Modelling the CO₂ hydrogenation reaction over Co, Ni and Ru/Al₂O₃

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Abstract

The CO₂ hydrogenation reaction was experimentally investigated over pristine Co, Ni and an Al₂O₃-supported Ru catalyst with 0.5 wt.% Ru loading. We developed a reaction model which takes the kinetical, diffusional and thermodynamic reaction regimes into account and enables the description of the reaction over a broad temperature range. The model is based on a fractional rate law with experimentally determined reaction orders. We found that the overall reaction orders on the different catalysts are in proximity to zero order (0.13 for Co, 0.14 for Ni and 0.38 for Ru/Al₂O₃), which leads to the interpretation that the reaction is limited by the available surface sites in the underlying reaction conditions. We demonstrate on the example of Ru/Al₂O₃ that the reaction rate strongly depends on the partial pressure of CO₂ in the gas phase. Upon reducing the partial pressure of CO₂ in the reaction gas stream via He dilution, the reaction approaches a higher reaction order. Furthermore, the supported Ru catalyst is less limited by pore-diffusion compared to pristine Co. With the derived model we can accurately calculate the CO₂ conversion over a broad temperature range; the temperature of maximum conversion is predicted within 15K and the deviation between simulation and experiment is mostly less than 20%. This enables the simple and rapid prediction of the influence of different reaction parameters such as the activation energy or the diffusional limitations on the CO₂ conversion.

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1. Introduction

Energy storage is one of the key challenges towards an energy supply solely based on renewable energy. To overcome the challenge of seasonal energy storage, an energy carrier with high gravimetric and stoichiometric energy density is favorable. Hydrocarbons synthesized from carbon dioxide and hydrogen were identified as the ideal energy carrier for this purpose [1]. If the CO₂ for this process is directly captured from air or point emitters and the hydrogen is obtained from water via electrolysis for synthesizing hydrocarbons, the carbon cycle is closed [2].

Current technology allows the conversion of CO₂ and hydrogen to methane with high selectivity via the Sabatier reaction [3–5]. The Sabatier reaction ($\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$) was first described in 1910 by French chemist Paul Sabatier and has important applications, for example in the Power-to-Gas technology [6]. An unselective path to longer chain hydrocarbons is via the Reverse Water Gas Shift reaction followed by the Fischer-Tropsch reaction. Current research efforts focus on the fundamental understanding of the CO₂ hydrogenation reaction towards hydrocarbons. This includes different approaches, such as ab initio calculations [7], the study of gas-surface interactions [8,9], the study of the support-metal interaction [10,11], the characterization of supported [12] –and unsupported transition metal catalysts [13], alloying and combining catalysts [14–16] and kinetic reaction modelling [17],[18]. The kinetic reaction description is the bridge between fundamental research and chemical reaction engineering towards real applications.

The kinetic reaction modelling over Ru/Al₂O₃ catalysts have been investigated intensively in the past [19], [20], [17], [21], [22], [23], which makes Ru/Al₂O₃ an ideal reference catalyst. The major findings in literature on the kinetic reaction investigation of the CO₂ hydrogenation reaction over Ru/Al₂O₃ are that the reaction order in respect to CO₂ is in the range between 0.07-0.34. The reaction order with respect to CO₂ changes due to different reaction conditions (partial pressures of CO₂, dilution, available active catalysts sites, different residence times). For a Ru/Al₂O₃ catalyst with 0.5 wt.% Ru loading, the reaction order of 0.225 with respect to CO₂ proposed by Lunde and Kester in 1973 [19] was reported. This dataset was later reinvestigated by Falbo et al. [20]. In this study it was found that the model of Lunde and Kester described the catalyst behavior in a wide range of CO₂ conversions satisfactorily and reported a reaction order of 0.14 with respect to CO₂. Upon further refinement and with additional experiments they report a reaction order with respect to CO₂ of 0.076. Furthermore, literature reports that the reaction mechanism can be either described with an Eley-Rideal [21] or Langmuir-Hinshelwood type mechanism [17],[23]. At the best of our knowledge, no detailed kinetic model is available in literature for the Sabatier reaction over the pristine Ni and Co catalysts. Kinetic models are available for supported Ni catalysts [27–29] but these are not representative of the actual properties of the pristine metal.

In this paper, the CO₂ hydrogenation reaction is investigated over the unsupported Co and Ni catalysts, with a 0.5 wt.% Ru/Al₂O₃ as a reference catalyst with the aim to develop an experimentally supported reaction model describing the CO₂ hydrogenation over a wide temperature range. In our previous study we reported the activity and Arrhenius parameters of the CO₂ hydrogenation reaction over the pristine Co, Ni, Fe, Cu and Ru/Al₂O₃ [13]. In contrast to this previous work, this paper aims to build a reaction model based on a detailed kinetic model. At low temperatures the CO₂ conversion is described by the reaction kinetics, at higher reaction temperatures approaching the thermodynamic limitations, diffusional limitations are also integrated into the reaction model. The catalysts Co and Ni have been chosen for this study since they were the most active pristine metal catalysts along with Ru/Al₂O₃ as reported in our previous work [13] and they are, less expensive, alternatives to substitute Ru based catalysts. However, their performance has to be further improved to match the high activity and selectivity of Ru in the CO₂ methanation reaction. For the development of improved catalysts for

the Sabatier reaction, it is important to understand the intrinsic activity and the limiting factors of the major active phase of the catalysts, the pristine metal, in order to address the challenge to synthesize improved catalyst systems with different supporting phases and promoters. According to the literature cited above, we used an empirical power law to describe the experimental data. We determined the reaction orders and the Arrhenius parameters and we estimated the diffusional limitations considering the catalyst structure and the thermodynamic limitations given by the observed reactions. Taking all three major reaction limitations into consideration, we present a reaction model that describes the CO₂ hydrogenation over a broad temperature range with high accuracy (max. 20% deviation between model and experiment). The model developed enables the simple and rapid prediction of the influence of different reaction parameters such as the activation energy or the diffusional limitations on the CO₂ conversion.

2. Materials and Methods

2.1 Materials

The pristine Ni and Co powders were purchased from Goodfellow (London, England) and are similar to the catalysts used in our previous work [13]. The main catalyst properties are reported in Table SI 1. The powders were examined for purity by means of X-ray photoelectron spectroscopy (XPS) and no impurities other than oxygen and carbon on the surface were detected (Figure SI 4). XRD powder analysis has been conducted, confirming the XPS results and showing that there are no impurities in the pristine metal catalysts. To avoid catalyst sintering and clogging of the reactor, the powders were pressed into pellets with a diameter of 8mm and a weight equivalent of four tons. In the following, they were broken into smaller grains with a specific length of approximately 1mm. The catalyst grains were mixed in an equal weight ratio with glass beads of similar size to separate the catalyst grains and avoid sintering. The borosilicate glass beads purchased from Schäfer Glass have a diameter of 1mm and were not affected by the reaction conditions, nor was the catalytic activity of the glass beads. The Al₂O₃-supported Ru catalyst was purchased from Sigma Aldrich. Each catalyst pellet has a cylindrical form with a length of 5mm and a diameter of 3.2mm. The catalyst pellets have an eggshell structure, as observable visually when they are cut along the long side. This has already been reported by Falbo et al. [20] and Porta et al. [24]. An image of the cross section of the Ru/Al₂O₃ catalyst used is provided in Figure SI 3. For all the experiments, 1000mg of each Co and Ni catalyst was used. The weight of the Ru/Al₂O₃ reference catalyst was 192mg.

2.2 Experimental setup

The experiments were carried out in a gas controlling and analysis system equipped with three mass flow controllers (MFC). A mass spectrometer (MS- Pfeiffer OmniStar 320) was used for quantification of the reaction products. The key towards high quality kinetic measurements is the fast sampling rate (approx. 120s per spectra) achieved with the MS, which enables a quasi *in situ* measurement of the reaction products. We followed the calibration procedure and partial pressure determination as described in depth in our previous work on the quantitative gas analysis by means of mass spectrometry [25]. The MS was calibrated for H₂, CO₂, CO and CH₄. The MFCs are of the Bronkhorst El Flow series. The flow range is 0.4-20 ml/min and the absolute measurement error in ml/min is 0.1% of the maximum set point (20ml/min) plus 0.5% of the set point. The reactor is a stainless-steel tube with a diameter of 7mm in the reaction zone. The reaction zone starts 75mm after the gas inlet. The catalyst is inserted after a small layer of glass wool is added on top of the in-tube sintered steel filter (Swagelok SS-2F-K4-60). The depth of the catalyst bed (l_{catalyst}) is measured to calculate the space velocity. The catalyst is then topped by another layer of glass wool in order to keep the material in place towards the reactor outlet. The length of the catalysts beds for Co and Ni is in a similar range with 24mm for Co and 20mm for Ni, resulting in an approximate space velocity of 1000^{-h} at a flow of 10ml/min. The Ru/Al₂O₃ catalyst bed length is with approximatively 5mm shorter.

All gas lines after the reactor oven are heated above 423 K in order to avoid water condensation in the tubes. The temperature is measured with a thermocouple directly placed after the catalyst bed.

2.3 Catalyst pretreatment

In a first step, the catalysts were dried in a constant He flow of 10ml/min at 423 K to evaporate moisture on the catalysts and in the reactor. In a second step the catalysts were reduced in a flow of 7.5ml/min H₂ with 2.5ml/min He as an internal standard and carrier gas at a heating rate of 5 K/min

up from the pretreatment temperature to 823 K. The temperature-programmed surface reduction (TPR) was carried out prior to each experiment to ensure a pure metallic catalyst surface.

2.4 CO₂ hydrogenation experiments

CO₂ conversion over a broad temperature range

The CO₂ conversion over Co, Ni and Ru/Al₂O₃ over a broad temperature range was measured at a constant pressure of one bar, a flow of 10ml/min with a H₂: CO₂ ratio of 4:1 and a temperature increase of 1K/min between 410 and 810K. The results of this experiment are the basis for the identification of the kinetic, diffusional and thermodynamically limited reaction range.

Determination of the reaction order

To determine the reaction order, the partial pressure of the reactants CO₂ and H₂ was varied, while keeping the other reaction parameters such as the reaction temperature, the total gas inflow (10ml/min) and the reaction pressure (1 bar) constant. Five ratios between H₂ and CO₂ were measured: 4, 3, 1.5, 1 and 0.5. The results of this experiment are discussed in section 4.1. For the further experiments, due to the limitations of the setting range of the mass flow controllers, we worked without He dilution.

Determination of the Arrhenius parameters

The rate constants k_f' for Co and Ni at three different temperatures were determined by varying the space velocity in the kinetically limited temperature range while keeping the other reaction parameters constant. The reaction pressure was one bar and the ratio of H₂:CO₂ was 4:1. To achieve the different SVs, the reaction gas flow was set to 20, 10, 7.5, 5 and 2.5 ml/min. The results of this experiment are discussed in section 4.3 and 4.4.

2.5 Computational details

The experimental data of CO₂ conversion and CH₄ selectivity are used for the development of the kinetic model. The kinetic model was defined progressively following the procedure in section 4.6. The linear regressions for the determination of the indicators for statistical evaluation (standard errors, confidence interval, t- and f-tests) of the kinetic parameters were performed in Excel. The simulations based on the kinetic model were created by integrating the 1D heterogeneous reactor model with the *ode23t* MATLAB® routine.

3. Theory and calculations

In the following we show the derivation of the fractional rate law for the CO₂ hydrogenation reaction, which is the fundament to determine the reaction orders experimentally. Furthermore, the integrated rate law and the fundamentals for the determination of the diffusional limitations are derived.

3.1 Fractional rate law

In the kinetically determined reaction range, CO formation is minimal over the Co and Ru/Al₂O₃ catalyst. The selectivity to CH₄ falls below 90% only at 790K for Co, respectively 755K for Ru/Al₂O₃ when the reverse water gas shift formation becomes thermodynamically favorable and the CO yield increases. In the kinetically determined temperature range the CO yield is below 9% for Co and below 1% for Ru/Al₂O₃. Since Ni activates significantly later than Co and Ru/Al₂O₃ and it is less selective for CH₄, the formation of CO is already more significant in the kinetically determined reaction range. The methane yield is nevertheless above 72%. The selectivity of the catalysts is relatively constant at around 70% for CH₄ up to 800K, where the CO yield increases.

The rate law was therefore derived for the Sabatier reaction which is given by Equation 1:

Equation 1: Sabatier reaction

The rate law was derived in the assumption of a fractional rate law. α is the reaction order with respect to CO₂ and β is the reaction order with respect to H₂. The exponents γ and δ are the reaction orders of the products CH₄ and H₂O, respectively. The rate is defined as the change in the partial pressure of CO₂ in the gas mixture over time and the general fractional rate law for the Sabatier reaction is given in Equation 2:

$$-\frac{dp_{\text{CO}_2}}{dt} = r(t) = \left(k_f \times p_{\text{CO}_2}^\alpha \times p_{\text{H}_2}^\beta \right) - \left(k_b \times p_{\text{CH}_4}^\gamma \times p_{\text{H}_2\text{O}}^\delta \right)$$

Equation 2: Fractional rate law for the Sabatier reaction. k_f is the kinetic constant of the forward reaction of the methanation reaction and k_b the kinetic constant of the backward reaction from the product to the reactant side.

The forward and backward reactions are linked by the equilibrium constant K_{eq} :

$$K_{\text{eq}} = \frac{k_f}{k_b}$$

Equation 3: Equilibrium constant defined by the kinetic constant of the forward reaction, k_f , and kinetic constant of the backward reaction k_b .

The kinetic constant of the forward reaction is given by the Arrhenius equation with the activation energy E_a of the reaction and the frequency factor k_0 :

$$k_f = k_0 \exp\left(-\frac{E_a}{RT}\right)$$

Equation 4: Arrhenius equation

The Sabatier reaction is exothermic and characterized by equilibrium, therefore the products are favored at low temperature. For this reason, k_b is close to zero in the kinetically determined temperature range. Furthermore, at low conversion, the partial pressure of CH₄ and H₂O is low, so that the reverse reaction rate approximates zero. Therefore, the term $k_b \times p_{\text{CH}_4}^\gamma \times p_{\text{H}_2\text{O}}^\delta$ in Equation 2 becomes negligible in the investigated reaction conditions.

With these approximations, Equation 2 is reformed to:

$$r(t) = k_f (p_{\text{CO}_2}^\alpha \times p_{\text{H}_2}^\beta)$$

Equation 5: Rate law for the Sabatier reaction under the assumption that the backwards reaction $k_b \cdot p_{\text{CH}_4}^\gamma \cdot p_{\text{H}_2\text{O}}^\delta$ in Equation 2 is negligible. This is valid under the assumption that the product formation is still small, and the equilibrium constant large in Equation 3.

The reaction orders α of CO_2 and β of H_2 are linked by the stoichiometry of the Sabatier reaction. Therefore, the change in the partial pressure of CO_2 is given by:

$$\Delta P_{\text{CO}_2} = \frac{\Delta P_{\text{H}_2}}{4}$$

Equation 6: The change of the partial pressure of CO_2 is linked to the change of the partial pressure of H_2 via the stoichiometry of the Sabatier reaction.

With Equation 6, the formulation of the reaction rate given in Equation 5 can be written as:

$$-\frac{dp_{\text{CO}_2}}{dt} = r(t) = k_f (p_{\text{CO}_2}^\alpha \times (4 \times p_{\text{CO}_2})^{4\alpha}) = k_f \times 4^{4\alpha} \times p_{\text{CO}_2}^{5\alpha} = k'_f \times p_{\text{CO}_2}^{5\alpha}$$

Equation 7: Rate law for the Sabatier reaction as a function of the CO_2 partial pressure.

Note that this simplification follows the reaction rate equation suggested by Lunde and Kester [19] and the model was confirmed to describe the Sabatier reaction well over a broad temperature range by Falbo et al. [20].

3.2 Reaction order

For the determination of the reaction order, we require an expression of α , the reaction order with respect to CO_2 , as a function of known reaction parameters. Therefore, we define the reaction rate $r(t)$ to equal the turnover rate (TOR) which we define as:

$$\text{TOR} \left[\frac{1}{s} \right] = \text{SV} \left[\frac{1}{s} \right] \times (1 - X_{\text{CO}_2}) = r(t)$$

Equation 8: The turnover rate can be equalized to the reaction rate, since it describes the number of CO_2 molecules that are turned over, therefore, the number of CO_2 molecules that are consumed in the reaction which equals the change of the partial CO_2 pressure as a function of time. This can be expressed via the space velocity (Equation SI 5) and the CO_2 conversion.

The TOR is a measure of how much CO_2 is converted per unit of time and can be expressed as a function of the space velocity (Equation SI 5) and the CO_2 conversion (Equation SI 1). The TOR equals the reaction rate $r(t)$ if we model the reaction from the inlet to the outlet of the reactor (integrated rate law). The assumption is that surface H^* is not the rate limiting step for the Sabatier reaction [17]. Therefore, $p_{\text{H}_2}^\beta$ is considered a constant in Equation 7. Inserting Equation 8 to the fractional rate law derived in Equation 7 results in:

$$r(t) = \text{SV} \times (1 - X_{\text{CO}_2}) = k''_f \times p_{\text{CO}_2}^\alpha$$

Equation 9: With $k''_f = k'_f \times p_{\text{H}_2}^{4\alpha}$

If we take the natural logarithm of Equation 9, it reforms to:

$$\ln(1 - X_{\text{CO}_2}) + \ln(\text{SV}) = \alpha \times \ln(p_{\text{CO}_2}) + \ln(k''_f)$$

Equation 10: This equation enables the graphical determination of the reaction order α . α is the slope of the curve in a plot of $\ln(1 - X_{CO_2})$ vs. $\ln(p_{CO_2,in})$. Note that the term $\ln(k_f'')$ only determines the axis intercept and has no influence on the slope of the curve.

Therefore, α is the slope of the curve in a plot of $\ln(1 - X_{CO_2})$ vs. $\ln(p_{CO_2,in})$. Note that the term $\ln(k_f'')$ only determines the axis intercept and has no influence on the slope of the curve.

3.3 Integrated rate law

Via the integration of the fractional rate law over the residence time of the reactants in the reactor, a relation between the partial pressure of CO_2 at the reactor outlet, $p_{CO_2,o}$, the kinetic constant k_f' and the residence time t_0 is derived.

To integrate over the reactor, Equation 7 is rearranged to:

$$-\frac{dp_{CO_2}}{p_{CO_2}^{5\alpha}} = k_f' \times dt$$

Equation 11: Rearranged rate law from Equation 7

Equation 11 is then integrated over the reactor length, therefore from the inlet partial pressure $p_{CO_2,i}$ to the outlet partial pressure $p_{CO_2,o}$ and from residence time 0 at the reactor inlet to the residence time t_0 .

$$\int_{p_{CO_2,i}}^{p_{CO_2,o}} \frac{dp_{CO_2}}{p_{CO_2}^{5\alpha}} = \int_0^{t_0} -k_f' dt$$

Equation 12: Integration of the rearranged rate law (Equation 11). The integration boundaries on the left-hand side of the equation are given by the inlet partial pressure of CO_2 to the reactor, $p_{CO_2,i}$ and the outlet partial pressure $p_{CO_2,o}$. The right-hand side is integrated over the residence time t_0 .

Solving the integral and substituting $p_{CO_2,o}$ with $p_{CO_2,o} = (1 - X_{CO_2})p_{CO_2,i}$ we get the following expression:

$$1 - \frac{(X_{CO_2})^{1-5\alpha}}{(1-5\alpha)} = -k_f' \times t_0 + C$$

Equation 13: Substitution: $p_{CO_2,o} = (1 - X_{CO_2})p_{CO_2,i}$. Discussion on the error of this approximated substitution is provided below. Note that $p_{CO_2,i}$ is a constant and is therefore included in the constant C.

Note that $p_{CO_2,i}$ is a constant and is therefore included in the constant C in equation 13. Furthermore, the error for the simplified substitution is low at low conversions (less than 4%, neglecting the change of number of moles over the Sabatier reaction, see error calculation Equation SI 22-27) in Equation 13.

With this equation, k_f' can be determined by means of a linear regression by plotting $\frac{(1-X_{CO_2})^{1-5\alpha}}{(1-5\alpha)}$ vs. t_0 . The constant C has no influence on the slope of the curve and therefore on k_f' .

3.4 Diffusional limitations

To quantify the rate limitations by diffusion, the Thiele modulus ϕ and the reaction effectiveness η are used [26].

The reaction effectiveness η is defined as ratio between the reaction rate observed r_{obs} and the theoretical reaction rate determined based on the reaction kinetics r_{th} .

$$\eta = \frac{r_{\text{obs}}}{r_{\text{th}}}$$

Equation 14: The reaction effectiveness factor η is defined by the ratio between the observed reaction rate and the theoretical reaction rate which is given by the reaction kinetics.

The generalized Thiele modulus was developed to describe the relationship between diffusion and reaction rate in porous catalyst pellets and is defined as follows [26]:

$$\phi = L \times \sqrt{\frac{5\alpha + 1}{2} \times \frac{k'_f}{D} \times p_A^{5\alpha-1}}$$

Equation 15: The thiele modulus ϕ is defined as a function of the reaction order α , the rate constant k'_f , the diffusional coefficient D and the partial pressure p_A of reactant A.

Where 5α is the overall reaction order and $p_A^{5\alpha-1}$ the partial pressure of the reactants outside of the diffusion boundary layer, L is the characteristic length of the catalyst grains and pellets, and D the diffusional coefficient.

For pronounced diffusional influence, the effectiveness factor is given by:

$$\eta = \frac{\tanh(\phi)}{\phi} \simeq \frac{1}{\phi}$$

Equation 16: Effectiveness factor as function of the Thiele modulus for catalysts with pronounced diffusional limitations. This assumption was taken since diffusional limitations were observed for all catalysts investigated in this chapter.

This is the case for the investigated reaction, since diffusional limitations are clearly observed on all catalysts.

$$\eta = \frac{1}{\phi} = \frac{r_{\text{obs}}}{r_{\text{th}}}$$

Equation 17: Expression for the effectiveness factor η derived from Equation 14 and Equation 15

Where:

$$r_{\text{th}} = k'_f \times p_A^{5\alpha}$$

Equation 18

From that, a relation between the observed kinetic constant k_{obs} and the real kinetic constant k_{kin} is derived.

$$r_{\text{obs}} = \frac{C}{\sqrt{k'_f}} \times k'_f = C \times \sqrt{k'_f}$$

Equation 19

with:

$$C = \frac{p_A^{5\alpha}}{\left(L \times \sqrt{\frac{5\alpha + 1}{2} \times \frac{p_A^{5\alpha-1}}{D}} \right)}$$

Equation 20

Therefore:

$$r_{\text{obs}}^{\text{new}} \sim \sqrt{k'_f}$$

Equation 21

And with the Arrhenius equation it follows:

$$r_{\text{obs}}^{\text{new}} = \sqrt{k'_0 \exp\left(-\frac{E_a}{RT}\right)} = \sqrt{k'_0} \times \exp\left(-\frac{E_a}{2} \times \frac{1}{RT}\right)$$

Equation 22

From that, it can be shown that the observed activation energy in the diffusion limited temperature ranges is in the range of half of the observed activation energy of the initial reaction:

$$E_a^{\text{obs,diff}} = \frac{E_a^{\text{obs}}}{2}$$

Equation 23: Under the assumption of pronounced diffusional limitations, the observed activation energy in the temperature range limited by diffusion, is approximatively half of the observed activation energy in the kinetic reaction range.

4. Results

In the first step the reaction orders of the CO₂ hydrogenation reaction over Co, Ni and Ru/Al₂O₃ are determined via a variation of the partial pressure of CO₂ in the Sabatier reaction. The sensitivity of the reaction order on He dilution of the reaction gas stream is presented on the example of Ru/Al₂O₃. Based on the fractional rate law and the determined reaction orders, the Arrhenius parameters of the CO₂ hydrogenation over the three catalysts are determined. The diffusional limitations are determined via the Arrhenius plot of a CO₂ conversion curve over Co, Ni and Ru/Al₂O₃. Based on the experimental results and the derived reaction model, the CO₂ conversions over the different catalysts is simulated.

4.1 Experimental determination of the reaction orders

The reaction orders are experimentally determined following experimental conditions described in section 2 and by means of Equation 10, where α is the slope of the curve in a plot of $\ln(1 - X_{\text{CO}_2})$ vs. $\ln(p_{\text{CO}_2,\text{in}})$. Alpha is determined by means of a linear regression. The overall reaction order for Ru/Al₂O₃ is 0.38, for Co 0.13 and 0.14 for Ni. Therefore, the reaction order with respect to CO₂ is 0.076 for Ru/Al₂O₃, 0.026 for Co and 0.028 for Ni. The linear regression result is given in Figure SI 6 and Table SI 4.

4.2 Catalyst saturation

To investigate the surface saturation of Ru/Al₂O₃, the CO₂ hydrogenation reaction was carried out in different He dilutions at ambient pressure and at elevated pressures without He dilution (See Table SI 7 for experimental conditions and results). The H₂ to CO₂ ratio is always kept constant at four according to the stoichiometry of the Sabatier reaction. The TOR, which has the unit of one over time, is given by the CO₂ conversion X_{CO_2} , which is dimensionless, and is multiplied by the space velocity, SV, which has the dimension one over time. The TOR is therefore a parameter to express how much CO₂ is converted per unit of time (note that in comparison to Equation 2, we use the inverse rate in this section). The apparent reaction order is the slope of the plot TOR against partial pressure of CO₂ in the reaction.

We found that by gradually lowering p_{CO_2} by means of He dilution, the TOR progressively increases and the reaction approximates a second order reaction. Anyhow, as shown in Figure 1, the reaction approaches a plateau at high CO_2 partial pressures. This suggests surface saturation and an approximation towards a zero-order reaction. The region of high partial pressures of CO_2 can be well described with a zero-order approximation, followed by a first order approximation for lower partial pressures of CO_2 (Figure SI 10).

Note that a comparable TOR is reached for the same CO_2 partial pressure (0.4bar) at two different space velocities (1500h^{-1} and 3000h^{-1}). One of the data-points at $p_{\text{CO}_2}=0.4\text{bar}$ is plotted in red in Figure 1. From this, we can conclude that the TOR only depends on gas composition and temperature. Therefore, the TOR does not depend on the SV/residence time.

Figure 1: The partial pressure of CO_2 in the reaction gas stream plotted versus the turnover rate for $\text{Ru}/\text{Al}_2\text{O}_3$. The blue points are experimental points. With the red point we confirmed that the reaction approximately exhibits the same TOR if the residence time is doubled, indicating that we operate in the solely kinetically determined temperature range. The blue line (B-Spline) is plotted to guide the eye. In region a) the reaction can be well approximated with a zero-order assumption ($\text{TOR} \propto p_{\text{CO}_2}$). Region b) is well described by a first order reaction ($\text{TOR} \propto \ln(p_{\text{CO}_2})$) and region c) is of higher reaction order.

4.3 Experimental determination of the Arrhenius parameters

The rate constants k'_f for Co and Ni at three different temperatures were determined by varying the space velocity in the kinetically limited temperature range while keeping the other reaction parameters constant. The experimental settings are given in section 2. The plot and table to determine k'_f at three different temperatures via linear regression are given in the supplementary material (Figure SI 7 and Table SI 5). The rate constant increases with increasing temperature and residence time for all catalysts. The high linearity of the plots ($R^2 > 0.99$) suggests that the kinetic constant is not influenced by the residence time.

4.4 Arrhenius plot

The Arrhenius plot to determine the activation energies and the frequency factors is plotted based on the kinetic constants at different temperatures (Figure SI 8). The experimental settings are given in section 2. We found an activation energy of 96 kJ/mol on Co, 74 kJ/mol on Ni and 97 kJ/mol on Ru/Al₂O₃. The results of the Arrhenius plot are given in Figure 2. The pre-exponential factor k_0 is exponentially sensitive on changes in the slope of the Arrhenius. Therefore, a sensitivity analysis was carried out to estimate the error on k_0 . The slope of the curve in the Arrhenius plot was varied by the standard error on the activation energies and the middle $k(T)$ was used as anchor point. The results of this sensitivity analysis along with the values of the activation energies and the pre-exponential factors are provided in Table 6 SI.

Figure 2 a) and b): Results from the Arrhenius plot from the kinetic constants for Co, Ni and Ru/Al₂O₃ determined via the linear regression of the rate constants at three different temperatures. The left plot a) shows the comparison of the activation energy, the right plot b) the comparison of the frequency factors k_0 . The red result points in a) and b) are Ru/Al₂O₃, green from Co and blue from Ni.

4.5 Diffusional limitations

It was found that the catalytic CO₂ hydrogenation over the catalysts Co, Ni and Ru/Al₂O₃ is first limited by the reaction kinetics at low temperatures, followed by the limitation due to reaction thermodynamics at higher temperatures. Anyhow, we found that diffusional limitations have a significant influence on the reaction between the kinetically and thermodynamically limited reaction range.

The temperature at which the diffusional limitations become predominant is determined by plotting the experimental CO₂ conversion curve and the rate constant of the forward reaction. The plots for Co, Ni and Ru/Al₂O₃ are given in the supplementary material.

The starting temperature of the diffusional limitations ($T_{diff,0}$) is the point at which the experimental curve deviates from the rate constant. To exclude strong thermodynamic influence in the range of the diffusional limitations, we calculated the equilibrium constant (Table 1). Following the theoretical derivations and Equation 17, we calculated the observed activation energy immediately above $T_{diff,0}$. For Cobalt the ratio between E_a^{obs} and $E_a^{obs,diff}$ is 0.42, indicating strong diffusional limitations. For Ni, the ratio is with 0.72, higher than Co, which leads to the assumption that the diffusional limitations are less pronounced. The ratio between E_a^{obs} and $E_a^{obs,diff}$ is also 0.72 for Ru/Al₂O₃, suggesting that the supported catalyst has less diffusional limitations in comparison to the bulk catalyst Co. As determined by SEM analysis (Figure Si 1), Ni has a larger particle size than Co, which facilitates diffusion.

Table 1: The temperature range of the predominant diffusional limited reaction range is given. Furthermore, the equilibrium constant in this range, the observed activation energy in the diffusion temperature range and the ratio between the observed activation energies in the diffusional and kinetically predominated temperature range are given. This ratio is a quantitative indicator for the diffusional limitations.

Catalyst	Temperature range of predominant diffusional limitations [K] $T_{\text{diff},0}$ to $T_{\text{diff},1}$	Equilibrium constant of Sabatier reaction $T_{\text{diff},0}$ to $T_{\text{diff},1}$	Observed E_a in range of predominant diffusional limitations [kJ/mol]	$\frac{E_a^{\text{obs,diff}}}{E_a^{\text{obs}}} \left[\frac{\text{kJmol}^{-1}}{\text{kJmol}^{-1}} \right]$
Co	560 to 580	9.10×10^5 to 2.44×10^5	40	$40/96=0.42$
Ni	670 to 700	1.62×10^3 to 4.00×10^2	54	$54/74=0.72$
Ru/Al ₂ O ₃	550 to 580	1.82×10^6 to 2.44×10^5	70	$70/97=0.72$

4.6 Reaction simulation

By combining the results from the kinetic reaction investigation, the identification and quantification of the diffusional limitations and the known thermodynamic constraints, the reaction over Co, Ni and Ru/Al₂O₃ was simulated. If we set $\eta = 1$ in the simulation (see eq. 14), the diffusional limitations are neglected in the simulation. With that the significant influence of the diffusional limitations at temperatures higher than the kinetic limitations and lower than the thermodynamic limitations become evident. The result is shown for Ru/Al₂O₃ in Figure 3 a) and for Co and Ni in Figure 3 b). The exact parameters used for the simulation are given in Table SI 8.

Figure 3a: Experimental CO₂ conversion over Ru/Al₂O₃ (blue dots) in comparison to the simulated reaction curve with (blue) -and without (red) diffusional limitations. The black curve is the calculated equilibrium conversion for the Sabatier reaction.

Figure 3b: Experimental vs. calculated CO_2 conversion over the pristine catalysts Co (red) and Ni (blue). The full lines are the calculated CO_2 conversion over Co and Ni. The dots are the measured CO_2 conversions as function of temperature. The black curve is the calculated equilibrium conversion for the Sabatier reaction. Both lines are obtained including the diffusional limitations in the reactor model.

5. Discussion

5.1 Reaction order

The experimentally determined reaction order of 0.076 on the Ru/Al₂O₃ catalyst (25% He dilution in the reaction gas stream) is in line with the reaction order reported in the study of Falbo et al. [20]. The results on the reaction order found in this study are additionally supported by the findings of Wang et al. [17] who reported a reaction order with respect to CO₂ of 0.07 at 533 K on a 0.5wt.% Ru/Al₂O₃ catalyst. The higher reaction order (0.34 with respect to CO₂ at 503K on a 10wt.% Ru/ γ -Al₂O₃) reported in Ref. [21] in comparison to this study is likely due to the less saturated surface of this catalyst. The catalyst load in their study is 20-fold larger compared to our 0.5 wt.% Ru/Al₂O₃ catalyst; therefore, there are more active sites available. Furthermore, the space velocity and He dilution are significantly larger. This leads to a less saturated surface and therefore to a higher reaction order, as we also proved in section 4.2.

The supporting phase of the catalyst can favor and enhance the CO₂ hydrogenation to CH₄ by adsorbing inactive reaction byproducts that accumulate on the surface and block active surface sites for reaction intermediates participating in the Sabatier reaction [11]. In this sense, the support operates as a reservoir of carbon species, giving a preferential way for the adsorption of carbon species and decreasing the amount of carbon that is present on the metallic surface. This supports our findings of lower reaction orders on the pristine metal catalysts in comparison to the supported Ru/Al₂O₃ catalysts. We suppose that the pristine metals have a limited number of surface site available for the reaction, thus revealing a low reaction order.

The low apparent reaction order at high surface coverage is predicted by both the Langmuir-Hinshelwood (LHM) and Eley Rideal model (ERM). Eley-Rideal mechanism refers to the reaction of an adsorbed species (in this case CO₂) with a gaseous species (H₂). Langmuir-Hinshelwood refers to the reaction of two species contemporarily present on the catalyst surface.

Both models are reported to adequately describe the CO₂ hydrogenation reaction over Ru/Al₂O₃ catalysts [17,21]. In order to determine the reaction mechanism, more detailed surface studies are required. Our experimental results lead to the assumption that the low reaction order is due to surface saturation, without the possibility of discriminating between various possible heterogeneous models.

We furthermore investigated the difference in the reaction order for a slightly diluted (25% He) and undiluted reaction gas on the Ru/Al₂O₃ catalyst. We found a slight decrease in the reaction order from 0.38 to 0.33. This can be explained with Figure 1 where we show that we approach higher reaction order upon dilution with He.

5.2 Arrhenius parameters

The findings of the activation energy based on the kinetic reaction model confirm the results reported in our previous work, where found an activation energy of 96 kJ/mol on Co, 78kJ/mol on Ni and 91kJ/mol on Ru/Al₂O₃ [13]. We show that we obtain comparable results with this more robust method, where the activation energy is not determined on a single conversion curve, and therefore we also confirm the liability of the previously reported method [13].

Anyhow, the values for k_0 are not directly comparable, since in this paper, we worked at different space velocities and k_0 is determined in the Arrhenius plot of $k(T)$ vs. the inverse temperature in contrast to the Arrhenius plot in [13], where the Turnover Frequency (TOF) is plotted against the

inverse temperature. Anyhow, the result that k_0 has the highest value on Ru/Al₂O₃, followed by Co and then Ni, is confirmed.

The absence of He as a dilution gas increases the activation energy since the reaction hot-spot is more pronounced if compared to a similar reaction in diluted conditions. The effect is more pronounced for Ru/Al₂O₃ and Co since they are active at lower temperatures than Ni. Wang et al.[17] reported an activation energy of 66 kJ/mol in the CO₂ hydrogenation reaction over a 0.5wt.% Ru/Al₂O₃ catalyst with a H₂:CO₂ ratio of 4:1. However, their reaction gas was diluted with 50% He, which significantly lowers the activation energy. Similar results were found by Duyar et al. [21] who worked in 80% He dilution and reported an activation energy of 66kJ/mol on a 10% Ru/ γ -Al₂O₃ catalyst. Furthermore, Falbo et al. [20] reported an activation energy on a 0.5wt.% Ru/Al₂O₃ catalyst of 65 kJ/mol, based on the re-analysis of the dataset of Lunde and Kester [19]. They also worked in N₂ and Ar diluted conditions. For what concerns Ni, the activation energy of 74 kJ/mol is sensibly lower than the value reported by Peebles et al. [30] for Ni (100), but in line with the 10 % Ni/SiO₂ catalyst. The result is also in line with the value reported by Xu and Froment [28] for Ni/Mg/A₂O₄.

5.3 Diffusional limitations

The diffusion limitations are identified at temperatures higher than the temperature of the initial reaction and lower than the temperatures at which the influence of the thermodynamic reaction limitations become significant. It was found that Co has the strongest diffusional limitations, followed by Ni and Ru/Al₂O₃. The limitation through diffusion can be explained as follows: At low temperatures, the reaction kinetics are slow in comparison to the diffusion of the reactants and the product in the single metal particles of the catalyst grains. Anyhow, the supported structure of the Ru/Al₂O₃ catalyst which is an eggshell type, prevents strong diffusional limitations. This clearly highlights the importance of a supporting phase for industrially relevant catalysts.

5.4 Reaction simulation

The kinetic region is well described by the model we developed based on the experimentally determined reaction parameters. A slight discrepancy exists between the model and the experimental data in the reaction activation temperature range. The presence of diffusional limitations is well considered by the model. The maximal conversion point is slightly overestimated on both catalysts. This might be due to deactivation phenomena that limit the experimental conversion values. However, the prediction results based on the reaction model represent the experimental curves accurately. The deviation between simulation and experiment is mostly below 20%, as shown in the parity plots which are given in the supporting information. For Co, the deviation exceeds 20% in the range where the reaction strongly increases with temperature (See Figure 3b). Therefore, this error is still acceptable.

With this model, the influence of changing activation energies, frequency factors, reaction orders and diffusional limitations on the CO₂ hydrogenation can be rapidly forecasted. This is a powerful tool to support the development of more efficient catalysts or to optimize a specific catalyst for the required reaction conditions.

6. Conclusion

This paper provides a kinetic investigation of the Sabatier reaction over pristine Co and Ni, and over supported Ru/Al₂O₃. It is shown that, in industrially relevant conditions (low or no He dilution, ambient pressure), the experimental results are explained with a low reaction order on all the catalysts investigated. The calculated orders are 0.14 on Co, 0.13 on Ni and 0.38 on Ru/Al₂O₃. The low reaction orders on Ni and Co are due to the limited available catalyst surface. We observed that Ru/Al₂O₃ undergoes the same saturation if the partial pressure of CO₂ is increased to 0.5 bar. On the other hand, the reaction order increases if the partial pressure of CO₂ is lowered (down to 0.04bar). The kinetic parameters of the reaction over the three catalysts were estimated by regression. The activation energies correspond to 96, 74 and 97 kJ/mol on Co, Ni and Ru/Al₂O₃ respectively. To model the reaction over the entire temperature range, we investigated the influence of diffusional limitations on the Sabatier reaction. It was found that the pristine metal catalysts (especially Co) suffer significantly from intrapore diffusional limitations close to the temperature of maximum conversion. The diffusional limitations on Ru/Al₂O₃ are reduced due to the eggshell structure of the catalyst used. Finally, the reaction model which we developed describes the CO₂ conversion of all the catalysts considered over the entire temperature range investigated with high accuracy. The temperature of maximum conversion is predicted within 15K and the deviation between simulation and experiment is mostly less than 20%.

With the in-depth investigation of pristine Co and Ni, which are important building blocks for industrial catalysts, we provide a basis for further investigations and improvements of the Sabatier reaction. In particular, the effects of the supports on the catalyst can now be investigated in direct comparison to the unsupported catalysts. This can facilitate the development of appropriate supported catalysts and the determination of relevant promoters that can form an optimal catalytic system, avoiding limitations due to saturation of the catalytic surface and to the presence of diffusional limitations.

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List of symbols

The list of symbols is order of appearance of the symbols in paper and the supporting information.

$p_{C,products}$	Sum of the partial pressures of carbon containing reaction products
p_{CH_4}	Partial pressure of methane
p_{CO}	Partial pressure of carbon monoxide
X_{CO_2}	CO ₂ conversion
$n_{CO_2,o}$	Molar outflow of the reactor of CO ₂
$n_{CO_2,i}$	Molar inflow of the reactor of CO ₂
$p_{CO_2,o}$	Partial pressure of CO ₂ after the reaction
Y_{CH_4}	Methane yield
Y_{CO}	Carbon monoxide yield
SV	Space velocity
$\dot{V}_{reactants}$	Volumetric flow of the reactants
$V_{reactor}$	Volume of the reactor
$l_{catalyst}$	Length of the catalyst bed
d_i	Diameter of the reactor
t_0	Residence time of the reactants in the catalysts bed
$a_{s,cat}$	Specific surface area of the catalyst
V_{cat}	Volume of one catalyst particle
ρ_{cat}	Density of the catalyst
r_{cat}	Radius of one catalyst particle
$n_{C,out}$	Molar outflow of carbon containing reaction products
Y_p	Product yield containing carbon atoms
$p_{p,i}$	Partial pressure of a specific carbon containing reaction product. This can be e.g. methane or carbon monoxide.
S_p	Yield to a specific carbon containing reaction product
$p_{CO_2,i}$	Partial pressure of carbon dioxide in the gas stream of the reactants
$p_{H_2,i}$	Partial pressure of hydrogen in the gas stream of the reactants
$p_{tot,i}$	Total pressure of the reactants
$n_{H_2,i}$	Molar flow of hydrogen in the reactant gas stream
$n_{tot,i}$	Total molar reactant flow
p_{CO_2}	Partial pressure of carbon dioxide
$r(t)$	Reaction rate
k_f	Rate constant of the forward reaction
k_b	Rate constant of the backwards reaction
α	Reaction order with respect to carbon monoxide
β	Reaction order with respect to hydrogen
γ	Reaction order with respect to methane
δ	Reaction order with respect to water
K_{eq}	Equilibrium constant

k_0	Frequency factor / preexponential factor of the Arrhenius equation
E_a	Activation energy
R	Universal gas constant
T	Temperature
TOR	Turnover rate
k'_f	Kinetic constant multiplied with a constant
k''_f	Modified kinetic constant taking the reaction order of hydrogen into account
η	reaction effectiveness
ϕ	Thiele modulus
r_{obs}	Observed reaction rate
r_{th}	Theoretical reaction rate
L	Characteristic catalyst length
D	Diffusional coefficient
p_A	General variable for a partial pressure of the reactants outside of the diffusion boundary layer
r_{obs}^{new}	Observed reaction rate considering diffusional limitations
$E_a^{obs,diff}$	Observed activation energy considering diffusional limitations
E_a^{obs}	Observed activation energy

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