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Kinetic studies of CO$_2$ methanation over a Ni/$\gamma$-Al$_2$O$_3$ catalyst using a batch reactor

Jin Yang Lim$^1$, J. McGregor$^2$, A. J. Sederman$^1$, J. S. Dennis$^1$

$^1$Department of Chemical Engineering and Biotechnology, University of Cambridge, Cambridge CB2 3RA, United Kingdom.

$^2$Department of Chemical and Biological Engineering, The University of Sheffield, Sir Robert Hadfield Building, Portobello Street, Sheffield, S1 3JD, United Kingdom.

Abstract

The methanation of CO$_2$ was investigated over a wide range of partial pressures of products and reactants using a gradientless, spinning-basket reactor operated in batch mode. The rate and selectivity of CO$_2$ methanation, using a 12 wt% Ni/$\gamma$-Al$_2$O$_3$ catalyst, were explored at temperatures 453 – 483 K and pressures up to 20 bar. The rate was found to increase with increasing partial pressures of H$_2$ and CO$_2$ when the partial pressures of these reactants were low; however, the rate of reaction was found to be insensitive to changes in the partial pressures of H$_2$ and CO$_2$ when their partial pressures were high. A convenient method of determining the effect of H$_2$O on the rate of reaction was also developed using the batch reactor and the inhibitory effect of H$_2$O on CO$_2$ methanation was quantified. The kinetic measurements were compared with a mathematical model of the reactor, in which different kinetic expressions were explored. The kinetics of the reaction were found to be consistent with a mechanism in which adsorbed CO$_2$ dissociated to adsorbed CO and O on the surface of the catalyst with the rate-limiting step being the subsequent dissociation of adsorbed CO.

Keywords: methanation of CO$_2$; kinetic measurements; nickel/alumina catalyst; modelling
1. Introduction

In response to anthropogenic climate change, it is expected that the number of carbon-capture schemes is expected to increase. As a result, the increased availability of CO$_2$ is likely to drive its cost down, so that heterogeneous catalysis could be used to convert CO$_2$ to various chemicals such as methane, methanol, formic acid and dimethyl carbonate (Aresta et al., 2007; Ma et al., 2009). Of course, CO$_2$ is thermodynamically very stable and the main challenge in converting it to other organic products is providing the free energy needed. In particular, the production of methane by reacting CO$_2$ with H$_2$ (CO$_2$ methanation) has the potential for producing synthetic natural gas (SNG), which could be distributed using the existing infrastructure for the distribution of natural gas (Kopyscinski, 2010). Furthermore, the study of the chemistry of CO$_2$ in methanation could provide insights into related reactions, such as the Fischer-Tropsch synthesis and CO methanation.

Various transition metals are active in catalysing the methanation of CO$_2$, i.e.

$$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}. \quad \text{(R1)}$$

A number of previous investigations of CO$_2$ methanation, particularly over Co and Fe catalysts, have arisen as a result of research designed to study, primarily, the conversion of CO$_2$ to long-chain paraffins or olefins via Fischer-Tropsch synthesis, where methane is inevitably produced as a major product (Zhang et al., 2002; Riedel et al., 2003). Ruthenium-based catalysts have received much attention, owing to their high reactivity and selectivity for the methanation of CO$_2$ (Kowalczyk et al., 2008; Zagli and Falconer, 1981; Marwood et al., 1997). Supported Rh catalysts have been investigated because of their ability to catalyse the methanation of CO$_2$ at very low temperatures, viz. below 100°C (Jacquemin et al., 2010). The field has been reviewed recently by Gao et al. (2015). Mixed Ni/Pt or Ni/Pd catalysts have also received attention (Porosoff and Chen, 2013) in batch reactor studies.

Although catalysts based on either Ru or Rh have been shown to be more active than nickel-based catalysts, the cost of such metals is prohibitive for their widespread use in industry. Nickel-based catalysts remain the most widely-studied materials owing to the abundance of Ni and its low cost. For the methanation of CO$_2$, nickel catalysts are often active at temperatures above 150°C, but the exact reaction mechanism is still subject to debate. The key question is whether the reaction occurs (i) by the dissociative adsorption of CO$_2$ to form CO and O on the surface of the catalyst (Falconer and Zagli, 1980; Weatherbee and Bartholomew, 1981; Fujita et al., 1991; Fujita et al., 1993), or (ii) by the conversion of
CO₂ to methane via carbonate or formate intermediates which do not involve CO, as suggested by Aldana et al. (2013).

It has become increasingly clear that the reaction pathway depends on the nature of the support. Whilst a number of studies have been performed on various types of supported nickel catalysts by characterising the structure and phases of the synthesised material (Aksoylu et al., 1996; Liu et al., 2013; Du et al., 2007), only a few investigations have performed rigorous kinetic studies on the rate and selectivity of CO₂ methanation at different temperatures, overall pressures and partial pressures of reactants and products. Given that the mechanistic pathways could differ for different catalysts, it is not unreasonable to expect that rate expressions differ for different catalysts, with important implications in reactor operation and design in industry.

The primary objective of this work was to investigate the kinetics of the methanation of CO₂ over nickel supported on Al₂O₃ over a wide range of partial pressures of reactants and products, and at relatively low temperatures < 210°C, to determine if the kinetics and rate expressions were consistent with previously-proposed theories. Only a few previous studies have proposed rate expressions for the methanation of CO₂ (e.g. Weatherbee and Bartholomew, 1982; van Herwijnen et al., 1973). The conclusions of these researchers were based on experiments which were performed on continuous, flow reactors. One way of validating the rate expressions is to examine their applicability over a wide range of partial pressures of reactants and products, conveniently achieved by conducting the reaction in a batch reactor. Here, we have undertaken a study of the kinetics of the methanation of CO₂ in a gradientless, spinning-basket reactor operating in batch.

2. Experimental

2.1. Catalyst and characterisation

A 12 wt% Ni catalyst was prepared by the incipient wetness impregnation of pellets of γ-alumina (Saint Gobain – SA 62125, 3 mm dia. spheres) using Ni(NO₃)₂·6H₂O as the precursor salt (Sigma-Aldrich). The pore volume of the support was reported to be 0.64 ml/g, experimentally verified by adding de-ionised (DI) water dropwise to the pellets until they had a glistening appearance, indicating that the pores were fully filled, and measuring the total volume of water used.
The impregnated catalyst was dried for 24 hours at 120°C in a hotbox oven prior to calcination at 450°C for 4 hours in 150 ml/min (as measured at 293 K and 1 bara) of air in a tubular quartz reactor and heated by a furnace at atmospheric pressure. Subsequently, H₂ was introduced at a flowrate of 100 ml/min (as measured at 293 K and 1 bara) at 700°C for 6 hours to reduce the calcined catalyst to metallic Ni. A temperature of 700°C was used to ensure that all available nickel oxide could be reduced to metallic nickel. The reduced catalyst was passivated in a mixture of 5 vol% O₂ and N₂ at 25°C, before being transferred to a Carberry spinning-basket reactor (described below) to investigate different reactions. Prior to each experiment in the Carberry reactor, the passivated catalyst was reduced in situ by hydrogen at 250°C overnight, for approximately 12 hours.

The catalyst was characterised by a BET surface area of 155 m² g⁻¹ and BJH pore volume of 0.46 cm³ g⁻¹. A dispersion of 12 % was obtained, based on pulse H₂ chemisorption experiments. Temperature programmed reduction was performed in a Hiden CATLAB microreactor, where the composition of the off-gas was measured by a mass spectrometer (Hiden QIC-20). The evolution of H₂O from the reduction of NiO to Ni by H₂ was used to study the reducibility of the different samples. The profiles of temperature programmed reduction (TPR) of the different samples are illustrated in Figure 1. In general, the investigations monitoring the off-gas of the reactor were consistent with the observations from a thermogravimetric analyser (TGA) (Mettler Toledo TGA/DSC 1 STARe system). For the calcined NiO/Al₂O₃ and the passivated Ni/Al₂O₃, two main H₂O peaks were observed, one at 280°C and another at 570°C. The H₂O peak at 180°C was attributed to evolution of moisture on the surface of the samples because no corresponding consumption of H₂ was observed (not shown). Figure 1 also shows that the passivated Ni/Al₂O₃ has significantly less NiO reduced at temperatures above 450°C, implying that the procedure for reduction at 700°C in the synthesis process had converted most of this NiO to metallic Ni. The passivation process appeared to have given rise to the NiO peak at 280°C. The passivated Ni/Al₂O₃ catalyst had to be reduced in situ in the Carberry reactor before catalytic reactions could be performed. The efficacy of this protocol was confirmed through temperature programmed reduction studies, the results of which are shown in Figure 1, where it is clear that negligible amounts of the ‘low temperature’ NiO remained after an isothermal reduction at 250°C for 9 hours.
Figure 1. H₂O signal versus temperature for a temperature programmed reduction on calcined NiO/Al₂O₃, passivated Ni/Al₂O₃ and passivated Ni/Al₂O₃ which was pre-treated with an isothermal reduction at 250°C for 9 hours.

The CATLAB apparatus was also used to perform temperature-programmed desorption of the spent catalyst following the reaction studies in the batch reactor: this will be elaborated on in Section 2.2. In-situ diffuse reflectance infrared spectroscopy (DRIFTS) was also performed on 50 mg of the catalyst in a flow of CO₂ and H₂ at 463 K under atmospheric pressure (Praying Mantis, Harrick Scientific). For each measurement, a series of 128 scans was performed with spectral resolution of 2 cm⁻¹ and a final spectrum was obtained by averaging the 128 scans. For every measurement a background spectrum was collected and automatically subtracted from the sample spectrum.

2.2. Studies of methanation in a batch reactor

A spinning-basket reactor was used to study the kinetics of CO₂ methanation, using the 12 wt% Ni/γ-Al₂O₃ catalyst. A schematic diagram of the experimental arrangement is shown in Figure 2. The reactor, made of 316 stainless steel (Carberry reactor, i.d. 75 mm, 401A-8801, Autoclave Engineers, USA), had a maximum operating temperature and pressure of, respectively, 250°C and 50 bar. The volume of the reactor was reported by the manufacturers to be 2.95 × 10⁻⁴ m³, which was confirmed by measuring the drop in the pressure of the sealed reactor after the removal, by the use of a syringe, of a known volume of gas at room temperature and elevated pressure. The reactor was equipped with a removable basket, which had a mesh size of 1.3 mm, connected to a rotating shaft. The baffles and impeller helped to
ensure that the reactor volume was gradientless in terms of heat and mass transfer external to
the catalyst particles. All connections in the apparatus, including tubes and fittings, were
made of 316 stainless steel. The reactor was heated externally by two band heaters
(Me5J1JP1, Watlow) with a total power output of 1 kW, capable of controlling the
temperature of the reactor to a precision of ± 0.1 K when steady-state was achieved.

In a typical experiment, the basket in the reactor was first loaded with a known
amount of catalyst and packed with a non-porous inert material, glass beads (1.4 mm diam.),
such that about 5.0 g of catalyst pellets were mixed with an equal mass of glass beads in the
basket. The reactor was sealed and the vacuum pump was turned on, with the valve to the
vent closed, to evacuate the gaseous content of the reactor. The reactor was heated to 250°C
and the catalyst was then subjected to a flow through the reactor of 100 ml/min (at room
temperature and pressure) of H₂ with a stirring at 1.7 Hz for 12 hours at 1 bar. The flow of H₂
was controlled by a rotameter and a needle valve. Following the reduction in H₂, the reactor
was evacuated once again using the vacuum pump and the internal temperature of the reactor
brought to the desired reaction temperature. The rate of the reaction of interest was studied in
batch by bringing the reactor to a desired initial pressure and composition, using gas supplied
from the cylinders connected to the reactor. During this period, the three-way valve was used
to isolate the rotameter for hydrogen, shown in [Figure 2], in order to prevent its exposure to
pressures above atmospheric pressure. Gas cylinders with pre-mixed gases were normally
used and the reactor could be brought to the desired pressure using one cylinder only. The
initial total pressure of the reactor was typically 10 – 20 bar. In order to raise the pressure of
the reactor, the pressure regulator on the gas cylinder of interest was first adjusted to about 2
bar higher than the desired pressure of the reactor. This was followed by fully opening the
needle valve at the inlet of the reactor and then opening the plug valve, raising the pressure of
the reactor. While the pressure was being raised, the flow of the gas from the cylinder into the
reactor was controlled by progressively closing the needle valve. As the pressure approached
the desired value, the needle valve would be almost fully closed. The plug valve of the
corresponding line was closed when the reactor reached the desired pressure. With this
procedure, the final pressure of the reactor could be consistently achieved to a precision of
± 0.1 bar, which was approximately the precision of pressure gauge PG1. The accuracy of the
measurement of pressure was confirmed by good agreement between the readings of the two
pressure gauges, PG1 and PG2. If the desired starting composition in the reactor was different
from that in any gas cylinder, different gases were introduced into the reactor in stages. This
was achieved by monitoring the total pressure, recorded by the two pressure gauges, of the
reactor after successive additions of gas from the various cylinders. A stirrer speed of 9.2 Hz was always used. The entire process of bringing the reactor to the desired pressure and starting the stirrer after the introduction of the gases typically took 10 – 15 s.

After the reactive gases were introduced, the changes in the composition of the reactor volume were measured over time. This was performed by taking volumes of 4 ± 0.2 ml (at atmospheric temperature and pressure) from the reactor using a gas-tight sampling syringe. Prior to the removal of the sample by the syringe, the gaseous contents of the lines after needle valve ‘A’ in Figure 2 were evacuated by the vacuum pump. The plug valves ‘B’ and ‘C’ were then closed and the volume enclosed by valves ‘A’, ‘B’ and ‘C’ was brought to 3 bar using the needle valve ‘A’ and monitored by pressure gauge PG3. The gas collected here was purged through the vent and the space evacuated once again before the actual sample was taken. The latter operation was performed as a precaution to minimise the effect of dead volume in the section of the reactor which might not have mixed well with the bulk phase of the reactor volume, i.e. within the connection through the walls of the reactor to the outlet at valve ‘A’. This procedure ensured that the composition of the sample of gas obtained from the reactor was representative of the contents of the bulk phase of the reactor volume. Only about 6 – 10 samples were taken for each experiment so as to minimise the errors incurred from the removal of gaseous contents from the reactor. The composition of the sample was analysed using off-line gas chromatography (Agilent 7890 GC Extended Refinery Gas Analysis) by passing the sample in the syringe through the sampling loop in the gas-chromatograph. The sampling loop in the gas chromatograph was evacuated using a vacuum pump before the gaseous contents of the syringe were introduced.

The composition of the gas given by off-line gas chromatography would only be equal to that in the bulk phase of the reactor if all species in the gas phase were above their dew point at room temperature and pressure. This was not the case for most reactions performed in this study because water was involved as a product or a reactant. Water was found to condense in the tubes before reaching the syringe. Furthermore, higher hydrocarbons might also have been produced in some experiments, evident from the detection of hydrocarbons heavier than pentane in the gas phase. The low temperature of the dew point of these heavy species would imply that some heavy hydrocarbons would have condensed and existed in the liquid phase. Since the analysis by gas chromatography provided a water-free composition of the gas, the partial pressures of different species in the gas phase of the reactor were determined by using argon as an internal standard, such that
\[ p_i = \frac{x_i}{x_{Ar}} \times p_{Ar,0} \]  \hspace{2cm} (1)

where \( p_i \) is the partial pressure of species \( i \), \( x_i \) is the mole fraction of species \( i \) in the syringe, \( x_{Ar} \) is the mole fraction of Ar in the syringe and \( p_{Ar,0} \) is the partial pressure of argon at the start of the reaction. In most experiments, gas cylinders (of different mixtures of H\(_2\), CO\(_2\) and CO) contained 4% Ar. Hence, \( p_{Ar,0} \) could be easily determined by measuring the total pressure of the reactor and multiplying with the known composition of the cylinder. This method of analysis allowed the measurement of the partial pressure of different species in the reactor over time.
Figure 2. Schematic diagram of the Carberry, spinning-basket reactor. The solid arrows represent the direction of flow of the gases and the red dotted lines represent transmissions of electrical or electronic signals.
3. Results

3.1. Parameters affecting the measurement of kinetics

3.1.1. Control experiment

To determine whether the high-surface area \( \gamma \)-Al\(_2\)O\(_3\) (3 mm dia. SA-62125 alumina spheres, Saint-Gobain), used as the support material, was active in the methanation of CO\(_2\), the basket of the reactor was packed with 5.0 g of the support and 5.0 g of non-porous glass beads. The Carberry reactor was sealed and emptied, as described in Section 2.2, and then the pressure was raised to 10 bar absolute by admitting 7.2 bar of H\(_2\), 2.4 bar CO\(_2\) and 0.4 bar Ar into the evacuated vessel, so that the initial partial pressures were \( p_{\text{CO}_2,0} = 2.4 \text{ bar} \) and \( p_{\text{H}_2,0} = 7.2 \text{ bar} \). Samples from the contents of the reactor were removed periodically using a gas-tight syringe and analysed using offline gas chromatography as described above. At both 293 K and 463 K, no significant decreases in \( p_{\text{CO}_2} \) and \( p_{\text{H}_2} \) were observed, indicating that the rate of any reaction was negligible. Therefore, the support material used in the synthesis of the Ni/Al\(_2\)O\(_3\) catalyst, the interior surface of the reactor and the nickel oxides present in the catalyst could collectively be taken as inert compared to the reduced nickel catalyst.

3.1.2. Catalyst deactivation

It would be challenging to obtain accurate kinetic measurements if the characteristic time for the rate of deactivation of the catalyst were comparable to the rate of methanation in each experiment. Furthermore, significant deactivation would also mean that each batch of catalyst could only be used once and would have to be replaced for each new experiment by a fresh batch of catalyst, which would have go through the reduction process before experimental measurements could be taken. Figure 3 illustrates the change in the partial pressures of CO\(_2\), CH\(_4\), H\(_2\) and C\(_2\)H\(_6\) over time for five consecutive, replicate methanation experiments, where the same batch of catalyst was used for the repeated runs. It is clear that the catalyst does not undergo significant deactivation over the total time of the experiments, with a total time-on-stream of about \( 4.5 \times 10^4 \) s. Figure 3 (d) shows a small increase in the amount of C\(_2\)H\(_6\) produced as the experiment was repeated. This observation was difficult to explain, but the apparent activation of the catalyst towards the production of C\(_2\)H\(_6\) could be a result of small changes to the surface of the catalyst after its initial exposure to H\(_2\) and CO\(_2\). Nevertheless,
the amount of C₂H₆ is very much smaller than that of CH₄, which is the primary product, and no significant influence of this change was observed in the profiles of the reactants.

Thus, the insignificant rate of deactivation and good reproducibility meant that experiments could be performed on the same batch of catalyst. As a precaution, the same batch of catalyst was used for no more than 10 experiments before being replaced by a fresh batch. The final experiment on a batch of catalyst was always performed at the same initial conditions, to provide a standard reference point in this study, viz. as shown in Figure 3 with initial partial pressures $p_{\text{CO}_2,0} = 2.4 \text{ bar}$, $p_{\text{H}_2,0} = 2.4 \text{ bar}$, $T = 463 \text{ K}$ and $m_{\text{cat}} = 5.0 \text{ g}$, in order to verify that no deactivation has occurred over the length of the past experiments.

Figure 3. The partial pressure of (a) CO₂, (b) CH₄, (c) H₂ and (d) C₂H₆ as a function of time for five consecutive, replicate batch experiments using the same catalyst. In all experiments, the initial partial pressures of CO₂ and H₂ were $p_{\text{CO}_2,0} = 2.4 \text{ bar}$, $p_{\text{H}_2,0} = 7.2 \text{ bar}$, with $T = 463 \text{ K}$ and $m_{\text{cat}} = 5.0 \text{ g}$.
3.1.3. Heat and mass transfer considerations

Figure 4 shows the experimental results when methanation of CO\textsubscript{2} was undertaken in the batch reactor at different impeller speeds. This was to investigate if there existed significant external gradients of concentration and, or, temperatures between the bulk gaseous phase of the reactor and the external surface of the catalyst pellets. At the extremes, the initial rate of production of methane when the impeller was stationary was about 20\% faster than at 9.2 Hz, the maximum speed used in the experiments. Each experiment was repeated twice for each impeller speed. The rate of reaction decreased asymptotically as the impeller speed was increased. At spinning speeds higher than 4.9 Hz, very little difference could be observed between the initial rates. All measurements of kinetics in this study were obtained with a stirrer speed of 9.2 Hz and the results shown in Figure 4 consequently suggest that negligible heat and mass transfer effects were present with the experimental conditions employed.

The Weisz-Prater number, \( N_{WP} \), was used to estimate any potential influence of diffusion within the pores of the catalyst pellet (Weisz and Prater, 1954). The Weisz-Prater criterion states that the value of \( N_{WP} < 0.3 \) if internal mass transfer limitations are negligible where

\[
N_{WP} = \frac{r' \rho_{cat} R_p^2}{C_s D_{eff}}.
\]

\( C_s \) being the concentration of CO\textsubscript{2} in mol m\textsuperscript{-3} and \( D_{eff} \) the effective diffusivity. \( N_{WP} \) was evaluated for CO\textsubscript{2} methanation at 463 K based on the reference conditions of Section 3.1.2. The average pore diameter, \( d_{pore} \), was taken to be 8.9 nm, as determined by BJH analysis and calculated using

\begin{align*}
\text{(a)} & \quad \text{Partial pressure, } P_{\text{CH}_4}/\text{bar} \\
\text{(b)} & \quad \text{Partial pressure, } P_{\text{CO}_2}/\text{bar} \\
& \quad \text{Time / s} \\
& \quad 0, 2000, 4000, 6000, 8000 \\
& \quad 0.0, 2.8, 4.8, 7.0, 9.2 \text{ Hz} \\
& \quad P_{\text{CO}_2,0} = 2.4 \text{ bar}, \ P_{\text{H}_2,0} = 7.2 \text{ bar}, \ T = 463 \text{ K and } m_{\text{cat}} = 5.0 \text{ g.}
\end{align*}
\[ d_{\text{pore}} = \frac{4V_{\text{pore, total}}}{A_{\text{pore, total}}} \]  

where \( V_{\text{pore, total}} \) is the total pore volume obtained and \( A_{\text{pore, total}} \) is the corresponding surface area of the pores, assuming that they are cylindrical. Given the small pore diameter, the effective diffusivity, \( D_{\text{eff}} \), was taken to be the product of the Knudsen diffusivity of \( \text{H}_2 \) and \((\varepsilon / \tau^2)\), with \( \varepsilon = 0.60 \) and \( \tau^2 \) assumed to be 3. Here, \( \varepsilon \) was determined from the cumulative pore volume of the \( \text{Al}_2\text{O}_3 \) support, accounting for pores ranging from 17 to 300 nm in diameter, of 0.55 cm\(^3\) g\(^{-1}\). The group \((\varepsilon / \tau^2)\) is appropriate for use with the model of Young and Todd (2005) to model diffusion within the particle of catalyst. \( N_{\text{WP}} \) was thus 0.09, much smaller than the value at which intra-particle mass transfer is important. Furthermore, the apparent activation energy, as discussed later, was \( 95 \pm 10 \) kJ mol\(^{-1}\), which is in agreement with previous investigations of \( \text{CO}_2 \) methanation (Weatherbee and Bartholomew, 1982; van Herwijnen et al., 1973). If significant intraparticle mass transfer had been present, the apparent activation energy would have been significantly smaller. (Levenspiel, 1972).

### 3.1.4. Effect of total pressure

The stoichiometry of Reaction (1) is such that in a batch reaction the total pressure in the vessel will decrease with progress of reaction. In order to examine the effects of total pressure on the rate of reaction, the reaction was performed for different initial partial pressures of \( \text{N}_2 \) at \( T = 463 \) K, \( p_{\text{CO}_2,0} = 2.4 \) bar, \( p_{\text{H}_2,0} = 7.2 \) bar for 5.0 g of catalyst. Figure 5 (a) shows that the total pressure of the system does not affect the rate because the profiles of \( \text{H}_2 \) with time essentially overlap for different initial partial pressures of \( \text{N}_2 \). Figure 5 (b) illustrates how \( S_{\text{CH}_4} \), the selectivity for \( \text{CH}_4 \), varies with \( X_{\text{CO}_2} \), the conversion of \( \text{CO}_2 \) at a given time. Here, \( X_{\text{CO}_2} \) is defined as

\[ X_{\text{CO}_2} = 1 - \frac{p_{\text{CO}_2}}{p_{\text{CO}_2,0}} \]  

and

\[ S_{\text{CH}_4} = \frac{p_{\text{CH}_4}}{\sum_{i=1}^{5} p_{i, \text{HC}}} \]  

where \( p_{i, \text{HC}} \) is the partial pressure of hydrocarbons with carbon number \( i \). The sum of the partial pressures of paraffins from carbon number 1 to 5 was evaluated in the denominator of Eq. (5). In all experiments, \( S_{\text{CH}_4} \) did not vary with \( X_{\text{CO}_2} \) and was found to be 0.995 at all conversions. Figure 5 (b)
also shows that total pressure did not affect the selectivity of the reaction. The values of $S_{\text{CH}_4}$ at $X_{\text{CO}_2} = 0$ were found to be slightly lower because $p_{\text{CH}_4}$ was small at the start of the reaction and the error incurred by trace hydrocarbons being in the lines of the sampling port or the syringe was relatively large.

Figure 5. (a) Partial pressure of $\text{H}_2$ over time and (b) the selectivity of $\text{CH}_4$ as a function of the conversion of $\text{CO}_2$ for different initial partial pressures of $\text{N}_2$. In all experiments, $p_{\text{CO}_2,0} = 2.4$ bar, $p_{\text{H}_2,0} = 7.2$ bar, $T = 463$ K and $m_{\text{cat}} = 5.0$ g.

### 3.2. Measurements of kinetics

The following Sections describe the kinetic measurements performed to elucidate the effects of $\text{H}_2$, $\text{CO}_2$, $\text{CH}_4$ and $\text{H}_2\text{O}$ on the rate and selectivity of the reaction for the temperature range 443 – 483 K. These experiments were performed by changing the initial partial pressures from the reference initial composition, i.e. $p_{\text{CO}_2,0} = 2.4$ bar and $p_{\text{H}_2,0} = 7.2$ bar, total pressure 10 bar (balance being Ar) and reference temperature, 463 K. The changes in the rate and selectivity were compared by observing the changes in the partial pressures of the reactants and the products.

The experimental results for the reference condition have already been illustrated in Figure 3 for five consecutive, replicated experiments. In Figure 3, $\text{CO}_2$ is in excess, evident from the remaining 0.5 bar of $p_{\text{CO}_2}$ after $p_{\text{H}_2}$ was depleted. The total amount of $p_{\text{CH}_4}$ formed was 1.8 bar. It has already been established that for these conditions, the methane selectivity was very close to unity. Hence, the carbon balance for the experiments could be estimated
from the sum of $p_{\text{CH}_4}$ and $p_{\text{CO}_2}$ at each measurement. This is shown in Figure 6, in which there is seen to be an overall decrease of about 0.1 bar over the length of the experiment, indicating that the maximum error from the removal of the contents of the reactor from sampling was approximately ± 0.1 bar, corresponding to a relative error of 4%.

Figure 6. Sum of $p_{\text{CH}_4}$ and $p_{\text{CO}_2}$ over time for five consecutive, replicated batch experiments using the same catalyst. In all experiments, $p_{\text{CO}_2,0} = 2.4$ bar, $p_{\text{H}_2,0} = 7.2$ bar, $T = 463$ K and $m_{\text{cat}} = 5.0$ g.

3.2.1. Effect of $p_{\text{H}_2}$

The effect of $p_{\text{H}_2}$ was investigated by performing CO$_2$ methanation with different initial partial pressures of H$_2$, $p_{\text{H}_2,0}$, at temperatures 453, 463 and 473 K. To compare the measurements with the reference initial condition of $p_{\text{CO}_2,0} = 2.4$ bar and $p_{\text{H}_2,0} = 7.2$ bar, the reactor was first filled with an additional quantity of H$_2$, typically 4 bar H$_2$, before a mixture of 2.4 bar CO$_2$ and 7.2 bar H$_2$ was introduced. This minimised the zero error on the time axis caused by initiating the reaction if the additional H$_2$ were introduced after the mixture of CO$_2$ and H$_2$ had already been admitted to the reactor. Figure 7 illustrates the profiles of CO$_2$ and CH$_4$ over time for different initial partial pressures of H$_2$. Figure 7 (a) shows that the addition of H$_2$, while keeping $p_{\text{CO}_2,0}$ constant at 2.4 bar, meant that H$_2$ was in stoichiometric excess compared to CO$_2$ for experiments with $p_{\text{H}_2,0} = 11.2$ and 15.2 bar. Hence, for these initial conditions, $p_{\text{CO}_2}$ eventually dropped to zero. Figure 7 (a) shows that the final amount of $p_{\text{CH}_4}$ increased to approximately 2.4 bar, consistent with the total loss of $p_{\text{CO}_2}$. The carbon balance, as determined by the sum of $p_{\text{CO}_2}$ and $p_{\text{CH}_4}$ and illustrated in Figure 8 (a), was within 5 % of the original $p_{\text{CO}_2}$, i.e. 2.4 bar. Figure 8 (b) shows that the selectivity of methane remained at
0.995 for different $p_{H_2,0}$. The initial rate of methanation, deduced either from the rate of increase of $p_{CH_4}$ or the decrease in $p_{CO_2}$ with time, was found to be unaffected by changes in $p_{H_2}$ for 7.2 bar $< p_{H_2,0} < 15.2$ bar. This can be seen in Figure 7 (a) where the profiles of $H_2$ and $CH_4$ overlap at low conversions levels, i.e. at the start of the reaction when $t < 1800$ s. However, the profiles of $p_{CO_2}$ and $p_{CH_4}$ for different $p_{H_2,0}$ begin to deviate during the later stages of the reaction, at $1800 < t < 5000$ s, during which period the rate was faster for experiments starting with a higher $p_{H_2,0}$. The deviation in the rate of reaction occurred when $p_{H_2}$ dropped below 6 bar, as observed in Figure 7 (c).

![Figure 7](image-url)

Figure 7. Partial pressures of (a) $CO_2$, (b) $CH_4$ and (c) $H_2$ with time for different initial partial pressures of $H_2$, i.e $p_{H_2,0} = 7.2, 11.2$ and 15.2 bar. In all experiments, $p_{CO_2,0} = 2.4$ bar, $T = 463$ K and $m_{cat} = 5$ g.
These observations suggest that at high partial pressures of H₂, the rate of reaction was not affected by changes in p_H₂. Increases in the rate with increase in p_H₂ only appeared at values of p_H₂ < 6 bar. If the rate of reaction was invariant in p_H₂ for all values of p_H₂, the profiles of p_{CO₂} and p_{CH₄} would overlap for p_{H₂,0} = 11.2 and 15.2 bar, which would be in conflict with the experimental observations here.

Figure 8. (a) The sum of p_{CH₄} and p_{CO₂} over time and (d) selectivity of CH₄ as a function of X_{CO₂} for different initial partial pressures of H₂, i.e. p_{H₂,0} = 7.2, 11.2 and 15.2 bar. In all experiments, p_{CO₂,0} = 2.4 bar, T = 463 K and m_{cat} = 5 g.

3.2.2. Effect of p_{CO₂}

The effect of p_{CO₂} was studied using the same method as outlined in Section 3.2.1, i.e. by first introducing additional CO₂ before the introduction of the mixture of CO₂ and H₂. The value of p_{H₂,0} was maintained at 15.2 bar and values of p_{CO₂,0} of 2.4, 2.9 and 3.4 bar were explored at T = 453 – 473 K, with 5.0 g of catalyst. Results are shown in Figure 9. There is good evidence that at high p_{CO₂}, as well as high p_{H₂}, the rate is insensitive to changes in p_{CO₂}. This is illustrated in the profiles of H₂, CH₄ and CO₂ in Figure 9 when t < 2400 s.

However, for low partial pressures of CO₂, i.e. when p_{CO₂} < ~0.2 bar, the rate was greater for higher partial pressures of CO₂. In these experiments, S_{CH₄} at complete conversion, i.e. X_{CO₂} = 1, only decreased from 0.996 for p_{CO₂,0} = 2.4 bar to 0.994 for p_{CO₂,0} = 3.4 bar. A slight overestimation in the measurement of p_{CO₂} was observed at t = 0 s for p_{CO₂,0} = 2.4 and 2.9 bar. This error occurred because CO₂ was introduced first into the reactor, filling all the
available evacuated space including the sampling lines. Because sampling lines were located a distance away from the impeller, when the reaction was initiated by adding H₂ and further CO₂ and the impeller being turned on, the volume of the sampling line, which had been filled with CO₂, was not mixed well with the bulk phase. The composition of the sample taken at this time did not therefore reflect the true composition of the bulk phase because the sample would have had a higher composition of CO₂. The sampling lines were purged three times before the actual sample was taken but the effect of the dead volume in the sampling lines was not completely eliminated. No such problems were observed for subsequent measurements at later times.

![Figure 9](image)

Figure 9. The partial pressure of (a) H₂, (b) CH₄ and (c) CO₂ versus time for different initial partial pressures of CO₂. (d) The selectivity of CH₄ as a function of the conversion of CO₂. Here, $p_{H_2,0} = 15.2$ bar, $T = 463$ K and $m_{cat} = 5.0$ g.

### 3.2.3. Effect of pCH₄

Running the reaction in batch means that the products accumulate in the reactor. Hence, it is important to determine whether the main products, i.e. CH₄ and H₂O, have any effect on
the rate and selectivity of the reaction. As before, it is easiest to elucidate the effect of CH₄ by performing batch reactions with various initial partial pressures of CH₄. The observations are illustrated in Figure 10, where CH₄ is shown to have no effect on the rate of reaction. For the purpose of comparison of measurements from different experiments, the profile of the net change in the partial pressure of CH₄, Δp_{CH₄}, defined as the difference between the measured p_{CH₄} at a given time t and that at t = 0, is plotted in Figure 10 (b). Furthermore, no change in selectivity was observed when additional CH₄ was introduced and it is clear that CH₄ simply acts as a spectator molecule in the bulk phase.

![Figure 10](image)

Figure 10. The partial pressure of (a) CO₂ and (b) H₂ over time for different initial partial pressures of CH₄. In all experiments, p_{CO₂₀} = 2.4 bar, p_{H₂₀} = 7.2 bar, T = 463 K and m_{cat} = 5.0 g.

### 3.2.4. Effect of pH₂O

Varying the amounts of H₂O present before the start of the CO₂ methanation reaction is difficult experimentally. The introduction of liquid H₂O via one of the inlet ports was found to be challenging because the H₂O would vaporise immediately on contact with the hot walls of the reactor and heated lines. The high expansion ratio of H₂O, where 1 ml of H₂O could lead to about 7.2 bar at 473 K if fully vaporised in the reactor, meant that such a procedure was not only operationally dangerous but also it was difficult to obtain a desired partial pressure of H₂O, p_{H₂O}.

It has already been established that the CO₂ methanation reaction over the 12 wt% Ni/γ-Al₂O₃ has a high selectivity for CH₄. This means that performing a batch reaction to completion with a stoichiometric ratio of H₂ to CO of 4:1 would yield a reactor containing mainly CH₄ and H₂O. Since CH₄ was had no effect on the rate and selectivity of the reaction,
if additional CO₂ and H₂ were introduced into the reactor, the subsequent measurements would account for the effect of H₂O on the reaction. In this study, 1 bar of CO₂ was added to 4 bar of H₂ in order to obtain a nominal \( p_{\text{H,O},0} \), the initial partial pressure of H₂O, of 2 bar. A \( p_{\text{H,O},0} \) of 4 bar was obtained with 2 bar CO₂ and 4 bar H₂. The reaction was deemed complete when no further drop in the total pressure was observed on the pressure gauge. This was also verified by checking that negligible amounts of H₂ and CO₂ were present in the gas chromatogram in a separate experiment with the same initial partial pressures of CO₂ and H₂. In order to decrease the errors introduced from sampling, for the experimental results presented here, no samples were taken from the reactor before additional CO₂ and H₂ were introduced.

![Graphs showing partial pressures of CO₂ and CH₄ versus time](image)

Figure 11. Partial pressure of (a) CO₂ and (b) CH₄ versus time for different initial partial pressures of H₂O. In all experiments, \( p_{\text{CO}_2,0} = 2.4 \text{ bar} \), \( p_{\text{H}_2,0} = 7.2 \text{ bar} \), \( T = 463 \text{ K} \) and \( m_{\text{cat}} = 5.0 \text{ g} \).

In this way, it was found that H₂O inhibited the rate of methanation of CO₂ significantly. This is illustrated in the profiles of CO₂ and CH₄ in Figures 11 (a) and (b). Figure 12 shows no observable change in CH₄ selectivity as partial pressures of H₂O are increased. Unlike the effect of CO₂ and H₂, the effect of H₂O on the rate of reaction could be seen from the beginning of the reaction. The initial rate of production of CH₄ decreased from \( 2.0 \times 10^{-6} \text{ mol CH}_4 \text{ s}^{-1} \text{ g}^{-1} \) when \( p_{\text{H,O},0} = 0 \) to \( 1.4 \times 10^{-6} \text{ mol CH}_4 \text{ s}^{-1} \text{ g}^{-1} \) with \( p_{\text{H,O},0} = 2 \text{ bar} \), a decrease of 30%. However, the rate only fell to \( 1.0 \times 10^{-6} \text{ mol CH}_4 \text{ s}^{-1} \text{ g}^{-1} \), a further decrease of only 20% when \( p_{\text{H,O},0} = 4 \text{ bar} \), suggesting that the rate is less sensitive to the presence of water at higher \( p_{\text{H,O}} \). It is evident that the gradual decrease in the rate of CO₂ methanation, as observed in a batch reactor, is not only because of the decreasing partial pressures of the
reactants but also because of the increase in $p_{H_2O}$. Since even small levels of $H_2O$ were found to inhibit the rate of reaction, it is important that this effect is accounted for when interpreting the measurements at higher conversions in the batch reactor.

![Figure 12](image-url)  
Figure 12. The selectivity CH$_4$ as a function of the conversion of CO$_2$ for different initial partial pressures of H$_2$O. In all experiments, $p_{CO_2,0} = 2.4$ bar, $p_{H_2,0} = 7.2$ bar, $T = 463$ K and $m_{cat} = 5.0$ g.

### 3.2.5. Effect of temperature

Figure 13 shows the variation of CO$_2$, H$_2$ and CH$_4$ over time for $p_{CO_2,0} = 2.4$ bar, $p_{H_2,0} = 7.2$ bar at different reaction temperatures, i.e. from 443 – 483 K. Figure 14 (a) shows a small change in selectivity of CH$_4$ over the temperature range, increasing from 0.990 at 443 K to about 0.997 at 483 K, at $X_{CO_2} = 0.8$. However, the effect of this increase in the selectivity of CH$_4$ with temperature on the overall consumption ratio of H$_2$ to CO$_2$ is negligible. This is evident from Figure 13 (a), where the excess $p_{CO_2}$ remained at ~0.5 bar, at all temperatures, after $p_{H_2}$ was depleted. The sum of $p_{CO_2}$ and $p_{CH_4}$ accounted for the majority of the carbon balance at all temperatures explored, as shown in Figure 14 (b). The sum of $p_{CO_2}$ and $p_{CH_4}$ generally increased with temperature because of the slight shift in CH$_4$ selectivity at higher temperatures. Nevertheless, even at the lowest temperature of 443 K, the sum of $p_{CO_2}$ and $p_{CH_4}$ still accounted for 92% of the initial $p_{CO_2}$.
Figure 13. Partial pressure of (a) $\text{H}_2$, (b) $\text{CO}_2$ and (c) $\text{CH}_4$ versus time at different reaction temperatures. In all experiments, $p_{\text{CO}_2,0} = 2.4$ bar, $p_{\text{H}_2,0} = 7.2$ bar and $m_{\text{cat}} = 5.0$ g.
3.3. Temperature-programmed studies

Following the batch reactions in the Carberry reactor, the spent sample of catalyst was removed and stored in a capped glass jar. Temperature programmed desorption (TPD) was performed on the stored catalyst in the CATLAB apparatus, where 40 ml/min (measured at room temperature and pressure) of He was passed through 50 mg of the spent catalyst in a cylindrical tubular reactor. The sample was held at 120°C for 1 hour under He before the temperature was increased at a ramp rate of 10°C/min. Figure 15 shows the evolution of H$_2$O, CO$_2$ and CH$_4$ in the off-gas, measured by a mass spectrometer, as a function of temperature. The calibration of the signals of the mass spectrometer was challenging because the absolute values of the signals are dependent on parameters other than the quantity of material, e.g. the total pressure within the spectrometer. As such there was a day-to-day variation in the signal intensity. The interpretation of the results from CATLAB was therefore performed by comparing the rate of change of the signals. There appeared to be three main regions for the evolution of CO$_2$: a shoulder at 200°C, a main peak at 300°C and a smaller peak at 350°C. The profile of water is extremely broad, as seen. The rate of evolution of methane was rather similar to that of water but its measurement was unlikely to have been accurate since the atomic mass of methane is identical to that of an oxygen fragment. No significant evolution of H$_2$ was observed between 100 and 700°C.
Figure 15. The profiles of H$_2$O, CO$_2$ and CH$_4$ versus temperature in a temperature-programmed desorption of the spent 12 wt% Ni/γ-Al$_2$O$_3$ after CO$_2$ methanation reaction in the batch reactor. Following a drying period at 120°C, the temperature was increased at a rate of 10°C/min under a flow of 40 ml/min (measured at room temperature and pressure) He.

### 3.4. DRIFTS measurements

Here, 50 mg of fresh, passivated 12 wt% Ni/γ-Al$_2$O$_3$ catalyst was packed as a differential bed and reduced at 450°C for 2 hours under 100 ml/min (at room temperature and pressure) of H$_2$. Following the reduction, a mixture of 24 vol% CO$_2$, 72 vol% H$_2$ and 4 vol% Ar was passed across the differential bed at a flow rate of 100 ml/min (at room temperature and pressure). Figure 16 illustrates the main features of the IR spectrum obtained at 463 K at steady-state under reaction conditions. The identification of the species was based on Fujita et al. (1993), who studied supported Ni on alumina using DRIFTS. The absorbance bands at 2050, 1920 and 1840 cm$^{-1}$ were attributed to straight and bridged carbonyl groups on the surface of the catalyst. The presence of formates was also detected, reflected in the large peaks at 1620, 1590, 1390, 1350, 1330 and 2890 cm$^{-1}$. Following the reaction at 463 K under CO$_2$ and H$_2$, the inlet flow was changed to 100 ml/min (at room temperature and pressure) of H$_2$ and spectra of the surface of the catalyst were obtained periodically. The carbonyl peaks at 2050, 1920 and 1840 cm$^{-1}$ decreased in magnitude very quickly and disappeared after approximately 5 mins. However, the formate groups persisted even after 40 minutes under a flow of H$_2$, indicating that they were bound more strongly to the surface of the catalyst than the carbonyl groups and were less reactive than the carbonyl species with H$_2$. 

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Figure 16. IR spectrum obtained at 463 K at steady-state under reaction conditions. The absorbance bands at 2050, 1920 and 1840 cm$^{-1}$ were attributed to straight and bridged carbonyl groups on the surface of the catalyst. The presence of formates was also detected, reflected in the large peaks at 1620, 1590, 1390, 1350, 1330 and 2890 cm$^{-1}$. Following the reaction at 463 K under CO$_2$ and H$_2$, the inlet flow was changed to 100 ml/min (at room temperature and pressure) of H$_2$ and spectra of the surface of the catalyst were obtained periodically. The carbonyl peaks at 2050, 1920 and 1840 cm$^{-1}$ decreased in magnitude very quickly and disappeared after approximately 5 mins. However, the formate groups persisted even after 40 minutes under a flow of H$_2$, indicating that they were bound more strongly to the surface of the catalyst than the carbonyl groups and were less reactive than the carbonyl species with H$_2$. 

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Figure 16. Infrared spectra of the adsorbed species in the range from (a) 1100 – 2200 cm\(^{-1}\) and (b) 2500 – 3300 cm\(^{-1}\) formed on reduced 12 wt% Ni/Al\(_2\)O\(_3\) in flow of 100 ml/min (at room temperature and pressure) of 24 vol% CO\(_2\), 72 vol% H\(_2\) and 4 vol% Ar at 463 K. The spectrum of the catalyst under He was used as the background.

4. Modelling

4.1.1. Reactor model

Reaction (1) has been established as the main reaction in CO\(_2\) methanation over the temperature range 443 – 493 K. Negligible levels of CO were detected in the bulk phase and the reaction was found to be at least 99.0% selective for methane. Therefore, it is reasonable to develop the model of the reactor based on the stoichiometry of the single Reaction (1). It has already been established in the above that there were no significant intra-particle or extra-particle gradients in concentration and temperature in the catalyst pellets. Hence, the transient changes of \( p_{\text{CO}_2} \), \( p_{\text{H}_2} \), \( p_{\text{CH}_4} \) and \( p_{\text{H}_2\text{O}} \) in the Carberry spinning-basket reactor could be modelled as a set of four ordinary differential equations:

\[
\frac{dp_{\text{CO}_2}}{dt} = \frac{-m_{\text{cat}}RT}{V_{\text{reactor}} \times 10^5} r',
\]

\[
\frac{dp_{\text{H}_2}}{dt} = \frac{4m_{\text{cat}}RT}{V_{\text{reactor}} \times 10^5} r',
\]

\[
\frac{dp_{\text{CH}_4}}{dt} = \frac{m_{\text{cat}}RT}{V_{\text{reactor}} \times 10^5} r',
\]

\[
\frac{dp_{\text{H}_2\text{O}}}{dt} = \frac{2m_{\text{cat}}RT}{V_{\text{reactor}} \times 10^5} r'.
\]
where $p_{CO_2}$, $p_{H_2}$, $p_{CH_4}$ and $p_{H_2O}$ are the partial pressures of $CO_2$, $H_2$, $CH_4$ and $H_2O$ respectively in bar. $r'$ is the rate of Reaction (1) in mol s$^{-1}$ g$^{-1}$cat, $t$ is time in seconds, $m_{cat}$ is the mass of the catalyst in the reactor in grams and $V_{reactor}$ is the volume of the reactor in m$^3$. The initial conditions for the experiments were

$$p_i = p_{i,0},$$  

(10)

where $p_i$ is the partial pressure of component $i$ in bar and $p_{i,0}$ is the initial partial pressure of species $i$. Given a rate expression for $r'$, which could be a function of $p_{CO_2}$, $p_{H_2}$, $p_{CH_4}$ and $p_{H_2O}$ at a given temperature, Equations (6) to (10) were solved using the MATLAB solver ode45 to give the variation of the partial pressure of $CO_2$, $H_2$, $CH_4$ and $H_2O$ over time for comparison with the experimental results.

4.1.2. Kinetic modelling

This Section investigates the validity of different rate expressions for $CO_2$ methanation using kinetic models based on a Langmuir-Hinshelwood approach. The active sites for the reaction were assumed to be identical and their distribution uniform throughout the catalyst. It was assumed that $CO_2$ methanation occurred via the dissociative adsorption of $CO_2$ (Weatherbee and Bartholomew, 1982). The sequence of elementary steps is outlined in Reactions (2) to (8):

$$H_2(\varepsilon) + 2\theta \xrightleftharpoons[k_1]{k_{-1}} 2\theta_H$$  

(R2)

$$CO_2(\varepsilon) + 2\theta \xrightleftharpoons[k_2]{k_{-2}} \theta_{CO} + \theta_O$$  

(R3)

$$\theta_{CO} \xrightarrow[k_3]{k_{-3}} CO(\varepsilon) + \theta$$  

(R4)

$$\theta_{CO} + \theta \xrightarrow[k_4]{k_{-4}} \theta_C + \theta_O$$  

(R5)

$$\theta_O + \theta_H \xrightarrow[k_5]{k_{-5}} \theta_{OH} + \theta$$  

(R6)

$$\theta_{OH} + \theta_H \xrightarrow[k_6]{k_{-6}} \theta_{H,O} + \theta$$  

(R7)

$$\theta_{H,O} \xrightarrow[k_7]{k_{-7}} H_2O(\varepsilon) + \theta$$  

(R8)
where \( k_i \) and \( k_{-i} \) are the forward and reverse rate of reaction for the specified elementary step and \( \theta_i \) presented adsorbed species \( i \) on an active site \( \theta \). Further steps include hydrogenation of the \( \theta_{CO} \) and the subsequent desorption of \( \theta_{CH_4} \) to form \( CH_4 \) and \( H_2O \) in the gas phase.

A number of different rate expressions were derived from this sequence of elementary steps, depending on assumptions about the rate-limiting step and the most abundant species on the surface of the catalyst. Table 1 gives four examples of rate expressions derived based on different rate-limiting steps and the most abundant surface species. It should be noted that some of the kinetic parameters in Eqs. (11)-(14) are a composite of a number of rate and equilibrium constants, produced during the derivations. It is beyond the scope of this study to determine the values of all of the individual constants and the investigation is limited to the evaluation of the four main kinetic parameters a, b, c and d. Three other rate expressions for \( CO_2 \) methanation, proposed by other investigators, are given in Table 2. The derivations of Eqs. (11) and (12) were largely based on the study by Weatherbee and Bartholomew (1982). However, in this study, \( H_2O \) was included as a dominant surface species in order to account for its inhibition on the rate of reaction, as observed in the experiments.

4.1.3. Model discrimination

Of course, not all the rate expressions in Tables 1 and 2 agree with the experimental results obtained in the present research. Equations (13) and (14) predict a finite rate when respectively either \( p_{CO_2} \) or \( p_{H_2} \) is zero. This is in conflict with the experimental evidence here. Figure 7 clearly illustrates that there was no further decrease in \( p_{CO_2} \) when \( H_2 \) was depleted and, similarly, Figure 9 shows no decrease in \( p_{H_2} \) when \( CO_2 \) was depleted. The same argument applies to Eq. (16).

The power law expression proposed by Chiang and Hopper (1983), Eq. (15), predicts that the rate of reaction would continue to increase indefinitely with \( p_{H_2} \) and \( p_{CO_2} \). This is contrary to the experimental results in Sections 3.2.1 and 3.2.2 where the rate of reaction was not affected by \( p_{H_2} \) and \( p_{CO_2} \) after values of \( p_{H_2} \) and \( p_{CO_2} \) exceeded certain threshold values. The inhibition of the rate of reaction by steam, evident in Section 3.2.4 was also not accounted for by Eqs. (13) – (17).
Table 1. Rate expressions based on different assumptions of the rate limiting step and the most abundant surface species. $p_i$ is the partial pressure of component $i$ and $r_{CH_4}$ is the rate of production of CH$_4$.

<table>
<thead>
<tr>
<th>Model</th>
<th>Rate expression</th>
<th>Rate-limiting step</th>
<th>Most abundant surface species</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$\frac{a_i P_{CO_2}^{0.5} P_{H_2}^{0.5}}{(1 + b_i \sqrt{P_{H_2}} + c_i P_{CO_2}^{0.5} P_{H_2}^{0.5} + d_i P_{H_2} + d_i P_{H_2} + d_i P_{H_2})^{2}}$</td>
<td>CO dissociation</td>
<td>H, CO and H$_2$O</td>
</tr>
<tr>
<td>II</td>
<td>$\frac{a_{II} P_{CO_2}^{0.5} P_{H_2}^{0.5}}{(1 + b_{II} (\frac{P_{CO_2}}{P_{H_2}})^{0.5} + c_{II} P_{CO_2}^{0.5} P_{H_2}^{0.5} + d_{II} P_{H_2} + d_{II} P_{H_2} + d_{II} P_{H_2})^{2}}$</td>
<td>CO dissociation</td>
<td>CO, O and H$_2$O</td>
</tr>
<tr>
<td>III</td>
<td>$\frac{a_{III} P_{H_2}}{(1 + b_{III} \sqrt{P_{CO_2}} + c_{III} \sqrt{P_{H_2}})^{2}}$</td>
<td>Adsorption of H$_2$</td>
<td>H, CO and O</td>
</tr>
<tr>
<td>IV</td>
<td>$\frac{a_{IV} P_{CO_2}}{(1 + b_{IV} \sqrt{P_{CO_2}} + c_{IV} \sqrt{P_{H_2}})^{2}}$</td>
<td>Adsorption of CO$_2$</td>
<td>H, CO and O</td>
</tr>
</tbody>
</table>

Table 2. Some rate expressions proposed by other investigators for CO$_2$ methanation.

<table>
<thead>
<tr>
<th>Rate expression</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r' = kp_{H_2}P_{CO_2}^{0.21}P_{CO_2}^{0.66}$</td>
<td>Chiang and Hopper (1983)</td>
</tr>
<tr>
<td>$r' = \frac{k_{PCO_2}}{1 + K_{CO_2}P_{CO_2}}$</td>
<td>van Herwijnen et al. (1973)</td>
</tr>
<tr>
<td>$r' = \frac{k\sqrt{P_{CO_2}P_{CO_2}}}{(1 + K_1 \sqrt{P_{CO_2}} + K_2 \sqrt{P_{CO_2}} + K_3 P_{CO_2})^2}$</td>
<td>Weatherbee and Bartholomew (1982)</td>
</tr>
</tbody>
</table>

The two most plausible rate expressions are those of Model I and II, i.e. Eqs. (11) and (12). Further comparison of these two models was performed here by substituting the rate expressions into the model of the reactor, given in Section 4.1.1 and comparing the predictions with the experimental measurements at different conditions. To do this, the
parameters, a, b, c and d for each model were estimated based on a least-squares minimisation developed in MATLAB. Thus, the agreement between the model and the experimental results was studied by comparing the solution of the system of ODEs with the temporal variation of the partial pressures of the various species measured in the batch experiments. In the minimisation routine, the difference, \( d_i(t) \), between these values were compared for each iteration at time \( t \) with the experimental measurements for \( p_{CO_2} \), \( p_{H_2} \) and \( p_{CH_4} \), such that

\[
d_i(t) = p_{i,\text{model}}(t) - p_{i,\text{exp}}(t)
\]  

where \( p_{i,\text{model}}(t) \) is the partial pressure of species \( i \) determined by the solution of the ODEs and \( p_{i,\text{exp}}(t) \) is the partial pressure of species \( i \) measured experimentally. The sum of all the squares of each component was evaluated at a given time, \( t \), such that

\[
D = \sum_i (d_i(t))^2.
\]

The values of the parameters a, b, c and d of Model I and II, were obtained by minimising the value \( D \) using the MATLAB optimisation routine lsqnonlin.

### 4.1.4. Model I

The derivation of Model I was based on the assumption that the rate-determining step is the dissociation of the CO and that the most abundant species on the surface of the catalyst are adsorbed \( H \), \( CO \) and \( H_2O \). Since, the parameter \( b_I \) is, in fact, the adsorption equilibrium constant of hydrogen on the surface of the catalyst, its value was obtained from Sehested et al. (2005), who studied the methanation of CO over a Ni/MgAl\(_2\)O\(_4\) catalyst, thus

\[
b_I = 7.7 \times 10^{-4} \exp \left( \frac{43000}{RT} \right).
\]

consistent with partial pressures expressed in bar. Alstrup (1995) and Aparicio (1997) have also reported values of \( b_I \). There is good agreement between the \( b_I \) obtained by Alstrup (1995) and Sehested (2005). The values of \( b_I \) obtained by Aparicio (1997) were an order of magnitude larger than those given by Eq. (20). However, the values of the heat of adsorption determined by Aparicio (1997) were found by to be in good agreement with Eq. (20) with the pre-exponential factor being responsible for the discrepancy between the reported values of \( b_I \). With the value of \( b_I \) predetermined, only three parameters were left to be determined using
the optimisation routine. Figure 17 compares the result of the least-squares minimisation routine for different initial $p_{H_2}$. It is clear that, because of the high value of $b_0$, the model predicts an increase in the rate of reaction at low $p_{H_2}$. The modelling results for $p_{H_2,0} = 7.2$ bar show that the profile of $p_{H_2}$ is approximately linear with time, in stark contrast with the experimental measurements where the rate decreased at higher conversions. Furthermore, the least-squares minimisation routine resulted in negative values of $c_i$, which have no physical interpretation.

![Graphs showing the partial pressures of $H_2$ and $CH_4$ over time for different initial partial pressures of $H_2$.](image)

Figure 17. Comparison between the modelling results (Model I, Eq. (20)) and the experimental results for different initial partial pressure of $H_2$: (a) shows the partial pressure of $H_2$ with time and (b) the partial pressure of $CH_4$ with time. $T = 463$ K, $p_{H_2,0} = 7.2$ bar, $p_{CO_2,0} = 2.4$ bar and $m_{cat} = 5$ g.

To proceed, the pre-exponential value of $b_0$ was allowed to vary in the least-squares minimisation routine. Table 3 gives the results of the optimisation. Figure 18 shows that by relaxing the pre-exponential term of $b_0$, a much better agreement was obtained with the experimental measurements. The agreement was verified with measurements taken from 443 – 483 K and the values of the kinetic constants are given in Table 3. Assuming that these parameters follow the Arrhenius relationship, the values of activation energy and heat of adsorption were obtained, given in Table 4. While the agreement with the experimental results was good, the pre-exponential factor $b_0$ was found to be $5 \times 10^{-7}$ bar$^{-0.5}$, very much smaller than that reported by Sehested et al. (2005). It could be argued that the surface of the catalyst in this study is different to that in other investigations, which were mainly studies
where high \( p_{\text{CO}_2} \) were involved. Alternatively, atomic H might not be one of the most abundant species on the surface of the catalyst under conditions for \( \text{CO}_2 \) methanation, which would explain the low level of affinity for the surface suggested by the value of \( b_1 \) determined here.

Table 3. Values of parameters from a fit of Model I to the experimental results.

<table>
<thead>
<tr>
<th>Temp / K</th>
<th>( a_1 / \text{mol bar}^{-1} \text{s}^{-1} )</th>
<th>( b_1 / \text{bar}^{-0.5} )</th>
<th>( c_1 / \text{bar}^{-1} )</th>
<th>( d_1 / \text{bar}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>443</td>
<td>((2.2 \pm 0.2) \times 10^{-5})</td>
<td>0.059 (\pm) 0.006</td>
<td>0.101 (\pm) 0.002</td>
<td>0.20 (\pm) 0.01</td>
</tr>
<tr>
<td>453</td>
<td>((3.8 \pm 0.1) \times 10^{-5})</td>
<td>0.046 (\pm) 0.002</td>
<td>0.091 (\pm) 0.002</td>
<td>0.16 (\pm) 0.01</td>
</tr>
<tr>
<td>463</td>
<td>((6.1 \pm 0.3) \times 10^{-5})</td>
<td>0.036 (\pm) 0.004</td>
<td>0.082 (\pm) 0.003</td>
<td>0.12 (\pm) 0.03</td>
</tr>
<tr>
<td>473</td>
<td>((9.0 \pm 0.5) \times 10^{-5})</td>
<td>0.028 (\pm) 0.004</td>
<td>0.074 (\pm) 0.008</td>
<td>0.12 (\pm) 0.02</td>
</tr>
<tr>
<td>483</td>
<td>((2.0 \pm 0.3) \times 10^{-4})</td>
<td>0.023 (\pm) 0.011</td>
<td>0.067 (\pm) 0.022</td>
<td>0.10 (\pm) 0.01</td>
</tr>
</tbody>
</table>

Table 4. Values of the activation energy, heat of adsorption and the corresponding pre-exponential factors of the parameters for Model I.

<table>
<thead>
<tr>
<th>( a_0 )</th>
<th>( b_0 )</th>
<th>( c_0 )</th>
<th>( d_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(49.4 \times 10^6) (\text{mol bar}^{-1} \text{s}^{-1})</td>
<td>(5.0 \times 10^{-7}) (\text{bar}^{-0.5})</td>
<td>(5.6 \times 10^{-2}) (\text{bar}^{-1})</td>
<td>(4.6 \times 10^{-4}) (\text{bar}^{-1})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( \Delta E_a )</th>
<th>( \Delta H_b )</th>
<th>( \Delta H_c )</th>
<th>( \Delta H_d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>92 (\text{kJ mol}^{-1})</td>
<td>-43 (\text{kJ mol}^{-1})</td>
<td>-1.5 (\text{kJ mol}^{-1})</td>
<td>-21.5 (\text{kJ mol}^{-1})</td>
</tr>
</tbody>
</table>

Figure 18. Comparison of the modelling results (Model I, with pre-exponential for Eq. 920) allowed to vary) and the experimental results for different initial partial pressure of \( \text{H}_2 \). (a) shows the partial pressure of \( \text{H}_2 \) with time and (b) the partial pressure of \( \text{CH}_4 \) with time. \( T = 463 \text{ K}, \ p_{\text{H}_2,0} = 7.2 \text{ bar}, \ p_{\text{CO}_2,0} = 2.4 \text{ bar} \) and \( m_{\text{cat}} = 5 \text{ g} \). The parameters in the kinetic model are given in Table 4.
4.1.5. Model II

The main difference between Model II and Model I is that Model II, given by Eq. (12), assumes that the most abundant species on the surface of the catalyst are H$_2$O, O and CO. The rate-limiting step of the reaction remains the dissociation of CO. As noted above, the derivations of these equations were largely based on Weatherbee and Bartholomew’s (1982) investigation but were extended in this research to account for the inhibitory effect of H$_2$O on the rate of reaction. Weatherbee and Bartholomew (1982) obtained values of $b_{II}$ over the range 500 – 600 K, and summarised their findings by

$$b_{II} = 4.27 \times 10^{-7} \exp \left( \frac{46000}{RT} \right).$$  \hspace{1cm} (21)

Given that their experiments were performed using a differential reactor, the conversion of CO$_2$, $X_{CO_2}$, was low. Hence, it is reasonable to assume that the effect of H$_2$O in their experiments was negligible because $p_{H_2O}$ could be taken to be small. In the present work, the values of $b_{II}$ at different temperatures were based on the extrapolation of Eq. (21) to temperatures of 443 – 483 K. The other parameters $a_{II}$, $c_{II}$ and $d_{II}$ were obtained by the least-squares fit algorithm, as described previously. The modelling results showed that $c_{II}$ was largely invariant over the range 443 – 483 K, with an average of 0.16 ± 0.02 bar$^{-1}$. It should be noted that $c_{II}$ is a composite of a number of kinetic and equilibrium constants: it is interesting that the resulting net “activation energy”, although not a true activation energy in the kinetic sense, appeared to be zero. In fact, the values of $c_{II}$ obtained by Weatherbee and Bartholomew (1982) did not show a clear trend with temperature, with a maximum value of 0.143 at 550 K. The values of the various kinetic constants obtained in the present work for Model II are given in Table 5 and the estimated values of activation energies, heats of adsorption and pre-exponential factors in Table 6.

Table 5. Values of parameters from the least-squares fit of Model II to the experimental results.

<table>
<thead>
<tr>
<th>Temp / K</th>
<th>$a_{II}$ / mol bar$^{-1}$ s$^{-1}$</th>
<th>$b_{II}$ / -</th>
<th>$d_{II}$ / bar$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>443</td>
<td>$(3.54 \pm 0.07) \times 10^{-5}$</td>
<td>0.039</td>
<td>0.23 ± 0.01</td>
</tr>
<tr>
<td>453</td>
<td>$(4.92 \pm 0.05) \times 10^{-5}$</td>
<td>0.051</td>
<td>0.19 ± 0.01</td>
</tr>
<tr>
<td>463</td>
<td>$(8.38 \pm 0.08) \times 10^{-5}$</td>
<td>0.066</td>
<td>0.16 ± 0.01</td>
</tr>
<tr>
<td>473</td>
<td>$(1.31 \pm 0.07) \times 10^{-4}$</td>
<td>0.085</td>
<td>0.13 ± 0.02</td>
</tr>
<tr>
<td>483</td>
<td>$(2.88 \pm 0.08) \times 10^{-4}$</td>
<td>0.110</td>
<td>0.11 ± 0.02</td>
</tr>
</tbody>
</table>
Table 6. Values of the activation energy, heat of adsorption and the corresponding pre-exponential factors for the parameters in Model II.

<table>
<thead>
<tr>
<th>(a_{II,0})</th>
<th>(b_{II,0})</th>
<th>(c_{II,0})</th>
<th>(d_{II,0}) bar(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3 \times 10^6 mol bar(^{-1}) s(^{-1})</td>
<td>4.3 \times 10^2</td>
<td>0.16 bar(^{-1})</td>
<td>3.4 \times 10^5 bar(^{-1})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(\Delta E_a)</th>
<th>(\Delta H_b)</th>
<th>(\Delta H_c)</th>
<th>(\Delta H_d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>95 kJ mol(^{-1})</td>
<td>-46 kJ mol(^{-1})</td>
<td>-</td>
<td>-32 kJ mol(^{-1})</td>
</tr>
</tbody>
</table>

For each set of initial conditions explored, all the experimental and modelling profiles of the three components, i.e. CO\(_2\), H\(_2\) and CH\(_4\), were compared. For illustration, Figure 19 shows \(p_{H_2}\) and \(p_{CH_4}\) as a function of time at \(T = 473\) K for different initial partial pressures of H\(_2\) while Figure 20 illustrates \(p_{CO_2}\) and \(p_{CH_4}\) versus time at \(T = 463\) K for different initial partial pressures of H\(_2\)O. It is clear that Model II correctly predicts a number of experimental observations. At high \(p_{CO_2}\) and \(p_{H_2}\), the rate is largely unaffected by changes in \(p_{CO_2}\) and \(p_{H_2}\), which is clearly observed in Figure 19 (a) and (b) at \(t < 1000\) s. Furthermore, the rate decreased at higher conversions, depicting a positive order on both \(p_{CO_2}\) and \(p_{H_2}\) on the rate of reaction at lower values of \(p_{CO_2}\) and \(p_{H_2}\). Figure 20 shows the decrease in the rate of reaction with higher partial pressures of H\(_2\)O.

![Figure 19](image-url)  
(a)  
![Figure 20](image-url)  
(b)  
Figure 19. Comparison between the modelling results and the experimental results for different initial partial pressures of CO\(_2\). (a) shows the partial pressure of H\(_2\) with time and (b) the partial pressure of CH\(_4\) with time. \(T = 473\) K, \(p_{CO_2,0} = 2.4\) bar and \(m_{cat} = 5.0\) g. Solid lines are the predictions of Model II and the symbols illustrate the corresponding experimental measurements.
Figure 20. Comparison between the modelling results and the experimental results for different initial partial pressures of H$_2$O. (a) shows the partial pressure of H$_2$ with time and (b) the partial pressure of CH$_4$ with time. T = 463 K, $p_{CO_2,0} = 2.4$ bar, $p_{H_2,0} = 7.2$ bar and $m_{cat} = 5.0$ g. Solid lines are the predictions of Model II and the symbols illustrate the corresponding experimental measurements.

5. Discussion

It has already been established in Section 4.1.3 that some of the rate expressions proposed by other studies, such as Eqs. (15) and (16), were not suitable for describing the experimental measurements obtained in the present research. Equation (16) was proposed by van Herwijnen et al. (1973), who performed the reaction over a similar temperature range to the present investigation. However, the experiments by van Herwijnen et al. (1973) only explored $p_{CO_2}$ up to 0.02 bar. They found that the rate followed a first-order dependence on $p_{CO_2}$ at $p_{CO_2} < 0.004$ bar changing to zero order at higher $p_{CO_2}$, in agreement with the observations in this study. The low threshold of $p_{CO_2}$ when the dependence on $p_{CO_2}$ changed to zero order is likely to the result of a very high ratio of H$_2$ to CO$_2$ exceeding 50:1 in their work. While the general trends in the study by van Herwijnen et al. (1973) were consistent with those in this study, Eq. (16) did not account for the effects of $p_{H_2}$ and $p_{H_2O}$. Rate expressions based on a power law, such as Eq. (15), were also found to be unsuitable for the modelling of the different species in the present research. Weatherbee and Bartholomew (1982) also observed that the reaction orders, based on power law expressions, changed significantly with temperature. Hence, the use of power law expressions for CO$_2$ methanation
is only suitable, at best, over a small range of temperature and partial pressures of reactants and products.

Good agreement between the experimental results and the predictions of Model I was only possible with a very small value of $b_1$, the adsorption equilibrium of $H_2$, compared to values reported in the literature (Sehested et al., 2005; Alstrup, 1995; Aparicio, 1997). This contradicts the assumption in Model I that atomic $H$ from the dissociative adsorption of $H_2$ is one of the most abundant species on the surface of the catalyst. Weatherbee and Bartholomew (1982) also derived an expression similar to Model I, albeit not accounting for $H_2O$ on the surface of the catalyst, and obtained negative parameters. Temperature-programmed desorption studies in the present work performed on the spent catalyst following CO$_2$ methanation in the Carberry reactor showed no significant evolution of $H_2$ above 100°C, suggesting that $H$ is not one of the main species on the surface under reaction conditions. Therefore, Model I was rejected on the basis of the evidence from the modelling efforts and experimental measurements.

When the value of $b_1$ from Weatherbee and Bartholomew (1982) was used, excellent agreement was obtained between Model II and the experimental results for different $p_{CO_2}$, $p_{H_2}$, $p_{H_2O}$ and temperatures. It has already been noted that Model II was based on a similar derivation to that of Eq. (17) but was extended to account for the effect of $p_{H_2O}$, which cannot be neglected in the present work because the batch operation performed as an integral reactor and the accumulation of $H_2O$ in the reactor was significant. Equation (17) also features an inhibition term involving CO. Weatherbee and Bartholomew (1982) consistently observed a small partial pressure of CO at the outlet of their reactor and attributed it to its being in equilibrium with the adsorbed CO, originating from the dissociative adsorption of CO$_2$ on the catalyst. However, their reactions were performed at a higher temperature than those described in this work. At 500 K, their lowest temperature, the amount of CO was only 0.003 mol%. Given that the temperature range in the present study was 443 – 483 K, it is likely that $p_{CO}$ was very much smaller because the adsorption of CO$_2$ is an activated process (Falconer and Zagli, 1980), viz. less CO$_2$ is adsorbed at lower temperatures. This was confirmed by the analysis of the gas samples in the present study, where no CO was detected at all. Furthermore, the thermodynamics of the reaction at such temperatures dictate that $p_{CO}$ is negligible. Therefore, the term involving CO was dropped in the derivation of Model II. This does not contradict the proposed rate mechanism where CO$_2$ dissociates into CO and O.
The absence of CO is most likely owing to the equilibrium lying heavily on the side of the adsorbed species and the detection limit of the gas chromatograph, approximately 0.05 bar.

The derivation of Model II assumed that CO\textsubscript{2} methanation involves the dissociative adsorption of CO\textsubscript{2} to form surface CO and O. TPD analysis on the spent catalyst following CO\textsubscript{2} methanation, illustrated in Figure 15, showed the evolution of CO\textsubscript{2} and CH\textsubscript{4} from 200 – 350°C, indicating the presence of some carbonaceous species on the catalyst. IR spectra obtained from in-situ DRIFTS analysis of the catalyst at 463 K, illustrated in Figure 16, clearly showed the presence of straight and bridged carbonyl groups. The high activity of these groups, evident from the fast decrease in the intensity of their corresponding IR bands when pure H\textsubscript{2} was passed through the catalyst, suggests the involvement of the carbonyl groups in the reaction pathway to form CH\textsubscript{4}. The DRIFTS analysis also revealed the presence of formate species, presumably from the hydrogenation of carbonyl and carbonate species. However, the DRIFTS measurements found that formate groups persisted even after 40 minutes under a flow of H\textsubscript{2}, indicating that they were bound much more strongly to the surface of the catalyst than the carbonyl groups, which decreased very rapidly. This provides further evidence that while hydrogen-modified groups were tightly bound to the surface, their reactivity is low and so they might not participate in the pathway to form CH\textsubscript{4}. These observations are consistent with those of Fujita et al. (1993), Jacquemin et al. (2010) and Aldana et al. (2013), who obtained similar spectra on Ni/SiO\textsubscript{2} and Ni/Al\textsubscript{2}O\textsubscript{3} to those observed in this study. Their studies also supported the dissociation of CO\textsubscript{2} followed by the subsequent hydrogenation of adsorbed C species for nickel supported on Al\textsubscript{2}O\textsubscript{3} or SiO\textsubscript{2}.

Finally, the derived model, with the accompanying parameters for Model II, was compared against additional independent experiments performed in the Carberry reactor. In Figure 21, CO\textsubscript{2} methanation was performed at 463 K with an initial inventory of 2.4 bar CO\textsubscript{2} and 7.2 bar H\textsubscript{2}. At 3180 s, additional CO\textsubscript{2} and H\textsubscript{2} were introduced and the composition of the bulk phase of the reactor was analysed periodically. In general, there is good agreement between the results predicted by the model and the measurements obtained from the batch reactor. It is noted that the rate of reaction after the introduction of additional reactants, viz. CO\textsubscript{2} and H\textsubscript{2}, was predicted to be slightly faster by the model than was the case in practice. This suggests that the inhibition term for H\textsubscript{2}O is slightly underestimated in Model II. Nevertheless, there is excellent agreement in Figure 22, where only additional H\textsubscript{2} was introduced at 3780 s. Kinetic expressions proposed by other studies, given in Table 2, were also compared against the experimental results in this study. They consistently predicted a
much faster rate of reaction after the introduction of additional reactants in Figure 21 and 22. This is probably the result of the absence of an inhibition term for $H_2O$, which limits their accuracy under conditions where $p_{H_2O}$ is high.

Figure 21. (a) Partial pressure of $CO_2$ and $CH_4$ and (b) partial pressure of $H_2$ versus time. Additional $CO_2$ and $H_2$ was introduced in a ratio of 3:1 at $t = 3180$ s. $T = 463$ K and $m_{cat} = 5.0$ g.

Figure 22. (a) Partial pressure of $CO_2$ and $CH_4$ and (b) partial pressure of $H_2$ versus time. Additional 4.5 bar of $H_2$ was introduced at $t = 3780$ s. $T = 463$ K and $m_{cat} = 5.0$ g.
6. Conclusions

An investigation of the methanation of CO\textsubscript{2} methanation was performed in a gradientless, spinning-basket reactor at temperatures of 443 – 483 K and pressures of up to 20 bar. The reactor was operated in batch and the composition of its contents was determined periodically. Additional analysis was performed using temperature-programmed studies and DRIFTS analysis in order to probe the surface of the catalyst.

The conclusions were as follows. At low $p_{\text{H}_2}$ and $p_{\text{CO}_2}$, the rate increases with the partial pressure of the reactants. At high $p_{\text{H}_2}$ and $p_{\text{CO}_2}$, the rate of reaction has a zeroth order relationship with the partial pressure of the reactants. H\textsubscript{2}O has a significant inhibitory effect on the rate of CO\textsubscript{2} methanation. Several rate expressions were tested against the experimental measurements and Eq. (12) was found to be the most satisfactory. It assumes a mechanism in which CO\textsubscript{2} dissociates to adsorbed CO and O on the surface of the catalyst. The rate-limiting step was taken to be the dissociation of adsorbed CO and the most abundant species were CO, O and H\textsubscript{2}O. The resulting adsorbed carbon on the surface would be further hydrogenated to form CH\textsubscript{4}. Temperature-programmed studies of the spent catalyst showed the presence of some carbonaceous species on the catalyst. Their presence was not sufficient to cause any deactivation but were consistent with the dissociation of CO\textsubscript{2} on the surface of the catalyst. The presence of carbonyl groups from in-situ DRIFTS analysis is also in agreement with this observation.

Overall, it has been demonstrated that the study of CO\textsubscript{2} methanation in batch has led to experimental measurements consistent with investigations, described in the literature, performed in reactors operated in continuous flow. Furthermore, the validity of different rate expressions could be easily determined over a wide range of partial pressures by using a batch reactor. A convenient method of determining the effect of H\textsubscript{2}O on the rate of reaction was discovered and the inhibitory effect of H\textsubscript{2}O was quantified.

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