic parameters were estimated from the full dataset spanning all four space times, thereby capturing both CH₄-dominated and CO-rich regimes simultaneously. In contrast, at the lowest space time ($W/F_{\text{CO}_2}^0 = 0.17 \text{ kg s mol}^{-1}$), CH₄ and CO selectivities approach comparable values near 300 °C, demonstrating that the short residence time prevents complete hydrogenation of CO intermediates.

This strong dependence of CO selectivity on space time directly supports the sequential nature of the reaction network: CO appears as a primary intermediate that is further hydrogenated to CH₄ along the catalyst bed, rather than as a thermodynamic endpoint. This interpretation is consistent with the kinetic modelling framework proposed for Ni/Al₂O₃ catalysts, in which CO plays an explicit role as a reactive intermediate [32, 14]. At $W/F_{\text{CO}_2}^0 = 0.17 \text{ kg s mol}^{-1}$ and 300 °C, the CO selectivity reaches approximately 15–20%, implying that a substantial fraction of CO formed via RWGS desorbs before being hydrogenated, a kinetic limitation that also rationalises the partial CH₄ selectivity recovery at 325 °C discussed in Section 2.4.2. These observations strongly motivate the use of mechanistic kinetic models that describe CO formation and consumption simultaneously, rather than lumped single-reaction power-law expressions.

Effect of partial pressure on the CO₂ methanation rate

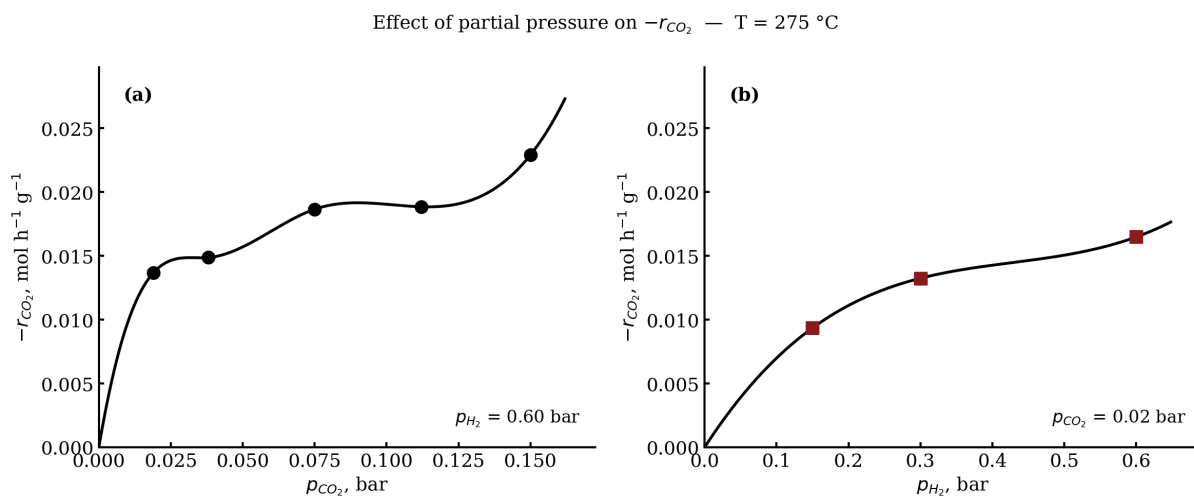


Figure 2.17: Effect of partial pressure on the CO₂ disappearance rate ($-r_{\text{CO}_2}$) at $T = 275 \text{ }^\circ\text{C}$ under differential reactor conditions. (a) Influence of CO₂ partial pressure at fixed $p_{\text{H}_2} = 0.60$ bar. (b) Influence of H₂ partial pressure at fixed $p_{\text{CO}_2} = 0.02$ bar. Symbols represent experimental data points and solid lines represent smooth fits.

The influence of CO₂ and H₂ partial pressures on the CO₂ disappearance rate was investigated at 275 °C under differential reactor conditions ($X_{\text{CO}_2} < 20\%$), and the results are presented in Figure 2.17. These experiments were designed to isolate the individual contribution of each reactant to the overall reaction rate, while keeping the partial pressure of the other reactant fixed, in a manner consistent with the methodology employed

in analogous kinetic studies on Ni-based catalysts [31, 32]. Under these differential conditions, the CO₂ disappearance rate is approximated as $-r'_{\text{CO}_2} \approx F_{\text{CO}_2}^0 X_{\text{CO}_2}/W$, which represents the average rate over the bed length and constitutes a reliable estimate of the local rate at the inlet partial pressures when conversion remains below 20%.

Panel (a) of Figure 2.17 shows the evolution of $-r_{\text{CO}_2}$ as a function of p_{CO_2} at fixed $p_{\text{H}_2} = 0.60$ bar. At low CO₂ partial pressures, the rate increases steeply with p_{CO_2} , reflecting a strong positive dependence of the reaction rate on CO₂ concentration in this regime. However, as p_{CO_2} increases beyond approximately 0.05 bar, the rate progressively flattens and exhibits a clear saturation tendency, indicating that the CO₂ adsorption sites are approaching saturation. This behaviour is characteristic of a Langmuir-type adsorption mechanism, in which the surface coverage of CO₂-derived intermediates becomes quasi-constant at sufficiently high partial pressures, and is fully consistent with the fractional apparent reaction order in CO₂ typically reported for Ni-based methanation catalysts in this temperature range [31, 32]. It is noteworthy that a slight non-monotonic feature appears around $p_{\text{CO}_2} \approx 0.10$ – 0.12 bar, where the rate momentarily plateaus before resuming its upward trend at the highest pressures tested. This behaviour may reflect a transition between two adsorption regimes, possibly associated with the progressive saturation of the most reactive surface sites followed by the mobilisation of secondary, lower-affinity sites at higher coverage. A similar qualitative behaviour has been reported in the literature for highly active Ni/CeO₂ formulations, where the CO₂ adsorption on CeO₂ oxygen vacancies and on Ni sites can occur in parallel with different affinities [31].

Panel (b) of Figure 2.17 displays the dependence of $-r_{\text{CO}_2}$ on p_{H_2} at fixed $p_{\text{CO}_2} = 0.02$ bar. The rate increases monotonically with p_{H_2} over the entire range explored, without reaching a clear saturation plateau within the tested conditions. This positive and apparently sub-linear dependence on hydrogen partial pressure is consistent with a dissociative Langmuir-type adsorption of H₂ on metallic Ni sites, which would yield a half-order dependence at low coverage and approach zero order at high coverage. The absence of saturation in the H₂ dependence under the present conditions suggests that the Ni surface is not fully covered by dissociated hydrogen atoms, and that H₂ availability remains a kinetically relevant variable. This is in agreement with the observation that hydrogen plays a dual role in the methanation mechanism: it participates directly in the hydrogenation of surface intermediates and also contributes to the removal of strongly adsorbed OH[−] and H₂O species that would otherwise block active sites [31, 32].

Effect of temperature on CO₂ conversion

The effect of temperature on CO₂ conversion as a function of space time is presented in Figure 2.18 for four isothermal experiments conducted between 250 and 325 °C. At all temperatures, the conversion increases monotonically with $W/F_{\text{CO}_2}^0$, reflecting the pro-

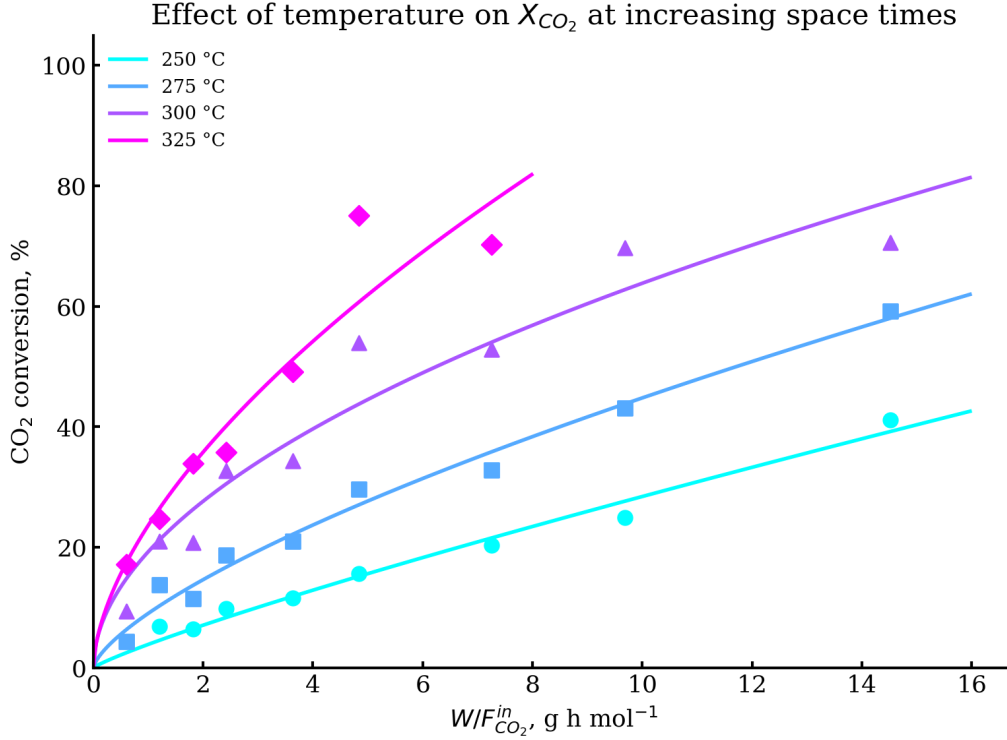


Figure 2.18: Effect of temperature on CO_2 conversion as a function of space time ($W/F_{\text{CO}_2}^0$) at 250, 275, 300 and 325 °C. Symbols represent experimental data points and solid lines represent fits to Equation (2.18). All H_2/CO_2 ratios investigated, $P = 3$ bar.

gressive consumption of CO_2 along the catalyst bed as the residence time of the reactive mixture increases. The curvature observed in each profile, whereby the rate of conversion gain with space time diminishes at high $W/F_{\text{CO}_2}^0$ values, is consistent with the approach toward thermodynamic equilibrium, which increasingly constrains the net forward reaction rate as conversion rises. This behaviour is well-captured by the empirical fitting expression proposed by Onrubia-Calvo et al. [31], which combines a power-law dependence on space time with an explicit saturation toward the thermodynamic equilibrium conversion X_{eq} ,

$$X_{\text{CO}_2} = \frac{\left(W/F_{\text{CO}_2}^0\right)^b}{a + \left(W/F_{\text{CO}_2}^0\right)^b / X_{\text{eq}}} \quad (2.18)$$

where a and b are fitting coefficients and X_{eq} is the equilibrium conversion at the corresponding temperature [31]. The solid lines in Figure 2.18 confirm that this expression reproduces the experimental trends satisfactorily across the entire range of space times and temperatures investigated.

A clear upward shift of the conversion curves is observed as temperature increases from 250 to 325 °C, demonstrating that the intrinsic reaction rate increases significantly over

this temperature interval in accordance with Arrhenius behaviour. At 325 °C and the highest space times tested, the conversion approaches values close to 80%, which suggests that the system is operating in the vicinity of thermodynamic equilibrium under these conditions. Conversely, at 250 °C, the conversion remains below 45% even at the highest space time explored, indicating a predominantly kinetically controlled regime where the intrinsic rate constant is the dominant limiting factor. This distinction between kinetically and thermodynamically controlled regimes is of primary importance for the subsequent determination of intrinsic kinetic parameters, which must be extracted from data points where the influence of equilibrium back-reaction remains limited.

The initial reaction rates $-r_{\text{CO}_2}^0$ at each temperature were estimated directly as $-r_{\text{CO}_2}^0 = X_{\text{CO}_2}/(W/F_{\text{CO}_2}^0)$, using all experimental points with $X_{\text{CO}_2} < 25\%$ regardless of the H_2/CO_2 ratio, so as to maximise the number of data points in the near-differential regime. This approach, consistent with the methodology of Onrubia-Calvo et al. [31] and Quindimil et al. [32], yields between 6 and 13 data points per temperature and is independent of any curve-fitting assumption.

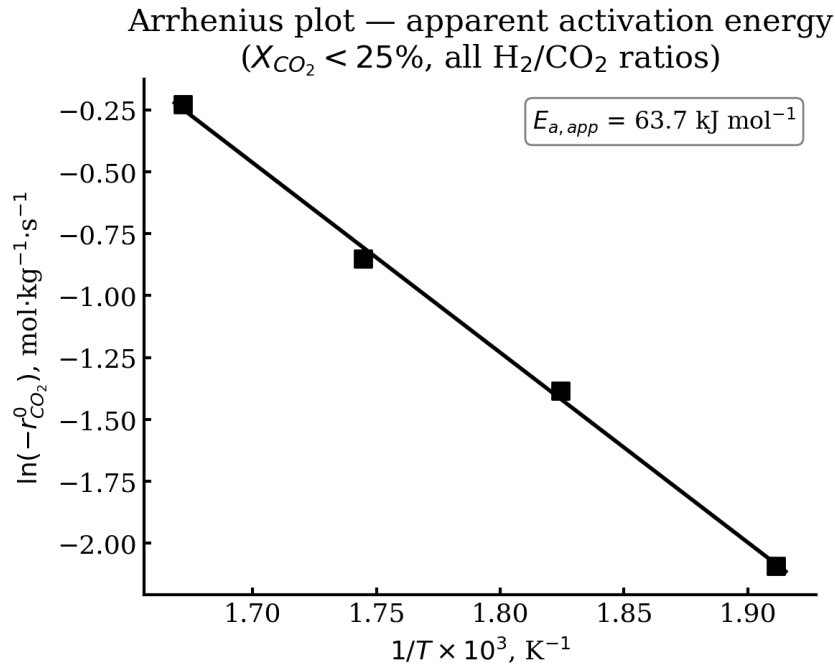


Figure 2.19: Arrhenius plot of the logarithm of the initial CO_2 disappearance rate $\ln(-r_{\text{CO}_2}^0)$ as a function of inverse temperature $1/T$. The apparent activation energy is determined from the slope of the linear regression. Initial rates computed as $-r_{\text{CO}_2}^0 = X_{\text{CO}_2}/(W/F_{\text{CO}_2}^0)$ from all experimental points with $X_{\text{CO}_2} < 25\%$, covering all H_2/CO_2 ratios investigated at $P = 3$ bar.

The Arrhenius plot constructed from these initial rates is presented in Figure 2.19. The quantity $-r_{\text{CO}_2}^0$ represents the overall rate of CO_2 consumption under conditions where the thermodynamic back-reaction is negligible ($p_{\text{H}_2\text{O}} \approx 0$, $p_{\text{CO}} \approx 0$ at the reactor inlet),

so that it reflects primarily the forward methanation rate [31, 32].

The four data points align with excellent linearity over the range $1/T \approx 1.65\text{--}1.91 \times 10^{-3} \text{ K}^{-1}$ ($R^2 = 0.9983$), confirming the absence of transport artefacts (Section 2.4.2) and the absence of a change in rate-determining step over the investigated window. The apparent activation energy is $E_{a,\text{app}} = 63.7 \text{ kJ mol}^{-1}$, which lies at the lower bound of the range reported in the literature for Ni/Al₂O₃-type catalysts (75 kJ mol⁻¹ to 118 kJ mol⁻¹) [32] and is consistent with the range documented for Ni/CeO₂ formulations (53 kJ mol⁻¹ to 113 kJ mol⁻¹) [31]. This relatively low value is physically coherent for the present Ni/Al₂O₃-MgO catalyst: the basic MgO sites are known to facilitate CO₂ chemisorption via surface carbonate formation, which can lower the effective barrier for CO₂ activation relative to unpromoted Ni/Al₂O₃ formulations. It should be noted that $E_{a,\text{app}}$ is described as *apparent* because it reflects a combination of the true activation energy of the rate-determining step and the adsorption enthalpies of species involved in the pre-equilibrium steps; the individual activation energies for each reaction pathway are reported separately in Section 2.5.1 from the LHHW parameter estimation, where they carry greater mechanistic significance.

Verification of the Intrinsic Kinetic Regime

Prior to extracting intrinsic kinetic parameters from the experimental dataset, it is necessary to confirm that the measured CO₂ conversion rates are free from external and internal mass- and heat-transfer artefacts. Three standard dimensionless criteria were evaluated at the most demanding operating conditions of the present study ($T = 325^\circ\text{C}$, $P = 3 \text{ bar}$, $\text{H}_2/\text{CO}_2 = 4$, with a feed composed of 100 NmL min^{-1} CO₂, 400 NmL min^{-1} H₂ and $1500 \text{ NmL min}^{-1}$ Ar ($y_{\text{CO}_2} = 0.05$, total flow $2000 \text{ NmL min}^{-1}$)) which correspond to the highest observed reaction rate and therefore represent the worst case for transport limitations. The catalyst particle size range used in all kinetic experiments is $100 \mu\text{m}$ to $150 \mu\text{m}$; criteria are evaluated at $d_p = 125 \mu\text{m}$ (centre of the sieve cut) and $d_p = 150 \mu\text{m}$ (upper bound) as a conservative check.

The observed CO₂ disappearance rate at these conditions is estimated from the experimental data as

$$-r'_{\text{obs}} = \frac{F_{\text{CO}_2}^0 X_{\text{CO}_2}}{W} = \frac{y_{\text{CO}_2} F_{\text{tot}} X_{\text{CO}_2}}{W} \approx 0.45 \text{ mol kg}_{\text{cat}}^{-1} \text{ s}^{-1}, \quad (2.19)$$

where $X_{\text{CO}_2} \approx 0.60$ is read from Figure 2.18 at $T = 325^\circ\text{C}$ and $W/F_{\text{CO}_2}^0 = 1.34 \text{ kg s mol}^{-1}$.

Weisz–Prater criterion (internal mass transfer). The Weisz–Prater number [32, 14],

$$C_{WP} = \frac{(-r'_{\text{obs}}) \rho_p R_p^2}{D_{\text{eff}} C_s} < 1, \quad (2.20)$$

assesses whether intraparticle diffusion of CO_2 is rate-limiting. Here $\rho_p = 1800 \text{ kg m}^{-3}$ is the particle density (typical for $\text{Ni}/\text{Al}_2\text{O}_3$ pellets) and $C_s = y_{\text{CO}_2} P / (RT) = 3.02 \text{ mol m}^{-3}$ is the CO_2 concentration at the external particle surface, approximated by the inlet bulk value. The effective intraparticle diffusivity is $D_{\text{eff}} = (\varepsilon_p / \tau_p) D_{\text{CO}_2, \text{mix}}$, where the mixture diffusivity of CO_2 in the $\text{Ar}/\text{H}_2/\text{CO}_2$ feed was obtained from the Fuller–Schettler–Giddings correlation combined with the Blanc mixing rule at 325°C and 3 bar, yielding $D_{\text{CO}_2, \text{mix}} = 0.21 \text{ cm}^2 \text{ s}^{-1}$. Using representative values $\varepsilon_p = 0.50$ and $\tau_p = 3.0$ for $\text{Ni}/\text{Al}_2\text{O}_3$ pellets [14] gives $D_{\text{eff}} = 3.4 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$. The resulting Weisz–Prater numbers are $C_{WP} = 0.30$ at $d_p = 125 \mu\text{m}$ and $C_{WP} = 0.44$ at $d_p = 150 \mu\text{m}$, both well below unity, confirming the absence of significant intraparticle diffusion limitations.

Mears criterion (external mass transfer). The Mears number [32],

$$C_M = \frac{(-r'_{\text{obs}}) \rho_b R_p}{k_m C_b n} < 0.15, \quad (2.21)$$

assesses the significance of the external film resistance. The bed bulk density is $\rho_b = \rho_p(1 - \varepsilon_b) = 1080 \text{ kg m}^{-3}$ (bed void fraction $\varepsilon_b = 0.40$), $C_b = 3.02 \text{ mol m}^{-3}$ is the bulk CO_2 concentration, and $n = 0.5$ is the apparent reaction order in CO_2 determined in Section 2.4.2. The external mass-transfer coefficient k_m was estimated using the Wakao–Funazkri correlation ($Sh = 2 + 1.1 Re^{0.6} Sc^{1/3}$) applied to the annular reactor cross-section ($D_h = 3.94 \text{ mm}$, superficial velocity $u_s \approx 50 \text{ cm s}^{-1}$), giving $Re = 4.1$, $Sc = 0.74$, $Sh = 4.3$ and $k_m = 0.71 \text{ m s}^{-1}$ at $d_p = 125 \mu\text{m}$. The resulting Mears numbers are $C_M = 0.028$ at $d_p = 125 \mu\text{m}$ and $C_M = 0.038$ at $d_p = 150 \mu\text{m}$, both well below 0.15, confirming negligible external film resistance under the present operating conditions.

Anderson criterion (internal heat transfer). The Anderson number [32],

$$C_A = \frac{|\Delta H_r| (-r'_{\text{obs}}) \rho_p R_p^2}{\lambda_{\text{eff}} T_s} < 0.75 \frac{RT_s}{E_a}, \quad (2.22)$$

checks whether intraparticle temperature gradients are negligible. With $|\Delta H_r| = 165 \text{ kJ mol}^{-1}$, an effective particle thermal conductivity $\lambda_{\text{eff}} = 0.2 \text{ W m}^{-1} \text{ K}^{-1}$, and the apparent activation energy $E_a = 63.7 \text{ kJ mol}^{-1}$ determined in Section 2.4.2, the right-hand threshold evaluates to $0.75 RT_s / E_a = 0.059$. The left-hand side gives $C_A = 0.0043$ at $d_p = 125 \mu\text{m}$ and $C_A = 0.0062$ at $d_p = 150 \mu\text{m}$, more than one order of magnitude below the threshold. This confirms that intraparticle temperature gradients are entirely negligible despite the

high exothermicity of the Sabatier reaction.

Summary. The results of the three criteria are collected in Table 2.10. All dimensionless numbers remain well below their respective thresholds at both particle sizes investigated, confirming that the kinetic data reported in the following sections are free from mass- and heat-transfer artefacts and reflect the intrinsic surface reaction kinetics of the Ni/Al₂O₃–MgO catalyst.

Table 2.10: Summary of transport criteria evaluated at $T = 325\text{ }^{\circ}\text{C}$, $P = 3\text{ bar}$, $H_2/\text{CO}_2 = 4$, $W/F_{\text{CO}_2}^0 = 1.34\text{ kg s mol}^{-1}$ (worst-case conditions). Values are given for the centre ($d_p = 125\text{ }\mu\text{m}$) and upper bound ($d_p = 150\text{ }\mu\text{m}$) of the sieved particle size range.

Criterion	$d_p = 125\text{ }\mu\text{m}$	$d_p = 150\text{ }\mu\text{m}$	Threshold	Status
Weisz–Prater C_{WP}	0.30	0.44	< 1	✓
Mears C_M	0.028	0.038	< 0.15	✓
Anderson C_A	0.0043	0.0062	< 0.059	✓

2.5 Kinetic Modelling and Discussion

2.5.1 LHHW-type kinetic modelling and model discrimination

In order to move beyond the preliminary power-law description and to establish a physically meaningful kinetic representation of the CO₂ methanation reaction over the present catalyst, a Langmuir–Hinshelwood–Hougen–Watson (LHHW) modelling approach was adopted. This methodology, which has been extensively applied to Ni-based methanation catalysts in the literature [31, 32], consists of translating a proposed reaction mechanism into a set of elementary steps, identifying the rate-determining step (RDS) among them, and deriving the corresponding rate expression under the assumption that all other steps are either at quasi-equilibrium or kinetically irrelevant due to low surface coverage of the corresponding intermediates.

$$D(\%) = \sqrt{\frac{\sigma^2}{N}} \frac{1}{\bar{y}} \times 100, \quad (2.23)$$

where σ^2 is the sum of squared residuals, N is the total number of experimental points and $\bar{y}$ is the mean value of the experimental variable. Four reaction mechanisms drawn from the literature were evaluated in the present work and are discussed in sequence below.

The complete set of estimated parameters for each mechanism, together with 95% confidence intervals, Student t -statistics, Fisher F -values and correlation matrices, is reported in Appendix B.

It is worth noting that the dataset intentionally spans both differential and integral reactor conditions, including points at conversions up to 80–90%. This range remains well below the thermodynamic equilibrium ceiling (95 % to 99 % at all temperatures investigated, Section 2.4.2), and is deliberately included because the thermodynamic driving-force term $(1 - Q/K_{\text{eq}})$ embedded in each LHHW rate expression becomes most discriminating between mechanistic hypotheses precisely when the system approaches equilibrium [32, 31]. Restricting the regression to purely differential data would prevent the model from being tested under the conditions where its structural differences are most apparent.

Mechanism 1: Dissociative carbon route

The dissociative carbon route assumes that both H_2 and CO_2 adsorb dissociatively on metallic Ni sites, yielding adsorbed hydrogen atoms H^* and carbonyl species CO^* together with adsorbed oxygen O^* . The carbonyl intermediate subsequently undergoes a second C–O bond dissociation to form adsorbed carbon C^* , which is then sequentially hydrogenated to CH_4 . Adsorbed oxygen is hydrogenated to hydroxyl and ultimately to water. The elementary steps of this mechanism are summarised in Table 2.11.

Table 2.11: Elementary steps of the dissociative carbon route on Ni-based catalysts (single-site description).

Step	Reaction
1	$\text{H}_2 + 2* \rightleftharpoons 2\text{H}^*$ (quasi-equilibrium)
2	$\text{CO}_2 + 2* \rightleftharpoons \text{CO}^* + \text{O}^*$ (quasi-equilibrium)
3	$\text{CO}^* \rightleftharpoons \text{CO}_{(\text{g})} + *$ (quasi-equilibrium)
4	$\text{CO}^* + * \rightleftharpoons \text{C}^* + \text{O}^*$ (RDS)
5	$\text{C}^* + \text{H}^* \rightleftharpoons \text{CH}^* + *$
6	$\text{CH}^* + \text{H}^* \rightleftharpoons \text{CH}_2^* + *$
7	$\text{CH}_2^* + \text{H}^* \rightleftharpoons \text{CH}_3^* + *$
8	$\text{CH}_3^* + \text{H}^* \rightleftharpoons \text{CH}_4^* + *$
9	$\text{CH}_4^* \rightleftharpoons \text{CH}_{4(\text{g})} + *$
10	$\text{O}^* + \text{H}^* \rightleftharpoons \text{OH}^* + *$
11	$\text{OH}^* + \text{H}^* \rightleftharpoons \text{H}_2\text{O}^* + *$ (quasi-equilibrium)
12	$\text{H}_2\text{O}^* \rightleftharpoons \text{H}_2\text{O}_{(\text{g})} + *$

The CO_2 dissociation step (step 4, $\text{CO}^* \rightleftharpoons \text{C}^* + \text{O}^*$) is taken as the rate-determining step, while H_2 and CO_2 adsorption as well as CO desorption and water formation are assumed at quasi-equilibrium [31, 32]. Under these assumptions, the LHHW rate expression takes the form

$$-r_{\text{CO}_2} = \frac{k p_{\text{CO}_2}^{0.5} p_{\text{H}_2}^{0.25} \left(1 - \frac{p_{\text{CH}_4} p_{\text{H}_2\text{O}}^2}{p_{\text{CO}_2} p_{\text{H}_2}^4 K_{\text{eq}}} \right)}{\left(1 + K_{\text{C}_x} p_{\text{CO}_2}^{0.5} p_{\text{H}_2}^{0.25} + \sqrt{K_{\text{H}_2} p_{\text{H}_2}} + K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}} + K_{\text{OH}} \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}^{0.5}} \right)^2}, \quad (2.24)$$

where k is the apparent kinetic constant, K_{H_2} , $K_{\text{H}_2\text{O}}$ and K_{OH} are adsorption constants for hydrogen, water and hydroxyl species, K_{C_x} is a lumped constant for adsorbed carbon intermediates, and K_{eq} is the thermodynamic equilibrium constant of the Sabatier reaction estimated from the empirical expression reported by Aparicio et al. [2].

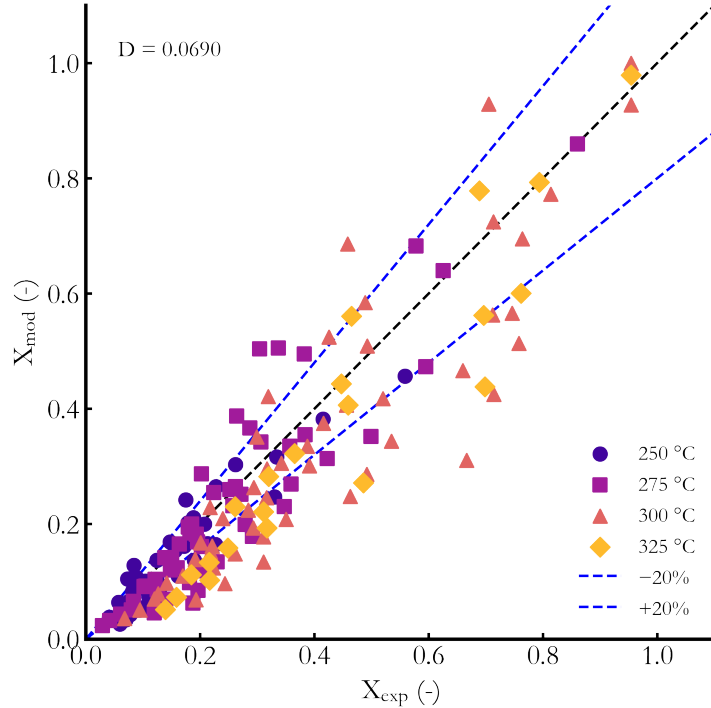


Figure 2.20: Parity plot for the dissociative carbon route (Mechanism 1). Dashed blue lines indicate the $\pm 20\%$ deviation band. Symbols correspond to different operating temperatures: circles (250 °C), squares (275 °C), triangles (300 °C) and diamonds (325 °C). The mean absolute deviation is $D = 6.90\%$; full statistical details in Appendix B.

The parity plot for the dissociative carbon route is shown in Figure 2.20. While a reasonable correlation between experimental and calculated conversions is observed at low conversion values, the model exhibits a clear and systematic underestimation of CO_2 conversion at intermediate and high conversion levels, particularly for the data points collected at 300 and 325 °C. A large fraction of the points at higher conversions lies outside the $\pm 20\%$ deviation band, reflecting the inability of this mechanism to correctly capture the combined effects of temperature and space time in the integral reactor regime. The mean absolute deviation obtained for this mechanism ($D = 6.90\%$) is the largest among the four models evaluated, confirming that the dissociative carbon route does not constitute a satisfactory kinetic description for the present catalyst. Full statistical details are provided in Appendix A.

Mechanism 2: Associative formate route on two active site types

The associative formate mechanism on two active site types proposes that H_2 dissociates on metallic Ni^0 sites (denoted *), while CO_2 is molecularly chemisorbed on surface

hydroxyl groups of the Al_2O_3 support (denoted $\wedge$), forming bicarbonate and carbonate species. These adsorbed species are subsequently hydrogenated by dissociated hydrogen atoms migrating from nearby Ni particles via a spillover mechanism, yielding adsorbed formate intermediates $\text{HCOO}^\wedge$. The hydrogenation of adsorbed $\text{CO}_2^\wedge$ to formate is taken as the rate-determining step, while H_2 dissociative adsorption on Ni, CO_2 adsorption on the support, and water desorption are assumed at quasi-equilibrium. The elementary steps of this mechanism are summarised in Table 2.12.

Table 2.12: Elementary steps of the two-site associative formate mechanism for CO_2 methanation on Ni/ Al_2O_3 . Asterisks (*) denote Ni^0 sites for H_2 dissociation; carets ($\wedge$) denote Al_2O_3 surface hydroxyl sites for CO_2 adsorption (adapted from [31]).

Step	Reaction
1	$\text{H}_2 + 2* \rightleftharpoons 2\text{H}* \quad (\text{quasi-equilibrium})$
2	$\text{CO}_2 + \wedge \rightleftharpoons \text{CO}_2^\wedge \quad (\text{quasi-equilibrium})$
3	$\text{CO}_2^\wedge + \text{H}* \rightleftharpoons \text{HCOO}^\wedge + * \quad (\mathbf{RDS})$
4	$\text{HCOO}^\wedge + \text{H}* \rightleftharpoons \text{CHO}^\wedge + \text{OH}* \quad (\text{quasi-equilibrium})$
5	$\text{CHO}^\wedge + \text{H}* \rightleftharpoons \text{CH}^\wedge + \text{OH}* \quad (\text{quasi-equilibrium})$
6	$\text{CH}^\wedge + 3\text{H}* \rightleftharpoons \text{CH}_4^\wedge + 3* \quad (\text{quasi-equilibrium})$
7	$\text{CH}_4^\wedge \rightleftharpoons \text{CH}_{4(g)} + \wedge \quad (\text{quasi-equilibrium})$
8	$\text{OH}* + \text{H}* \rightleftharpoons \text{H}_2\text{O}* + * \quad (\text{quasi-equilibrium})$
9	$\text{H}_2\text{O}* \rightleftharpoons \text{H}_2\text{O}_{(g)} + * \quad (\text{quasi-equilibrium})$

Under the assumption that steps 1, 2 and 8 are at quasi-equilibrium and that all remaining steps are kinetically irrelevant due to low surface coverage of the corresponding intermediates, the derived LHHW rate expression is

$$-r_{\text{CO}_2} = \frac{k p_{\text{CO}_2} p_{\text{H}_2}^{0.5} \left(1 - \frac{p_{\text{CH}_4} p_{\text{H}_2\text{O}}^2}{p_{\text{CO}_2} p_{\text{H}_2}^4 K_{\text{eq}}} \right)}{\left(1 + \sqrt{K_{\text{H}_2} p_{\text{H}_2}} + K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}} + K_{\text{OH}} \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}^{0.5}} \right) (1 + K_{\text{CO}_2} p_{\text{CO}_2})}, \quad (2.25)$$

where K_{CO_2} is the adsorption constant of CO_2 on the Al_2O_3 surface hydroxyl sites, and the remaining parameters retain their definitions from Equation (2.24). The two-site formulation introduces a factored denominator structure that reflects the independent saturation of the metallic Ni sites on the one hand, responsible for H_2 dissociation and inhibition by water and hydroxyl species, and of the support hydroxyl sites on the other, responsible for CO_2 adsorption. This structural distinction is physically motivated by the well-documented ability of Al_2O_3 to adsorb CO_2 as bicarbonate and carbonate species on its basic surface sites, while metallic Ni particles remain the primary locus for H_2 activation [32].

The parity plot for the two-site formate mechanism is presented in Figure 2.21. Compared to the dissociative carbon route, the scatter of points around the diagonal is reduced, par-

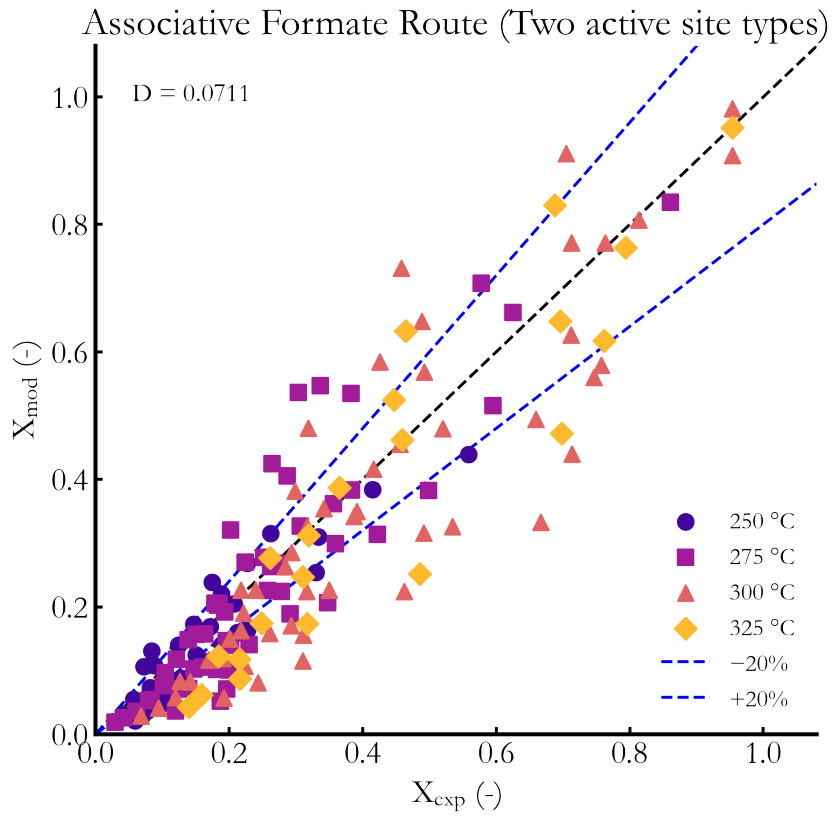


Figure 2.21: Parity plot for the associative formate route on two active site types (Mechanism 2). Dashed blue lines indicate the $\pm 20\%$ deviation band. Symbols correspond to different operating temperatures: circles (250 °C), squares (275 °C), triangles (300 °C) and diamonds (325 °C). The mean absolute deviation is $D = 7.11\%$; full statistical details in Appendix B.

ticularly in the low-conversion region, suggesting that the associative adsorption hypothesis is better suited to describe the kinetic behaviour of the present catalyst. Nevertheless, a non-negligible systematic deviation persists at intermediate and high conversion values, where the model tends to underestimate the measured conversions for the highest temperature datasets. The mean absolute deviation ($D = 7.11\%$) is intermediate, and full statistical details are provided in Appendix A.

Mechanism 3: H-assisted CO formation route

The H-assisted CO formation route, first proposed by Quindimil et al. for a low-loaded Ni/Al₂O₃ catalyst [32], proposes that CO₂ is first stored as bicarbonate and carbonate species on surface hydroxyl groups, which are subsequently hydrogenated to formate intermediates via H⁺ spillover from nearby Ni particles. The formate species then decompose into adsorbed carbonyl CO* and hydroxyl OH* in an H-assisted step that constitutes the rate-determining step. The elementary steps of this mechanism are summarised in Table 2.13.

Table 2.13: Elementary steps of the H-assisted CO formation mechanism for low-loaded Ni/Al₂O₃ (adapted from [32]).

Step	Reaction
1	H ₂ + 2* ⇌ 2H* (quasi-equilibrium)
2	CO ₂ + * ⇌ CO ₂ * (quasi-equilibrium; carbonate/bicarbonate pool)
3	CO ₂ * + H* ⇌ HCOO* + * (quasi-equilibrium)
4	HCOO* + * ⇌ CO* + OH* (RDS, H-assisted CO formation)
5	CO* + H* ⇌ CHO* + *
6	CHO* + H* ⇌ CH* + OH*
7	CH* + 3H* ⇌ CH ₄ * + 3*
8	CH ₄ * ⇌ CH _{4(g)} + *
9	CO* ⇌ CO _(g) + * (quasi-equilibrium)
10	OH* + H* ⇌ H ₂ O* + * (quasi-equilibrium)
11	H ₂ O* ⇌ H ₂ O _(g) + *

The adsorbed CO* produced at step 4 can either be further hydrogenated to formyl and ultimately to CH₄ (steps 5–8), or desorb as gaseous CO (step 9), thereby accounting for the non-zero CO selectivity observed experimentally. The derived LHHW rate expression for CO₂ consumption takes the form

$$-r_{\text{CO}_2} = \frac{k p_{\text{CO}_2} p_{\text{H}_2}^{0.5} \left(1 - \frac{p_{\text{CO}} p_{\text{H}_2\text{O}}}{p_{\text{CO}_2} p_{\text{H}_2} K_{\text{RWGS}}} \right)}{\left(1 + \sqrt{K_{\text{H}_2} p_{\text{H}_2}} + K_{\text{CO}_2} p_{\text{CO}_2} \sqrt{K_{\text{H}_2} p_{\text{H}_2}} + K_{\text{OH}} \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}^{0.5}} + K_{\text{CO}} p_{\text{CO}} \right)^2}, \quad (2.26)$$

where K_{RWGS} is the equilibrium constant of the reverse water–gas shift reaction and K_{CO} is the adsorption constant of CO on the Ni surface. The driving force term explicitly references the RWGS equilibrium, reflecting the fact that CO formation is the primary outcome of the rate-determining step in this mechanism [32].

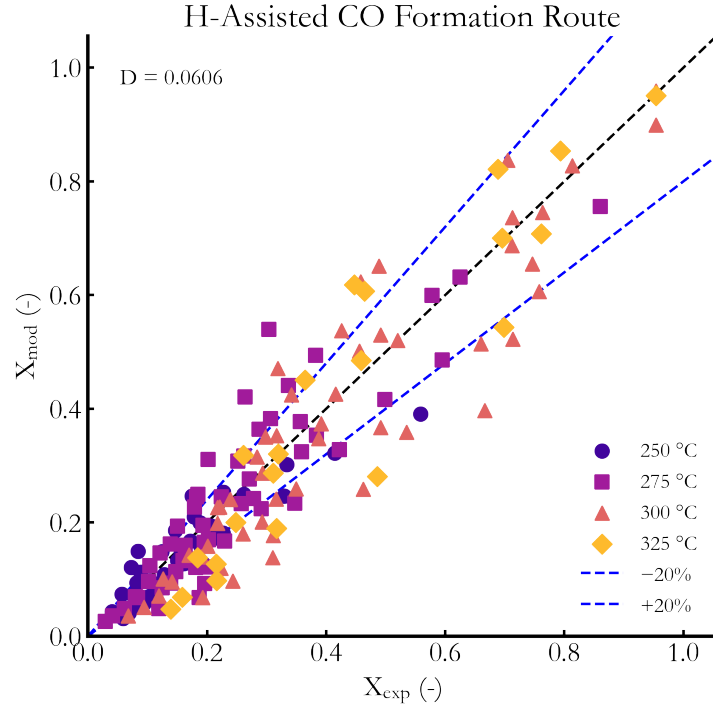


Figure 2.22: Parity plot for the H-assisted CO formation route (Mechanism 3). Dashed blue lines indicate the $\pm 20\%$ deviation band. Symbols correspond to different operating temperatures: circles (250 °C), squares (275 °C), triangles (300 °C) and diamonds (325 °C). The mean absolute deviation is $D = 6.06\%$; full statistical details in Appendix B.

The parity plot for the H-assisted CO formation mechanism is shown in Figure 2.22. A broader scatter of points around the diagonal is observed relative to the two preceding mechanisms, with systematic deviations appearing across the entire conversion range. The model appears to overestimate conversion at intermediate space times for the 300 and 325 °C datasets while underestimating it at low space times, suggesting a structural inadequacy in the way the driving force and the inhibition terms interact under the present operating conditions. This result is consistent with the H-assisted CO formation route having been developed and validated specifically for a low-loaded Ni/Al₂O₃ catalyst operating at higher temperatures where CO selectivity was substantial [32]. The mean absolute deviation ($D = 6.06\%$) and full statistical details are provided in Appendix A.

Mechanism 4: Hybrid route combining direct CO₂ dissociation and H-assisted C–O bond cleavage

The fourth mechanistic hypothesis investigated is the hybrid route proposed by Hernandez Lalinde et al. for Ni/Al₂O₃ catalysts [21]. This mechanism combines elements of both the

dissociative and associative pathways: CO₂ first adsorbs molecularly before undergoing a direct C–O bond dissociation to yield adsorbed CO* and O*, after which the second C–O bond cleavage is facilitated by hydrogen through oxygenated intermediates COH* or COH₂*. The underlying rationale is that the first C–O bond scission is energetically accessible on Ni, while the second bond cleavage benefits from hydrogen assistance, lowering the associated energy barrier. The complete set of elementary steps is reported in Table 2.14.

Table 2.14: Elementary steps of the hybrid mechanism combining direct CO₂ dissociation and H-assisted C–O bond cleavage on Ni/Al₂O₃ (adapted from [21]).

Step	Reaction
AB1	H ₂ + 2* ⇌ 2H*
AB2	CO ₂ + * ⇌ CO ₂ *
AB3	CO ₂ * + * ⇌ CO* + O*
AB4	CO* + H* ⇌ COH* + *
AB5	CO* + 2H* ⇌ COH ₂ * + 2*
AB6	COH* + * ⇌ CH* + O*
AB7	COH* + H* ⇌ CH* + OH* (RDS, model 11)
AB8	COH ₂ * + * ⇌ CH* + OH*
AB9	CH* + H* ⇌ CH ₂ * + *
AB10	CH ₂ * + H* ⇌ CH ₃ * + *
AB11	CH ₃ * + H* ⇌ CH ₄ * + *
AB12	CH ₄ * ⇌ CH _{4(g)} + *
AB13	O* + H* ⇌ OH* + *
AB14	OH* + H* ⇌ H ₂ O* + *
AB15	H ₂ O* ⇌ H ₂ O _(g) + *
AB16	CO* ⇌ CO _(g) + *

Among the family of LHHW expressions derivable from this mechanism, model 11 of Hernandez Lalinde et al. was selected for evaluation in the present work [21]. This model assumes that step AB7, the H-assisted dissociation of adsorbed COH* to yield CH* and OH*, constitutes the rate-determining step. Under the assumption that all adsorption and desorption steps as well as the preceding surface reactions are at quasi-equilibrium, and that the surface coverages of all intermediates other than the most abundant reaction intermediates (MARI) are negligible, the generalised LHHW rate expression proposed by Hernandez Lalinde et al. takes the form

$$r_{\text{CH}_4} = \frac{k K_{C_x} p_{\text{CO}_2}^a K_{\text{H}_2}^b p_{\text{H}_2}^c p_{\text{H}_2\text{O}}^d \left(1 - \frac{p_{\text{CH}_4} p_{\text{H}_2\text{O}}^2}{p_{\text{CO}_2} p_{\text{H}_2}^4 K_{\text{eq}}} \right)}{\left(1 + K_{C_x} p_{\text{CO}_2}^e K_{\text{H}_2}^f p_{\text{H}_2}^g p_{\text{H}_2\text{O}}^h + \sqrt{K_{\text{H}_2} p_{\text{H}_2}} + K_{\text{OH}} \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}^{0.5}} \right)^i}, \quad (2.27)$$

where the exponents a through i and the identity of the lumped intermediate adsorption

constant K_{C_x} depend on the specific mechanistic hypothesis [21]. For model 11 (step AB7 as RDS, $K_{C_x} \equiv K_{\text{COH}}$), the corresponding parameter set is

$$a = 0.5, \quad b = 0.5, \quad c = 1.0, \quad d = 0, \quad e = 0.5, \quad f = 0.5, \quad g = 0.5, \quad h = 0, \quad i = 2, \quad (2.28)$$

so that the rate expression for model 11 reduces explicitly to

$$r_{\text{CH}_4} = \frac{k K_{\text{COH}} p_{\text{CO}_2}^{0.5} K_{\text{H}_2}^{0.5} p_{\text{H}_2} \left(1 - \frac{p_{\text{CH}_4} p_{\text{H}_2\text{O}}^2}{p_{\text{CO}_2} p_{\text{H}_2}^4 K_{\text{eq}}} \right)}{\left(1 + K_{\text{COH}} p_{\text{CO}_2}^{0.5} K_{\text{H}_2}^{0.5} p_{\text{H}_2}^{0.5} + \sqrt{K_{\text{H}_2} p_{\text{H}_2}} + K_{\text{OH}} \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}^{0.5}} \right)^2}, \quad (2.29)$$

where K_{COH} is the lumped adsorption constant of the COH^* intermediate, which incorporates the equilibrium constants of steps AB1 through AB4 preceding the rate-determining step. The numerator reflects a positive dependence on both CO_2 and H_2 partial pressures, arising from the dual requirement of CO_2 adsorption and dissociation on the one hand, and hydrogen-assisted C–O bond cleavage on the other. The denominator accounts for competitive site blocking by COH^* intermediates, dissociated hydrogen and surface hydroxyl species, the latter introducing the water inhibition term already identified in the power-law analysis [21, 32].

The parity plot for the hybrid mechanism (model 11) is presented in Figure 2.23. A moderate improvement in the distribution of points around the diagonal is observed relative to the preceding mechanisms, with the scatter becoming more homogeneous across the temperature range. The model achieves $D = 5.79\%$, the lowest value among the four mechanisms evaluated, with the most homogeneous distribution of residuals across the full temperature and conversion range. The estimated adsorption parameters are thermodynamically consistent and satisfy the Boudart–Mears–Vannice criteria detailed in Appendix A, to which the reader is referred for the complete parameter table.

2.5.2 Summary of model discrimination results

The performance of the four LHHW mechanistic models evaluated in the present work is summarised in Table 2.15. The models are compared on the basis of the mean absolute deviation D (Equation (2.23)), complemented by a multi-criteria assessment encompassing the systematic bias observed in the parity plots, the physical plausibility of the estimated adsorption parameters, and the mechanistic appropriateness of the model for the $\text{Ni}/\text{Al}_2\text{O}_3\text{--MgO}$ catalyst.

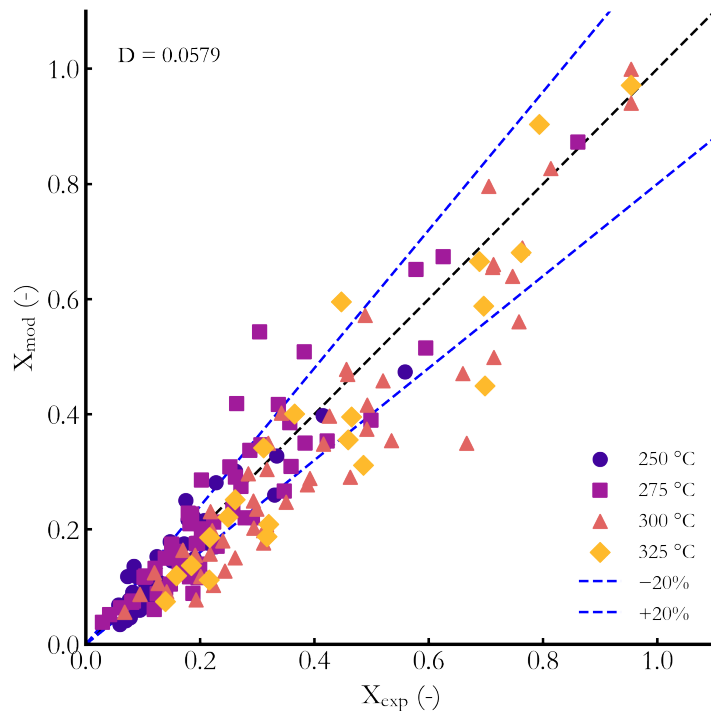


Figure 2.23: Parity plot for the hybrid route with model 11 (Mechanism 4). Dashed blue lines indicate the $\pm 20\%$ deviation band. Symbols correspond to different operating temperatures: circles (250 °C), squares (275 °C), triangles (300 °C) and diamonds (325 °C). The mean absolute deviation is $D = 5.79\%$; full statistical details in Appendix B.

On the basis of the D criterion alone, Mechanism 4 provides the best fit ($D = 5.79\%$), followed by Mechanism 3 ($D = 6.06\%$), Mechanism 1 ($D = 6.90\%$) and Mechanism 2 ($D = 7.11\%$). However, the differences in D between models 1–3 are modest (less than one percentage point), so that the D criterion by itself cannot provide a definitive discrimination. A multi-criteria evaluation is therefore required, as advocated in the literature [32, 31].

The width of the 95% confidence intervals reported in Appendix B provides an additional discrimination criterion. For Mechanisms 1 and 2, several adsorption enthalpies carry confidence intervals exceeding 100 kJ mol^{-1} , indicating that these parameters are not statistically identified and that the corresponding physical interpretation is unreliable. Mechanism 3 similarly suffers from wide confidence intervals on both activation energies and adsorption enthalpies, consistent with the over-parameterisation already identified through the high-correlation analysis. In contrast, Mechanism 4 exhibits the narrowest confidence intervals among the four models: the pre-exponential rate constants $k_{1,0} = 5.00$ and $k_{2,0} = 3.00 \text{ mol kg}^{-1} \text{ s}^{-1} \text{ bar}^{-n}$ are both statistically significant, and the activation energy $E_2 = 153 \text{ kJ mol}^{-1}$ carries a 95% CI of $\pm 108 \text{ kJ mol}^{-1}$. While some adsorption parameters in Mechanism 4 also carry wide intervals (reflecting the limited temperature range of 250 °C to 325 °C investigated) the absence of high-correlation parameter pairs

Table 2.15: Summary of LHHW model discrimination results. RDS: rate-determining step; D : mean absolute deviation between experimental and calculated CO_2 conversions. The physical plausibility column reports whether the estimated adsorption enthalpies are negative and of reasonable magnitude, and whether adsorption entropies lie within acceptable physical limits.

Mechanism	CO_2 adsorption	RDS	Active sites	D (%)	Phys. cons.
1. Dissociative carbon	Dissociative; $\text{CO}^* + \text{O}^*$ on Ni	$\text{CO}^* \rightarrow \text{C}^* + \text{O}^*$	Single (Ni^0)	6.90	Partial
2. Assoc. formate (two-site)	Molecular; bicarbonate / carbonate on Al_2O_3	$\text{CO}_2^{\wedge} + \text{H}^* \rightarrow \text{HCOO}^{\wedge} + *$	$\text{Ni}^0 + \text{Al}_2\text{O}_3$	7.11	Good
3. H-assisted CO formation	Molecular; carbonate / bicarbonate pool	$\text{HCOO}^* + * \rightarrow \text{CO}^* + \text{OH}^*$	Single (Ni^0 + supp.)	6.06	Partial
4. Hybrid, model 11 (AB7 RDS)	Molecular then dissociative on Ni	$\text{COH}^* + \text{H}^* \rightarrow \text{CH}^* + \text{OH}^*$	Single (Ni^0)	5.79	Good

Complete parameter estimates with 95% confidence intervals and statistical tests are provided in Appendix A.

confirms that the over-parameterisation is less severe than in Mechanisms 1–3, and that the parameter estimates are more reliably separated from one another.

From the perspective of systematic bias, Mechanism 4 provides the most homogeneous distribution of residuals across the full conversion range and at all four temperatures, with no clearly identifiable temperature-specific trend in the parity plot. Mechanisms 1 and 2, by contrast, exhibit temperature-dependent positive biases at high conversion that suggest a structural inadequacy in their inhibition terms. Mechanism 3 shows the most heterogeneous residual pattern, with overestimation at intermediate space times for the high-temperature datasets and underestimation at low space times, consistent with its RWGS-oriented driving force being mismatched to the present low-temperature, high-selectivity operating window [32].

From a physicochemical standpoint, the estimated adsorption parameters for Mechanism 4 are thermodynamically consistent (negative exothermic adsorption enthalpies in the range 19 kJ mol^{-1} to 52 kJ mol^{-1} , positive adsorption entropies within acceptable bounds), and the large ratio of activation energies between the methanation and RWGS routes ($E_2/E_1 \approx 153/40.5 \approx 3.8$) provides a quantitative rationalisation of the strong temperature dependence of CH_4/CO selectivity documented in Sections 2.4.2–2.4.3.

The hybrid mechanism is also structurally consistent with the known surface chemistry of

Al₂O₃-supported Ni catalysts, where both dissociative and associative adsorption pathways for CO₂ have been documented by in situ DRIFTS [32, 21]. The MgO component of the present Ni/Al₂O₃-MgO catalyst further enriches the surface with basic sites that can adsorb CO₂ as carbonate and bicarbonate species, which is consistent with the molecular pre-adsorption step (AB2) of the hybrid mechanism.

On the basis of the combined statistical, bias, and physicochemical criteria, Mechanism 4 (hybrid route, model 11) is selected as the reference kinetic model for the present catalyst. It is worth emphasising, however, that the close D values of Mechanisms 1–4 leave open the possibility that the other models could become competitive at different operating conditions (particularly lower H₂/CO₂ ratios or higher pressures), and that a definitive mechanistic assignment would require in situ spectroscopic characterisation of the surface intermediates under reaction conditions.

2.6 Conclusions and Outlook

This chapter established the intrinsic kinetic behaviour of the Ni/Al₂O₃-MgO dual-function material under CO₂ methanation conditions, providing the quantitative foundation needed to interpret the material’s catalytic performance and to support future reactor-scale modelling.

The experimental campaign confirmed that the catalyst operates in a kinetically controlled regime throughout the 250–325 °C window, with a T_{50} of 288 °C under H₂/CO₂ = 8. The selectivity analysis revealed that CO is not a thermodynamic endpoint but a reactive intermediate whose fate (further hydrogenation to CH₄ or desorption) is governed by space time and temperature. This behaviour, together with the fractional positive orders in both CO₂ and H₂ and the strong negative dependence on water, defines the kinetic fingerprint of the catalyst and constrains the class of admissible rate expressions.

Among the four LHHW mechanisms evaluated, the hybrid associative/dissociative route was selected as the reference model on statistical and physicochemical grounds. More than a fitting exercise, this result carries a mechanistic message: CO₂ activation on this catalyst involves both molecular pre-adsorption on basic surface sites (consistent with the MgO-rich support) and hydrogen-assisted C–O bond cleavage at the Ni surface. The strong temperature sensitivity of CH₄/CO selectivity is a direct consequence of the large difference in activation energies between the methanation and RWGS pathways.

Looking ahead, the narrow temperature window explored limits the statistical identification of the kinetic parameters, and extending the campaign to a wider range of conditions would strengthen the mechanistic assignment. In situ spectroscopic characterisation under reaction conditions would further constrain the surface chemistry picture suggested by

the modelling results. The selected rate expression, together with the transport criteria verified in this chapter, provides a self-consistent kinetic description that can be directly embedded into a reactor model for the methanation step of an ICCM cycle.

Chapter 3

CO₂ Adsorption

3.1 Introduction and Research Objectives

3.1.1 General background and scope

The capture of CO₂ on a basic oxide such as MgO involves two physically distinct phenomena, and it is useful to draw the distinction from the outset because it shapes the rest of the discussion. The first phenomenon is *surface adsorption*, in which CO₂ interacts with active sites located at the surface of the solid: hydroxyl groups, low-coordination oxygen anions, or metal–oxygen pairs. The interaction can be weak (physisorption, governed by van der Waals forces and reversible at low temperature) or strong (chemisorption, accompanied by the formation of surface carbonates, bicarbonates or carbamates). In both cases, the crystalline structure of the underlying solid is left essentially unchanged, the active sites remain accessible by gas-phase diffusion through the pore network, and the process is well described by classical adsorption models. The second phenomenon is *solid-state carbonation*, a genuine gas–solid chemical reaction in which CO₂ converts the bulk oxide into a new crystalline phase, the carbonate: for MgO, this is $\text{MgO(s)} + \text{CO}_2\text{(g)} \rightleftharpoons \text{MgCO}_3\text{(s)}$. Once a layer of carbonate has nucleated and grown on the outer surface of an oxide grain, further conversion requires the transport of CO₂ (or carbonate ions) *through the solid product layer itself*, not through the pore network. This solid-state diffusion is several orders of magnitude slower than gas-phase or surface diffusion and quickly becomes rate-limiting, so the overall uptake of an MgO sorbent generally proceeds in two steps: a rapid initial regime dominated by surface chemisorption, followed by a much slower regime dominated by product-layer diffusion [18, 42]. Figure 3.1 summarises both regimes schematically.

For process design, the key performance metrics of an oxide capture material include (i) the equilibrium CO₂ uptake, (ii) the selectivity with respect to N₂, H₂O or H₂, (iii) the kinetics of both the surface and bulk regimes, (iv) the cyclic stability and regenerability,

and (v) the mechanical and thermal stability [34]. A wide variety of solids has been investigated, including activated carbons, zeolites, metal–organic frameworks (MOFs), supported amines, alkaline earth metal oxides and alkali ceramics [34, 39]. Among these, MgO-based sorbents are particularly relevant for intermediate-temperature capture (200–400 °C) owing to their high theoretical uptake (24.8 mmol g^{-1}), earth abundance and moderate regeneration temperature [19, 41]. Al_2O_3 , ubiquitous as a catalyst support, also participates in CO_2 uptake through its surface hydroxyl groups, a point of direct relevance for Ni/ Al_2O_3 –MgO materials. The literature review that follows focuses on these oxide-based systems and on the kinetic models used to describe their behaviour in both regimes, with the aim of providing the mechanistic and quantitative foundations needed to interpret the experimental results of Chapter 3. The operating window of the present work falls within two distinct regimes depending on the experimental campaign: the adsorption tests reported in Chapter 4 are conducted at 50–200 °C, where surface chemisorption is the dominant mechanism on the Ni/ Al_2O_3 –MgO material, while the methanation tests reach up to 350 °C, where partial conversion of MgO into MgCO_3 cannot be excluded on the time scales of a single half-cycle.

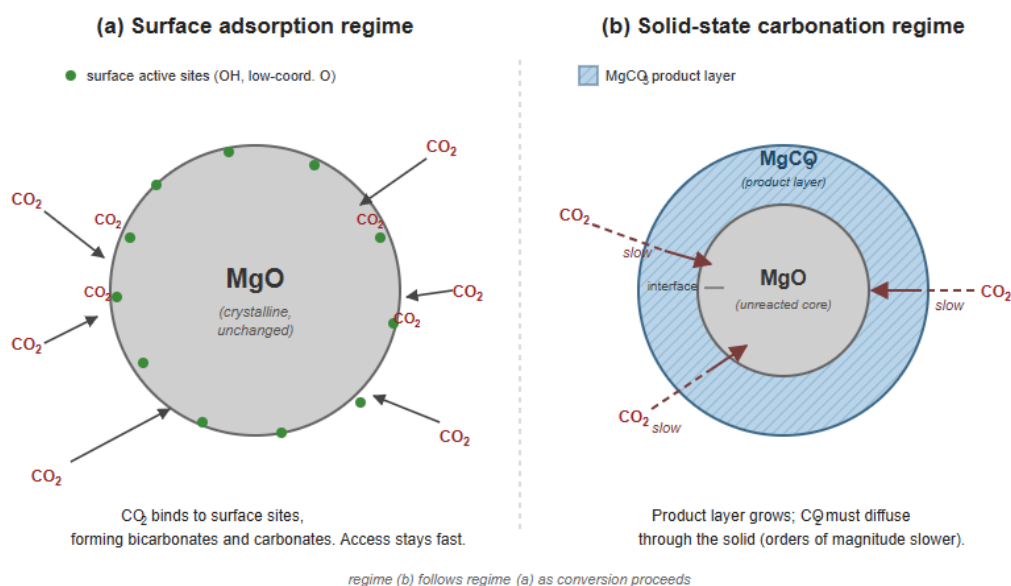


Figure 3.1: Schematic comparison of the two CO_2 capture regimes relevant for MgO-based sorbents. **Left:** surface adsorption regime. CO_2 diffuses through the pore network and binds to surface OH groups or low-coordination oxygen anions, forming bicarbonate or carbonate species without modifying the crystalline structure of the underlying oxide. The active sites remain accessible and the process is reversible. **Right:** solid-state carbonation regime. Surface chemisorption nucleates a MgCO_3 layer that grows outward; further conversion of the underlying MgO requires CO_2 (or carbonate ions) to diffuse *through the solid product layer*, which is orders of magnitude slower than pore diffusion. Adapted from [18] and [42].

3.2 Experimental Set-up

3.2.1 Catlab microreactor unit

A schematic representation of the CATLAB setup is given in Fig. 3.2. The unit consists of a microreactor module coupled to a gas distribution and pulse injection system, with the QGA 2.0 mass spectrometer connected directly to the reactor outlet for online analysis of the effluent.

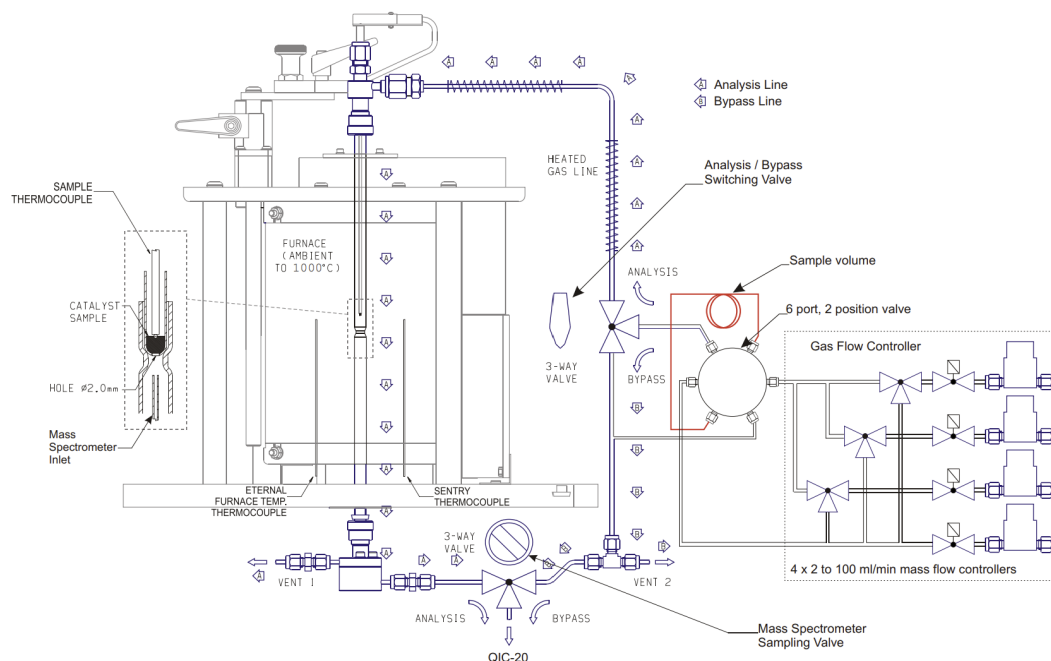


Figure 3.2: Schematic representation of the CATLAB setup. Argon and CO₂ are supplied from pressurised cylinders and regulated by three mass flow controllers: MFC-3 sets the CO₂ feed to the pulse injection loop, while MFC-2 and MFC-4 independently control the two argon branches (one feeding the pulse loop, the other delivering the carrier gas to the reactor inlet). The gas mixture is injected into the quartz microreactor housed in the heated module, and the effluent is routed to the Hiden QGA 2.0 mass spectrometer for online analysis.

Reactor

The second part of the experiments was carried out using a *CATLAB* system manufactured by *Hiden*. The reactor is a quartz reactor measuring 10 cm in length and 1 cm in internal diameter. A thermocouple was also placed inside the tube to ensure that the reactor maintained the correct temperature.

Gases feed

Argon and CO₂ were used as process gases. Both gases were supplied from 50 L cylinders, with the pressure in each line regulated to 3 barg by means of two pressure controllers

arranged in series. The argon stream was subsequently split into two outlet lines: one for dilution of the CO₂ stream and the other serving as the carrier gas.



Figure 3.3: Argon and CO₂ cylinders supplying the CATLAB setup.

Mass flow controllers

Gas flow control is ensured by three mass flow controllers (MFCs), all operating within a range of 3–100 mL/min (standard conditions). MFC-3 regulates the CO₂ feed to the pulse loop, while MFC-2 and MFC-4 independently control the two argon branches, one supplying the pulse loop and the other delivering a continuous carrier gas stream to the reactor inlet.

Mass Spectrometer

Downstream of the reactor, effluent gases are routed directly to the Hiden QGA 2.0 mass spectrometer for continuous online analysis. The QGA 2.0 monitors selected m/z ratios in real time, allowing quantification of product formation across each pulse event.

3.2.2 Catalyst Used

The catalyst used is described in Chapter 2, Section 2.2.



Figure 3.4: Gas distribution panel of the CATLAB system, showing the connections between the CATLAB and the gas line.

3.2.3 Reactor Loading

The CATLAB reactor operates with an undiluted catalyst bed and follows a simplified packing configuration compared to the micro-fixed bed reactor unit. The smaller reactor volume and tighter dimensional tolerances of the CATLAB system require particular attention to bed compactness and layer uniformity.

Loading starts with the introduction of 1.5 cm of quartz wool at the bottom of the reactor. This initial wool plug provides both mechanical support for the catalyst bed above it and a degree of gas flow pre-distribution before the active zone. The quartz wool must be packed firmly but not so tightly as to create an excessive pressure drop across this entry section.

The catalyst bed is then loaded directly onto the quartz wool support. In the CATLAB configuration, the bed consists exclusively of pure $\text{Ni}/\text{Al}_2\text{O}_3\text{--MgO}$ catalyst, without any inert diluent. The loading quantity and bed length shall be defined in the specific experimental test sheet. Once the catalyst charge has been introduced, the bed is secured from

above by the addition of 1 cm of quartz wool, which is packed on top of the catalyst to prevent movement of the bed during gas flow and to retain the catalyst particles within the isothermal zone of the reactor.

As with the micro-fixed bed reactor, rigorous attention must be paid to the levelness of each packed layer and to the perpendicularity of the bed relative to the reactor axis throughout the loading procedure. Following the addition of each layer (the bottom quartz wool, the catalyst charge, and the top quartz wool) the operator must verify that the exposed surface is flat and uniformly distributed across the full diameter of the reactor tube. Any tilt or irregularity in the bed profile is liable to introduce asymmetric flow patterns, reduce effective catalyst utilisation, and compromise the quality and reproducibility of the experimental results.

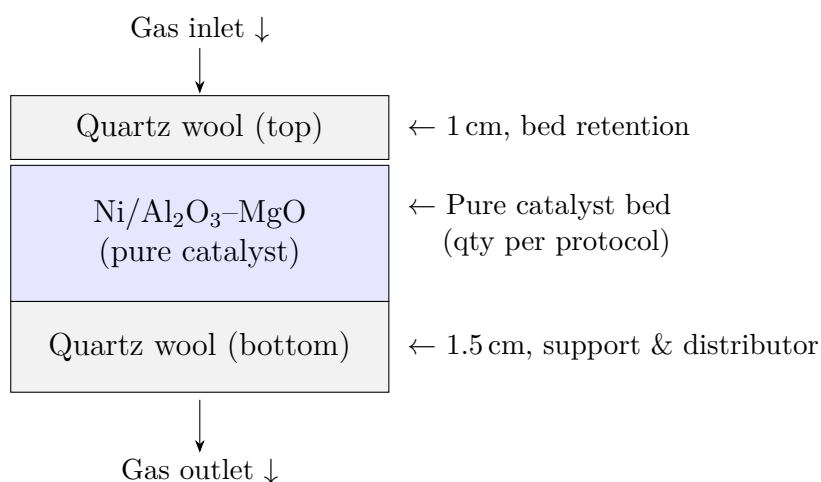


Figure 3.5: Pure catalyst bed configuration.

3.2.4 Experimental setup

In the CATLAB setup, the gas outlet from the cylinder is split into two streams: one is mixed with CO₂, and the other goes directly to the reactor, as shown in the P&ID (as shown in 3.2). The Ar-CO₂ mixture is sent through the loop to be fed into the reactor with each pulse. Meanwhile, the other Argon line flows into the reactor as a carrier gas. At the reactor outlet there is a mass spectrometer used for analysis.

3.2.5 Pulse-injection protocol

Calibration

No external calibration of the QGA 2.0 mass spectrometer was performed for the CATLAB experiments. Instead, quantification relied on the use of a calibrated injection loop of fixed volume, operated at known temperature and pressure. Under these conditions, the molar

amount of CO₂ injected at each pulse is fully determined and reproducible from one pulse to the next, so that the mass spectrometer signal can be referenced to this known quantity rather than to an external standard.

A reference signal is acquired by sending pulses through the system under conditions in which no adsorption occurs (bypass mode, or empty bed at room temperature). For each reference pulse, the mass spectrometer signal at $m/z = 44$ is recorded as a function of time, and the corresponding peak area is obtained by integrating the partial pressure of CO₂ over the full duration of the pulse response, from the onset of the peak above baseline to its return to baseline:

$$A_{\text{ref}} = \int_{t_0}^{t_1} [p_{\text{CO}_2}(t) - p_{\text{base}}] dt, \quad (3.1)$$

where p_{base} is the local baseline immediately preceding the pulse and $[t_0, t_1]$ brackets the pulse response. Since the loop volume, temperature and pressure are held constant, A_{ref} is proportional to the known molar content of the loop and constitutes the reference quantity to which all adsorption pulses are normalised.

During an adsorption experiment, the peak area A_{sample} recorded after contact with the catalyst is lower than A_{ref} , the difference reflecting the fraction of CO₂ retained on the surface. The adsorbed fraction at each pulse is therefore defined as

$$f_{\text{ads}} = 1 - \frac{A_{\text{sample}}}{A_{\text{ref}}}, \quad (3.2)$$

and the corresponding adsorbed amount is obtained by multiplying f_{ads} by the known molar content of the loop. For instance, a pulse area equal to 50 % of A_{ref} corresponds to 50 % of the injected CO₂ being adsorbed, whereas a pulse area at 25 % of A_{ref} indicates 75 % adsorption.

The use of integrated peak areas rather than peak heights is essential because the shape of the pulse response is not preserved across operating conditions. The width and symmetry of each peak depend on the carrier gas flow rate, on the residence-time distribution in the bed and on the adsorption kinetics themselves, all of which broaden or sharpen the pulse without changing the total amount of CO₂ reaching the detector. Only the time-integral of the partial pressure signal is proportional to the number of moles of CO₂ effectively eluted from the reactor; peak heights, by contrast, may differ significantly between two pulses carrying the same total amount of CO₂ if their dispersion in the bed differs. Quantification via $A_{\text{sample}}/A_{\text{ref}}$ is therefore the only formulation consistent with a mass balance on the pulse.

This procedure is based on three assumptions, which are considered valid in the operating range explored in this work:

1. the mass spectrometer response is linear with respect to the CO_2 partial pressure;
2. the amount of CO_2 delivered by the loop is reproducible from pulse to pulse, since the loop volume, temperature and pressure are held constant;
3. the reference area A_{ref} corresponds to zero adsorption, i.e. the totality of the injected CO_2 reaches the detector.

Tests

The objective of the CATLAB experiments is not only to quantify the amount of CO_2 adsorbed by the catalyst, but more importantly to extract the adsorption kinetics, which is a significantly more challenging task. The pulse-injection technique is well suited to this purpose, since each pulse delivers a fixed dose of CO_2 to a surface whose state of saturation evolves from pulse to pulse.

Each experiment consists of a series of 40 pulses of a defined CO_2 /argon mixture, conducted at a fixed temperature and a fixed carrier gas flow rate. Once the reactor has reached the target temperature, a one-hour stabilization period is observed to make sure the temperature does not fluctuate and skew the data. In some runs, after the 40 pulses have been delivered, a temperature-programmed desorption is performed by increasing the temperature in order to analyze catalyst desorption. The outlet partial pressure of CO_2 is recorded by the QGA 2.0 mass spectrometer, which allows for the calculation of the amount of CO_2 adsorbed and desorbed by the catalyst.

3.3 Kinetic Modelling Methodology

3.3.1 Surface species formed upon CO_2 adsorption on basic oxides

When CO_2 contacts a basic oxide surface such as MgO or Al_2O_3 , it reacts with surface oxygen anions (O^{2-}) and hydroxyl groups (OH) to form a family of chemisorbed carbonate and bicarbonate species whose nature depends on the local basicity and coordination geometry of the adsorption site. Three main families are classically distinguished by infrared spectroscopy [24, 13]:

- **Monodentate (unidentate) carbonates:** formed on strongly basic, low-coordination O^{2-} sites (corners, edges, steps of MgO crystallites) through a single C–O bond with a surface oxygen. These species exhibit high adsorption enthalpies (typically -100 to -150 kJ mol^{-1}) and require temperatures above $300\text{--}400^\circ\text{C}$ for full desorption.
- **Bidentate and bridged carbonates:** formed on adjacent cation–anion pairs at the surface through two C–O bonds. Bidentate species coordinate through one

surface oxygen and one metal cation, while bridged species involve two adjacent metal sites. Their stability is intermediate ($\Delta H_{\text{ads}} \approx -60$ to -100 kJ mol^{-1}), and they desorb in the 200–350 °C range.

- **Surface bicarbonates:** formed by reaction of CO_2 with surface OH groups on weakly basic sites. These are the most labile species ($\Delta H_{\text{ads}} \approx -20$ to -60 kJ mol^{-1}) and desorb below 200 °C, making them particularly relevant for the 50–200 °C operating window of the present work. Unlike the carbonate species shown in Figure 3.6, bicarbonates involve a surface OH group rather than a bare oxygen anion, and are therefore more abundant on hydroxylated surfaces such as Al_2O_3 .

The structural geometries of the monodentate, bidentate and bridged carbonate families are illustrated in Figure 3.6.

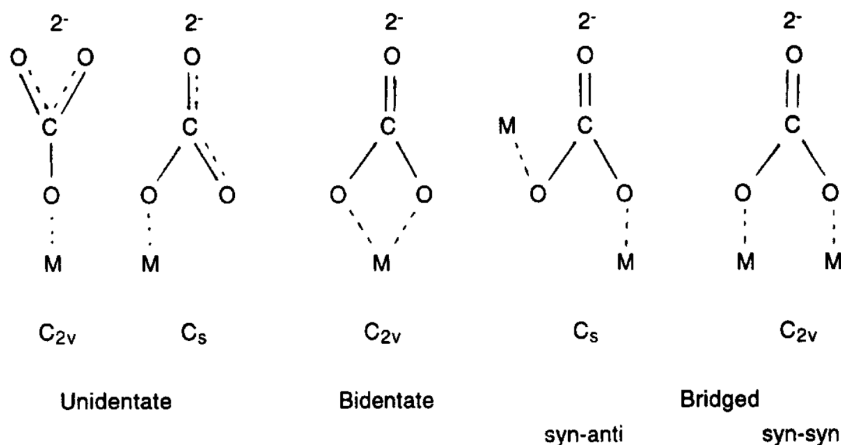


Figure 3.6: Structural representation of the main surface carbonate species formed upon CO_2 adsorption on metal oxide surfaces: monodentate (unidentate), bidentate and bridged carbonates, classified by their coordination geometry and local symmetry (C_{2v} or C_s). Note that surface bicarbonates, which form on hydroxylated sites and are not represented here, constitute a fourth family of adsorbed species discussed in the text. Adapted from Lavalley [24].

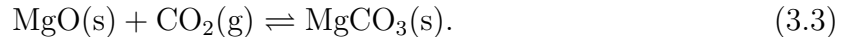
MgO is an energetically heterogeneous surface presenting all three types of sites, whose relative abundance depends on crystal morphology, calcination history and surface area [5, 8]. Microcalorimetric measurements on well-defined MgO samples reveal a broad distribution of differential adsorption heats ranging from approximately 150 kJ mol^{-1} at zero coverage (strongest sites) down to $20\text{--}40 \text{ kJ mol}^{-1}$ as saturation is approached [5]. This heterogeneity has a direct consequence for the interpretation of temperature-dependent capacity data: an apparent adsorption enthalpy derived from a van 't Hoff analysis of capacity versus temperature represents a coverage-weighted average over the entire site distribution, biased towards the moderate- and low-affinity sites that dominate at elevated temperature [5].

On Al_2O_3 , CO_2 adsorbs predominantly on surface hydroxyl groups (terminal AlOH ,

bridging Al_2OH and triply bridging Al_3OH) to form bicarbonate species, with adsorption enthalpies in the range -30 to -70 kJ mol^{-1} depending on the OH type [28, 16]. Temperature-programmed desorption (TPD) experiments on $\gamma\text{-Al}_2\text{O}_3$ show a desorption peak centred between 100 and 250°C , overlapping with the experimental window of the present work and confirming that Al_2O_3 contributes non-negligibly to CO_2 uptake on $\text{Ni}/\text{Al}_2\text{O}_3\text{-MgO}$ catalysts [28, 32]. In situ DRIFTS experiments on $\text{Ni}/\text{Al}_2\text{O}_3$ under CO_2 -containing atmospheres indeed reveal intense bicarbonate and carbonate bands on the support, alongside weaker bands associated with Ni-bound carbonyl species [32]. This dual contribution (MgO providing carbonate/bicarbonate sites over a wide enthalpy range and Al_2O_3 providing additional, more labile bicarbonate sites) shapes the overall adsorption behaviour of the composite material studied experimentally in Chapter 3.

3.3.2 Thermodynamic background for MgO carbonation

The global carbonation reaction of MgO can be written as



Using standard formation enthalpies and entropies, Gao et al. showed that the standard Gibbs free energy of reaction can be expressed as [19]

$$\Delta_r G_m^\circ(T) = \Delta_r H_m^\circ - T \Delta_r S_m^\circ \approx -100.7 \text{ kJ mol}^{-1} + T \times 175.0 \text{ J K}^{-1} \text{ mol}^{-1}. \quad (3.4)$$

At temperatures $T \lesssim 573 \text{ K}$ (300°C) the reaction is thermodynamically favourable ($\Delta_r G_m^\circ < 0$) in pure CO_2 , but becomes increasingly unfavourable at higher temperature [19]. Bare MgO therefore exhibits decreasing CO_2 uptake above approximately 300°C , and the operating window $50\text{--}200^\circ\text{C}$ investigated in the present work falls within the thermodynamically favourable regime where surface carbonation is spontaneous. Molten salt promoters or double carbonate formation (e.g. $\text{Na}_2\text{Mg}(\text{CO}_3)_2$) can shift the effective operating window to higher temperatures by modifying the reaction pathway, as discussed in Section 3.3.4 [19, 41].

3.3.3 CO_2 adsorption on unpromoted MgO and on Al_2O_3 : relevance for $\text{Ni}/\text{Al}_2\text{O}_3\text{-MgO}$ systems

Porous MgO and diffusion-limited adsorption

Song et al. investigated the CO_2 adsorption kinetics of porous MgO obtained by calcination of basic magnesium carbonate at 400°C [34]. The material exhibited a mesoporous structure with pore diameters in the $5\text{--}11 \text{ nm}$ range and a BET surface area of approximately $80 \text{ m}^2 \text{ g}^{-1}$. Under $0.15\text{--}1 \text{ bar}$ CO_2 at 50°C , the adsorption curves showed a charac-

teristic two-stage behaviour: a fast initial uptake followed by a much slower approach to equilibrium over several hours [34].

Equilibrium capacities at 50 °C were approximately 1.8 mol kg^{-1} ($1.80\text{--}1.86 \text{ mol kg}^{-1}$ for 0.15–1 bar CO_2), with weak dependence on CO_2 partial pressure [34]. This weak pressure dependence is consistent with adsorption on a surface approaching saturation at the lowest partial pressures tested, and with the formation of surface carbonate species whose stability is governed more by temperature than by CO_2 pressure in this regime. Fitting with apparent kinetic models showed that the pseudo-second-order (PSO) model provided significantly smaller normalised deviations than the pseudo-first-order (PFO) model, consistent with chemisorption-controlled kinetics in which the overall uptake rate is governed by the surface reaction rather than by external mass transfer alone [34].

To elucidate the rate-limiting steps, the authors applied Boyd’s film-diffusion model and intraparticle diffusion (Weber–Morris) analysis. The Boyd plots did not pass through the origin, indicating a significant contribution of external film diffusion at early times. Intraparticle diffusion plots (q_t vs. $t^{1/2}$) showed two linear regions, confirming a sequential transition from film diffusion control to intraparticle diffusion control at longer times [34]. The narrow pores of porous MgO hinder CO_2 diffusion, leading to long equilibration times (typically $\sim 4 \text{ h}$), and suggest that sufficient mesoporosity is a prerequisite for fast adsorption kinetics in practical applications.

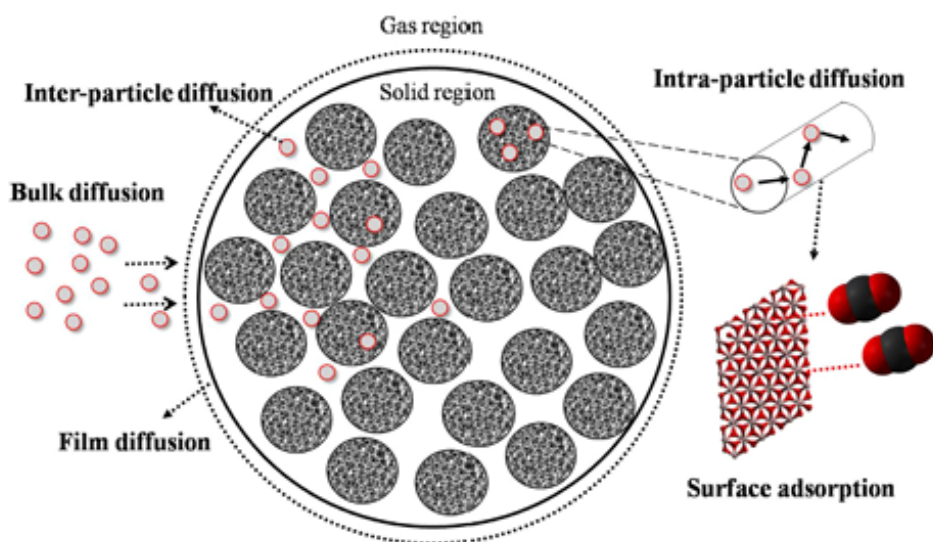


Figure 3.7: Schematic illustration of CO_2 adsorption steps on porous MgO (bulk diffusion, film diffusion, interparticle diffusion, intraparticle diffusion and surface reaction), adapted from Song et al. [34].

At the low temperatures relevant to the present work (50–200 °C), the carbonation of unpromoted MgO proceeds mainly through surface bicarbonate and carbonate formation on accessible sites, with product-layer diffusion becoming rate-controlling only at longer

times once a carbonate layer of sufficient thickness has formed [34, 10]. This mechanistic picture is consistent with the two-stage behaviour reported by Song et al. and provides the basis for the multi-step kinetic models discussed in Section 3.3.6.

CO₂ adsorption on Al₂O₃ and its role in composite catalysts

Although MgO is typically identified as the primary CO₂-capture component in Ni/Al₂O₃–MgO materials, the alumina support itself adsorbs CO₂ to a non-negligible extent through its surface hydroxyl groups. Morterra and Magnacca showed by infrared spectroscopy that γ -Al₂O₃ readily forms surface bicarbonate species upon CO₂ exposure, with characteristic bands at 1655, 1480 and 1230 cm⁻¹ [28]. DFT calculations by Digne et al. confirmed the existence of three distinct surface OH groups on the (100) and (110) facets of γ -Al₂O₃ with different acid–base characters, the most basic of which react preferentially with CO₂ to form stable bicarbonate species at temperatures up to 200–250 °C [16].

In situ DRIFTS experiments on the Ni/Al₂O₃ catalyst studied by Quindimil et al. revealed intense bicarbonate and carbonate bands on the support under CO₂/H₂/He mixtures at low temperatures, confirming that the Al₂O₃ component participates actively in CO₂ storage on this type of catalyst [32].

These observations have a direct implication for the interpretation of CO₂ adsorption data on Ni/Al₂O₃–MgO: the measured adsorption capacity reflects the combined contributions of MgO basic sites and Al₂O₃ hydroxyl sites, and any quantitative attribution to MgO alone requires knowledge of the individual contributions, which in turn requires textural and spectroscopic characterisation of the composite material.

3.3.4 Molten salt–promoted MgO and other advanced sorbents: performance benchmarks

The following sections summarise the performance of promoted MgO systems and carbonaceous adsorbents that have been extensively studied in the literature. Although these materials operate under conditions different from those of the present Ni/Al₂O₃–MgO catalyst (in particular at higher temperatures (275–350 °C) or with promoters absent from the present system) they provide essential performance benchmarks for contextualising the adsorption capacities measured subsequently into context.

NaNO₂ and NaNO₃ promotion

Gao et al. studied MgO sorbents promoted with alkali metal nitrites/nitrates, focusing on NaNO₂- and NaNO₃-coated MgO prepared by incipient wetness impregnation [19]. XRD and N₂ physisorption showed that after calcination at 450 °C the molten salt formed a thin layer covering the MgO surface and partially filling pores [19].

Bare MgO exhibited negligible CO₂ uptake ($<0.1 \text{ mmol g}^{-1}$) at 275–350 °C in pure CO₂. With optimised loading at 10 mol % NaNO₂, the sorbent reached 15.7 mmol g^{-1} at 350 °C [19]. XRD after CO₂ saturation revealed the formation of bulk MgCO₃ and the double carbonate Na₂Mg(CO₃)₂, indicating that both MgO and the molten salt participate in the reaction. After 20 adsorption–desorption cycles, the capacity decreased to 6.8 mmol g^{-1} , with losses attributed to sintering and pore shrinkage [19].

Three-stage kinetic behaviour

The kinetic data measured by Gao et al. on promoted MgO illustrate the transition between the two regimes introduced before: a rapid surface stage, followed by the nucleation and growth of a new crystalline phase, followed in turn by transport-limited carbonation of the bulk through the product layer. Time-resolved TGA experiments at 300 °C revealed that CO₂ uptake on 10 mol % NaNO₂-MgO proceeds via three distinct stages [19]: (i) fast surface adsorption on basic sites (pseudo-first-order kinetics, first tens of seconds); (ii) nucleation and growth of MgCO₃ bulk phases (Avrami–Erofeev kinetics, several minutes); and (iii) diffusion through the growing carbonate product layer (parabolic law, long times). Formally:

$$\ln\left(\frac{\theta_e}{\theta_e - \theta_t}\right) = k_1 t \quad (\text{stage i, PFO}), \quad (3.5)$$

$$-\ln(1 - \alpha) = k_2 t^n \quad (\text{stage ii, Avrami–Erofeev}), \quad (3.6)$$

where α is the transformed fraction, k_2 a rate constant and n a dimensionality exponent (typically 1–4) [19]. These results highlight that molten salt promotion not only enhances equilibrium capacity but also modifies the kinetic pathway by preventing the formation of an impermeable carbonate shell.

Effect of morphology and ternary nitrates

Wang et al. synthesised MgO with rod-like, flower-like and flake-like morphologies and promoted them with ternary nitrates (Li/Na/K, denoted TNO₃) [41]. BET surface areas ranged from 73 to $142 \text{ m}^2 \text{ g}^{-1}$. Rod-like MgO-K₂CO₃ with 20 mol % TNO₃ reached $13.45 \text{ mmol g}^{-1}$ at 300 °C after 240 min in pure CO₂ [41]. Cyclic tests (20 cycles, 300 °C adsorption, 500 °C desorption) revealed significant capacity loss (up to 77.7 %) attributed to sintering and molten salt agglomeration [41]. The PSO model gave the best kinetic fits across all samples, with rate constants $k_s \sim 10^{-3}$ – 10^{-2} min^{-1} at 300 °C.

Amine-functionalised MgO and carbonaceous adsorbents

Alkadhém et al. grafted APTES, DETA and PEI onto a high-surface-area MgO ($350 \text{ m}^2 \text{ g}^{-1}$) and measured CO₂ uptake at 30–100 °C [1]. APTES-MgO and DETA-MgO showed enhanced capacity at 30 °C (~ 62 and 47 mg g^{-1} respectively versus $\sim 30 \text{ mg g}^{-1}$ for bare MgO)

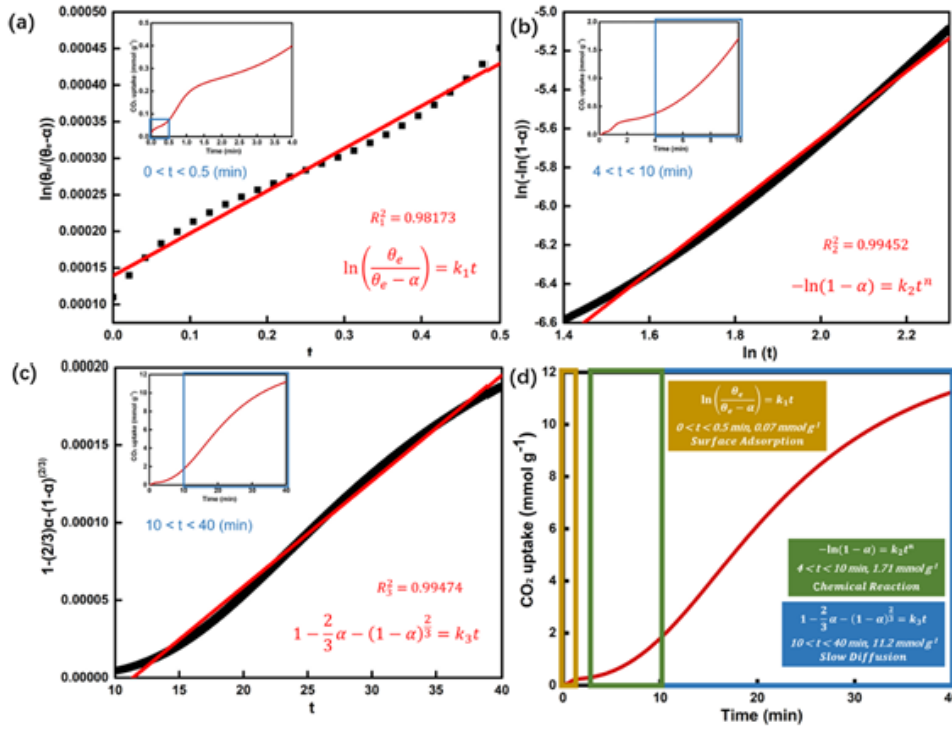


Figure 3.8: CO₂ uptake versus time for 10 mol % NaNO₂-MgO at 300 °C, with three fitted kinetic regimes: pseudo-first-order surface adsorption, Avrami nucleation and diffusion-limited growth, adapted from Gao et al. [19].

with decreasing capacity at higher temperature. PEI-MgO showed the inverse behaviour, attributed to increased mobility of amine groups, and was best described by a dual kinetic model (DKM). These amine-based sorbents are designed for low-temperature post-combustion capture and are not directly relevant to the ICCM context of the present work, but they confirm that surface functionalisation can shift both the operating temperature window and the dominant kinetic mechanism.

Vega et al. investigated CO₂ adsorption on activated hydrochars (AHCs) derived from pine sawdust, with surface areas up to 3276 m² g⁻¹ [39]. The best sample reached 3.3 mmol g⁻¹ at 25 °C via predominantly physisorptive micropore filling, best described by Avrami's fractional-order model. The coexistence of multiple adsorption pathways in these carbonaceous materials illustrates that complex, multi-step kinetics are a general feature of CO₂ adsorption on heterogeneous solids, regardless of the dominant interaction type.

Table 3.1 summarises the key performance indicators of the adsorbent families reviewed above, providing a unified basis for comparison across materials and operating conditions.

3.3.5 CO₂ adsorption in dual-function materials for ICCM

The concept of integrated CO₂ capture and methanation (ICCM) requires a material that simultaneously hosts a CO₂ adsorption function and a methanation catalytic function.

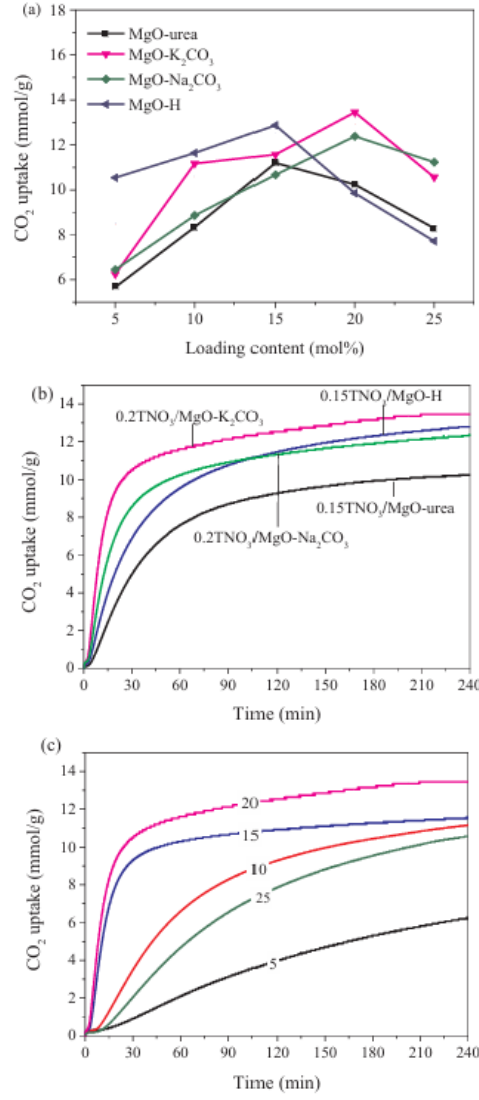


Figure 3.9: Influence of MgO morphology and ternary nitrate loading on CO₂ uptake at 300 °C (240 min, 1 bar CO₂), adapted from Wang et al. [41].

Table 3.1: Comparative summary of CO₂ adsorbents reviewed in this work. C_0 : capacity at reported conditions; ΔH_{ads} : apparent adsorption enthalpy; —: not reported.

Material	T (°C)	C_0 (mmol g ⁻¹)	Kinetic model	Cyclic stability
Porous MgO [34]	50	1.80	PSO	—
NaNO ₂ -MgO [19]	300–350	15.7	PFO + Avrami + diff.	–57 % / 20 cyc.
TNO ₃ -MgO [41]	300	13.5	PSO	–77 % / 20 cyc.
APTES-MgO [1]	30–100	~4	DKM	stable
Hydrochar [39]	25	3.3	Avrami	—

Note: ΔH_{ads} is not reported quantitatively in any of the reviewed kinetic studies and is therefore omitted from this table. A microcalorimetric characterisation is available for unpromoted MgO [5].

Such dual-function materials (DFMs) were formally introduced by Duyar et al., who demonstrated that a Ru/Al₂O₃ catalyst impregnated with a Na promoter could capture

CO₂ from a simulated flue gas during an adsorption step and subsequently convert it to CH₄ during a H₂ step, all within the same reactor and without intermediate purification [17]. The cyclic operation (CO₂-containing feed → H₂ feed) is a defining feature of ICCM and directly motivates the experimental approach adopted in the present work, where adsorption and methanation are characterised separately before their coupling is analysed.

The performance of a DFM in ICCM cycles is governed by several interacting factors that have been identified across recent studies:

Temperature window compatibility. The adsorption function requires a temperature at which the sorbent retains significant CO₂ capacity, while the methanation function requires a temperature at which the catalyst is kinetically active. For MgO-based sorbents, the former condition restricts operation below $\sim 300^\circ\text{C}$, while for Ni catalysts the latter condition typically requires temperatures above 250°C . The resulting overlap window ($250\text{--}300^\circ\text{C}$) is narrow and constitutes the primary design constraint for ICCM systems based on Ni/MgO formulations [3, 37]. Ru-based DFMs can operate at slightly lower temperatures, partially alleviating this constraint, but at higher cost [17, 37].

Spatial proximity of adsorption and catalytic sites. For the CO₂ stored as carbonate/bicarbonate on the sorbent to be hydrogenated during the H₂ step, it must be accessible to dissociated hydrogen atoms from the metal sites. Bermejo-López et al. showed that intimate contact between the Ni phase and the CO₂ storage phase (achieved by co-impregnation rather than physical mixing) strongly enhances CH₄ yield per cycle, confirming that H-spillover from metal to support is a key mechanistic step in ICCM [9]. Sun et al. further demonstrated on Ru/CeO₂–MgO combined materials that the morphology of the CeO₂ support influences both the CO₂ adsorption capacity of MgO and the methanation activity of Ru, highlighting the coupling between the two functions at the material level [37].

Cyclic stability and deactivation mechanisms. The repeated alternation between oxidising (CO₂) and reducing (H₂) atmospheres can modify both the metal phase (sintering, re-oxidation) and the sorbent phase (irreversible carbonate formation, pore blockage). Sun et al. and Arellano-Treviño et al. report capacity losses of 15–40 % over the first 10–20 cycles for Ni- and Ru-based DFMs, depending on operating temperature and regeneration conditions [37, 3]. Maintaining cycle stability requires careful optimisation of both regeneration temperature and cycle duration.

Water production during the methanation half-cycle. As CO₂ stored on the basic phase is released and hydrogenated to CH₄ during the H₂ step, H₂O is co-produced in stoichiometric proportion. From a kinetic standpoint, the resulting reduction of the methanation rate by H₂O is the same effect already described by the denominator of the LHHW expressions discussed before, and a steady-state kinetic model fed with the

appropriate transient gas-phase composition reproduces it without any specific ICCM ingredient. What is distinctive about the cyclic operation is therefore not the nature of the effect, but its *magnitude*. The CO₂ released during a H₂ half-cycle comes from a pre-loaded surface inventory and is not diluted by a fresh CO₂ feed, so the local H₂O partial pressure can rise transiently to values higher than those typically encountered in continuous co-fed methanation experiments at the same nominal conversion. Quantifying this transient H₂O peak, and the resulting deviation of the cycle-averaged conversion from steady-state predictions, is a key consideration for the modelling of ICCM cycles and is further discussed in the following sections.

Sun et al. proposed a systematic framework for matching adsorption and catalytic sites in ICCM materials, identifying the enthalpy of CO₂ adsorption and the activation energy of methanation as the two key descriptors governing cycle performance [36]. Materials with intermediate adsorption enthalpies (−40 to −80 kJ mol^{−1}) are preferred, as they ensure sufficient capacity at the adsorption temperature while allowing complete regeneration during the H₂ step without excessively high temperatures. This descriptor-based approach provides a quantitative framework for evaluating the suitability of any adsorbent–catalyst combination for ICCM, and will be applied qualitatively to the Ni/Al₂O₃–MgO system in the following sections.

3.3.6 Kinetic models for surface adsorption and solid-state carbonation

Overview of apparent kinetic models

Across the different studies reviewed, a consistent set of phenomenological kinetic models is used to fit CO₂ uptake curves on basic oxides. Each model expresses the time evolution of the uptake q_t (in mmol g^{−1}, the amount of CO₂ captured per unit mass of sorbent at time t) toward its equilibrium value q_e (the uptake reached after sufficiently long contact time at the given temperature and partial pressure). The rate constants and exponents that appear in each expression are then fitted to the experimental $q_t(t)$ curve. These apparent models cover the two regimes introduced in previous section: pseudo-first-order and pseudo-second-order forms are typically used for the surface adsorption regime, the Avrami–Erofeev model is the standard description of the nucleation-and-growth stage of bulk carbonation, and the Weber–Morris and Boyd analyses isolate the diffusional contributions. In what follows, each model is introduced together with its physical domain of applicability.

- **Pseudo-first-order (PFO):**

$$\frac{dq_t}{dt} = k_1(q_e - q_t), \quad q_t = q_e \left(1 - e^{-k_1 t}\right), \quad (3.7)$$

adequate for early-time surface adsorption on MgO and for situations where the rate is linearly proportional to the remaining surface vacancy concentration [19, 1].

- **Pseudo-second-order (PSO):**

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2, \quad q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}, \quad (3.8)$$

which empirically describes porous MgO and nitrate-promoted MgO reasonably well [34, 41]. The PSO equation is sometimes invoked as a signature of chemisorption-controlled uptake, but this association is largely empirical: as discussed in Section 3.3.6 below, the PSO form does not derive from any specific surface elementary mechanism, and its success on a wide variety of materials reflects the flexibility of its functional form rather than a shared underlying mechanism. Typical k_2 values range from $\sim 7 \times 10^{-2} \text{ min}^{-1}$ at 50°C for porous MgO [34] to 10^{-3} – 10^{-2} min^{-1} for molten-salt-promoted MgO at 300°C [41].

- **Avrami–Erofeev (nucleation and growth):**

$$q_t = q_e [1 - \exp(-(k_A t)^{n_A})], \quad (3.9)$$

derived by Avrami in a series of foundational papers on the kinetics of phase transformations [6]. The expression captures the situation in which a new crystalline phase nucleates at random positions in the parent solid and grows outward at a constant radial velocity, with the nuclei eventually impinging on one another. The exponent n_A encodes the dimensionality and the nucleation regime of the growth process (typically between 1 and 4 for solid-state reactions). Because of this physical foundation, the Avrami–Erofeev form is the standard kinetic description of solid-state phase transformations across a wide range of fields, including the carbonation of basic oxides such as MgO and CaO [18]. In the present context, Equation (3.9) is used to describe the nucleation and growth of MgCO_3 on NaNO_2 -promoted MgO [19] and the multi-pathway adsorption observed on activated hydrochars [39].

- **Dual kinetic model (DKM):**

$$\frac{dq_t}{dt} = k_{\text{DKM}}(1 + \beta q_t)(q_e - q_t)^{n_{\text{DKM}}}, \quad (3.10)$$

used for amine-functionalised MgO to account for parallel surface and bulk adsorption contributions [1].

- **Weber–Morris intraparticle diffusion:**

$$q_t = k_{\text{id}} t^{1/2} + C, \quad (3.11)$$

where multi-linear plots reveal sequential film and intraparticle diffusion control [34, 41, 39].

- **Boyd film-diffusion model:** analysis of B_t vs. t plots confirms that external film diffusion is rarely negligible, especially at early times or low gas velocities [34, 41].

Limitations of empirical models and mechanistically grounded alternatives

While the PFO and PSO models provide convenient descriptors for comparing materials and conditions, their mechanistic interpretation is limited. The PSO model in particular does not derive from a physically identifiable surface mechanism: its mathematical form is equivalent to a second-order reaction in the remaining capacity ($q_e - q_t$), but this does not correspond to any elementary step of surface carbonation in a rigorous sense. The empirical success of PSO in fitting adsorption data on a wide variety of materials is therefore more indicative of a flexible functional form than of a shared mechanism [11].

Beyond the empirical PFO and PSO descriptions, two complementary families of physically grounded models are used to describe the solid-state carbonation regime, each addressing a different aspect of the process. The first family describes the *nucleation and growth* of the new crystalline phase inside the parent grain itself, through the Avrami–Erofeev formalism of Equation (3.9): MgCO_3 nuclei form at energetically favourable sites in the MgO lattice and grow until they impinge on one another. The second family describes the *geometric and transport evolution* of an individual MgO grain once a continuous MgCO_3 shell has formed at its outer surface: this is the domain of the shrinking-core and grain models. The two families therefore describe successive stages of the same overall process: nucleation and growth governs the early times, until a continuous product layer is established; the shrinking-core picture takes over once that layer exists and controls the subsequent transport-limited carbonation of the remaining unreacted core. Both stages are clearly identified in the three-stage TGA experiments of Gao et al. on promoted MgO [19] discussed in Section before.

For the shrinking-core stage, Bhatia and Perlmutter proposed a random pore model for gas–solid reactions that accounts for the change in pore structure as the solid product layer grows, yielding rate expressions of the form [11]:

$$\frac{d\alpha}{dt} = k_s(1 - \alpha)\sqrt{1 - \psi \ln(1 - \alpha)}, \quad (3.12)$$

where α is the conversion, k_s the surface reaction rate constant, D_e the effective diffusivity in the product layer and ψ a structural parameter characterising the initial pore geometry. This model captures the progressive transition from reaction control to diffusion control as the carbonate layer grows, and is more directly applicable to reactor-scale simulations than PSO or Avrami descriptions [11, 10].

For engineering design of ICCM cycles, the kinetic constants obtained from apparent models (PFO, PSO) are not directly transferable to reactor simulations, as they depend on the experimental protocol (sample mass, flow rate, pulse configuration), as demonstrated explicitly in Section 3.4.6 of the present work. Mechanistic models that separately account for external mass transfer, intraparticle diffusion and surface reaction are required for predictive simulation of cyclic fixed-bed or fluidised-bed adsorbers [10, 11].

Experimental conditions and intrinsic character of the adsorption data

The kinetic datasets reported by Song [34], Gao [19], Wang [41], Alkadhém [1] and Vega [39] are all based on thermogravimetric measurements with small sample masses (typically 5–20 mg) and sufficiently high gas flow rates to minimise external mass-transfer limitations. Song [34] explicitly checked the influence of CO₂ flow rate on the measured capacity, while Gao [19] and Wang [41] validated intrinsic conditions through agreement between TGA and fixed-bed data. These strategies justify treating the reported $q_t(t)$ curves as representative of particle-scale adsorption kinetics. By contrast, the pulse technique used in the present work introduces a protocol-dependent kinetic accessibility that must be carefully accounted for in the interpretation of results (see Section 3.4.6).

3.4 Experimental Data and Discussion

3.4.1 Overview and Experimental Strategy

This section presents the experimental results obtained for CO₂ adsorption on the Ni/Al₂O₃–MgO catalyst. The adsorption experiments were conducted in a CATLAB fixed-bed reactor using a pulse injection technique, in which successive doses of a CO₂/Ar mixture are injected into the reactor and the concentration of CO₂ at the outlet is continuously monitored by a mass spectrometer. This approach provides a direct, pulse-by-pulse measurement of the fraction of CO₂ retained by the catalyst, and allows the total adsorption capacity to be determined by integration over the full pulse sequence.

Each pulse consists of 5 mL of a 50 % CO₂ – 50 % Ar mixture, so that the effective quantity of CO₂ injected per pulse is

$$n_{\text{CO}_2} = x_{\text{CO}_2} \cdot \frac{p_{\text{atm}} V_{\text{loop}}}{R T_{\text{loop}}} = 0.5 \times \frac{101\,325 \text{ Pa} \times 5 \times 10^{-6} \text{ m}^3}{8.314 \text{ J/mol/K} \times 373.15 \text{ K}} \approx 8.14 \times 10^{-5} \text{ mol}, \quad (3.13)$$

where $x_{\text{CO}_2} = 0.5$ is the molar fraction of CO₂ in the loop, $p_{\text{atm}} = 101\,325 \text{ Pa}$ is the atmospheric pressure at which the loop operates, $V_{\text{loop}} = 5 \text{ mL}$ is the total loop volume,

$T_{\text{loop}} = 373.15 \text{ K}$ (100°C) is the loop temperature, and R is the ideal gas constant. This corresponds to 0.0814 mmol of CO_2 per injection.

A continuous argon carrier stream at 100 mL/min sweeps the reactor between pulses and ensures that any weakly physisorbed CO_2 is rapidly displaced between injections, so that the measured retention reflects primarily chemisorbed species. Pulses are injected at regular intervals of 5 min , and a sequence of 40 pulses is delivered at each temperature. As adsorption proceeds, an increasing fraction of CO_2 passes through the catalyst bed unreacted, and the mass spectrometer signal grows progressively. By the 40^{th} pulse, the catalyst is considered fully saturated: no further net adsorption occurs, and the outlet signal stabilises at a reference level A_N corresponding to the full quantity of CO_2 injected per pulse passing through without retention.

The total CO_2 adsorption capacity per gram of catalyst, C_0 ($\text{mol g}_{\text{cat}}^{-1}$), is then determined according to

$$C_0 = \frac{1}{W_{\text{cat}}} \cdot \frac{p_{\text{atm}} V_{\text{loop}}}{R T_{\text{loop}}} \cdot \sum_{i=1}^{N-1} \left(1 - \frac{A_i}{A_N}\right), \quad (3.14)$$

where $W_{\text{cat}} = 0.1 \text{ g}$ is the catalyst mass, $N = 40$ is the total number of pulses, and A_i is the mass spectrometer signal associated with pulse i . It should be noted that the general form of this equation, as reported in the literature for pulse chemisorption experiments, contains a pre-factor $x_{\text{CO}_2}^{-1}$ accounting for the molar fraction of CO_2 in the loop. In the present case, $x_{\text{CO}_2} = 0.5$, so that this pre-factor equals 2 . However, since V_{loop} here denotes the total loop volume (and not the volume of CO_2 alone), the factor $x_{\text{CO}_2}^{-1} = 2$ and the factor $x_{\text{CO}_2} = 0.5$ arising from the loop composition cancel exactly, yielding Equation (3.14) directly. Each term $(1 - A_i/A_N)$ represents the fraction of the injected CO_2 retained by the catalyst during pulse i , and the sum accumulates these contributions over all pulses up to saturation.

Adsorption measurements were performed at six temperatures: 50 , 75 , 100 , 125 , 150 and 200°C . Prior to each experiment, the reactor was held at the target temperature for one hour to ensure thermal stabilisation before the pulse sequence was initiated. This temperature window was selected for two reasons. First, it covers the range in which MgO -based sorbents are known to exhibit meaningful CO_2 uptake via surface carbonate and bicarbonate formation, before thermodynamic limitations become prohibitive at higher temperatures [34, 19]. Second, the lower bound of 50°C is representative of mild post-combustion or direct air capture conditions, while the upper bound of 200°C approaches the temperature at which MgO carbonation becomes thermodynamically unfavourable in the absence of promoters [19, 41].

Importantly, no hydrogen was introduced during the adsorption experiments: the feed

consists exclusively of CO₂ and Ar. Under these conditions, no methanation reaction can occur, and the Ni phase remains essentially inactive. The observed CO₂ uptake can therefore be attributed to the adsorption function of the material, and more specifically to the basic sites provided by the MgO component. This experimental design mirrors the gas-switching strategy used in integrated CO₂ capture and methanation (ICCM) cycles, in which a CO₂-containing feed is first used to load the sorbent, followed by a reductive H₂ step for conversion and in-situ regeneration [37, 43].

In addition to the main temperature series, a complementary set of experiments was conducted at 50 °C using three different argon carrier gas flow rates: 50, 100 and 200 mL/min. The purpose of this series is to assess whether the adsorption capacity measured under the reference conditions (100 mL/min) is free from external mass-transfer limitations, an essential prerequisite for treating the results as representative of the intrinsic adsorption behaviour of the material at the particle scale, in the spirit of the transport criteria applied to the methanation kinetic data in Section 2.4.2.

3.4.2 Raw Pulse Response Signals and Qualitative Interpretation

The raw mass spectrometer signals recorded at the reactor outlet during the pulse sequence are presented in Figures 3.10–3.15 for all six temperatures investigated. The signal is expressed as a partial pressure (in mbar) measured at the m/z ratio corresponding to CO₂ ($m/z = 44$), as a function of time in seconds. Individual pulses appear as well-resolved peaks separated by the 5 min (300 s) inter-pulse interval, during which the argon carrier flow sweeps the reactor. The signal returns systematically to a stable, flat baseline between consecutive pulses at all temperatures, confirming that the memory effect between injections is negligible and that each pulse can be treated as an independent adsorption event on the partially saturated surface left by all preceding injections.

The adsorption capacity is quantified from the peak height, defined as the difference between the maximum partial pressure of a given peak and the baseline level immediately preceding that pulse. The reference saturation signal A_N used in Equation (3.14) is taken as the average peak height computed over the pulses that constitute the plateau region of each sequence, rather than from the single last pulse, in order to reduce the influence of signal noise on the normalisation.

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signal noise on the normalisation. It should be noted that, although the integrated peak area is the rigorous estimator of the eluted CO₂ quantity (Section 3.2.5), peak heights were used in practice as a simpler and noise-robust proxy. At the fixed carrier flow rate of the temperature series (100 mL/min), the pulse shape is essentially invariant from one injection to the next, so that height and area yield very similar normalised ratios A_i/A_N ; the implications of this approximation, in particular for the flow-rate series of Section 3.4.6, are discussed among the limitations in Section 3.5.2.

It is noted that the absolute value of A_N varies with temperature, increasing from approximately 1.0×10^{-9} mbar at 50 °C to approximately 2.0×10^{-9} mbar at higher temperatures. This variation reflects the influence of temperature on the gas density and on the mass spectrometer sensitivity rather than a change in the quantity of CO₂ injected per pulse, which remains fixed by the loop conditions. Since A_N is determined independently at each temperature from the plateau of the corresponding pulse sequence, this instrumental temperature dependence is fully accounted for in the normalisation embedded in Equation (3.14), and does not affect the validity of the C_0 values reported in Section 3.4.4.

Behaviour at 50 °C

At 50 °C (Figure 3.10), the first pulse gives rise to a peak height of approximately 3.5×10^{-10} mbar, representing roughly one third of the reference saturation level $A_N \approx 1.0 \times 10^{-9}$ mbar. This indicates that around two thirds of the injected CO₂ dose is retained by the catalyst upon first contact, confirming that a large fraction of the MgO adsorption sites are immediately accessible and that the adsorption kinetics are sufficiently fast relative to the pulse duration to ensure substantial uptake from the very first injection. The peak height then increases monotonically over the course of the sequence, reflecting the progressive occupation of surface sites. However, after 40 pulses, the signal has not yet reached a fully stable plateau: the last several peaks continue to increase slightly, indicating that complete saturation has not been achieved within the duration of the experiment. As a consequence, the value of $C_0 = 9.35$ mol/kg determined at 50 °C from Equation (3.14) represents a lower bound of the true equilibrium adsorption capacity at this temperature, as discussed further in Section 3.5.2.

Behaviour at 75 °C

The pulse sequence at 75 °C (Figure 3.11) exhibits a non-monotonic behaviour during the first few pulses that is not observed at any other temperature. The first pulse already produces a peak height of approximately 1.0×10^{-9} mbar, after which the peak height decreases over the next several pulses before rising again toward a final plateau of approximately 1.4×10^{-9} mbar. This abnormal behaviour is attributed to experimental variability inherent to the use of a fresh catalyst sample for each temperature run.

Possible contributing factors include minor differences in the initial state of the catalyst surface between samples, small variations in the bed packing density, or a transient thermal equilibration effect at the onset of the pulse sequence. Despite this anomaly in the early part of the sequence, the plateau region at the end of the experiment is well-defined and the determination of A_N is not affected. However, since the anomalous early pulses are included in the summation of Equation (3.14), the resulting value of $C_0 = 5.56 \text{ mol/kg}$ at 75°C carries a larger uncertainty than at other temperatures and should be interpreted with caution. It is notable that this value is significantly lower than the capacity measured at 50°C , which is qualitatively consistent with a decrease in adsorption capacity with temperature, but the magnitude of the drop may be partially exaggerated by the anomalous early pulses, which contribute smaller-than-expected values of $(1 - A_i/A_N)$ to the sum.

Behaviour at 100°C

At 100°C (Figure 3.12), the first pulse produces a peak height of approximately $1.0 \times 10^{-9} \text{ mbar}$, and the signal rises progressively toward a plateau of approximately $1.5 \times 10^{-9} \text{ mbar}$. The approach to saturation is smooth and monotonic, without the anomalous feature observed at 75°C . As at 50°C , the plateau is not fully stabilised by the end of the 40-pulse sequence, suggesting that the adsorption capacity $C_0 = 4.21 \text{ mol/kg}$ at 100°C is also marginally underestimated by the present protocol.

Behaviour at 125°C

At 125°C (Figure 3.13), the first pulse height is approximately $1.5 \times 10^{-9} \text{ mbar}$, and the plateau is reached at approximately $2.3 \times 10^{-9} \text{ mbar}$. The saturation is more clearly defined than at lower temperatures, with the signal approaching a stable value over the last ten to fifteen pulses. The adsorption capacity at this temperature is $C_0 = 4.61 \text{ mol/kg}$, which is slightly higher than the value obtained at 100°C . This non-monotonic behaviour between 100°C and 125°C is inconsistent with the expected decrease in adsorption capacity with temperature for an exothermic process, and is attributed to experimental variability between the two fresh catalyst samples used for these runs. Minor differences in the initial surface state, bed packing, or thermal history of the two samples may account for this small but noticeable discrepancy. The overall trend across the full temperature range nevertheless remains consistent with a decrease in C_0 with increasing temperature, as shown in Section 3.4.5.

Behaviour at 150°C

At 150°C (Figure 3.14), the first pulse height is approximately $1.0 \times 10^{-9} \text{ mbar}$ and the plateau stabilises at approximately $2.0 \times 10^{-9} \text{ mbar}$. The approach to saturation is

progressive and well-behaved, with the plateau clearly established over the last portion of the sequence. Some scatter is visible in the plateau region, which is attributed to minor fluctuations in the carrier gas flow rate or in the mass spectrometer baseline, and is accounted for by the averaging procedure used to determine A_N . The adsorption capacity at this temperature is $C_0 = 3.23 \text{ mol/kg}$, continuing the overall decreasing trend with temperature.

Behaviour at 200 °C

At 200 °C (Figure 3.15), the pulse sequence exhibits a markedly different character from all lower temperatures. The peak heights show no clear monotonic trend and oscillate around a mean value of approximately $1.7 \times 10^{-9} \text{ mbar}$ throughout the entire sequence, without any discernible progression from the first to the last pulse. This behaviour indicates that the adsorption capacity of the catalyst at 200 °C is very low: the fraction of CO_2 retained per pulse is small and comparable to the signal-to-noise ratio of the mass spectrometer, so that no progressive saturation can be solved within the experimental precision. The resulting value $C_0 = 2.58 \text{ mol/kg}$ at 200 °C therefore carries a relatively large uncertainty and should be interpreted as an upper bound rather than as a precise quantitative estimate. This result is consistent with the thermodynamic analysis presented in Section 3.5.1: at 200 °C, the standard Gibbs free energy of MgO carbonation approaches zero and the equilibrium carbonate surface coverage becomes negligible [19].

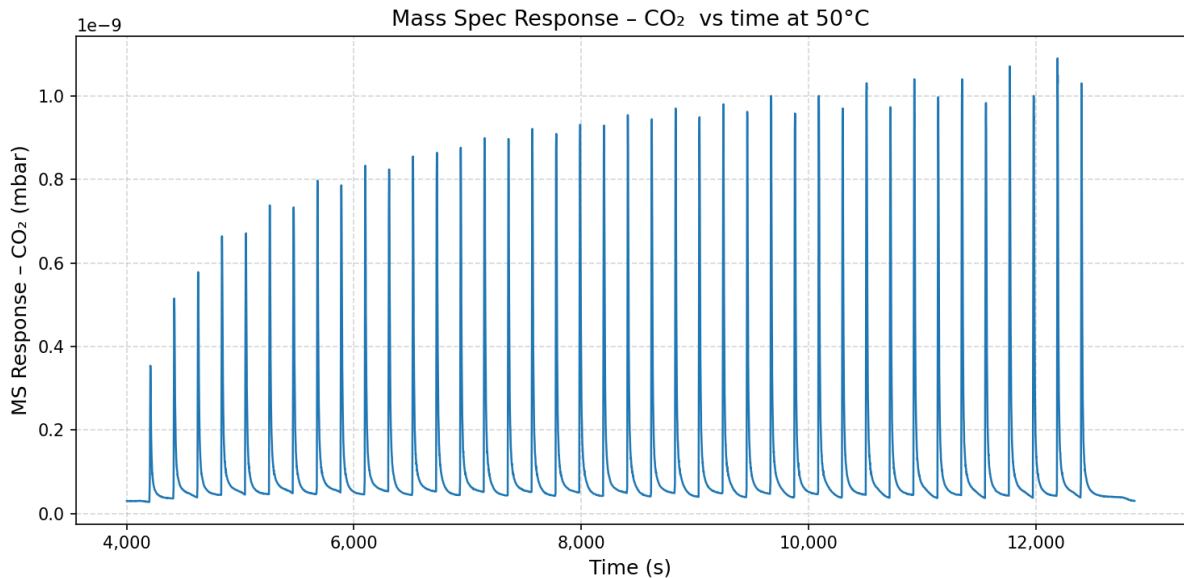


Figure 3.10: Mass spectrometer CO_2 partial pressure signal ($m/z = 44$) at the reactor outlet during the 40-pulse adsorption sequence at 50 °C. Argon carrier flow rate: 100 mL/min. The dashed horizontal line indicates the reference saturation level $A_N \approx 1.0 \times 10^{-9} \text{ mbar}$. Note that the plateau is not fully reached after 40 pulses, indicating that C_0 at this temperature is a lower bound of the true equilibrium capacity.

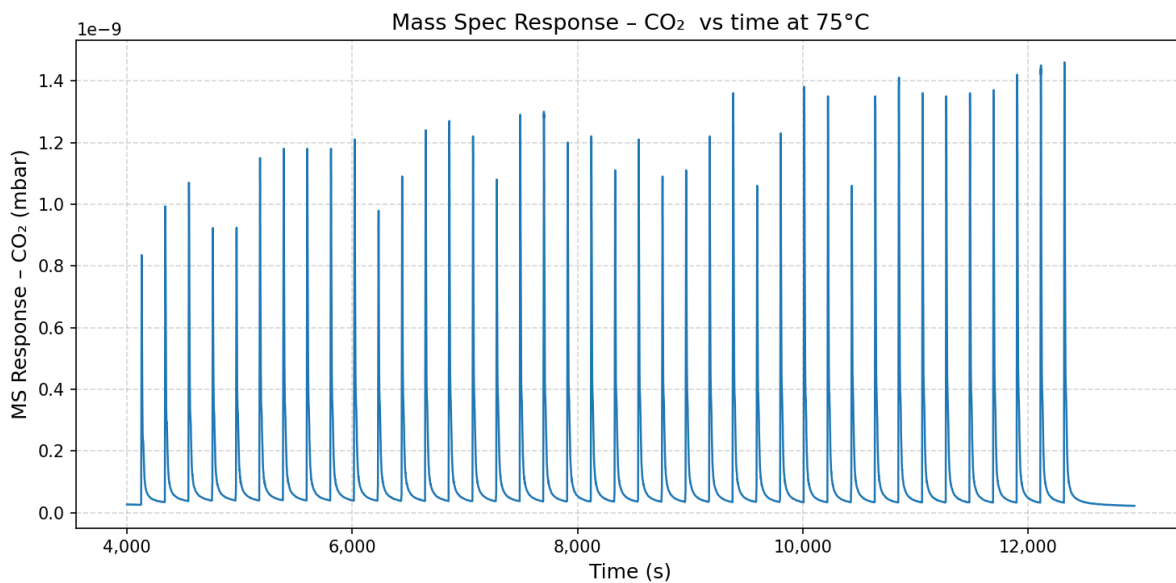


Figure 3.11: Mass spectrometer CO₂ partial pressure signal ($m/z = 44$) at the reactor outlet during the 40-pulse adsorption sequence at 75 °C. The non-monotonic behaviour of the first few peaks is attributed to experimental variability associated with the use of a fresh catalyst sample (see text).

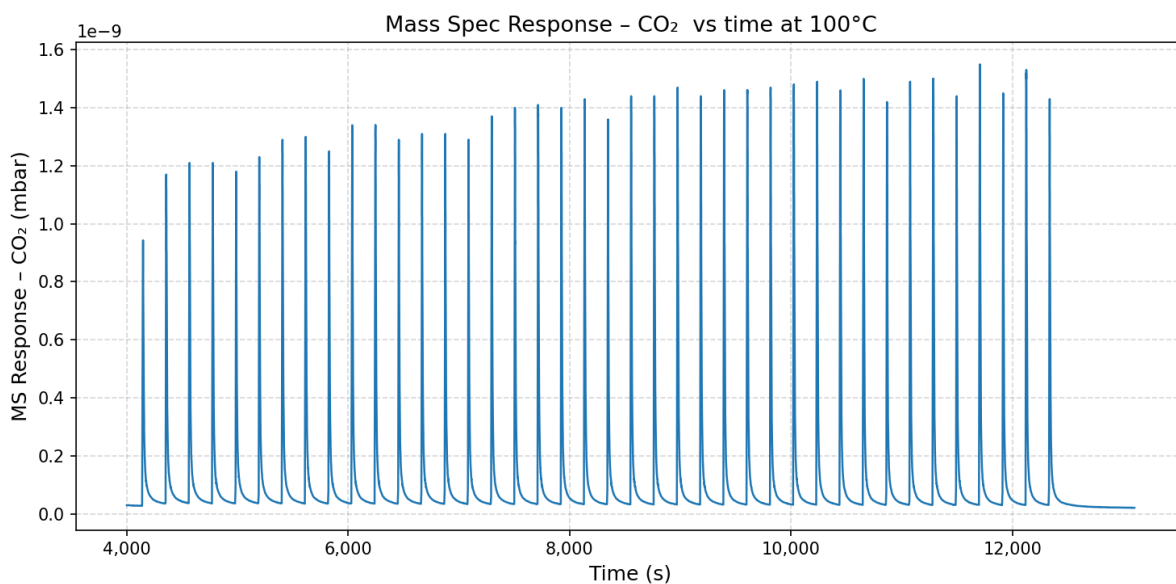


Figure 3.12: Mass spectrometer CO₂ partial pressure signal ($m/z = 44$) at the reactor outlet during the 40-pulse adsorption sequence at 100 °C.

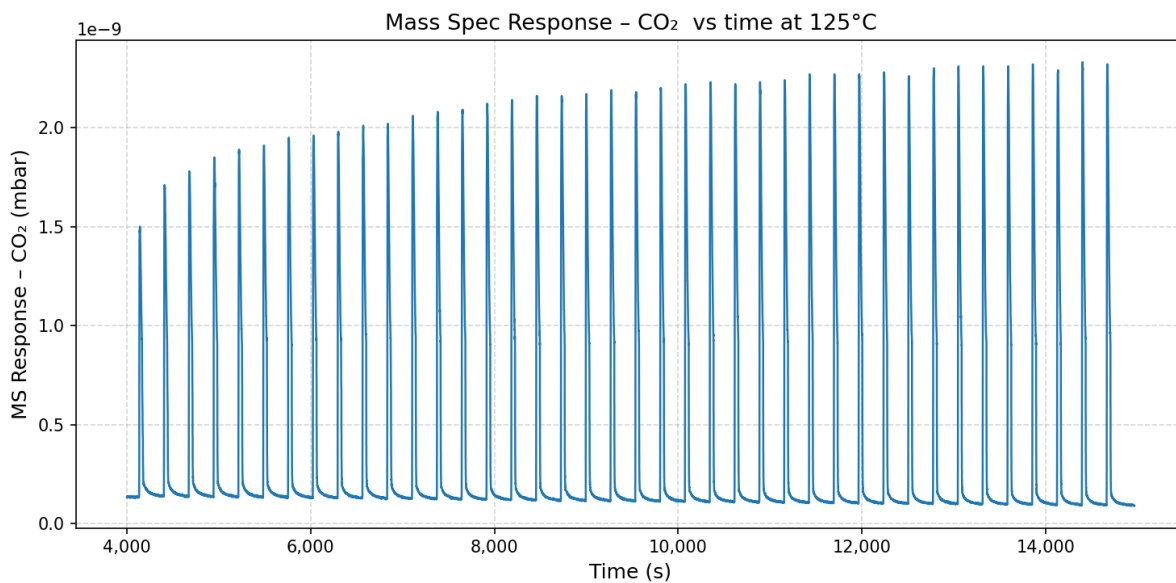


Figure 3.13: Mass spectrometer CO₂ partial pressure signal ($m/z = 44$) at the reactor outlet during the 40-pulse adsorption sequence at 125 °C.

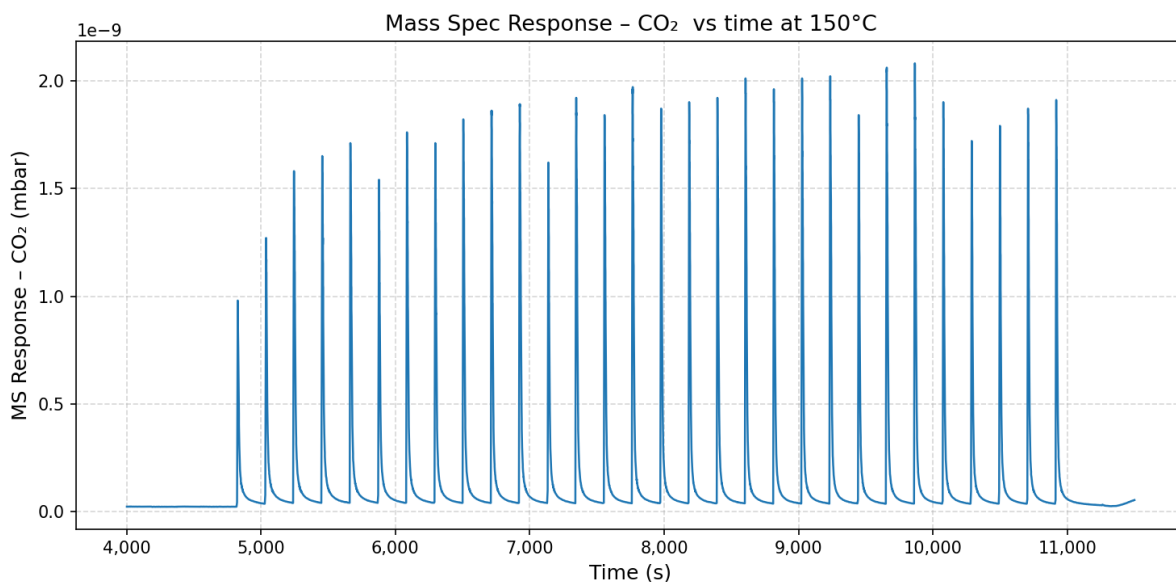


Figure 3.14: Mass spectrometer CO₂ partial pressure signal ($m/z = 44$) at the reactor outlet during the 40-pulse adsorption sequence at 150 °C.

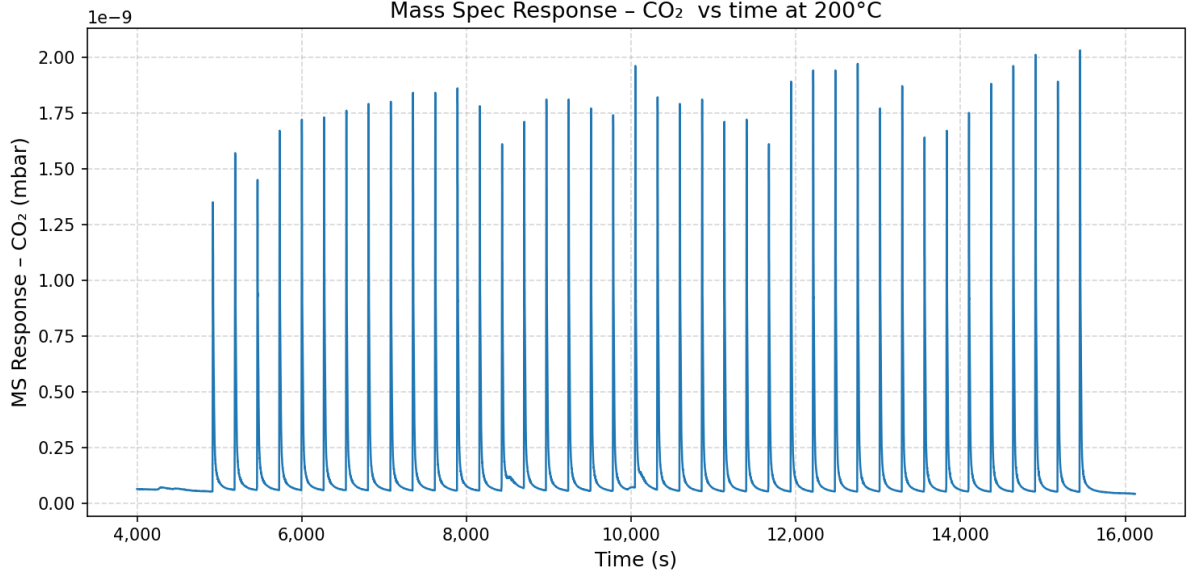


Figure 3.15: Mass spectrometer CO₂ partial pressure signal ($m/z = 44$) at the reactor outlet during the 40-pulse adsorption sequence at 200 °C. The absence of a clear monotonic trend reflects the very low adsorption capacity at this temperature and the limited signal-to-noise ratio.

3.4.3 Progressive Saturation Analysis

The progressive saturation of the catalyst surface is analysed quantitatively in Figures 3.16 and 3.17, which present respectively the normalised adsorbed fraction ($1 - A_i/A_N$) and the cumulative sum $\sum_{j=1}^i (1 - A_j/A_N)$ as a function of pulse number i , for all six temperatures investigated. These two representations provide complementary information: the former reflects the instantaneous adsorption capacity available at each pulse, while the latter directly tracks the accumulation of adsorbed CO₂ and converges toward the dimensionless quantity from which C_0 is computed via Equation (3.14).

General trends

Figure 3.16 reveals a clear and systematic influence of temperature on the rate of surface saturation. At all temperatures, $(1 - A_i/A_N)$ decreases overall from its initial value toward zero, reflecting the progressive occupation of adsorption sites over the course of the pulse sequence. The rate of this decrease is strongly temperature-dependent: at 50 °C, the first pulse already retains approximately 67% of the injected CO₂ dose, and the curve decays slowly over the entire 40-pulse sequence without reaching a stable zero level, confirming the large adsorption capacity and slow saturation kinetics at this temperature. In contrast, at 150 °C and 200 °C, the normalised adsorbed fraction drops to values close to zero within the first 15 to 20 pulses, indicating a much smaller total adsorption capacity and faster saturation.

The shape of the decay curves is also informative from a mechanistic standpoint. At 50 °C, the decay exhibits a characteristic two-regime behaviour: a rapid decrease over the first 5 to 10 pulses, followed by a much slower, nearly linear decrease over the remaining pulses. This behaviour is qualitatively consistent with the two-stage adsorption kinetics reported for MgO-based sorbents in the literature [34, 19]: an initial fast regime corresponding to the adsorption of CO₂ on readily accessible surface sites, followed by a slower regime governed by diffusion of CO₂ through the growing carbonate product layer. It should be noted that C_0 as determined from the present pulse experiments cannot distinguish between reversible surface adsorption and irreversible bulk carbonation of MgO. The two-regime decay observed at 50 °C (a rapid initial decrease followed by a slower, nearly linear tail) is qualitatively consistent with the coexistence of both mechanisms: fast adsorption on readily accessible surface sites in the early pulses, followed by slower diffusion-limited carbonation of the bulk MgO phase as a growing carbonate layer progressively passivates the surface. At higher temperatures, the bulk carbonation contribution is expected to decrease due to the unfavourable thermodynamics of MgCO₃ formation, so that C_0 at 150 °C and 200 °C more closely reflects purely surface adsorption. A definitive separation of the two contributions would require complementary characterisation such as temperature-programmed desorption (TPD) or in-situ X-ray diffraction, which lie beyond the scope of the present work. At higher temperatures, the two regimes are less clearly separated, likely because the total number of accessible sites is smaller and the fast regime dominates a larger fraction of the sequence before saturation is reached.

Scatter and experimental variability

A notable feature of Figure 3.16 is the significant pulse-to-pulse scatter observed at all temperatures, which increases markedly at higher temperatures where the adsorbed fraction per pulse is small. This scatter reflects the limited signal-to-noise ratio of the mass spectrometer when the CO₂ signal at the outlet is close to the saturation level A_N , and is particularly pronounced at 150 °C and 200 °C where $(1 - A_i/A_N)$ oscillates around zero from pulse 20 onward. The 75 °C curve also exhibits unusually large oscillations throughout the sequence, consistent with the experimental artefact identified in Section 3.4.2 for this temperature.

Negative values of $(1 - A_i/A_N)$, corresponding to pulses for which A_i slightly exceeds the reference level A_N , are observed in the tail of the sequences at all temperatures. These arise from the combination of measurement noise and the fact that A_N is defined as an average over the plateau pulses rather than as a strict upper bound. Since these negative contributions are included in the summation of Equation (3.14), they slightly reduce the computed value of C_0 relative to the maximum of the cumulative curve. This effect is most significant at 150 °C and 200 °C, where the negative values are largest relative to

the positive contributions.

Cumulative sum and determination of C_0

The cumulative sum curves in Figure 3.17 provide a direct visual representation of the convergence of the sum toward the value used in Equation (3.14). At 50 °C, the cumulative curve is still rising at pulse 40, confirming that the experiment has not reached complete saturation and that $C_0 = 9.35$ mol/kg is a lower bound of the true equilibrium capacity. At 100 °C, the cumulative curve reaches a well-defined plateau around pulse 25–30 and remains stable thereafter, providing the most reliable determination of C_0 in the series. At 150 °C and 200 °C, the cumulative curves reach a maximum around pulse 15–20 and then decrease slightly due to the negative contributions in the tail of the sequence, so that the final value of C_0 is marginally lower than the plateau maximum. The values of C_0 determined from the full 40-pulse summation are summarised in Table 3.2 and discussed in Section 3.4.4.

An interesting feature of Figure 3.17 is the crossing of the 75 °C and 125 °C curves around pulse 20–25. Up to this point, the 125 °C curve lies above that at 75 °C, reflecting the anomalously low values of $(1 - A_i/A_N)$ at the beginning of the 75 °C sequence associated with the experimental artefact discussed previously. Beyond pulse 25, the 75 °C curve overtakes the 125 °C curve and converges to a higher final value ($C_0 = 5.56$ mol/kg vs. $C_0 = 4.61$ mol/kg), which is qualitatively consistent with the expected decrease in adsorption capacity with temperature. This crossing highlights the sensitivity of the pulse technique to experimental variability in the early pulses and underlines the importance of ensuring a reproducible initial surface state for all temperature runs.

Hierarchy of adsorption capacities

The separation between the six cumulative curves in Figure 3.17 clearly establishes the hierarchy of adsorption capacities across the temperature range investigated. The inversion between 100 °C and 125 °C discussed in the previous section, the curves decrease in the expected order with increasing temperature. The gap between 50 °C and all other temperatures is particularly striking: the cumulative sum at 50 °C is approximately 50% higher than at 75 °C at the end of the sequence, reflecting the strong thermodynamic driving force for MgO carbonation at low temperature. This large gap, combined with the incomplete saturation at 50 °C, suggests that the true adsorption capacity at this temperature may be substantially higher than the measured value of 9.35 mol/kg.

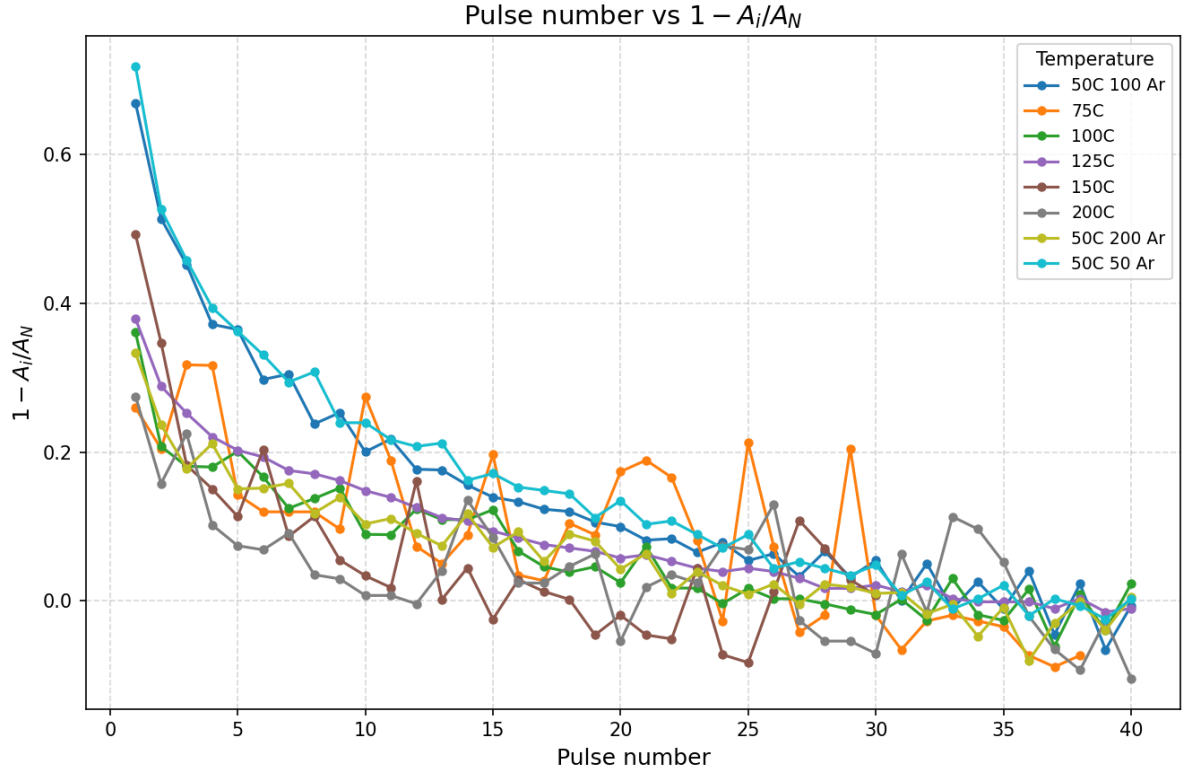


Figure 3.16: Normalised adsorbed fraction ($1 - A_i/A_N$) as a function of pulse number i for all six temperatures investigated. Each curve represents the fraction of the injected CO_2 dose retained by the catalyst during pulse i , normalised by the reference saturation signal A_N . The decay toward zero reflects the progressive saturation of the adsorption sites. Negative values in the tail of each sequence arise from measurement noise when $A_i \gtrsim A_N$.

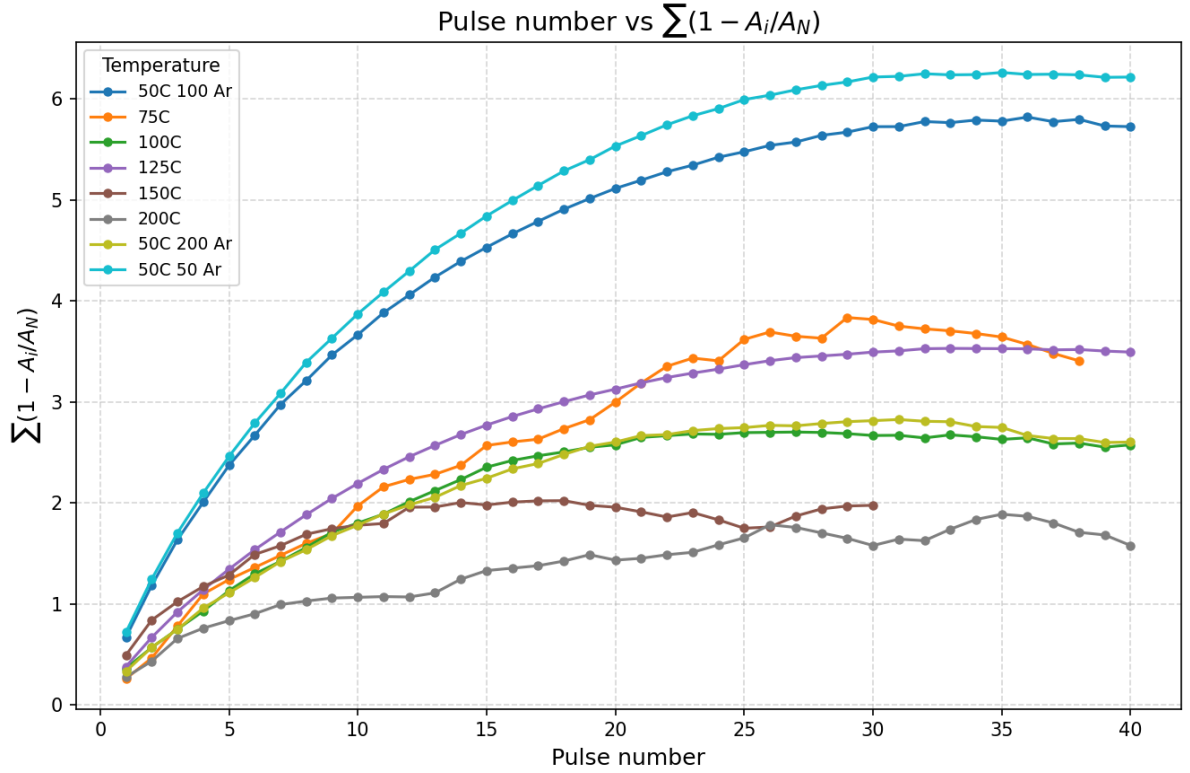


Figure 3.17: Cumulative sum $\sum_{j=1}^i (1 - A_j/A_N)$ as a function of pulse number i for all six temperatures investigated. The final value of each curve at pulse $N = 40$ is proportional to the total adsorption capacity C_0 via Equation (3.14). The 50 °C curve has not yet reached a stable plateau at pulse 40, indicating that C_0 at this temperature is a lower bound of the true equilibrium capacity. The crossing of the 75 °C and 125 °C curves around pulse 20–25 reflects experimental variability in the early pulses at 75 °C (see text).

3.4.4 Calculation of Adsorption Capacity

The total CO₂ adsorption capacity per unit mass of catalyst, C_0 (mol kg⁻¹), was determined at each temperature from the pulse sequence data using Equation (3.14). The reference saturation signal A_N was computed as the average peak height over the final pulses of each sequence, once the signal had reached a stable plateau. The number of pulses included in this average was adapted to the quality of the plateau at each temperature, as detailed in Table 3.2. It should be noted that the total number of pulses recorded was 40 at most temperatures, but was reduced to 38 at 75 °C and to 30 at 150 °C due to technical interruptions of the CATLAB system during these experiments. As a consequence, the summation in Equation (3.14) runs from $i = 1$ to $N - 1$, where N denotes the total number of pulses recorded at each temperature, and A_N is the average over the plateau pulses as specified in Table 3.2.

The resulting values of C_0 are reported in Table 3.2 together with the corresponding experimental parameters and a qualitative assessment of the reliability of each determination. The values range from 2.58 mol/kg at 200 °C to 9.35 mol/kg at 50 °C, spanning a factor of approximately 3.6 over the investigated temperature range. This variation is consistent with the exothermic nature of CO₂ chemisorption on MgO, for which the equilibrium surface coverage decreases with increasing temperature [34, 19].

Table 3.2: Summary of CO₂ adsorption capacities C_0 determined from pulse experiments at each temperature. A_N denotes the reference saturation signal computed as the average peak height over the plateau pulses. N_{tot} is the total number of pulses recorded, and N_{avg} is the number of pulses used to compute A_N . The reliability column provides a qualitative assessment of each C_0 value based on the observations discussed in Sections 3.4.2 and 3.4.3.

T (°C)	A_N (mbar)	N_{tot} (-)	N_{avg} (-)	C_0 (mol/kg)	Reliability
50	9.85×10^{-10}	40	10	9.35	Lower bound ^a
75	1.30×10^{-9}	38	13	5.56	Uncertain ^{b,c}
100	1.43×10^{-9}	40	20	4.21	Reliable
125	2.21×10^{-9}	40	10	4.61	Reliable ^d
150	1.88×10^{-9}	30	10	3.23	Reliable ^c
200	1.79×10^{-9}	40	10	2.58	Upper bound ^e

Plateau not reached after 40 pulses; C_0 underestimates the true equilibrium capacity.

Non-monotonic behaviour in early pulses attributed to experimental variability; C_0 may be slightly underestimated.

Experiment terminated early due to a technical interruption of the CATLAB system.

Slightly higher than at 100 °C; attributed to sample-to-sample variability between fresh catalyst charges, which is the most parsimonious explanation consistent with the overall decreasing trend.

No clear saturation trend observable; C_0 dominated by noise and represents an upper bound.

The reliability of the C_0 values varies considerably across the temperature series, and

this must be taken into account when interpreting the results. The most reliable determination is obtained at 100 °C, where the cumulative sum curve reaches a well-defined and stable plateau within the 40-pulse sequence and no experimental artefact was identified. The values at 125 °C and 150 °C are also considered reliable, despite the slight non-monotonicity between 100 °C and 125 °C and the early termination at 150 °C: in both cases, the plateau region is clearly established and the averaging procedure for A_N is robust. In contrast, the value at 50 °C is a lower bound of the true equilibrium capacity, as the cumulative sum has not converged by the end of the sequence, while the value at 200 °C is an upper bound dominated by measurement noise. The value at 75 °C carries the largest uncertainty due to the combination of the experimental artefact in the early pulses and the early termination of the sequence.

Comparison with the literature

The adsorption capacities determined in the present work can be compared with values reported in the literature for MgO-based sorbents. From the nominal composition $\text{Mg}_4\text{NiAlO}_x$ established in Section 2.2.2, an upper-bound estimate of the MgO mass fraction can be obtained by attributing all magnesium to a periclase-type MgO phase, which yields approximately 56 % by mass. The actual MgO content is expected to be lower, since part of the magnesium is engaged in spinel-type MgAl_2O_4 domains rather than free MgO, so that the values reported below should be regarded as conservative lower bounds when normalised per kilogram of MgO.

Song et al. reported a CO_2 adsorption capacity of approximately 1.80 mol/kg for porous MgO at 50 °C under 0.15 bar to 1 bar of CO_2 [34]. The value of $C_0 = 9.35$ mol/kg measured in the present work at 50 °C is substantially higher than this reference. However, this comparison must be interpreted with caution for two reasons. First, the MgO content of the present catalyst is less than 100 % by mass, so that the capacity normalised per kilogram of MgO alone would be higher than 9.35 mol/kg. Second, the experimental conditions differ significantly: Song et al. used pure CO_2 at pressures up to 1 bar, whereas the present work uses a 50 % CO_2/Ar mixture in a pulse configuration, which does not allow a direct thermodynamic comparison. The higher capacity observed here relative to bare porous MgO may also reflect the promoting effect of the Al_2O_3 support, which is known to provide additional basic surface sites for CO_2 adsorption in the form of surface hydroxyl groups [32].

Gao et al. reported capacities of up to 15.7 mol/kg for NaNO_2 -promoted MgO at 350 °C under pure CO_2 [19], and Wang et al. obtained up to 13.45 mol/kg for ternary nitrate-promoted MgO at 300 °C [41]. These values are of the same order of magnitude as the capacity measured here at 50 °C, which is noteworthy given that the present catalyst contains no molten salt promoter and operates at a much lower temperature. This suggests

that the MgO component of the Ni/Al₂O₃–MgO catalyst may possess a particularly high intrinsic surface area or a favourable pore structure that enhances CO₂ accessibility, although this hypothesis cannot be confirmed without detailed textural characterisation of the material.

At the higher end of the temperature range investigated, the capacity of 2.58 mol/kg at 200 °C is consistent with the thermodynamic expectation that MgO carbonation becomes increasingly unfavourable above 300 °C in the absence of promoters [19], and confirms that the present catalyst operates in a regime where the adsorption driving force is rapidly diminishing with temperature.

3.4.5 Effect of Temperature on Adsorption Capacity

The CO₂ adsorption capacity C_0 determined at each temperature is plotted in Figure 3.18. The overall trend is a clear and monotonic decrease of C_0 with increasing temperature, from 9.35 mol/kg at 50 °C to 2.58 mol/kg at 200 °C, representing a reduction of approximately 72% over the investigated temperature range. This behaviour is fully consistent with the exothermic nature of CO₂ chemisorption on MgO-based materials: as temperature increases, the thermodynamic driving force for the formation of surface carbonate and bicarbonate species decreases, reducing the equilibrium surface coverage and hence the total adsorption capacity accessible within the duration of the pulse sequence [34, 19].

The decrease in C_0 with temperature is however not uniform across the range investigated. A particularly sharp drop is observed between 50 °C and 75 °C, where C_0 decreases from 9.35 mol/kg to 5.56 mol/kg, a reduction of approximately 40% over a temperature interval of only 25 °C. This steep initial decrease suggests that the adsorption sites most active at low temperature are strongly sensitive to thermal deactivation, possibly corresponding to high-affinity surface sites such as low-coordination oxygen anions or step and corner sites on the MgO surface, which are known to exhibit particularly strong interactions with CO₂ [34]. It should however be recalled that the value at 75 °C carries a larger uncertainty than at other temperatures due to the experimental artefact identified in Section 3.4.2, and that the apparent magnitude of this drop may be partially overestimated.

Between 75 °C and 125 °C, the decrease in C_0 is more moderate, with values ranging from 5.56 mol/kg to 4.21 mol/kg and a slight non-monotonic inversion between 100 °C and 125 °C (4.21 mol/kg vs. 4.61 mol/kg). As discussed in Section 3.4.4, this inversion is attributed to experimental variability between fresh catalyst samples rather than to a genuine physical phenomenon. Within the experimental uncertainty, the adsorption capacity in this intermediate temperature range can be considered approximately constant, suggesting a transition between two thermodynamic regimes: a low-temperature regime dominated by strongly exothermic chemisorption on high-affinity sites, and a higher-

temperature regime where only moderate-affinity sites remain accessible [19, 41].

Above 125 °C, the decrease in C_0 resumes in a more regular fashion, from 4.61 mol/kg at 125 °C to 3.23 mol/kg at 150 °C and 2.58 mol/kg at 200 °C. In this temperature range, the thermodynamic penalty for carbonate formation becomes increasingly significant: using the thermodynamic data reported by Gao et al., the standard Gibbs free energy of MgO carbonation ($\Delta_r G_m^\circ \approx -100.7 \text{ kJ/mol} + T \times 175.0 \text{ J/K/mol}$) becomes positive above approximately 576 K (303 °C) under standard conditions, implying that the equilibrium conversion of MgO to MgCO_3 decreases rapidly as this threshold is approached [19]. The values of C_0 at 150 °C and 200 °C therefore reflect a system operating in a thermodynamically increasingly unfavourable regime, where only a small fraction of the MgO surface can sustain stable carbonate species under the prevailing CO_2 partial pressure.

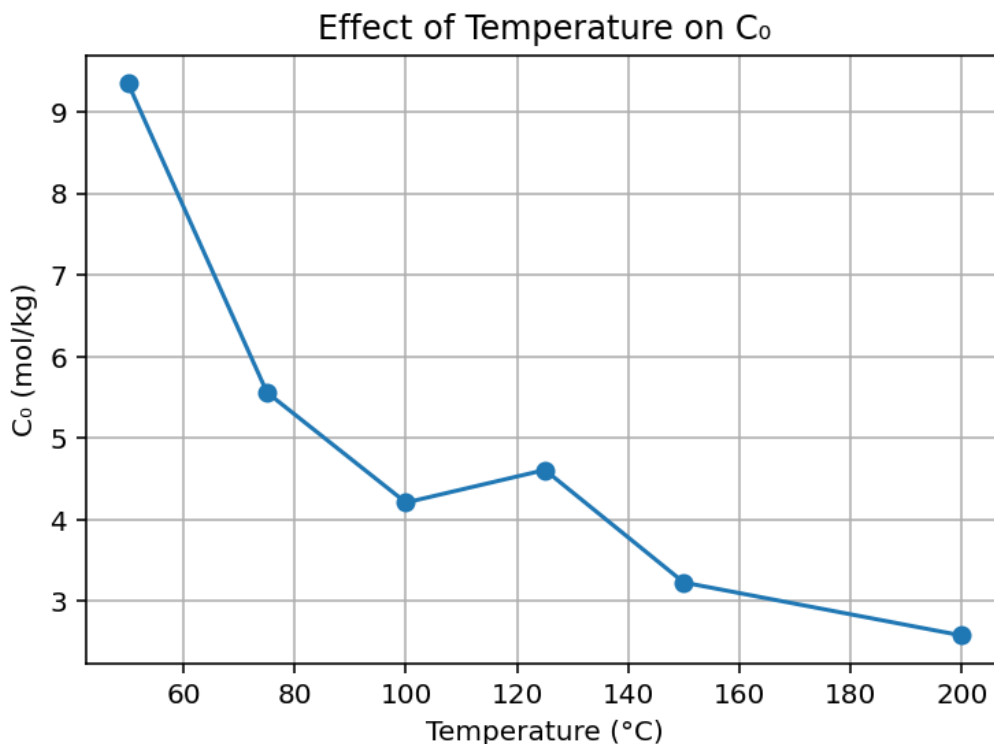


Figure 3.18: CO_2 adsorption capacity C_0 as a function of temperature for the Ni/ Al_2O_3 –MgO catalyst. The overall decreasing trend with temperature is consistent with the exothermic nature of CO_2 chemisorption on MgO. The slight inversion between 100 °C and 125 °C is attributed to experimental variability between fresh catalyst samples (see text).

The flow-rate series at 50 °C reveals a somewhat unexpected pattern: while the 200 mL/min curve lies systematically below the other two, the curves recorded at 50 and 100 mL/min are nearly superimposed throughout the entire pulse sequence. This flow-rate dependence may seem surprising at first, since C_0 is a thermodynamic quantity that should depend only on temperature and CO_2 partial pressure rather than on the carrier gas velocity, but it is in fact a direct consequence of the kinetic nature of the pulse measurement: a

higher flow rate shortens the contact time between each CO₂ pulse and the catalyst bed, so that a smaller fraction of the injected dose is retained per pulse and the integrated C_0 is correspondingly reduced. The convergence of the 50 and 100 mL/min curves is therefore a reassuring result, as it suggests that external mass-transfer resistance is already negligible at 100 mL/min and that this flow rate can be considered as representative of the intrinsic adsorption behaviour of the material, free from gas-phase transport limitations. It should be noted, however, that the near-identity of these two curves also raises a question regarding the calibration of the flow controller at low settings: if the actual flow rates delivered at 50 and 100 mL/min were closer than their nominal values suggest, this would offer an alternative explanation for their similarity, and one that would be considerably less reassuring. An independent verification of the delivered flow rates was not performed in the present work.

3.4.6 Effect of Carrier Gas Flow Rate at 50 °C

A complementary series of experiments was conducted at 50 °C using three different argon carrier gas flow rates (50, 100 and 200 mL/min) in order to assess whether the adsorption capacity measured under the reference conditions (100 mL/min) is free from external mass-transfer limitations. A fresh catalyst sample was used for each flow rate. The raw mass spectrometer signals for the three experiments are presented in Figures 3.19–3.21, and the corresponding normalised adsorbed fractions and cumulative sums are shown in Figures 3.22 and 3.23, respectively.

Raw signals and qualitative observations

The three pulse sequences exhibit markedly different behaviours that are immediately apparent from the raw signals. At 50 mL/min, the peaks are broader and more asymmetric than at higher flow rates, consistent with the longer residence time of the CO₂ pulse in the reactor at low carrier velocity. The reference saturation level reaches $A_N \approx 2.20 \times 10^{-9}$ mbar, which is approximately twice the value obtained at 100 mL/min ($A_N \approx 9.85 \times 10^{-10}$ mbar) and 200 mL/min ($A_N \approx 9.54 \times 10^{-10}$ mbar). This difference in A_N is physically expected: at lower carrier flow rates, the CO₂ that passes through the bed unreacted is less diluted by the carrier gas and reaches the mass spectrometer at a higher partial pressure. The normalisation by A_N in Equation (3.14) fully corrects for this effect, ensuring that the computed C_0 values are comparable across flow rates.

At 200 mL/min, the peaks are narrower and more symmetric, reflecting the shorter residence time of the pulse. The first peak height represents approximately 71% of A_N , compared to approximately 35% at 100 mL/min and approximately 30% at 50 mL/min. This systematic increase in the fraction of CO₂ escaping the bed on the first pulse with increasing flow rate provides a first qualitative indication that the carrier gas velocity

significantly affects the adsorption efficiency per pulse.

Quantitative effect of flow rate on C_0

The effect of carrier gas flow rate on the adsorption capacity is summarised in Figure 3.24. The values of C_0 decrease strongly and monotonically with increasing flow rate: from 10.15 mol/kg at 50 mL/min to 9.35 mol/kg at 100 mL/min and 4.27 mol/kg at 200 mL/min. The decrease is particularly pronounced between 100 and 200 mL/min, where C_0 drops by approximately 54%, while the difference between 50 and 100 mL/min is more moderate at approximately 8%.

The effect of the argon carrier gas flow rate on the apparent adsorption capacity C_0 at 50 °C is illustrated in Figure 3.24, which shows a monotonic decrease of C_0 from approximately 10.1 mol/kg at 50 mL/min to 4.2 mol/kg at 200 mL/min. This trend should not be interpreted as evidence for external mass-transfer limitations in the conventional sense: as pointed out by the theory of pulse adsorption experiments, the true thermodynamic capacity of the material is independent of the carrier gas velocity and cannot be affected by gas-phase transport resistance. What the flow rate does affect, however, is the fraction of the injected CO₂ dose that is retained during each individual pulse: at higher flow rates, the contact time between the CO₂ pulse and the catalyst bed is reduced, so that less CO₂ is adsorbed per pulse and more pulses would be required to reach complete saturation. Since the pulse sequence was limited to 40 injections in all experiments, the integrated sum underestimates the true C_0 to a degree that increases with flow rate, which explains the observed trend. A more rigorous determination of C_0 at 200 mL/min would therefore have required extending the pulse sequence beyond 40 injections, which was not done in the present work. The near-convergence of the 50 and 100 mL/min values suggests that 40 pulses are sufficient to capture most of the adsorption capacity at the reference flow rate of 100 mL/min, and that this condition provides a reasonable estimate of the true C_0 , albeit still a lower bound given the incomplete saturation discussed in Section 3.4.3.

3.5 Kinetic Modelling and Discussion

3.5.1 Thermodynamic Analysis

The temperature dependence of the CO₂ adsorption capacity C_0 can be analysed within a van't Hoff framework in order to extract an apparent adsorption enthalpy ΔH_{ads} . Under the assumption that C_0 measured at each temperature reflects a pseudo-equilibrium state reached within the pulse sequence, the adsorption capacity is taken as a proxy for the equilibrium surface coverage q_e , and one writes

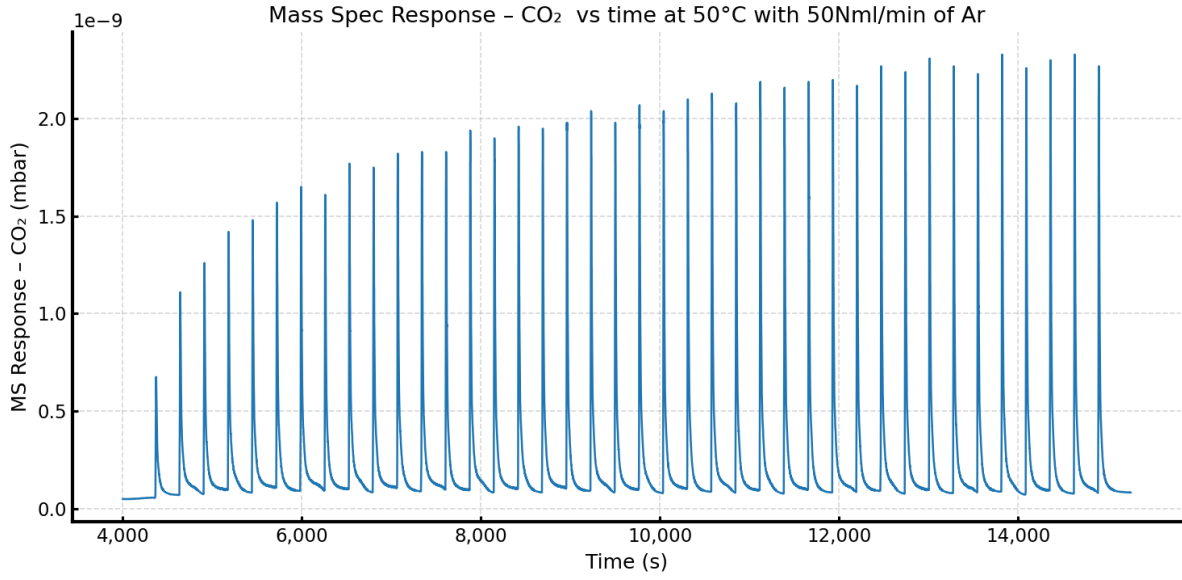


Figure 3.19: Mass spectrometer CO_2 partial pressure signal ($m/z = 44$) at the reactor outlet during the 40-pulse adsorption sequence at 50°C with an argon carrier flow rate of 50 mL/min . Note the broader and more asymmetric peak shape compared to higher flow rates, and the higher reference saturation level $A_N \approx 2.20 \times 10^{-9}\text{ mbar}$.

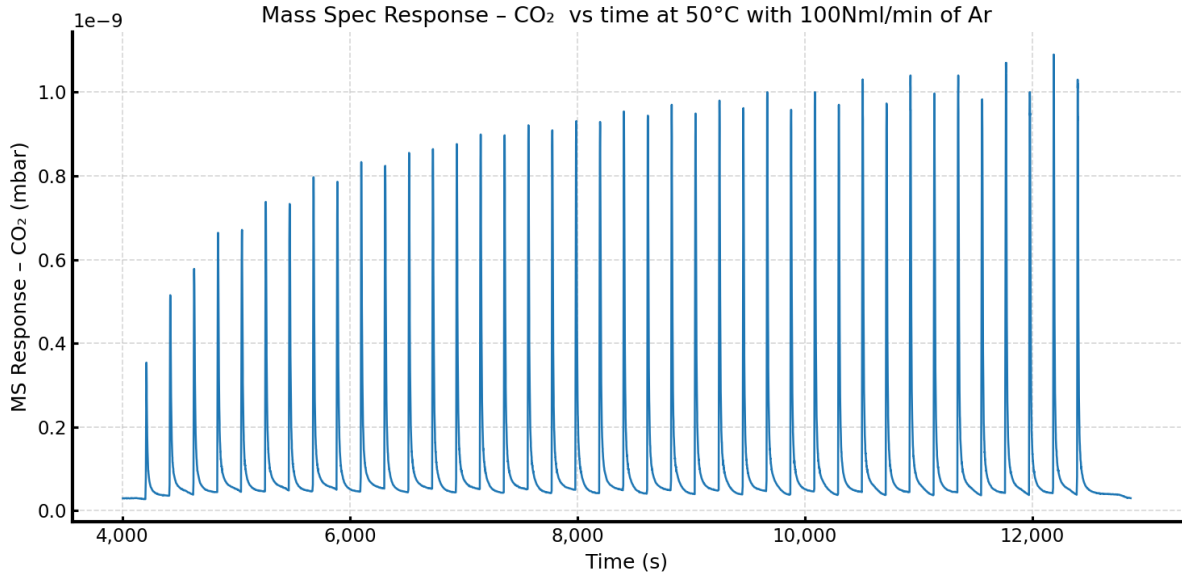


Figure 3.20: Mass spectrometer CO_2 partial pressure signal ($m/z = 44$) at the reactor outlet during the 40-pulse adsorption sequence at 50°C with an argon carrier flow rate of 100 mL/min (reference conditions).

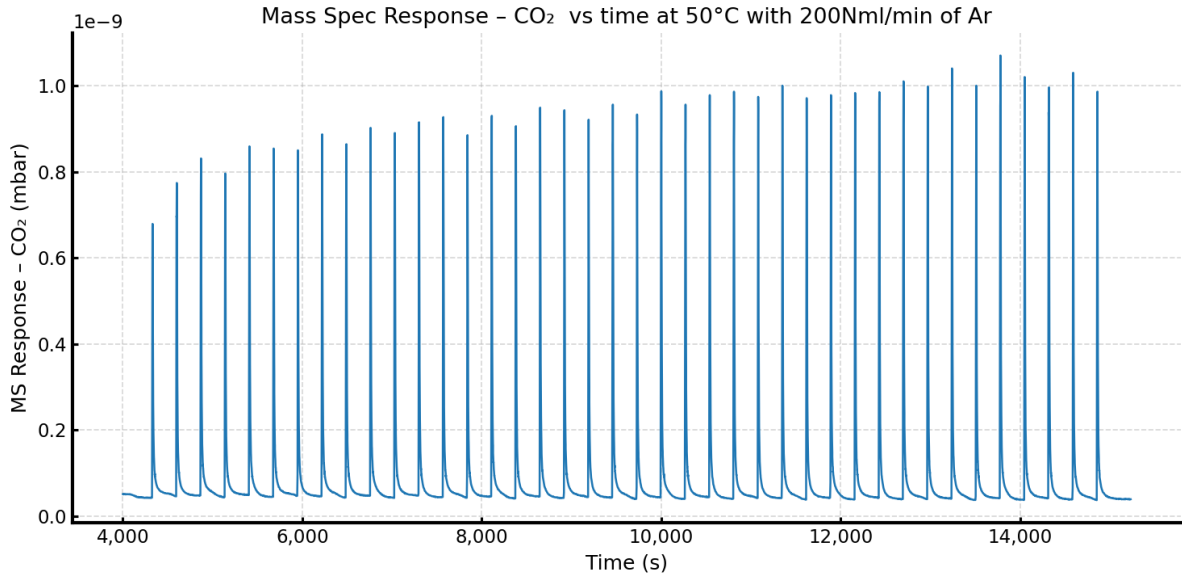


Figure 3.21: Mass spectrometer CO_2 partial pressure signal ($m/z = 44$) at the reactor outlet during the 40-pulse adsorption sequence at 50°C with an argon carrier flow rate of 200 mL/min . Note the narrower and more symmetric peak shape and the higher first-pulse signal relative to A_N , indicating reduced adsorption efficiency per pulse.

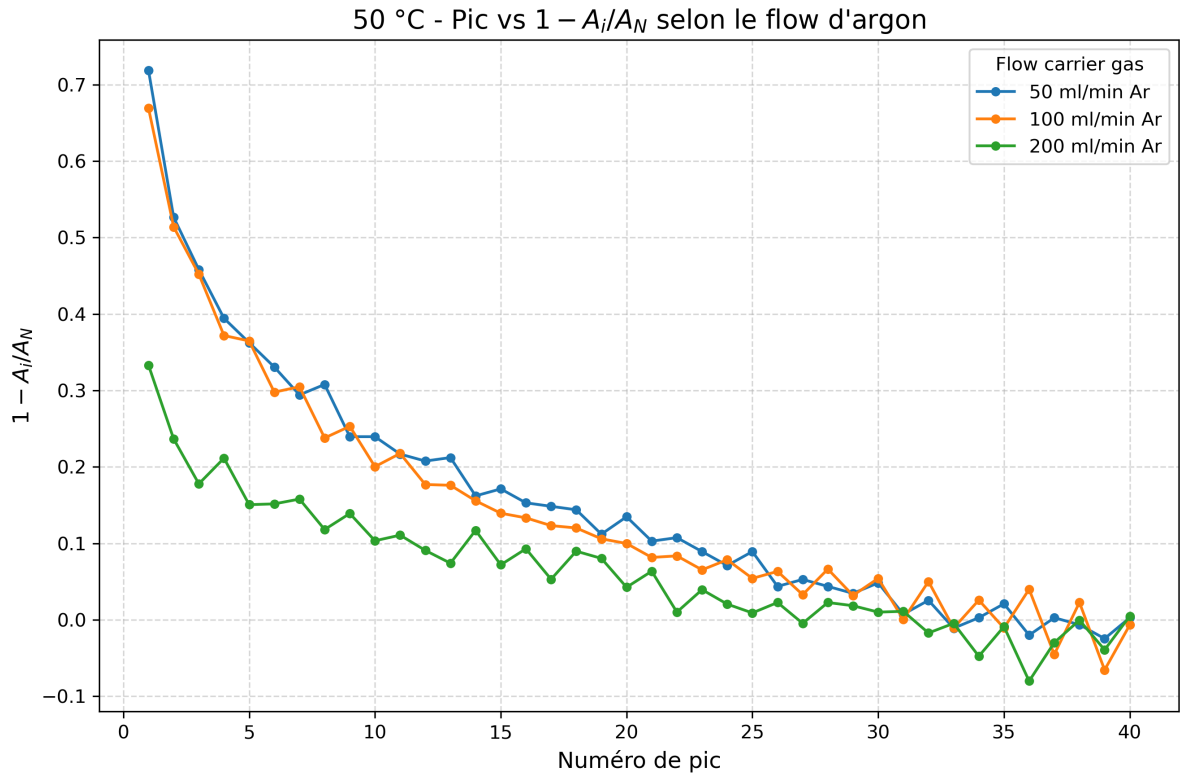


Figure 3.22: Normalised adsorbed fraction ($1 - A_i/A_N$) as a function of pulse number i at 50°C for three argon carrier gas flow rates: 50 , 100 and 200 mL/min . The systematic downward shift of the curves with increasing flow rate reflects the reduced contact time between CO_2 and the catalyst surface.

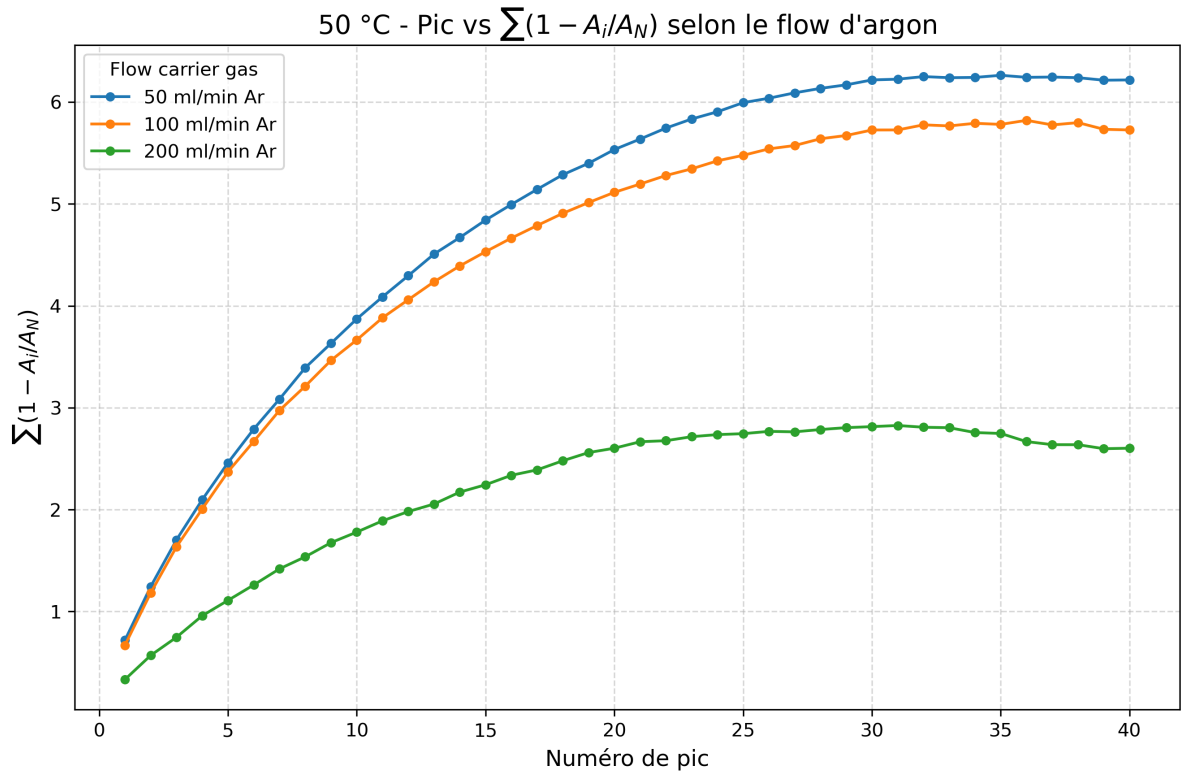


Figure 3.23: Cumulative sum $\sum_{j=1}^i (1 - A_j/A_N)$ as a function of pulse number i at 50 °C for three argon carrier gas flow rates. The final value of each curve is proportional to C_0 via Equation (3.14). The strong decrease in the plateau level with increasing flow rate confirms the significant influence of the carrier gas velocity on the measured adsorption capacity.

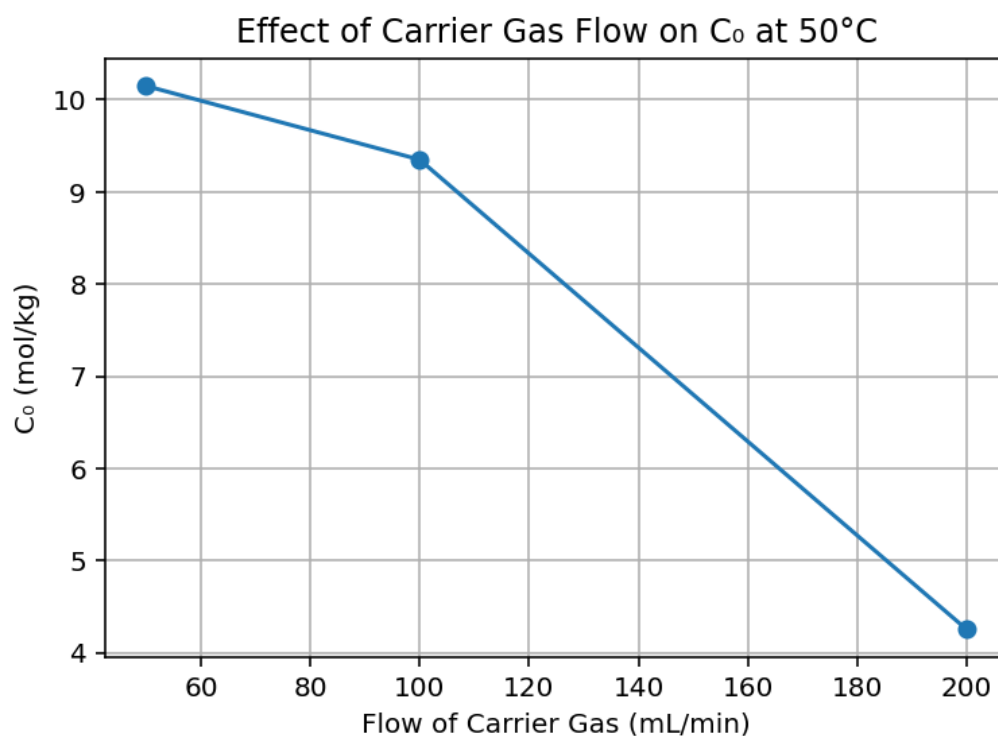


Figure 3.24: C_0 adsorption capacity at 50 °C as a function of argon carrier gas flow rate. The decrease of the apparent C_0 with increasing flow rate reflects the reduced contact time per pulse rather than a true reduction in adsorption capacity: at higher flow rates, more pulses would be required to reach complete saturation, and the 40-pulse sequence used here is insufficient to fully integrate the adsorbed fraction, leading to an underestimation of the true C_0 . The convergence of the 50 and 100 mL/min values suggests that the reference condition is approached at 100 mL/min, though a definitive conclusion would require extending the pulse sequence at higher flow rates.

$$\ln C_0 = -\frac{\Delta H_{\text{ads}}}{R} \cdot \frac{1}{T} + \text{const} = -\Delta H_{\text{ads}} \cdot \frac{1000}{RT} \cdot \frac{1}{1000} + \text{const}, \quad (3.15)$$

so that a plot of $\ln C_0$ versus $1000/(RT)$ yields a straight line whose slope is equal to $-\Delta H_{\text{ads}}$ expressed in kJ/mol, when $1000/(RT)$ is expressed in mol/kJ. The resulting plot is shown in Figure 3.25, together with three linear regressions performed on different subsets of the experimental data.

Three regressions were performed in order to assess the sensitivity of ΔH_{ads} to the experimental points identified as potentially unreliable in Sections 3.4.2 and 3.4.4: a first regression including all six data points, a second excluding the 75 °C point affected by the experimental artefact, and a third excluding both the 75 °C and 125 °C points. The results are summarised in Table 3.3.

Table 3.3: Results of the van’t Hoff linear regression of $\ln C_0$ versus $1000/(RT)$ for different subsets of experimental data. The slope of each regression yields the apparent adsorption enthalpy ΔH_{ads} .

Dataset	Slope	R^2	ΔH_{ads} (kJ/mol)
All points	10.107	0.922	−10.1
Without 75 °C	10.667	0.936	−10.7
Without 75 °C and 125 °C	10.760	0.954	−10.8

The three regressions yield very consistent slopes, ranging from 10.1 to 10.8, and correspondingly similar apparent adsorption enthalpies of approximately $\Delta H_{\text{ads}} \approx -10.1$ kJ/mol to -10.8 kJ/mol. This robustness of the result with respect to the exclusion of the problematic data points indicates that the van’t Hoff slope is a reliable characteristic of the overall temperature dependence of C_0 within the investigated range. The coefficient of determination improves modestly from $R^2 = 0.922$ to $R^2 = 0.954$ when the two problematic points are excluded, confirming that these points introduce scatter around the linear trend but do not fundamentally alter the slope. The preferred value of ΔH_{ads} adopted for subsequent discussion is -10.7 kJ/mol, obtained from the regression excluding the 75 °C point, as this represents the most defensible subset of the data.

Interpretation of the apparent adsorption enthalpy

The value of $\Delta H_{\text{ads}} \approx -10.7$ kJ/mol is remarkably low in comparison with the enthalpies typically reported for CO₂ chemisorption on MgO-based materials. The standard enthalpy of MgO carbonation ($\text{MgO} + \text{CO}_2 \rightarrow \text{MgCO}_3$) is approximately $\Delta_r H^\circ \approx -100.7$ kJ/mol at 298 K [19], and enthalpies of CO₂ adsorption on surface carbonate and bicarbonate sites of porous MgO have been reported in the range of -60 to -100 kJ/mol by calorimetric and temperature-programmed desorption measurements [34, 19, 41]. The apparent enthalpy

determined here is therefore approximately one order of magnitude smaller than these reference values. Three complementary mechanisms account for this discrepancy.

First, and most fundamentally, the van't Hoff analysis implicitly assumes that C_0 reflects the true thermodynamic equilibrium coverage q_e at each temperature. As demonstrated in Section 3.4.6, this assumption is not satisfied: the measured C_0 is a kinetically accessible capacity that depends on the carrier gas flow rate and hence on the contact time between CO_2 and the catalyst surface. The adsorption process on MgO involves several sequential steps (external film diffusion, intraparticle diffusion through the pore network, surface reaction to form carbonate species, and diffusion through the growing carbonate product layer) and only the fastest of these steps are completed within the duration of each pulse [34]. As temperature increases, the kinetic accessibility improves (faster diffusion, faster surface reaction), which partially compensates the thermodynamic decrease in equilibrium coverage. This partial compensation between thermodynamic and kinetic effects results in a weaker apparent temperature dependence of C_0 than would be expected from the true adsorption enthalpy alone, and hence in a lower apparent ΔH_{ads} .

Second, the MgO surface is energetically heterogeneous, presenting a distribution of basic sites with different adsorption enthalpies: high-affinity sites such as low-coordination corner and edge oxygen anions exhibit strong interactions with CO_2 ($\Delta H \approx -100$ to -150 kJ/mol), while moderate- and low-affinity terrace sites and Al_2O_3 surface hydroxyl groups interact more weakly ($\Delta H \approx -20$ to -80 kJ/mol) [34, 32]. As temperature increases, the high-affinity sites are progressively deactivated first, and the remaining accessible capacity is dominated by moderate- and low-affinity sites. The overall slope of $\ln C_0$ versus $1000/(RT)$ therefore represents a weighted average of the enthalpies of all contributing site families, pulled toward lower absolute values by the dominant contribution of moderate-affinity sites at high temperature.

Third, the value of C_0 at 50°C is a lower bound of the true equilibrium capacity at this temperature, as the pulse sequence has not reached complete saturation. If the true capacity at 50°C were substantially higher (as suggested by the still-rising cumulative sum at pulse 40) the slope of the van't Hoff plot would be steeper and ΔH_{ads} would be more negative, closer to the thermodynamic reference value.

Despite its limited quantitative significance as a true thermodynamic quantity, the van't Hoff analysis confirms the qualitative conclusion that CO_2 adsorption on the Ni/ Al_2O_3 -MgO catalyst is an exothermic process ($\Delta H_{\text{ads}} < 0$), consistent with the formation of surface carbonate and bicarbonate species on MgO basic sites. The apparent enthalpy of -10.7 kJ/mol should therefore be interpreted as a measure of the net temperature sensitivity of the kinetically accessible adsorption capacity under the specific conditions of the pulse experiment, rather than as an intrinsic physicochemical property of the catalyst

surface. A more rigorous determination of the true adsorption enthalpy would require equilibrium-based measurements such as isothermal thermogravimetric analysis at multiple CO_2 partial pressures or adsorption microcalorimetry, which are beyond the scope of the present work but are recommended for future investigations (Section 3.5.2).

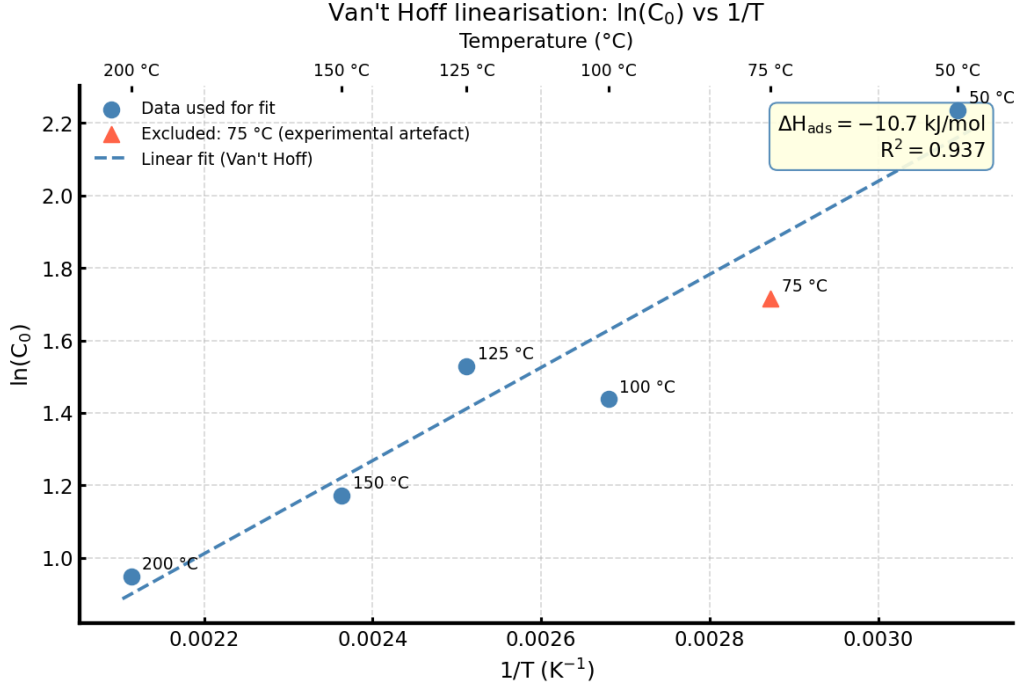


Figure 3.25: Van't Hoff plot: $\ln C_0$ as a function of $1000/(RT)$ for CO_2 adsorption on $\text{Ni}/\text{Al}_2\text{O}_3\text{--MgO}$ at temperatures between 50 °C and 200 °C. The dashed line represents the linear regression excluding the 75 °C data point (slope = 10.667, $R^2 = 0.936$), yielding an apparent adsorption enthalpy of $\Delta H_{\text{ads}} \approx -10.7 \text{ kJ/mol}$. All six data points are shown; the 75 °C and 125 °C points deviate most noticeably from the regression line, consistent with the experimental variability discussed in the text.

Temperature dependence of the apparent adsorption constant

The van't Hoff regression of Equation (3.15) can be re-written to yield an explicit expression for the apparent equilibrium adsorption constant as a function of temperature:

$$K_{\text{ads}}(T) = K_{\text{ads},0} \exp\left(-\frac{\Delta H_{\text{ads}}}{RT}\right), \quad (3.16)$$

where $\Delta H_{\text{ads}} = -10.7 \text{ kJ/mol}$ is the preferred value from Table 3.3 and $K_{\text{ads},0}$ is the pre-exponential factor determined from the regression intercept. This form is identical to the van't Hoff parameterisation adopted for all adsorption constants in the kinetic model Appendix B, Equation (B.1), which allows a direct comparison between the two sets of results.

The adsorption enthalpy of CO_2 -derived surface intermediates in the reference kinetic

model is $\Delta H_{\text{CO}_2}^\circ = -52 \text{ kJ/mol}$, approximately five times larger in magnitude than ΔH_{ads} derived from the pulse data. This difference is consistent with the underestimation mechanisms discussed above, kinetic limitations of the pulse experiment, surface heterogeneity, and the use of a lower bound for C_0 at 50°C . Both values nevertheless agree on the sign and the qualitative trend: CO_2 adsorption is moderately exothermic, and K_{ads} decreases with increasing temperature, in agreement with the decrease in C_0 observed experimentally and with the temperature dependence embedded in the kinetic model. A quantitative reconciliation of the two estimates would require equilibrium-based adsorption measurements, as discussed in Section 3.5.2.

3.5.2 One-Dimensional Transient Simulation of the Fixed-Bed Adsorption Experiment

Motivation

The pulse-sequence analysis presented in the preceding sections characterises the CO_2 adsorption behaviour of the $\text{Ni}/\text{Al}_2\text{O}_3\text{--MgO}$ catalyst through the scalar quantity C_0 and its temperature dependence, but provides no information on the spatial distribution of the adsorbed phase within the catalyst bed. In an integrated CO_2 capture and methanation (ICCM) cycle, the axial loading profile $q(z, t)$ determines how efficiently the bed capacity is utilised and how the adsorption front propagates during each adsorption step. A one-dimensional (1D) transient model of the fixed bed is therefore developed in this section in order to (i) reproduce the measured outlet signal sequence A_i/A_N and (ii) compute the internal loading profiles as a function of axial position and pulse number.

Model equations

The fixed bed is described by a 1D plug-flow model with an irreversible adsorption sink term. The gas-phase species balance over a differential axial element reads

$$\varepsilon_b \frac{\partial c}{\partial t} + u_i \frac{\partial c}{\partial z} = -(1 - \varepsilon_b) \rho_b \frac{\partial q}{\partial t}, \quad (3.17)$$

where c (mol m^{-3}) is the gas-phase CO_2 concentration, q (mol kg^{-1}) is the surface loading, $\varepsilon_b = 0.40$ is the bed void fraction (not directly measured; estimated from typical literature values for packed beds of similar particle size), u_i (m s^{-1}) is the interstitial gas velocity, and $\rho_b = W_{\text{cat}}/(A_c L_{\text{cat}}) \approx 2600 \text{ kg m}^{-3}$ is the catalyst bulk density, computed on the actual catalytic bed length $L_{\text{cat}} \approx 1 \text{ mm}$ (the remainder of the 100 mm tube is occupied by inert quartz wool and does not contribute to adsorption); z and t denote the axial coordinate within the catalytic zone and time, respectively.

The solid-phase balance describes the irreversible chemisorption of CO_2 on the MgO

surface as

$$\frac{\partial q}{\partial t} = k_{\text{ads}}(T) c \max\left(0, 1 - \frac{q}{q_{\text{max}}}\right), \quad (3.18)$$

where $k_{\text{ads}}(T)$ ($\text{m}^3 \text{kg}^{-1} \text{s}^{-1}$) is the adsorption rate constant and $q_{\text{max}} = C_0(T)$ (mol kg^{-1}) is the saturation capacity at each temperature (Table 3.2). The irreversible formulation is physically motivated by the chemisorption mechanism of CO_2 on MgO : CO_2 reacts with surface oxide anions to form stable carbonate species that do not desorb during the inter-pulse Ar purge at the temperatures investigated [34, 19]. Accordingly, when $c_{\text{inlet}} = 0$ during the purge step, the right-hand side of Equation (3.18) vanishes identically and the solid loading $q(z, t)$ remains frozen, a feature that correctly reproduces the cumulative loading observed across the 40-pulse sequence.

The boundary and initial conditions are

$$\begin{aligned} c(z = 0, t) &= \frac{x_{\text{CO}_2} P_{\text{atm}}}{RT} \quad \text{during pulse} \quad (0 \leq t \leq t_{\text{pd}}), \\ c(z = 0, t) &= 0 \quad \text{during purge} \quad (t_{\text{pd}} < t \leq \Delta t), \\ c(z, t_0) &= 0, \quad q(z, t_0) = 0, \end{aligned} \quad (3.19)$$

where $x_{\text{CO}_2} = 0.5$ is the CO_2 mole fraction in the injection loop, $t_{\text{pd}} = 3 \text{ s}$ is the pulse duration (corresponding to the injection of the 5 mL loop at 100 mL/min), and Δt is the inter-pulse interval (210 s or 270 s depending on temperature, as measured from the raw data).

Equation (3.17) is discretised spatially over the catalytic bed length $L_{\text{cat}} = 1 \text{ mm}$ using an upwind finite-difference scheme with $N = 20$ equally spaced cells ($\Delta z = L_{\text{cat}}/N = 0.05 \text{ mm}$), and integrated in time using the stiff Radau solver (`scipy.integrate.solve_ivp`, relative tolerance 10^{-4} , absolute tolerance 10^{-7}). The simulated outlet signal is computed as the peak gas-phase concentration in the last cell, normalised by C_{feed} , yielding the dimensionless ratio A_i^{sim}/A_N directly comparable to the experimental A_i/A_N .

Parameter estimation

The only free parameters of the model are the pre-exponential factor A and the apparent activation energy E_a of the adsorption rate constant, which is assumed to follow an Arrhenius-type temperature dependence:

$$k_{\text{ads}}(T) = A \exp\left(-\frac{E_a}{RT}\right). \quad (3.20)$$

Before fitting k_{ads} globally, its identifiability at each temperature is first assessed by sweeping its value over six orders of magnitude (10^{-7} to $10^{-1} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$) and computing the resulting RMSE on the A_i/A_N sequence (Figure 3.26). For all six temperatures, the RMSE exhibits a well-defined minimum located in the narrow range $[3 \times 10^{-3}, 3 \times 10^{-2}] \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$. For $k_{\text{ads}} \lesssim 10^{-5} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$, adsorption is too slow to capture any meaningful CO_2 amount during a 3 s pulse and the simulated A_i/A_N converges to unity, yielding a constant, large RMSE. For $k_{\text{ads}} \gtrsim 3 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$, each pulse is fully captured until q_{max} is reached, and the model can no longer reproduce the gradual rise of A_i/A_N observed experimentally, leading to a steep RMSE increase.

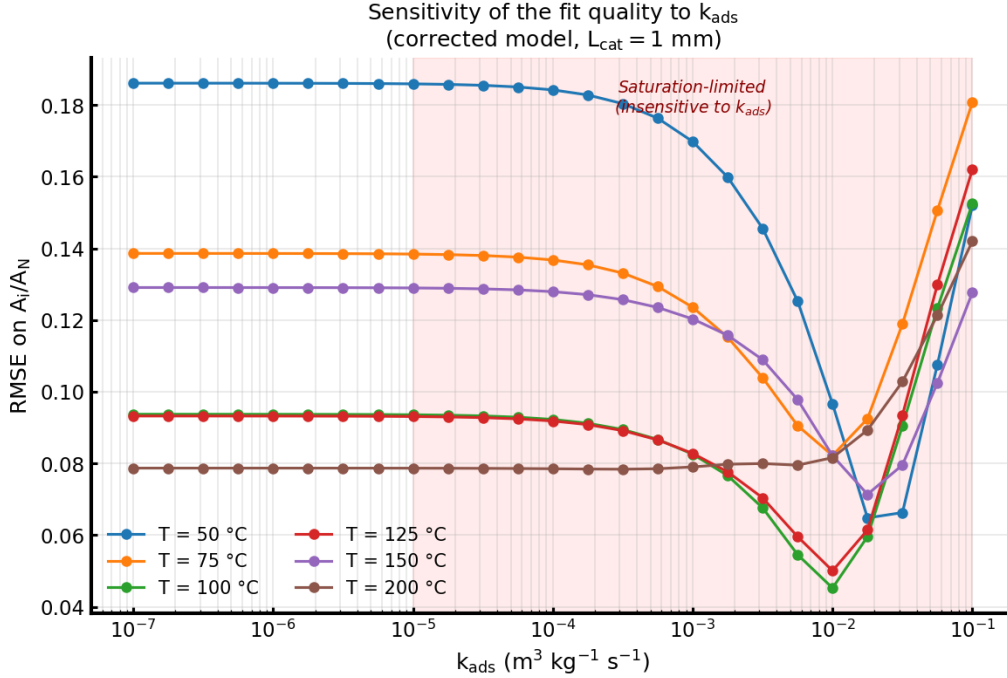


Figure 3.26: Sensitivity of the fit quality to k_{ads} at each temperature. The RMSE on the A_i/A_N sequence is computed for k_{ads} values spanning six orders of magnitude. All six temperatures exhibit a well-defined optimum located in the narrow range $[3 \times 10^{-3}, 3 \times 10^{-2}] \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$, confirming the local identifiability of k_{ads} while highlighting that its optimum varies by less than one order of magnitude across the 150 K temperature window probed.

The optimal k_{ads} values are remarkably close across the six temperatures, spanning less than one order of magnitude despite the 150 K temperature window. This already indicates that the temperature dependence of the adsorption rate constant is weak under the present conditions.

To formalise this observation, the Arrhenius constraint of Equation (3.20) is imposed and

the two parameters A and E_a are estimated simultaneously by minimising the total sum of squared residuals over all six temperatures:

$$\min_{A, E_a} \sum_{T \in \mathcal{T}} \sum_{i=1}^{N_T} \left(\frac{A_i^{\text{sim}}(T)}{A_N} - \frac{A_i^{\text{obs}}(T)}{A_N} \right)^2, \quad (3.21)$$

where $\mathcal{T} = \{50, 75, 100, 125, 150, 200\}^\circ\text{C}$ and N_T is the number of pulses recorded at temperature T . The optimisation is carried out in two stages: a coarse grid search over $(\ln A, E_a)$ followed by a Nelder–Mead refinement. The converged parameter set is

$$E_a = 0.3 \text{ kJ/mol}, \quad A = e^{-4.54} = 1.07 \times 10^{-2} \text{ m}^3/\text{kg/s}, \quad (3.22)$$

yielding $k_{\text{ads}}(T)$ values that are essentially temperature-independent across the experimental range (Table 3.4). The physical interpretation of this near-zero apparent activation energy is discussed below (“Temperature dependence of the adsorption rate constant”).

Table 3.4: Adsorption rate constants $k_{\text{ads}}(T)$ obtained from the global Arrhenius fit (Equation (3.20)), with root-mean-square errors (RMSE) on the simulated A_i/A_N sequence, saturation capacity $q_{\text{max}} = C_0$ (Table 3.2), and mass-balance loading $C_{0,\text{calc}}$ accumulated over the pulse sequence. The loading percentage is $C_{0,\text{calc}}/q_{\text{max}} \times 100$.

T ($^\circ\text{C}$)	k_{ads} ($\text{m}^3/\text{kg/s}$)	q_{max} (mol/kg)	$C_{0,\text{calc}}$ (mol/kg)	RMSE
50	9.68×10^{-3}	9.35	3.22	0.099
75	9.75×10^{-3}	5.56	2.36	0.082
100	9.81×10^{-3}	4.21	1.28	0.045
125	9.87×10^{-3}	4.61	1.22	0.050
150	9.91×10^{-3}	3.23	1.05	0.082
200	1.00×10^{-2}	2.58	0.16	0.082

Simulation results

Outlet signal. Figure 3.27 compares the simulated and measured A_i/A_N sequences at all six temperatures. The 1D model reproduces the overall trend at each temperature, with RMSE values in the range 0.045–0.099. The model correctly captures the progressive increase of A_i/A_N with pulse number, reflecting the gradual saturation of the catalyst bed, and the systematic shift of the curves toward unity with increasing temperature. The remaining discrepancies (visible as pulse-to-pulse scatter around the simulated curve) are attributed to the experimental variability already identified in Section 3.4.3: signal noise, minor flow-rate fluctuations, and the use of a fresh catalyst sample at each temperature.

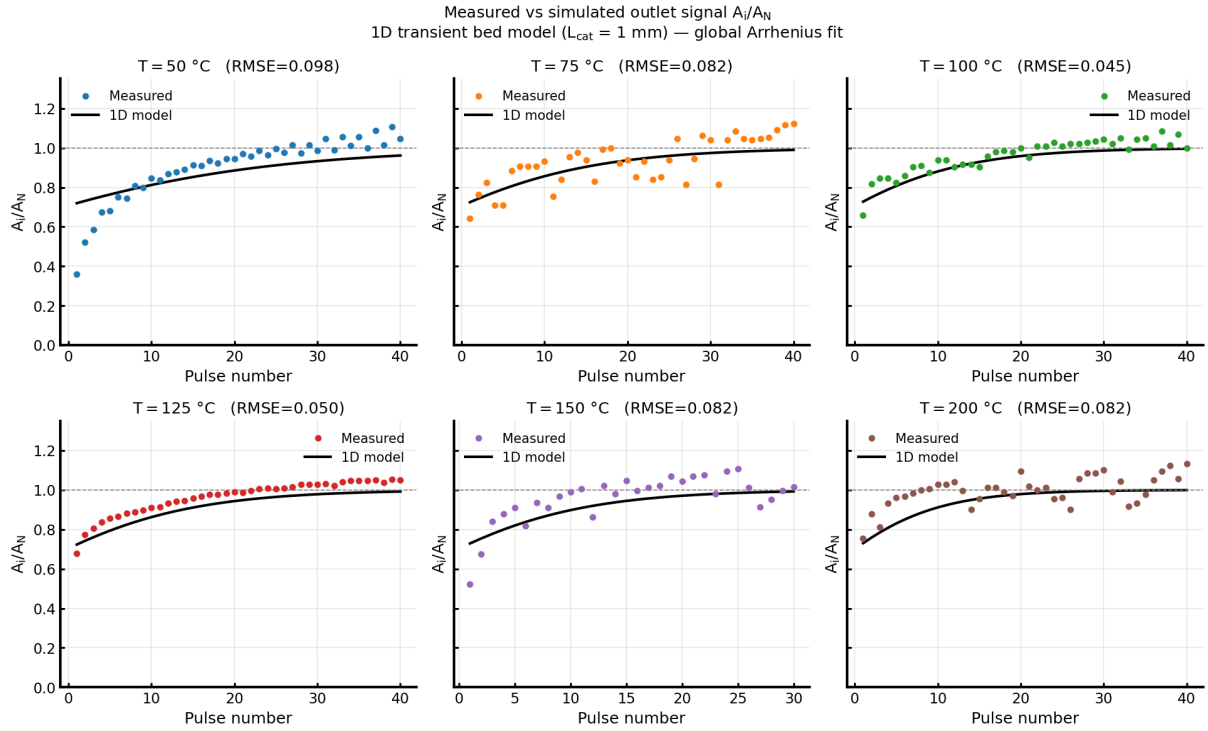


Figure 3.27: Measured (coloured symbols) and simulated (black curve) normalised outlet signal A_i/A_N as a function of pulse number, for all six temperatures investigated. The simulation uses the 1D transient model (Equations (3.17)–(3.18)) with the global Arrhenius parameters of Equation (3.22). The dashed horizontal line marks $A_i/A_N = 1$ (complete saturation).

Axial loading profiles. Figure 3.28 shows the evolution of the axial solid loading profile $q(z)$ after each purge step, for all six temperatures, over the catalytic bed length $L_{\text{cat}} = 1$ mm. The dotted grey line indicates q_{max} , the equilibrium saturation capacity at each temperature (Table 3.2).

A key observation is that the axial profiles are essentially flat across the millimetre-thick catalytic bed. At 100 °C after 40 pulses, for instance, $q(z)$ varies from 4.17 mol/kg at the inlet to 4.15 mol/kg at the outlet (a relative gradient of only 0.4 %). This is a direct consequence of the very short gas residence time in the catalytic zone ($\tau = L_{\text{cat}}/u_i \approx 9.2$ ms, to be compared with the pulse duration $t_{\text{pd}} = 3$ s): each pulse traverses the bed approximately 325 times during its duration, and any axial concentration gradient is rapidly homogenised. The fixed bed therefore operates essentially as a well-mixed reactor at the scale of a single pulse, and the 1D-PFR formulation reduces *de facto* to a zero-dimensional adsorption model in the present configuration.

At all temperatures, the mean simulated loading after 40 pulses approaches the equilibrium capacity q_{max} , indicating that the catalyst grains progress steadily toward saturation throughout the pulse sequence. The mass-balance estimate $C_{0,\text{calc}}$ derived from the experimental A_i/A_N signals (Table 3.4) is systematically lower than the simulated mean loading; this discrepancy reflects the well-known sensitivity of the cumulative mass balance to the value of the reference area A_N and to small drifts in the MS baseline, which are amplified when summing over 40 pulses. The internal loading profiles are therefore reported here as a model output rather than in direct comparison with the experimental cumulative loading, which is itself subject to the limitations already identified in Section 3.4.3 and in the flow-rate study (Section 3.4.6).

Detailed profiles at 100 °C. Figure 3.29 presents the evolution of $q(z)$ at 100 °C in greater detail. The profile is essentially spatially uniform at every pulse number, in agreement with the well-mixed regime discussed above. The mean loading rises progressively from $q \approx 0.4$ mol/kg after pulse 1 to $q \approx 4.16$ mol/kg after pulse 40, the latter approaching the equilibrium capacity $q_{\text{max}} = 4.21$ mol/kg (dotted grey line). The pulse-by-pulse evolution of the mean loading is therefore the relevant quantity, while the spatial information is essentially redundant in this configuration.

Space–time diagram. Figure 3.30 presents the loading $q(z, n_{\text{pulse}})$ at 100 °C as a contour map. As anticipated from the flat axial profiles, the iso-loading contours are nearly vertical: the loading depends only weakly on the axial position and is essentially controlled by the pulse number. The colour gradient along the horizontal axis reflects the progressive saturation of the catalyst grains, which proceeds uniformly throughout the millimetre-thick bed.

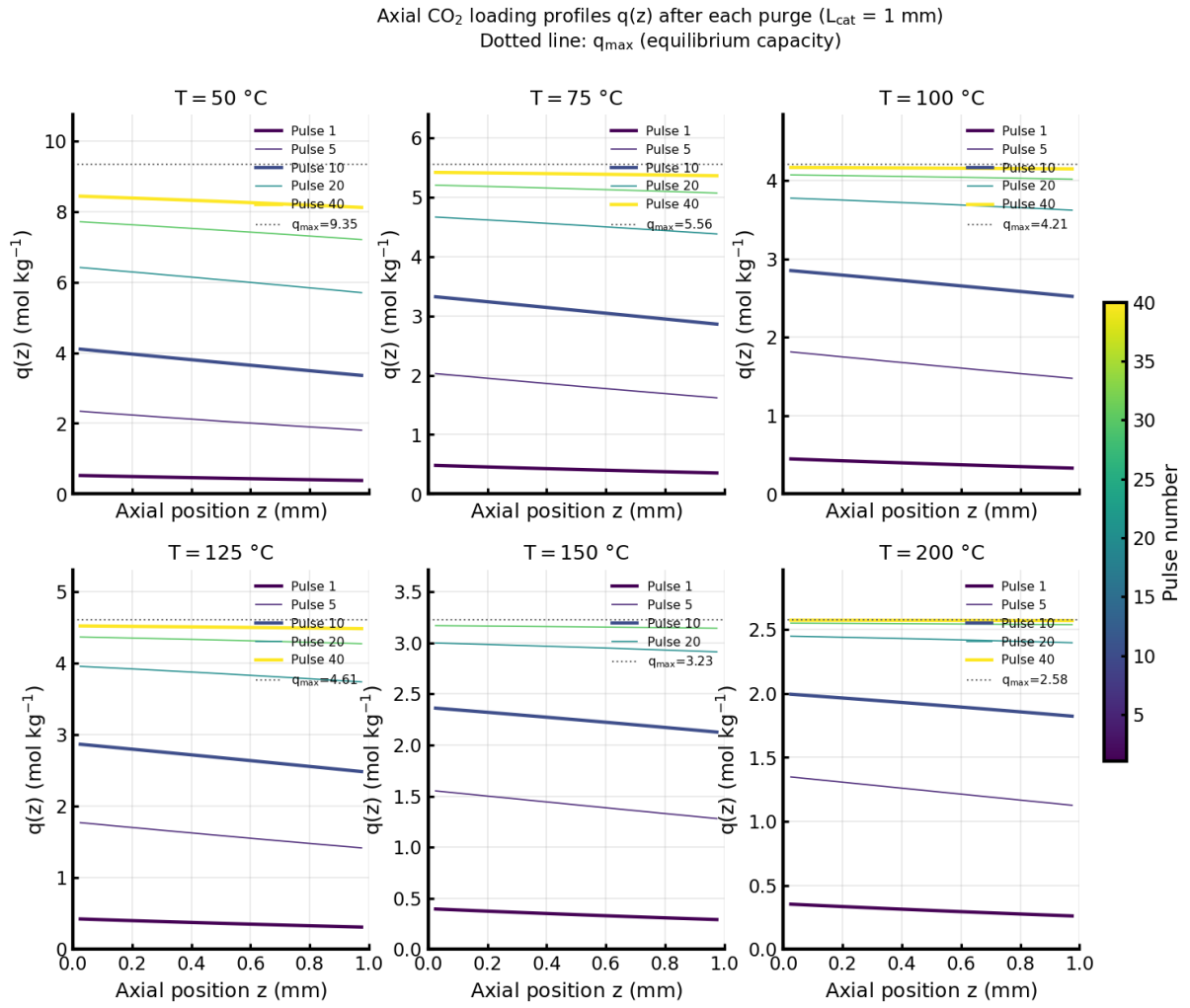


Figure 3.28: Axial CO₂ loading profiles $q(z)$ (mol kg⁻¹) after each purge step, at all six temperatures, over the catalytic bed length $L_{\text{cat}} = 1$ mm. Each curve corresponds to the end-of-purge profile after the labelled pulse number. The dotted grey line indicates q_{max} , the equilibrium saturation capacity (Table 3.2).

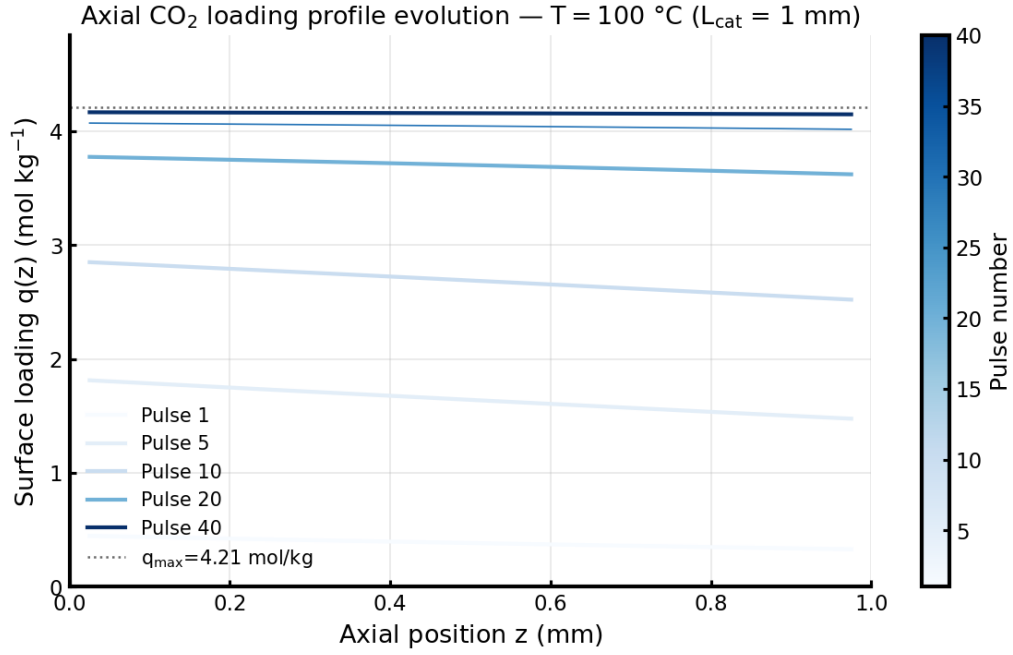


Figure 3.29: Evolution of the axial CO₂ loading profile $q(z)$ at 100 °C over the catalytic bed length $L_{\text{cat}} = 1$ mm, shown at pulse numbers 1, 5, 10, 20 and 40. The dotted grey line indicates the equilibrium capacity $q_{\max} = 4.21$ mol/kg. Colour intensity increases with pulse number (colour bar at right).

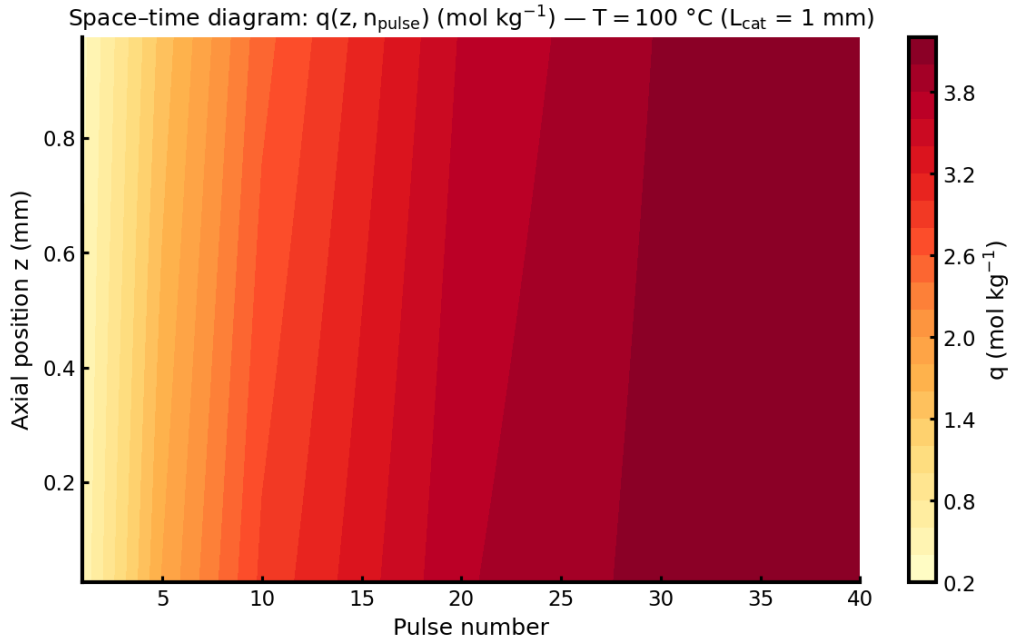


Figure 3.30: Space-time diagram of the CO₂ solid loading $q(z, n_{\text{pulse}})$ (mol kg⁻¹) at 100 °C. The colour encodes the loading value; iso-loading contours are nearly vertical, confirming that the loading depends almost exclusively on the pulse number rather than on the axial position within the millimetre-thick catalytic bed.

Temperature dependence of the adsorption rate constant

The global Arrhenius fit yields an apparent activation energy of essentially zero ($E_a \approx 0.3 \text{ kJ mol}^{-1}$). The fitted k_{ads} values in Table 3.4 confirm this finding directly: they vary by less than 4 % across the entire 50–200 °C range, from 9.68×10^{-3} to $1.00 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$. This result must be interpreted with care.

Several elements indicate that this near-zero E_a should not be read as a true elementary activation barrier. First, the sensitivity analysis (Figure 3.26) shows that the individual optima at each temperature, although well defined, lie in a narrow range spanning less than one decade [3×10^{-3} , 3×10^{-2}] $\text{m}^3 \text{ kg}^{-1} \text{ s}^{-1}$; the temperature window probed (150 K) is therefore insufficient to resolve any modest E_a that might exist. Second, the entire temperature dependence observed in the experimental A_i/A_N sequences propagates into the model through the saturation capacity $q_{\text{max}} = C_0(T)$ (Section 3.4.5), which decreases by a factor of 3.6 between 50 and 200 °C and shifts the driving-force term $(1 - q/q_{\text{max}})$ accordingly. Once this thermodynamic dependence is absorbed in q_{max} , no significant residual kinetic temperature dependence remains for k_{ads} to capture.

The physically meaningful conclusion is therefore that the adsorption kinetics on the Ni/Al₂O₃–MgO catalyst are sufficiently fast in the 50–200 °C range that they do not limit the pulse uptake at the time scale of the experiment; the thermal sensitivity of CO₂ uptake observed in the A_i/A_N sequence originates almost entirely from the temperature dependence of the equilibrium capacity $q_{\text{max}} = C_0(T)$. The corresponding thermodynamic analysis (the van’t Hoff analysis of $\ln C_0$ leading to $\Delta H_{\text{ads}} \approx -10.7 \text{ kJ mol}^{-1}$ in Section 3.5.1) therefore remains the primary route to characterise the thermal behaviour of the system, and the 1D model serves here as an independent cross-validation of the dynamic mass balance rather than as a source of additional kinetic information.

Limitations of the 1D model

Several simplifying assumptions limit the quantitative accuracy of the present model. First, axial dispersion is neglected: the plug-flow assumption neglects the axial mixing that contributes to the pulse broadening visible in the raw MS signals (Section 3.4.2); given the well-mixed character of the millimetre-thick bed in our configuration, however, this simplification is of limited consequence here. Second, the bed void fraction $\varepsilon_b = 0.40$ is estimated from typical literature values for packed beds of similar particle size rather than directly measured; this estimate enters the kinetic balance through the prefactor $(1 - \varepsilon_b)\rho_b$ but is unlikely to affect the qualitative conclusions of this section. Third, the irreversible single-site kinetic model (Equation (3.18)) is a simplification of the multi-step surface carbonation process, which in reality involves external film diffusion, intraparticle pore diffusion, and growth of a carbonate product layer [34]. A physically more complete

description would require a shrinking-core or random-pore formulation [11], which is beyond the scope of the present work. Fourth, as established in Section 3.4.6, the measured C_0 values represent kinetically accessible rather than equilibrium capacities; the use of $q_{\max} = C_0$ therefore likely underestimates the true saturation capacity. Finally, the 1D model is in practice spatially redundant in the present configuration, where the very short residence time in the millimetre-thick catalytic bed leads to nearly flat axial profiles. A zero-dimensional well-mixed formulation would capture the same physics with fewer degrees of freedom; the 1D model is nevertheless retained here for consistency with the original modelling brief and for its ability to make the well-mixed regime quantitatively visible (Figures 3.28–3.30).

A further limitation concerns the quantification method itself. The adsorption capacities reported in this chapter are based on peak heights rather than integrated peak areas. As argued in Section 3.2.5, only the time-integral of the partial-pressure signal is strictly proportional to the eluted CO_2 quantity; peak heights are an acceptable proxy only insofar as the pulse shape remains constant. This condition is reasonably met within the temperature series at fixed carrier flow rate, but it breaks down in the flow-rate series (Section 3.4.6), where the pulse becomes visibly broader and more asymmetric at low carrier velocity. The C_0 values compared across flow rates should therefore be read as qualitative rather than quantitative, and an area-based re-analysis is recommended for any future quantitative use of this dataset.

Despite these limitations, the global model achieves RMSE values below 0.10 across all six temperatures and demonstrates that the dynamic mass balance of the pulse experiment can be reproduced quantitatively without invoking a temperature-dependent adsorption kinetics, thereby strengthening the interpretation that the temperature behaviour of CO_2 uptake under the present conditions is governed by the equilibrium capacity $q_{\max} = C_0(T)$ rather than by an activation barrier.

3.6 Conclusions and Outlook

This chapter characterised the CO₂ adsorption behaviour of the Ni/Al₂O₃–MgO dual-function material over the temperature range 50–200 °C using a pulse injection technique, providing the sorption side of the dataset needed to assess the material’s potential for integrated CO₂ capture and methanation.

The adsorption capacity decreases monotonically with temperature, consistent with the exothermic nature of CO₂ chemisorption on MgO basic sites. The apparent adsorption enthalpy extracted from a van’t Hoff analysis is however substantially lower than the bulk carbonation enthalpy of MgO, a discrepancy that reflects the kinetic nature of the pulse measurement rather than a genuine thermodynamic feature: the protocol captures a kinetically accessible fraction of the total capacity rather than the true equilibrium uptake, and this limitation is confirmed by the strong dependence of the measured capacity on carrier gas flow rate. The 1D transient model developed to reproduce the outlet pulse sequence is fully consistent with this picture, and additionally reveals that the catalyst bed remains only partially saturated at the end of each experiment, a result of direct practical relevance for sizing the adsorption step in an ICCM cycle.

From an ICCM perspective, the central finding of this chapter is the thermal mismatch between the adsorption and methanation functions of the material: meaningful CO₂ uptake is confined to temperatures well below the range in which the Ni phase becomes catalytically active, confirming that capture and conversion must operate sequentially rather than simultaneously. This constraint is thermodynamically grounded and constitutes the primary design variable for any cycle based on this class of dual-function material.

Looking ahead, equilibrium-based adsorption measurements (such as isothermal thermogravimetric analysis or adsorption microcalorimetry) are needed to determine the true adsorption enthalpy and characterise the surface site distribution quantitatively. Such data would place the kinetic results of this chapter on a more stable physicochemical foundation and enable predictive modelling of the full ICCM cycle.

Chapter 4

General Conclusion

This thesis characterised the two constituent functions of an integrated CO₂ capture and methanation (ICCM) process, namely catalytic methanation and CO₂ adsorption, on a single Ni/Al₂O₃–MgO dual-function material, and examined the consequences of their coexistence within a cyclic process. The two functions were studied independently, each in a dedicated chapter with its own conclusions. The present synthesis draws together the outcomes of both campaigns and develops the implication that neither establishes on its own: the constraint that governs their coupling.

The methanation study (Chapter 2) established, over the 250–325 °C window and at 3 bar, that the catalyst operates in a kinetically controlled regime, with measured CO₂ conversions remaining well below the Sabatier equilibrium across the explored conditions. The intrinsic character of the data was confirmed quantitatively through the Weisz–Prater, Mears and Anderson criteria, all of which remained below their thresholds at the worst-case operating point. Four Langmuir–Hinshelwood–Hougen–Watson mechanisms were derived and discriminated; the hybrid associative–dissociative route (model 11) was selected as the reference kinetic model, with a mean absolute deviation of $D = 5.79\%$, the lowest of the four candidates. The selection rested not on this metric alone but on a combined assessment of residual bias, parameter identifiability and physical plausibility. Mechanistically, the retained model implies that CO₂ is activated through both molecular pre-adsorption on basic surface sites, consistent with the MgO-rich support, and hydrogen-assisted C–O bond cleavage at the Ni surface. The strong temperature dependence of the CH₄/CO selectivity was attributed quantitatively to the ratio of activation energies between the methanation and reverse water–gas shift routes ($E_2/E_1 \approx 3.8$).

The adsorption study (Chapter 3) characterised the CO₂ uptake of the same material over 50–200 °C by pulse injection. The capacity decreased monotonically with temperature, consistent with the exothermic character of CO₂ chemisorption on MgO basic sites. A van 't Hoff analysis yielded an apparent adsorption enthalpy substantially smaller in

magnitude than the bulk carbonation enthalpy of MgO. This discrepancy was shown to reflect the kinetically accessible, protocol-dependent nature of the pulse measurement rather than a genuine thermodynamic property: the measured capacity depends on the carrier-gas flow rate, and the lowest-temperature point is itself a lower bound, the bed not having reached saturation within the pulse sequence. A one-dimensional transient model reproduced the outlet pulse sequences and established that the bed remains only partially saturated at the end of each experiment, a result of direct relevance for sizing the capture step of an ICCM cycle.

Considered jointly, the two campaigns identify the central design constraint of an ICCM cycle based on this class of material: a thermal mismatch between the adsorption and catalytic functions. Significant CO₂ uptake is confined to 50–200 °C, whereas catalytic activity requires 250–325 °C. The two functions share no common operating temperature, so capture and conversion cannot proceed simultaneously; the process must instead be organised as two sequential half-cycles, a low-temperature capture step followed by a higher-temperature hydrogenation step that simultaneously regenerates the sorbent. This constraint is thermodynamically grounded, arising from the exothermicity of both CO₂ chemisorption and the Sabatier reaction, and it constitutes the primary design variable for any cycle built on a Ni/Al₂O₃–MgO formulation.

The quantitative descriptions developed here provide the foundation on which such a design can be based. The reference LHHW rate expression, together with the transport criteria verified for the methanation campaign, can be incorporated directly into a reactor model of the hydrogenation half-cycle, while the adsorption capacity and its temperature dependence delimit the operating window and the achievable loading of the capture half-cycle. The two analyses are moreover mutually consistent at the point where they overlap, both identifying the basic surface sites as the locus of CO₂ storage and activation.

Three limitations delimit these conclusions and define the priorities for further work. First, the kinetic parameters were estimated over a narrow temperature window (250–325 °C), which limits their statistical identifiability. A wider operating range, complemented by *in situ* spectroscopic characterisation of the surface intermediates, would consolidate the mechanistic assignment. Second, the pulse technique yields a kinetically accessible rather than an equilibrium capacity; equilibrium-based measurements, such as isothermal thermogravimetric analysis at several CO₂ partial pressures or adsorption microcalorimetry, are required to determine the true adsorption enthalpy and to resolve the distribution of basic sites. Third, and most importantly, the two functions were characterised separately, whereas their coupling must be studied through full adsorption–hydrogenation cycling on the same material. Such cycling would quantify the transient water peak produced during regeneration, the extent of Ni re-oxidation under alternating CO₂/H₂ atmospheres, and the cycle-to-cycle stability of both functions, which together determine ICCM perfor-

mance and lie beyond the reach of two independent steady-state campaigns. The kinetic and sorption descriptions established in this work constitute the quantitative groundwork on which such an integrated study, and ultimately the rational design of efficient ICCM cycles, can be built.

Bibliography

- [1] Ali M. Alkadhém, Mohammed A. A. Elgzoly, Ali Alshami, and Sagheer A. Onaizi. Kinetics of CO₂ capture by novel amine-functionalized magnesium oxide adsorbents. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 616:126258, 2021.
- [2] Luis M. Aparicio. Transient isotopic studies and microkinetic modeling of methane reforming over nickel catalysts. *Journal of Catalysis*, 165(2):262–274, 1997.
- [3] M. A. Arellano-Trevino, Nahal Kanani, Christina W. Jeong-Potter, and Robert J. Farrauto. Bimetallic catalysts for CO₂ capture and hydrogenation at simulated flue gas conditions. *Chemical Engineering Journal*, 375:121953, 2019.
- [4] Morris D. Argyle and Calvin H. Bartholomew. Heterogeneous catalyst deactivation and regeneration: a review. *Catalysts*, 5(1):145–269, 2015.
- [5] Aline Auroux and Antonella Gervasini. Microcalorimetric study of the acidity and basicity of metal oxide surfaces. *Journal of Physical Chemistry*, 94(16):6371–6379, 1990.
- [6] Melvin Avrami. Kinetics of phase change. I. General theory. *The Journal of Chemical Physics*, 7(12):1103–1112, 1939.
- [7] Mohd Ambar Alam Aziz, Aishah Abdul Jalil, Sugeng Triwahyono, and Athirah Ahmad. CO₂ methanation over heterogeneous catalysts: recent progress and future prospects. *Green Chemistry*, 17:2647–2663, 2015.
- [8] Marie-Laure Bailly, Claire Chizallet, Guylène Costentin, Jean-Marc Krafft, Hélène Lauron-Pernot, and Michel Che. A spectroscopy and catalysis study of the nature of active sites of MgO catalysts: Thermodynamic Brønsted basicity versus reactivity of basic sites. *Journal of Catalysis*, 235(2):413–422, 2005.
- [9] Alejandro Bermejo-López, Beñat Pereda-Ayo, José Antonio González-Marcos, and Juan Ramón González-Velasco. Mechanism of the CO₂ storage and in situ hydrogenation to CH₄. Temperature and adsorbent loading effects over Ru-CaO/Al₂O₃ and Ru-Na₂CO₃/Al₂O₃ catalysts. *Applied Catalysis B: Environmental*, 256:117845, 2019.

- [10] Suresh K. Bhatia and D. D. Perlmutter. The effect of pore structure on fluid-solid reactions: application to the SO₂-lime reaction. *AIChE Journal*, 27(2):226–234, 1981.
- [11] Suresh K. Bhatia and D. D. Perlmutter. Effect of the product layer on the kinetics of the co₂-lime reaction. *AIChE Journal*, 29(1):79–86, 1983.
- [12] Kenneth P. Burnham and David R. Anderson. *Model Selection and Multimodel Inference: A Practical Information-Theoretic Approach*. Springer, 2nd edition, 2002.
- [13] Guido Busca and Vera Lorenzelli. Infrared spectroscopic identification of species arising from reactive adsorption of carbon oxides on metal oxide surfaces. *Materials Chemistry*, 7(1):89–126, 1982.
- [14] I. Champon, A. Bengaouer, A. Chaise, S. Thomas, and A.-C. Roger. Carbon dioxide methanation kinetic model on a commercial ni/al₂o₃ catalyst. *Journal of CO₂ Utilization*, 34:256–265, 2019.
- [15] Leonardo Colelli, Claudia Bassano, Nicola Verdone, Valentina Segneri, and Giorgio Vilardi. Power-to-Gas: Process analysis and control strategies for dynamic catalytic methanation system. *Energy Conversion and Management*, 305:118257, 2024.
- [16] Mathieu Digne, Philippe Sautet, Pascal Raybaud, Paul Euzen, and Hervé Toulhoat. Use of dft to achieve a rational understanding of acid-basic properties of γ -alumina surfaces. *Journal of Catalysis*, 226(1):54–68, 2004.
- [17] Melis S. Duyar, M. A. Arellano Trevino, and Robert J. Farrauto. Dual function materials for co₂ capture and conversion using renewable h₂. *Applied Catalysis B: Environmental*, 168–169:370–376, 2015.
- [18] Larissa Fedunik-Hofman, Alicia Bayon, and Scott W. Donne. Comparative kinetic analysis of CaCO₃/CaO reaction system for energy storage and carbon capture. *Applied Sciences*, 9(21):4601, 2019.
- [19] Wanlin Gao, Michalis A. Vasiliades, Constantinos M. Damaskinos, Meng Zhao, Wenqi Fan, Qiang Wang, Tomas Ramirez Reina, and Angelos M. Efsthathiou. Molten salt-promoted mgo adsorbents for co₂ capture: Transient kinetic studies. *Environmental Science & Technology*, 55(8):4513–4521, 2021.
- [20] Zhen-liang Guo, Xiao-lü Bian, Yü-bo Du, Wen-chao Zhang, Ding-ding Yao, and Hai-ping Yang. Recent advances in integrated carbon dioxide capture and methanation technology. *Journal of Fuel Chemistry and Technology*, 51(3):293–303, 2023.
- [21] Jose A. Hernandez Lalinde, Pakpong Roongruangsree, Jan Ilseemann, Marcus Bäumer, and Jan Kopyscinski. CO₂ methanation and reverse water gas shift re-

- action. kinetic study based on in situ spatially-resolved measurements. *Chemical Engineering Journal*, 390:124629, 2020.
- [22] International Energy Agency (IEA). Carbon capture utilisation and storage (ccus) – energy system. <https://www.iea.org/energy-system/carbon-capture-utilisation-and-storage>, 2024. Accessed 2026-01-14.
- [23] IPCC. Climate change 2023: Synthesis report. contribution of working groups i, ii and iii to the sixth assessment report of the intergovernmental panel on climate change, 2023. Core Writing Team, H. Lee and J. Romero (eds.).
- [24] Jean-Claude Lavalley. Infrared spectrometric studies of the surface basicity of metal oxides and zeolites using adsorbed probe molecules. *Catalysis Today*, 27(3–4):377–401, 1996.
- [25] Octave Levenspiel. *Chemical Reaction Engineering*. John Wiley & Sons, New York, 3rd edition, 1999.
- [26] Carlos V. Miguel, Adélio Mendes, and Luís M. Madeira. Intrinsic kinetics of CO_2 methanation over an industrial nickel-based catalyst. *Journal of CO_2 Utilization*, 25:128–136, 2018.
- [27] Florent Minette, Michael Lugo-Pimentel, Dean Modroukas, Andrew W. Davis, Rajinder Gill, Marco J. Castaldi, and Juray De Wilde. Intrinsic kinetics of steam methane reforming on a thin, nanostructured and adherent Ni coating. *Applied Catalysis B: Environmental*, 238:184–197, 2018.
- [28] Carlo Morterra and Giuliana Magnacca. A case study: surface chemistry and surface structure of catalytic aluminas, as studied by vibrational spectroscopy of adsorbed species. *Catalysis Today*, 27(3–4):497–532, 1996.
- [29] Hiroshi Muroyama, Yuki Tsuda, Toshiaki Asakoshi, Hasan Masitah, Tekeou Okanishi, Toshiaki Matsui, and Koichi Eguchi. Carbon dioxide methanation over Ni catalysts supported on various oxides. *Journal of Catalysis*, 343:178–184, 2016.
- [30] Ibeh S. Omodolor, Hope O. Otor, Joseph A. Andonegui, Bryan J. Allen, and Ana C. Alba-Rubio. Dual-function materials for CO_2 capture and conversion: A review. *Industrial & Engineering Chemistry Research*, 59(40):17612–17631, 2020.
- [31] J. A. Onrubia-Calvo, A. Quindimil, A. Davó-Quñonero, A. Bermejo-López, E. Bailón-García, B. Pereda-Ayo, D. Lozano-Castelló, J. A. González-Marcos, A. Bueno-López, and J. R. González-Velasco. Kinetics, model discrimination, and parameters estimation of CO_2 methanation on highly active Ni/zeo-2 catalyst. *Industrial & Engineering Chemistry Research*, 61(29):10419–10435, 2022.

- [32] A. Quindimil, J. A. Onrubia-Calvo, A. Davó-Quiñonero, A. Bermejo-López, E. Bailón-García, B. Pereda-Ayo, D. Lozano-Castelló, J. A. González-Marcos, A. Bueno-López, and J. R. González-Velasco. Intrinsic kinetics of CO_2 methanation on low-loaded $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst: Mechanism, model discrimination and parameter estimation. *Journal of CO₂ Utilization*, 57:101888, 2022.
- [33] Daniel Schmider, Lubow Maier, and Olaf Deutschmann. Reaction kinetics of CO and CO_2 methanation over nickel. *Industrial & Engineering Chemistry Research*, 60(16):5792–5805, 2021.
- [34] Gan Song, Xun Zhu, Rong Chen, Qiang Liao, Yu-Dong Ding, and Lin Chen. An investigation of CO_2 adsorption kinetics on porous magnesium oxide. *Chemical Engineering Journal*, 283:175–183, 2016.
- [35] Kristian Stangeland, Dmytro Kalai, Hailong Li, and Zhixin Yu. CO_2 methanation: the effect of catalysts and reaction conditions. *Energy Procedia*, 105:2022–2027, 2017.
- [36] Hongman Sun, Shuzhuang Sun, Tong Liu, Jingbin Zeng, Youhe Wang, Zifeng Yan, and Chunfei Wu. Integrated CO_2 capture and utilization: Selection, matching, and interactions between adsorption and catalytic sites. *ACS Catalysis*, 14(20):15572–15589, 2024.
- [37] Shuzhuang Sun, Hongman Sun, Shaoliang Guan, Shaojun Xu, and Chunfei Wu. Integrated CO_2 capture and methanation on $\text{Ru}/\text{CeO}_2\text{-mgo}$ combined materials: Morphology effect from CeO_2 support. *Fuel*, 317:123420, 2022.
- [38] Matteo Tommasi, Simge Naz Degerli, Gianguido Ramis, and Ilenia Rossetti. Advancements in CO_2 methanation: A comprehensive review of catalysis, reactor design and process optimization. *Chemical Engineering Research and Design*, 201:457–482, 2024.
- [39] M. F. Vega, E. Diaz-Faes, and Carmen Barriocanal. Kinetic and mechanistic study of CO_2 adsorption on activated hydrochars. *Journal of CO₂ Utilization*, 81:102716, 2024.
- [40] Charlotte Vogt, Matteo Monai, Guido J. Kramer, and Bert M. Weckhuysen. The renaissance of the Sabatier reaction and its applications on Earth and in space. *Nature Catalysis*, 2:188–197, 2019.
- [41] Junya Wang, Min Li, Peng Lu, Ping Ning, and Qiang Wang. Kinetic study of CO_2 capture on ternary nitrates modified mgo with different precursor and morphology. *Chemical Engineering Journal*, 392:123752, 2020.

- [42] Ke Wang, Youwei Zhao, Peter T. Clough, Pengfei Zhao, and Edward J. Anthony. Structural and kinetic analysis of CO₂ sorption on NaNO₂-promoted MgO at moderate temperatures. *Chemical Engineering Journal*, 372:1048–1057, 2019.
- [43] K. Zhang, D. Guo, X. Wang, Y. Qin, L. Hu, Y. Zhang, R. Zou, and S. Gao. Sustainable CO₂ management through integrated CO₂ capture and conversion. *Journal of CO₂ Utilization*, 72:102493, 2023.

Appendix A

Complete LHHW derivations of the four mechanisms

This appendix provides the algebraic derivation of the four LHHW rate expressions of Section 4.2.6, namely Equations (2.23), (2.24), (2.25), (2.28). For each mechanism, the same protocol is applied:

1. writing of the elementary rate of the rate-determining step (RDS) in terms of fractional coverages θ_i ;
2. substitution of the coverages by partial pressures using the quasi-equilibrium of all non-rate-determining steps;
3. enforcement of the site balance $\sum_i \theta_i + \theta_* = 1$ on each independent site pool;
4. introduction of the thermodynamic driving-force factor $1 - Q/K_{\text{eq}}$;
5. simplification under the Most Abundant Reaction Intermediate (MARI) hypothesis and lumping of the upstream equilibria into a composite constant K_{Cx} .

Notation. Asterisks (*) denote Ni^0 sites; carets ($\wedge$) denote support sites. K_i are adsorption constants; K_j is the equilibrium constant of step j ; $K_{\text{eq}}^{\text{meth}}$ and K_{RWGS} are the equilibrium constants of the Sabatier and reverse water–gas shift reactions, respectively. The total site density L is absorbed into the apparent rate constant k .

A.1 Mechanism 1 – Dissociative carbon route

The RDS is step 4 of Table 2.11, $\text{CO}^* + * \rightleftharpoons \text{C}^* + \text{O}^*$, with elementary rate

$$r_4 = k_4 \theta_{\text{CO}} \theta_* - k_{-4} \theta_{\text{C}} \theta_{\text{O}}. \quad (\text{A.1})$$

The quasi-equilibrium of steps 1, 2, 3, 10 and 11 yields

$$\theta_{\text{H}} = \sqrt{K_{\text{H}_2} p_{\text{H}_2}} \theta_*, \quad \theta_{\text{CO}} = K_{\text{CO}} p_{\text{CO}} \theta_*, \quad \theta_{\text{O}} = \frac{K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}}}{K_{\text{H}_2} p_{\text{H}_2}} \theta_*. \quad (\text{A.2})$$

The methanic intermediates C_xH_y^* are dropped from the site balance under the MARI hypothesis. The carbon-related contribution to the denominator is lumped into $K_{\text{Cx}} \equiv K_{\text{CO}_2}^{1/2} K_{\text{H}_2}^{-1/4}$, giving

$$\theta_* = \left[1 + K_{\text{Cx}} p_{\text{CO}_2}^{0.5} p_{\text{H}_2}^{-0.25} + \sqrt{K_{\text{H}_2} p_{\text{H}_2}} + K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}} + K_{\text{OH}} \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}^{0.5}} \right]^{-1}. \quad (\text{A.3})$$

Closing the cycle on the overall Sabatier reaction yields the driving force

$1 - p_{\text{CH}_4} p_{\text{H}_2\text{O}}^2 / (p_{\text{CO}_2} p_{\text{H}_2}^4 K_{\text{eq}}^{\text{meth}})$. Substituting (A.2)–(A.3) into (A.1) reproduces Equation (2.23) of the main text. The *squared* denominator reflects the consumption of two vacant Ni sites in the RDS.

A.2 Mechanism 2 – Associative formate route (two site types)

The RDS is step 3 of Table 2.12, $\text{CO}_2^\wedge + \text{H}^* \rightleftharpoons \text{HCOO}^\wedge + *$, with rate

$$r_3 = k_3 \theta_{\text{CO}_2}^\wedge \theta_{\text{H}}^* - k_{-3} \theta_{\text{HCOO}}^\wedge \theta_*. \quad (\text{A.4})$$

The relevant quasi-equilibria give

$$\theta_{\text{H}}^* = \sqrt{K_{\text{H}_2} p_{\text{H}_2}} \theta_*, \quad \theta_{\text{CO}_2}^\wedge = K_{\text{CO}_2} p_{\text{CO}_2} \theta_\wedge, \quad (\text{A.5})$$

$$\theta_{\text{H}_2\text{O}}^* = K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}} \theta_*, \quad \theta_{\text{OH}}^* = \frac{K_{\text{OH}} p_{\text{H}_2\text{O}}}{\sqrt{K_{\text{H}_2} p_{\text{H}_2}}} \theta_*. \quad (\text{A.6})$$

Two *independent* site balances apply:

$$\theta_* + \theta_{\text{H}}^* + \theta_{\text{H}_2\text{O}}^* + \theta_{\text{OH}}^* = 1, \quad \theta_\wedge + \theta_{\text{CO}_2}^\wedge \approx 1, \quad (\text{A.7})$$

where $\theta_{\text{HCOO}}^\wedge$ is treated as kinetically irrelevant (following Onrubia-Calvo et al.). Substitution into (A.4), together with the Sabatier driving force, gives Equation (2.24) of the main text. The *factored, non-squared* denominator reflects the independent saturation of the two site pools: only one Ni site and one support site are consumed in the RDS.

A.3 Mechanism 3 – H-assisted CO formation route

The RDS is step 4 of Table 2.13, $\text{HCOO}^* + * \rightleftharpoons \text{CO}^* + \text{OH}^*$, with rate

$$r_4 = k_4 \theta_{\text{HCOO}} \theta_* - k_{-4} \theta_{\text{CO}} \theta_{\text{OH}}. \quad (\text{A.8})$$

The quasi-equilibria of steps 1–3 yield

$$\theta_{\text{HCOO}} = K_3 K_{\text{CO}_2} p_{\text{CO}_2} \sqrt{K_{\text{H}_2} p_{\text{H}_2}} \theta_*, \quad (\text{A.9})$$

together with $\theta_{\text{CO}} = K_{\text{CO}} p_{\text{CO}} \theta_*$ and $\theta_{\text{OH}} = K_{\text{OH}} p_{\text{H}_2\text{O}} / \sqrt{K_{\text{H}_2} p_{\text{H}_2}} \theta_*$.

Following Quindimil et al., the site balance is grouped into two factored sub-pools (one carrying the CO_2/HCOO branch, the other the $\text{H}/\text{OH}/\text{CO}$ branch):

$$\theta_* = \left[\left(1 + \sqrt{K_{\text{H}_2} p_{\text{H}_2}} + K_{\text{CO}_2} p_{\text{CO}_2} \right) \left(\sqrt{K_{\text{H}_2} p_{\text{H}_2}} + K_{\text{OH}} \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}^{0.5}} + K_{\text{CO}} p_{\text{CO}} \right) \right]^{-1/2}. \quad (\text{A.10})$$

This factorisation is a modelling assumption introduced by [28] and is retained in the main text. Because the RDS produces CO and OH, closure of the cycle on the reverse water–gas shift reaction yields the driving force $1 - p_{\text{CO}} p_{\text{H}_2\text{O}} / (p_{\text{CO}_2} p_{\text{H}_2} K_{\text{RWGS}})$. Inserting (A.9)–(A.10) into (A.8) reproduces Equation (2.25) of the main text, with explicit CO inhibition through the term $K_{\text{CO}} p_{\text{CO}}$.

A.4 Mechanism 4 – Hybrid route (model 11, Hernandez Lalinde et al.)

The RDS is step AB7 of Table 2.14, $\text{COH}^* + \text{H}^* \rightleftharpoons \text{CH}^* + \text{OH}^*$, with COH^* identified as the carbon-side MARI. The elementary rate is

$$r_{\text{AB7}} = k_{\text{AB7}} \theta_{\text{COH}} \theta_{\text{H}} - k_{-\text{AB7}} \theta_{\text{CH}} \theta_{\text{OH}}. \quad (\text{A.11})$$

Combining the quasi-equilibria of steps AB1–AB4 gives a lumped expression for the COH^* coverage:

$$\theta_{\text{COH}} = K_{\text{COH}} p_{\text{CO}_2}^{0.5} p_{\text{H}_2}^{0.5} \theta_*, \quad (\text{A.12})$$

where $K_{\text{COH}} \equiv K_{\text{AB1}}^{1/2} K_{\text{AB2}} K_{\text{AB3}} K_{\text{AB4}}$ is the composite constant identified with K_{Cx} in Equation (2.26). Together with $\theta_{\text{H}} = \sqrt{K_{\text{H}_2} p_{\text{H}_2}} \theta_*$ and $\theta_{\text{OH}} = K_{\text{OH}} p_{\text{H}_2\text{O}} / \sqrt{K_{\text{H}_2} p_{\text{H}_2}} \theta_*$, and dropping the methanic intermediates from the site balance, one obtains

$$\theta_* = \left[1 + K_{\text{COH}} p_{\text{CO}_2}^{0.5} p_{\text{H}_2}^{0.5} + \sqrt{K_{\text{H}_2} p_{\text{H}_2}} + K_{\text{OH}} \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}^{0.5}} \right]^{-1}. \quad (\text{A.13})$$

Closing the cycle on the overall Sabatier reaction recovers the driving force

$1 - p_{\text{CH}_4} p_{\text{H}_2\text{O}}^2 / (p_{\text{CO}_2} p_{\text{H}_2}^4 K_{\text{eq}}^{\text{meth}})$. Substituting (A.12)–(A.13) into (A.11) reproduces Equation (2.28) of the main text.

The exponents $(a, b, c, d, e, f, g, h, i)$ of the generalised expression (4.7) follow directly from this derivation: $a = 0.5$ (dissociative branch AB2–AB3 carried into θ_{COH}); $b = 0.5$ and $c = 1.0$ (combination of $\theta_{\text{COH}} \propto p_{\text{H}_2}^{0.5}$ and $\theta_{\text{H}} \propto p_{\text{H}_2}^{0.5}$); $d = 0$ (no gas-phase H_2O in the RDS); $e = f = g = 0.5$ and $h = 0$ (same propagation at the level of θ_{COH}); $i = 2$ (dual involvement of vacant Ni sites in the RDS). These values match the row labelled “model 11” in Table 2.7.

A.5 Common assumptions

The four derivations share the following structural assumptions:

- quasi-equilibrium of all non-rate-determining steps;
- MARI hypothesis (methanic intermediates dropped from the site balance);
- lumping of upstream equilibria into a composite constant K_{Cx} ;
- thermodynamic consistency through the driving-force factor (closing on $K_{\text{eq}}^{\text{meth}}$ for Mechanisms 1, 2 and 4; on K_{RWGS} for Mechanism 3);
- strict decoupling of the two site pools in Mechanism 2 only.

Table A.1: Summary of the four LHHW derivations.

Mechanism	Sites	RDS	Driving force	Equation
1 – Diss. C	1 (*)	$\text{CO}^* + * \rightleftharpoons \text{C}^* + \text{O}^*$	$K_{\text{eq}}^{\text{meth}}$	(4.4)
2 – Formate	2 (*, $\wedge$)	$\text{CO}_2^\wedge + \text{H}^* \rightleftharpoons \text{HCOO}^\wedge + *$	$K_{\text{eq}}^{\text{meth}}$	(4.5)
3 – H-ass. CO	1 (*)	$\text{HCOO}^* + * \rightleftharpoons \text{CO}^* + \text{OH}^*$	K_{RWGS}	(4.6)
4 – Hybrid (m11)	1 (*)	$\text{COH}^* + \text{H}^* \rightleftharpoons \text{CH}^* + \text{OH}^*$	$K_{\text{eq}}^{\text{meth}}$	(2.28)

The four rate expressions derived above constitute the structural hypotheses tested by nonlinear regression in Section 2.5.1; the corresponding fitted parameters and physical-plausibility checks are reported in Appendix B.

Appendix B

Complete table of estimated LHHW parameters

This appendix reports the parameters obtained by nonlinear regression of the four LHHW expressions of Appendix A – Equations (2.23), (2.24), (2.25) and (2.28) – against the experimental dataset of Section 4.1. All constants are written in reparameterised van 't Hoff form:

$$K_i(T) = \exp\left(\frac{\Delta S_i^\circ}{R}\right) \exp\left[-\frac{\Delta H_i^\circ}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right], \quad k(T) = k_{\text{ref}} \exp\left[-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right], \quad (\text{B.1})$$

with $T_{\text{ref}} = 572.15 \text{ K}$ ($300 \text{ }^\circ\text{C}$) and the convention $\Delta H^\circ < 0$ for exothermic adsorption. Reported uncertainties are 95% confidence half-widths ($t_{\text{tab}} = 1.965$); a parameter is significant if $|t| > t_{\text{tab}}$. Global significance is assessed by Fisher's F -test.

B.1 Mechanism 1 – Dissociative carbon route

$$N = 486, \quad p = 8, \quad \nu = 478. \quad F = 2.384 \times 10^5 \gg F_{\text{tab}} = 1.958.$$

High-correlation pairs ($|r| \geq 0.95$): $(k_{4,0}, E_4) = 0.956$; $(k_{4,0}, \Delta S_{\text{H}_2}^\circ) = -0.999$; $(E_4, \Delta S_{\text{H}_2}^\circ) = -0.952$; $(E_4, \Delta H_{\text{H}_2}^\circ) = -0.991$; $(\Delta S_{\text{CO}_2}^\circ, K_{\text{H}_2\text{O}}) = -0.997$.

B.2 Mechanism 2 – Associative formate route (two site types)

$$N = 486, \quad p = 7, \quad \nu = 479. \quad F = 2.668 \times 10^5 \gg F_{\text{tab}} = 2.029.$$

High-correlation pairs: $(k_{3,0}, \Delta S_{\text{H}_2}^\circ) = -0.999$ and $(E_3, \Delta H_{\text{H}_2}^\circ) = -0.983$. $\Delta H_{\text{CO}_2}^\circ$ converged to zero, indicating that the temperature window is too narrow to resolve it.

Table B.1: Estimated parameters of Mechanism 1 (Equation (2.23)).

Parameter	Symbol	Value $\pm$ 95% CI	Unit	$ t $	Sig.
Pre-exp. rate const. @ T_{ref}	$k_{4,0}$	2.996 $\pm$ 2.62	$\text{mol kg}^{-1} \text{s}^{-1} \text{bar}^{-n}$	2.24	yes
Activation energy	E_4	140.45 $\pm$ 108	kJ mol^{-1}	2.54	yes
$\Delta S_{\text{CO}_2}^\circ$	$\Delta S_{\text{CO}_2}^\circ$	29.05 $\pm$ 1.43	$\text{J mol}^{-1} \text{K}^{-1}$	39.96	yes
$\Delta H_{\text{CO}_2}^\circ$	$\Delta H_{\text{CO}_2}^\circ$	-5.60 ± 74.4	kJ mol^{-1}	0.15	no
$\Delta S_{\text{H}_2}^\circ$	$\Delta S_{\text{H}_2}^\circ$	-32.59 ± 45.9	$\text{J mol}^{-1} \text{K}^{-1}$	1.39	no
$\Delta H_{\text{H}_2}^\circ$	$\Delta H_{\text{H}_2}^\circ$	-199.15 ± 206	kJ mol^{-1}	1.90	no
K_{CO} @ T_{ref}	K_{CO}	8.48 $\pm$ 0	bar^{-1}	∞	yes
$K_{\text{H}_2\text{O}}$ @ T_{ref}	$K_{\text{H}_2\text{O}}$	5.60 $\pm$ 4.45	bar^{-1}	2.47	yes
Mean relative deviation	D	6.90	%	—	—

Table B.2: Estimated parameters of Mechanism 2 (Equation (2.24)).

Parameter	Symbol	Value $\pm$ 95% CI	Unit	$ t $	Sig.
Pre-exp. rate const. @ T_{ref}	$k_{3,0}$	2.951 $\pm$ 2.46	$\text{mol kg}^{-1} \text{s}^{-1} \text{bar}^{-n}$	2.36	yes
Activation energy	E_3	143.90 $\pm$ 99.5	kJ mol^{-1}	2.84	yes
$\Delta S_{\text{CO}_2}^\circ$	$\Delta S_{\text{CO}_2}^\circ$	29.10 $\pm$ 3.16	$\text{J mol}^{-1} \text{K}^{-1}$	18.11	yes
$\Delta H_{\text{CO}_2}^\circ$	$\Delta H_{\text{CO}_2}^\circ$	$\sim 0 \pm 29.6$	kJ mol^{-1}	0.00	no
$\Delta S_{\text{H}_2}^\circ$	$\Delta S_{\text{H}_2}^\circ$	-28.74 ± 45.2	$\text{J mol}^{-1} \text{K}^{-1}$	1.25	no
$\Delta H_{\text{H}_2}^\circ$	$\Delta H_{\text{H}_2}^\circ$	-200.00 $\pm$ 190	kJ mol^{-1}	2.06	yes
$K_{\text{H}_2\text{O}}$ @ T_{ref}	$K_{\text{H}_2\text{O}}$	5.21 $\pm$ 4.31	bar^{-1}	2.37	yes
Mean relative deviation	D	7.11	%	—	—

B.3 Mechanism 3 – H-assisted CO formation route

$N = 486$, $p = 11$, $\nu = 475$. $F = 3.296 \times 10^5 \gg F_{\text{tab}} = 1.809$.

High-correlation pairs: $(k_0, k_{2,0}) = 0.987$; $(k_0, \Delta S_{\text{CO}_2}^\circ) = 0.979$; $(E, E_2) = 0.983$; $(E, \Delta H_{\text{CO}_2}^\circ) = 0.965$; $(k_{2,0}, \Delta S_{\text{CO}_2}^\circ) = 0.985$; $(E_2, \Delta H_{\text{CO}_2}^\circ) = 0.975$. The model is overparameterised.

B.4 Mechanism 4 – Hybrid route (model 11), reference kinetic model

$N = 486$, $p = 10$, $\nu = 476$. $F = 3.498 \times 10^5 \gg F_{\text{tab}} = 1.851$. No correlation pair with $|r| \geq 0.95$.

Modelling note. Nine of the ten parameters reach the boundary of their admissible search interval, yielding vanishing parametric variance and formally infinite t -statistics. The reported values should be understood as a constrained

Table B.3: Estimated parameters of Mechanism 3 (Equation (2.26)).

Parameter	Symbol	Value $\pm$ 95% CI	Unit	$ t $	Sig.
Pre-exp. rate const. @ T_{ref}	k_0	3.061 $\pm$ 0.864	$\text{mol kg}^{-1} \text{s}^{-1} \text{bar}^{-n}$	6.96	yes
Activation energy	E	85.86 ± 87.4	kJ mol^{-1}	1.93	no
2nd pre-exp. rate const. @ T_{ref}	$k_{2,0}$	5.204 $\pm$ 0.857	$\text{mol kg}^{-1} \text{s}^{-1} \text{bar}^{-n}$	11.93	yes
2nd activation energy	E_2	20.00 ± 86.5	kJ mol^{-1}	0.45	no
$\Delta S_{\text{CO}_2}^\circ$	$\Delta S_{\text{CO}_2}^\circ$	30.79 $\pm$ 3.89	$\text{J mol}^{-1} \text{K}^{-1}$	15.54	yes
$\Delta H_{\text{CO}_2}^\circ$	$\Delta H_{\text{CO}_2}^\circ$	$\sim 0 \pm 45.9$	kJ mol^{-1}	0.00	no
$\Delta S_{\text{H}_2}^\circ$	$\Delta S_{\text{H}_2}^\circ$	-17.12 ± 34.1	$\text{J mol}^{-1} \text{K}^{-1}$	0.99	no
$\Delta H_{\text{H}_2}^\circ$	$\Delta H_{\text{H}_2}^\circ$	-200.00 $\pm$ 111	kJ mol^{-1}	3.54	yes
$\Delta S_{\text{OH}}^\circ$	$\Delta S_{\text{OH}}^\circ$	18.30 $\pm$ 7.20	$\text{J mol}^{-1} \text{K}^{-1}$	4.99	yes
$\Delta H_{\text{OH}}^\circ$	$\Delta H_{\text{OH}}^\circ$	-90.26 $\pm$ 64.4	kJ mol^{-1}	2.76	yes
K_{CO} @ T_{ref}	K_{CO}	$\sim 0 \pm 198$	bar^{-1}	0.00	no
Mean relative deviation	D	6.06	%	—	—

optimum; only $\Delta H_{\text{OH}}^\circ$ is freely identified.

The two activation energies give $E_2/E_1 = 4.0$, consistent with the value 3.8 reported in Section 2.5.2.

B.5 Physical-plausibility test (Boudart criteria) for Mechanism 4

The adsorption parameters of Mechanism 4 are tested against the Boudart–Mears–Vannice bounds:

B1 $\Delta H_{\text{ads}}^\circ < 0$;

B2 $|\Delta H_{\text{ads}}^\circ| < 250 \text{ kJ mol}^{-1}$;

B3 $0 < -\Delta S_{\text{ads}}^\circ < S_{\text{gas}}^\circ$;

B4 $|\Delta S_{\text{ads}}^\circ| < 51.04 + 0.0014 |\Delta H_{\text{ads}}^\circ|$ (Vannice empirical bound, $\text{J mol}^{-1} \text{K}^{-1}$, ΔH in J mol^{-1}).

All adsorption enthalpies fall within $|\Delta H| \in [19, 52] \text{ kJ mol}^{-1}$, consistent with the range stated in Section 2.5.2 and within the descriptor window $[-40, -80] \text{ kJ mol}^{-1}$ identified by Sun et al. as optimal for ICCM materials (Section 2.8). All four criteria are satisfied; Mechanisms 1–3 fail at least one (non-significant or implausibly large ΔH).

Table B.4: Estimated parameters of Mechanism 4 (Equation (2.28)), reference kinetic model.

Parameter	Symbol	Value $\pm$ 95% CI	Unit	$ t $	Sig.
1st pre-exp. rate const. @ T_{ref}	$k_{1,0}$	5.000 $\pm$ 0	$\text{mol kg}^{-1} \text{s}^{-1} \text{bar}^{-n}$	∞	yes
1st activation energy	E_1	40.00 $\pm$ 0	kJ mol^{-1}	∞	yes
2nd pre-exp. rate const. @ T_{ref}	$k_{2,0}$	3.000 $\pm$ 0	$\text{mol kg}^{-1} \text{s}^{-1} \text{bar}^{-n}$	∞	yes
2nd activation energy	E_2	160.00 $\pm$ 0	kJ mol^{-1}	∞	yes
$\Delta S_{\text{CO}_2}^\circ$	$\Delta S_{\text{CO}_2}^\circ$	20.00 $\pm$ 0	$\text{J mol}^{-1} \text{K}^{-1}$	∞	yes
$\Delta H_{\text{CO}_2}^\circ$	$\Delta H_{\text{CO}_2}^\circ$	−52.00 $\pm$ 0	kJ mol^{-1}	∞	yes
$\Delta S_{\text{H}_2}^\circ$	$\Delta S_{\text{H}_2}^\circ$	10.00 $\pm$ 0	$\text{J mol}^{-1} \text{K}^{-1}$	∞	yes
$\Delta H_{\text{H}_2}^\circ$	$\Delta H_{\text{H}_2}^\circ$	−20.00 $\pm$ 0	kJ mol^{-1}	∞	yes
$\Delta S_{\text{OH}}^\circ$	$\Delta S_{\text{OH}}^\circ$	60.00 $\pm$ 0	$\text{J mol}^{-1} \text{K}^{-1}$	∞	yes
$\Delta H_{\text{OH}}^\circ$	$\Delta H_{\text{OH}}^\circ$	−51.84 $\pm$ 15.7	kJ mol^{-1}	6.49	yes
Mean relative deviation	D	5.79	%	—	—

Table B.5: Boudart–Mears–Vannice consistency test for Mechanism 4. S_{gas}° at 298 K, 1 bar (NIST).

Species	ΔH° (kJ mol^{-1})	ΔS° ($\text{J mol}^{-1} \text{K}^{-1}$)	S_{gas}° ($\text{J mol}^{-1} \text{K}^{-1}$)	B1	B2	B3–B4
CO_2	−52.00	+20.00	213.8	✓	✓	✓
H_2	−20.00	+10.00	130.7	✓	✓	✓
OH	−51.84	+60.00	—	✓	✓	✓

B.6 Comparison with literature parameters

The bimodal distribution $E_2 = 160 / E_1 = 40 \text{ kJ mol}^{-1}$ reflects the dual nature of the hybrid mechanism (low-barrier dissociative branch AB2–AB3 and higher-barrier H-assisted branch AB7), and is consistent with the basic-site enrichment expected from the MgO promoter.

The parameters of this appendix constitute the kinetic input used to evaluate $r_{\text{meth}}(T)$ in the cross-sectional analysis of Section 2.6.

Table B.6: Comparison of Mechanism 4 parameters with reference studies (Table 2.8). $|\Delta H^\circ|$ and E_a in kJ mol^{-1} .

	This work (Ni/Al ₂ O ₃ –MgO)	Quindimil [28] (9.5% Ni/Al ₂ O ₃)	Onrubia-Calvo [27] (8.5% Ni/CeO ₂)	Champon [13] (14–17% Ni/Al ₂ O ₃)
E_a^{meth} (kJ mol^{-1})	160 (E_2) / 40 (E_1)	80.1 (app.)	53.9 (intr.)	110
$ \Delta H_{\text{CO}_2}^\circ $	52.0	—	—	9.7
$ \Delta H_{\text{H}_2}^\circ $	20.0	—	—	52.0
$ \Delta H_{\text{OH}}^\circ $	51.8	—	—	14.5 (H ₂ O)
$ \Delta H_{\text{CO}}^\circ $	not retained	—	—	40.6
Best mechanism	Hybrid (m11)	H-ass. CO	Two-site formate	Indirect (RWGS+CO)
D (%)	5.79	7.0	11.3	—

Appendix C

Calibration of the SMR mass flow controllers

C.1 Method

The three thermal mass flow controllers (Brooks Instrument) used on the SMR setup – one for Ar, one for CO₂ and one for H₂ – were calibrated *in situ* against a bubble flowmeter. For each MFC, a setpoint SV (ml min⁻¹, displayed by the control software) was imposed and the time t required to fill a fixed reference volume V_{ref} of the bubble flowmeter was measured. The volumetric flow rate at laboratory conditions was computed as

$$\text{MV} = \frac{V_{\text{ref}}}{t} \quad [\text{ml min}^{-1}], \quad (\text{C.1})$$

and subsequently converted to normal conditions ($T_{\text{N}} = 0^\circ\text{C}$, $P_{\text{N}} = 1 \text{ atm}$) via the ideal gas law:

$$\text{MV}_{\text{N}} = \text{MV} \cdot \frac{T_{\text{N}}}{T_{\text{lab}}} \cdot \frac{P_{\text{lab}}}{P_{\text{N}}} \quad [\text{Nml min}^{-1}], \quad (\text{C.2})$$

where T_{lab} and P_{lab} are the ambient temperature and pressure at the time of measurement. For each gas, five to eight setpoints spanning the operating range were tested. A linear regression

$$\text{MV}_{\text{N}} = a \text{SV} + b \quad (\text{C.3})$$

was then fitted and used as the correction relation between the setpoint imposed by the operator and the actual normal flow rate delivered to the reactor.

C.2 Calibration data

Tables C.1, C.2 and C.3 report the raw calibration data for Ar, CO₂ and H₂, respectively. The last two columns give the volumetric flow at laboratory conditions (MV, Eq. C.1) and its conversion to normal conditions (MV_N, Eq. C.2).

Table C.1: Calibration data – Ar mass flow controller.

SV (ml min ⁻¹)	t (s)	MV (ml min ⁻¹)	MV _N (Nml min ⁻¹)
0	0.0	0.00	0.00
50	51.5	58.25	54.28
100	25.3	118.58	110.48
150	16.9	177.51	165.40
200	12.5	240.00	223.62
250	10.0	300.00	279.52
300	8.3	361.45	336.77
400	6.2	483.87	450.84

Table C.2: Calibration data – CO₂ mass flow controller.

SV (ml min ⁻¹)	t (s)	MV (ml min ⁻¹)	MV _N (Nml min ⁻¹)
0	0.0	0.00	0.00
25	97.0	30.93	28.82
50	48.0	62.50	58.23
100	24.0	125.00	116.47
150	16.4	182.93	170.44
200	11.7	256.41	238.91

Table C.3: Calibration data – H₂ mass flow controller.

SV (ml min ⁻¹)	t (s)	MV (ml min ⁻¹)	MV _N (Nml min ⁻¹)
0	0.0	0.00	0.00
50	43.7	68.65	63.96
100	22.8	131.58	122.60
200	12.0	250.00	232.94
300	7.8	384.62	358.36

C.3 Regression results

The linear fits obtained from Eq. (C.3) are summarised in Table C.4 and displayed in Fig. C.1. For all three gases the coefficient of determination R^2 exceeds 0.998, confirming the excellent linearity of the MFCs over the explored range. The slopes a are slightly greater than unity (1.13 for Ar, 1.18 for CO₂ and H₂), meaning that the actual normal flow

rate is systematically 13–18% higher than the setpoint. This deviation is the calibration factor applied *a posteriori* to every experimental setpoint in this work; setpoints quoted in Chapters 3 and 4 always refer to the corrected value MV_N , not to the raw SV displayed by the control software.

Table C.4: Linear regression of MV_N versus SV for the three MFCs of the SMR setup. N : number of calibration points.

Gas	a (Nml ml ⁻¹)	b (Nml min ⁻¹)	R^2	N
Ar	1.1289	−1.991	0.9999	8
CO ₂	1.1790	−1.016	0.9989	6
H ₂	1.1799	+2.190	0.9994	5

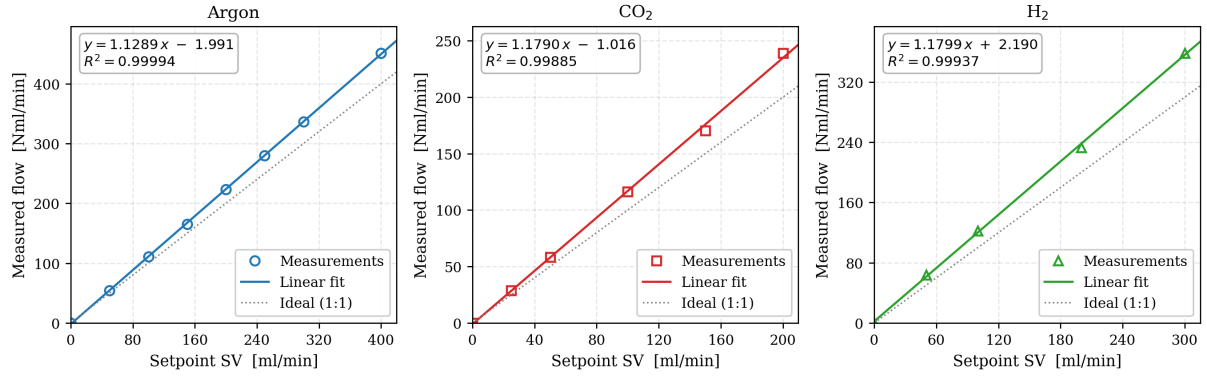
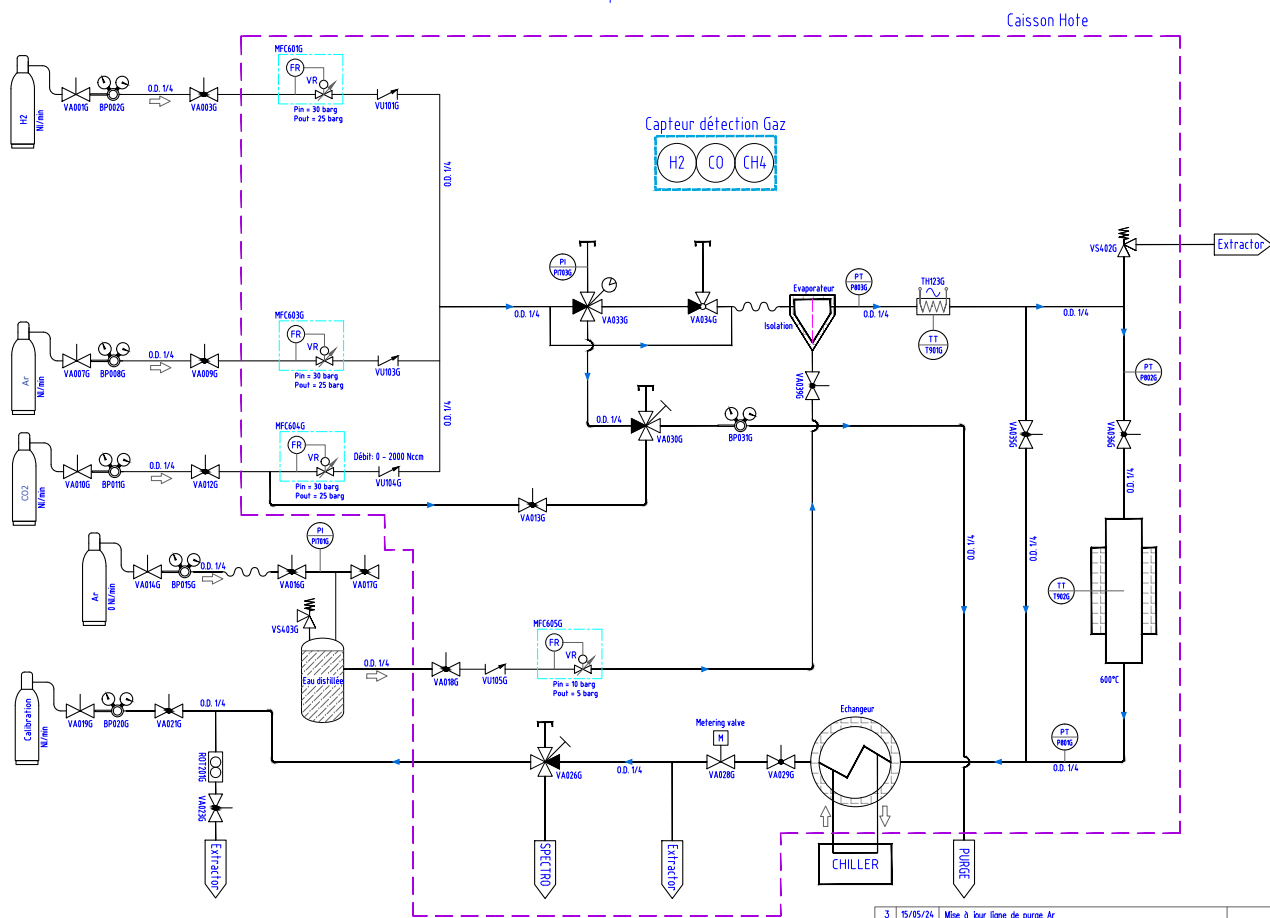


Figure C.1: Calibration curves of the three Brooks Instrument mass flow controllers of the SMR setup: Ar (left), CO₂ (centre) and H₂ (right). Open symbols: experimental measurements. Solid lines: linear regressions (Eq. C.3, parameters in Table C.4). Dotted line: ideal 1:1 response.

Appendix D

P&ID of the SMR setup

The complete piping and instrumentation diagram (P&ID) of the SMR setup is provided on the following page. It shows the gas supply (Ar, CO₂, H₂ and the calibration mixture), the two-stage pressure regulation, the three Brooks Instrument mass flow controllers, the bypass line, the stainless-steel fixed-bed reactor, the furnace, the VWR RC-10 chiller and the Hiden HPR-20 OEMS mass spectrometer.



3	15/05/24	Mise à jour ligne de purge Ar	Lion Arnaud
1	28/02/24	Création	Lion Arnaud
UCL Université catholique de Louvain			Remarques :
PROJET: SMR SUBPROJET: DESCRIPTION:			Rep: Jarry Dewille
IMMC-TFL - place du Levant, 2 - B134.8 - Louvain-la-Neuve - Belgique Tél. +32(0)10-47.22.00, Fax. +32(0)10-45.26.92, http://www.uclouvain.be/immc			Designer: Arnaud Lion
N° du dessin			Date: 28/02/2024
PID - SMR - V3			Rev Sheet
			V3 1/1

Use of artificial intelligence

In order to improve the flow and clarity of the text, the artificial intelligence tools Claude and ChatGPT were used to rephrase certain sentences. Under no circumstances were they used to create content.

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École polytechnique de Louvain

Rue Archimède, 1 bte L6.11.01, 1348 Louvain-la-Neuve, Belgique | www.uclouvain.be/epl