Syngas Production via Reverse Water-Gas Shift Reaction over a Ni-Al$_2$O$_3$ Catalyst: Catalyst Stability, Reaction Kinetics, and Modeling

The synthesis of liquid fuels from CO$_2$, e.g., separated from flue gases of power plants, and H$_2$ from renewables, i.e., water electrolysis, is a concept for substituting fossil fuels in the transport sector. It consists of two steps, syngas production via reverse water-gas shift (RWGS) and synfuel production by Fischer-Tropsch synthesis. Research is concentrated on the RWGS using a Ni-catalyst. The catalyst shows an appropriate performance in catalyzing the RWGS. The catalyst is stable at technically relevant temperatures. The intrinsic and effective kinetics were determined and considerations on a technical application of the process are proposed.

Keywords: Ni catalyst, Power-to-liquid process, Reverse water-gas shift, Synfuel production, Syngas production

Received: September 11, 2015; revised: November 17, 2015; accepted: February 09, 2016
DOI: 10.1002/ceat.201500548

1 Introduction

During the last decades, the increasing global energy demand has been almost solely satisfied by fossil fuels and has thereby led to rising CO$_2$ emissions. With regard to the last 40 years, CO$_2$ emissions per year doubled from 16 Gt in 1973 to 32 Gt in 2012 [1]. Thus, the CO$_2$ concentration in the atmosphere has increased from 280 ppm in pre-industrial time to today’s 400 ppm, which can be linked to climate change. Therefore, the reduction of CO$_2$ emissions is regarded as one of today’s most ambitious issues.

Within the last years, renewables such as wind and solar energy have started substituting fossil power plants; however, the transport sector, sharing 22 % of global CO$_2$ emissions [2], is lacking alternatives to fossil fuels like gasoline, jet fuel, and diesel oil. Hence, the production of liquid fuels by Fischer-Tropsch synthesis (FTS) based on H$_2$ (electrolysis) and CO$_2$ are options to reduce CO$_2$ emissions.

The FTS has also regained research attraction because of lack of efficient storage options for electrical energy. Due to strong fluctuations in supply on a daily or weekly basis, renewable electricity produced by solar and wind energy is not able to provide the base load. An option for storage of large amounts of electrical energy is transformation into chemical energy. An obvious way is H$_2$ production by water electrolysis, based on renewable electricity, but storage is complex and costly. Instead of storing pure H$_2$, it may be transformed to liquid hydrocarbons like diesel or jet oil, which offers a much higher volumetric energy density and the advantage that the existing infrastructure for storage and transportation can be used. For such a synthesis, a carbon source is needed with CO$_2$ being an encouraging option. Such a power-to-liquid (PTL) process based on CO$_2$ and renewable H$_2$ is a multistep process and consists of the following three subsequent stages (Fig. 1), details in [3–6]:

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Figure 1. Concept of a process for the production of synfuels from CO$_2$, e.g., separated from flue gases of power plants, and regenerative H$_2$ (water electrolysis based on renewable energy/electrification is not shown).

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1) At first, H$_2$ is produced by water electrolysis, e.g., by use of renewable (off peak) electrical energy:

\[
\text{H}_2\text{O}_{\text{liq}} \rightarrow \text{H}_2 + 0.5 \text{O}_2, \quad \Delta_h^{\circ} H^{\circ}_{298} = 286 \text{ kJ mol}^{-1}
\]
2) Secondly, CO₂ is converted to CO via reverse water-gas shift (RWGS) at temperatures above 800 °C:

\[ \text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}; \Delta_H^{\text{f}}_{298} = 41 \text{ kJ mol}^{-1} \] \hspace{1cm} (2)

3) In the final step, syngas is converted to liquid hydrocarbons by FTs:

\[ \text{CO} + 2\text{H}_2 \rightarrow (\text{CH}_2) - + \text{H}_2\text{O}; \Delta_H^{\text{f}}_{298} = -152 \text{ kJ mol}^{-1} \] \hspace{1cm} (3)

Thereby, \((\text{CH}_2)\) represents a methylene group of a normal paraffin.

Further treatment of the FTs products gains liquid fuels, which can be distributed in the existing infrastructure of the transportation sector.

Whereas various research work on FTs within this concept has already been published [5–7], this work focuses on the syngas production via RWGS on a commercial Ni catalyst (Eq. (2)). Thereby methane formations from CO and CO₂ have to be considered as unwanted side reactions:

\[ \text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}; \Delta_H^{\text{f}}_{298} = -206 \text{ kJ mol}^{-1} \] \hspace{1cm} (4)

\[ \text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}; \Delta_H^{\text{f}}_{298} = -165 \text{ kJ mol}^{-1} \] \hspace{1cm} (5)

High temperatures are needed to shift the thermodynamic equilibrium of the RWGS towards CO (Fig. 2). CH₄ and carbon (although carbon may probably not likely to occur, due to kinetics), are only stable below 700 °C and 900 °C, respectively. Thus, temperatures of about 900 °C are needed for the efficient production of CO (syngas) without any danger of coke formation. However, coke formation is likely to cause catalyst coking during syngas production, especially if the H₂-to-CO ratios of the syngas are lower as in the present concept, e.g., for the CH₄ dry reforming process, and has been examined by different authors recently [8–10].

Moreover, knowledge of the reaction kinetics is crucial in order to design a technical reactor. Up to now, various authors have attempted to describe the reaction mechanisms and kinetics of CO₂ hydrogenation on Ni catalysts. Especially the hydrogenation of CO₂ to CH₄ was deeply examined [11–14]. As different reactions occur and adsorption effects influence the kinetics, most of the reported kinetic rate equations are based on Langmuir-type expressions.

With regard to the RWGS reaction, recently several studies of new catalysts and catalytic stability were conducted [15–17], but only a few kinetic and mechanistic studies were performed exclusively on the RWGS reaction [18–21]. Thereby the reaction kinetics was either described by Langmuir kinetics or power law equations.

However, the references mentioned above studied the kinetics at temperatures ranging only up to 500 °C, which is, due to thermodynamics, not relevant for the proposed concept. Therefore, in this work, intrinsic and effective RWGS kinetics were examined for technically relevant temperatures of up to 1000 °C. A respective kinetic model was derived and validated by experiments. Finally, considerations on a technical reactor are proposed with regard to pressure and temperature (profile). Carbon formation, probably occurring only below 900 °C (Fig. 2 b), may lead to catalyst deactivation and has to be avoided. Thus, this work also examined the stability of the used Ni catalyst.

![Figure 2. Influence of temperature on the thermodynamic equilibrium of the RWGS at 1 bar (p\text{CO}_2=0.75 \text{bar}; \ p\text{CO}_2=0.25 \text{bar}. (a) Calculation with coke formation "allowed"; (b) coke formation suppressed.](image)

2 Experimental Setup

Most of the experiments were conducted in an inert quartz glass tube with 2 cm diameter at ambient pressure and temperatures between 600 °C and 1000 °C. Mass flow controllers set the feed gas rate and composition. A commercial Ni-Al₂O₃ steam reforming catalyst was used with 11 wt % Ni, a BET surface area of 7 m² g⁻¹, and an ρₕ,mean₁ of 150 nm. Technical particles, i.e., cylinders with 3 mm diameter and length, as well as crushed particles of 60–150 μm size were applied. Downstream the reactor, a cooling trap removed the water, and gas analysis was conducted online via infrared gas analyzer (CO, CO₂, CH₄).

After long-term experiments, the coke content was determined by burning off the carbon. Detection of the burn-off products CO and CO₂ took place via IR gas analysis; integrated signals represent the mass of coke formed.

The conversion rates of CO₂ were calculated by regarding the carbon balance of CO, CO₂, and CH₄. The kinetic approach considered only the conversion of CO₂. It was assumed that the formation of CH₄ originated from consecutive methanation of CO. The data points of the kinetic experiments were recorded from high to low temperature. The reactor was held...
at each temperature until steady state was reached, in order to minimize catalytic deactivation during the experiment.

3 Model Derivation and Approach

For the design of an industrial RWGS plant, it is necessary to know the reaction kinetics including internal and external mass transport effects as well as the thermodynamic equilibrium of the RWGS.

3.1 Intrinsic Kinetics

The intrinsic reaction kinetics was examined at low residence times of about 0.4 ms. Therefore, CO$_2$ conversion was less than 25% and the reverse reaction could be neglected. In order to exclude an influence of pore diffusion and external mass transfer, crushed particles with a diameter of about 100 µm were used and not the original particles with a size of 3 mm. Based on experiments with varied temperature and concentrations of CO$_2$ and H$_2$, the following power law rate equation for the RWGS was derived in which $f$ indicates the forward reaction:

$$r_{m,CO_2, intrinsic} = k_m \cdot CO_2 \cdot T \cdot CO_2$$

$$= k_{m,CO_2} \cdot T_{\infty} e^{-\frac{T_{\infty}}{T}}$$  \hspace{1cm} (6)

The kinetic parameters are summarized in Tab. 1.

Table 1. RWGS kinetic parameters (100-µm particles, 1 bar, $p_{CO_2} = 0.45$ bar, $p_{CO_2} = 0.15$ bar, rest N$_2$, $X_{CO_2} = 18–25 \%$, $T = 796–839 \degree C$).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{m,CO_2}$ [m$^3$ kg$^{-1}$ s$^{-1}$ mol$^{-1}$]</td>
<td>3100</td>
</tr>
<tr>
<td>$E_A$ [kJ mol$^{-1}$]</td>
<td>82</td>
</tr>
<tr>
<td>$n_{CO_2}$ [-]</td>
<td>1</td>
</tr>
<tr>
<td>$n_{H_2}$ [-]</td>
<td>0.3</td>
</tr>
</tbody>
</table>

However, for the implementation of a reactor model, the reverse reaction, i.e., conversion of CO to CO$_2$ with rate $r_{m,CO_{intrinsic}}$, has to be considered to derive the overall intrinsic rate of CO$_2$ conversion:

$$r_{m, CO_2, intrinsic} = r_{m, CO, intrinsic} \cdot f - r_{m, CO, intrinsic}$$  \hspace{1cm} (7)

Applying the equilibrium constant

$$K_{C, RWGS} = \frac{c_{CO}^f \cdot c_{H_2O}^f \cdot c_{H_2}^{0.3}}{c_{CO_2}^f \cdot c_{CO}^{0.7}}$$  \hspace{1cm} (8)

in combination with Eqs. (6) and (7) leads to the correlation for the reverse reaction only:

$$r_{m, CO_{intrinsic}} = k_m \cdot CO_2 \left( c_{CO} \cdot c_{H_2}^{0.3} - \frac{1}{K_{C, RWGS}} c_{CO_2} \cdot c_{H_2O}^{0.7} \right)$$  \hspace{1cm} (9)

During RWGS the number of moles does not change, the equilibrium constant expressed in molar concentrations equals the constant in terms of partial pressures:

$$K_{P, RWGS} = K_{C, RWGS}$$  \hspace{1cm} (10)

The equilibrium constant was calculated as proposed by Twigg [22]:

$$K_{P, RWGS} = \left( \frac{1}{e^{-0.29353 Z^3 + 0.63508 Z^2 + 4.1778 Z + 0.31888}} \right)$$  \hspace{1cm} (11)

3.2 Effective Kinetics

The intrinsic rate and rate constant, respectively, almost grows exponentially with temperature (Arrhenius law). For a particle size relevant for a technical fixed-bed reactor, the observed (effective) reaction rate may be lower as predicted by the intrinsic kinetic data, since pore or external diffusion influences limits the reaction rate. Here, only the mass transport of CO$_2$ was considered; a limitation by H$_2$ was excluded as i) the proposed system offers an excess of H$_2$ and ii) both molecular and Knudsen diffusivity of H$_2$ is about six times higher than CO$_2$ diffusivity.

3.2.1 External Mass Transport Limitations

The external mass transport describes the diffusion of reactants to the catalyst’s external surface.

$$r_{m, eff} = \beta_{CO_2} \cdot A_m \left( \frac{c_{CO_2} - c_{CO_2,s}}{c_{CO_2}} \right)$$  \hspace{1cm} (12)

$\beta_{CO_2}$ is the mass transport coefficient, $A_m$ the specific external catalyst surface area, and $c_{CO_2}$ and $c_{CO_2,s}$ the concentration of CO$_2$ in the bulk phase and at the external surface, respectively. High conversion rates on and inside the catalyst particle lead to low CO$_2$ surface concentrations. The mass transport coefficient $\beta_{CO_2}$ is calculated, based on the Sherwood number $Sh$:

$$\beta_{CO_2} = \frac{Sh \cdot DCO_2 \cdot \text{molecular}}{d_p}$$  \hspace{1cm} (13)

For a fixed bed with porosity $\epsilon_{\text{bed}}$, $Sh$ is given by (with $Re$ based on $u_0/\epsilon_{\text{bed}}$ as velocity in Eq. (17)):

$$Sh = (1 + 1.5 (1 - \epsilon_{\text{bed}})) \cdot Sh_p$$  \hspace{1cm} (14)

The Sherwood number $Sh_p$ for single particles is given by:

$$Sh_p = 2 + 0.69 \cdot \sqrt{Re \cdot \sqrt{Sc}}$$  \hspace{1cm} (15)

The Schmidt number $Sc$ and Reynolds number $Re$ are defined as:

$$Sc = \frac{\nu}{DCO_2 \cdot \text{molecular}}$$  \hspace{1cm} (16)

$$Re = \frac{u \cdot d_p}{\nu}$$  \hspace{1cm} (17)
3.2.2 Internal Mass Transport Limitations

The influence of internal mass transport on the effective rate is calculated by the pore effectiveness factor \( \eta_{\text{pore}} \), which relates the effective rate in the particle to the intrinsic reaction rate for reactant concentrations on the particle’s external surface:

\[
\eta_{\text{pore}} = \frac{r_{\text{CO}_2, \text{eff}}}{r_{\text{CO}_2, \text{intrinsic}}(c_{\text{CO}_2, s})}
\]  
(18)

For the estimation of \( \eta_{\text{pore}} \), the Thiele modulus \( \Phi_{\text{reversible}} \) valid for reversible reactions was applied [17, 18]. Thereby, the following assumptions and simplifications were made:

i) For the catalyst particle, a spherical shape was assumed.

ii) The kinetic equation of the (forward) RWGS rate was simplified as the \( \text{H}_2 \) concentration has only little influence on the rate, due to stoichiometry, surplus of \( \text{H}_2 \) in the feed gas, and the low reaction order of \( \text{H}_2 = 0.3 \) (\( n_{\text{CO}_2} = 1 \)).

\[
r_{\text{m,CO}_2, \text{intrinsic}, f} = k_{\text{m,CO}_2, \text{total}} c_{\text{CO}_2, s} \]
(19)

with

\[
k_{\text{m,CO}_2, \text{total}} = k_{\text{m,CO}_2} c_{\text{H}_2, \text{mean}}^{0.3}
\]

and

\[
c_{\text{H}_2, \text{mean}} = \frac{c_{\text{H}_2, \text{in}} + c_{\text{H}_2, \text{out}}}{2}
\]

iii) The reversible Thiele modulus for reversible first-order reactions (\( \text{CO}_2 \rightleftharpoons \text{CO} \)) was employed.

iv) The reverse reaction was also transformed into a first-order approach with respect to \( \text{CO} \):

\[
r_{\text{m,CO}} = k_{\text{m,CO}, \text{total}} c_{\text{CO}}
\]

(20)

Combination of Eqs. (7), (9), and (19) leads to:

\[
k_{\text{m,CO}, \text{total}} = k_{\text{m,CO}_2, \text{total}} \frac{1}{K_C} c_{\text{H}_2, \text{mean}}^{0.3}
\]

(21)

with

\[
k_{\text{C,CO}_2, \text{CO}} = \frac{c_{\text{H}_2}}{c_{\text{H}_2, \text{mean}}} K_{\text{C, RWGS}}
\]

(22)

derived from the equilibrium condition:

\[
r_{\text{m,CO}, f} = r_{\text{m,CO}} \quad \text{with} \quad k_{\text{C,CO}_2, \text{CO}} = \frac{k_{\text{m,CO}_2, \text{total}}}{k_{\text{m,CO}, \text{total}}}
\]

(23)

Based on these assumptions, the effectiveness factor and the effective reaction rate can be calculated as follows (a complete derivation is given in [23]):

\[
r_{\text{CO}_2, \text{eff}} = \eta_{\text{pore}} k_{\text{m,CO}_2, \text{total}} \left( \frac{c_{\text{CO}_2, s} - c_{\text{CO}}}{K_{\text{C,CO}_2, \text{CO}}} \right)
\]

(24)

The pore effectiveness factor \( \eta_{\text{pore}} \) is calculated by:

\[
\eta_{\text{pore}} = \frac{1}{\Phi_{\text{reversible}}} \left( \frac{1}{\tanh(3\Phi_{\text{reversible}})} - \frac{1}{3\Phi_{\text{reversible}}} \right)
\]

(25)

The Thiele modulus is thereby defined as:

\[
\Phi_{\text{reversible}} = \frac{d_p}{6} \sqrt{\frac{k_{\text{m,CO}_2, \text{total}}(T) \rho_p}{D_{\text{CO}_2, \text{eff}}} \left( 1 + K_{\text{C,CO}_2, \text{CO}} \right)}
\]

(26)

The effective diffusion coefficient was estimated using Eq. (27):

\[
D_{\text{CO}_2, \text{eff}} = \frac{\varepsilon_p}{\tau_p} D_{\text{CO}_2, \text{pore}}
\]

(27)

with

\[
D_{\text{CO}_2, \text{pore}} = \left( \frac{1}{D_{\text{CO}_2, \text{Knudsen}}} + \frac{1}{D_{\text{CO}_2, \text{molar}}} \right)^{-1}
\]

(28)

and

\[
D_{\text{CO}_2, \text{Knudsen}} = \frac{d_{\text{pore}}}{3} \sqrt{\frac{8 \ R \ T}{\pi \ M_{\text{CO}_2}}}
\]

(29)

3.2.3 External and Internal Mass Transport

The effective reaction rate may be influenced by external and internal mass transport limitations. The unknown \( \text{CO}_2 \) surface concentration can be calculated by combining Eq. (12) with Eq. (24):

\[
c_{\text{CO}_2, s} = \frac{\beta_{\text{CO}_2} \ R \ M_{\text{CO}_2} \ e_{\text{pore}}^\text{bulk} + \eta_{\text{pore}} k_{\text{m,CO}_2, \text{total}}^\text{pore} \ c_{\text{CO}_2, s}^\text{pore} \ K_{\text{C,CO}_2, \text{CO}}} {\beta_{\text{CO}_2} \ R \ M_{\text{CO}_2} \ e_{\text{pore}}^\text{bulk} + \eta_{\text{pore}} k_{\text{m,CO}_2, \text{total}}^\text{pore}}
\]

(30)

Inserting Eq. (30) either in Eq. (12) or in Eq. (24) leads to the overall reaction rate. In order to discriminate between external and internal mass transport influences, the overall efficiency and the pore efficiency (Eq. (18)) can be compared. The overall efficiency \( \eta_{\text{overall}} \) is defined as:

\[
\eta_{\text{overall}} = \frac{r_{\text{CO}_2, \text{eff}}}{r_{\text{CO}_2, \text{intrinsic}}(c_{\text{CO}_2, \text{bulk}})}
\]

(31)

Tab. 2 summarizes the parameters for the modeling of the effective reaction kinetics.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Crushed particle</th>
<th>Technical particle</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d_p ) [m]</td>
<td>( 1.2 \times 10^{-4} )</td>
<td>( 3 \times 10^{-3} )</td>
</tr>
<tr>
<td>( d_{\text{pore}} ) [m]</td>
<td>( 150 \times 10^{-9} )</td>
<td></td>
</tr>
<tr>
<td>( \rho_p ) [kg m(^{-3})]</td>
<td>1800</td>
<td></td>
</tr>
<tr>
<td>( \rho_{\text{pore}} ) [kg m(^{-3})]</td>
<td>1020</td>
<td></td>
</tr>
<tr>
<td>( \varepsilon_p / \tau_p )</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>( D_{\text{mole, CO}_2, 298K} ) [m(^3) s(^{-1})]</td>
<td>( 2.17 \times 10^{-5} )</td>
<td></td>
</tr>
</tbody>
</table>
### 3.3 Fixed-Bed Reactor Model

The software package Berkeley Madonna was used for the implementation of a 1D fixed-bed reactor model, being isothermal for the lab-scale reactor and adiabatic for the technical process. It is based on the intrinsic and effective kinetics of the RWGS including consideration of the thermodynamic equilibrium of the RWGS. The methanation is neglected because only temperatures above 600°C were considered, i.e., methane is not formed because of thermodynamic constraints. A mass balance was set up for each species (CO₂, H₂, CO, H₂O) as illustrated for CO₂ in Eq. (32) with \( u_s \) as superficial gas velocity:

\[
-u_s r_g \pi \frac{dc_{CO_2}}{dt_{Cat}} = r_{m,CO_2,eff}
\]  

Initial conditions and physical parameters used in the simulation model are summarized in Tab. 3.

#### Table 3. Feed gas properties at a H₂-to-CO₂ ratio of 3, a temperature of 273 K and a pressure of 1 bar.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c_{CO_2,0} ) [mol m⁻³]</td>
<td>6.6</td>
</tr>
<tr>
<td>( c_{H_2,0} ) [mol m⁻³]</td>
<td>19.9</td>
</tr>
<tr>
<td>( c_{CO,0} ) [mol m⁻³]</td>
<td>0</td>
</tr>
<tr>
<td>( c_{H_2O,0} ) [mol m⁻³]</td>
<td>0</td>
</tr>
<tr>
<td>( v_g ) [m s⁻¹]</td>
<td>1.9×10⁻⁵</td>
</tr>
<tr>
<td>( \rho_g ) [kg m⁻³]</td>
<td>0.83</td>
</tr>
<tr>
<td>( c_P ) [J mol⁻¹ K⁻¹] (1173 K)</td>
<td>36.9</td>
</tr>
</tbody>
</table>

### 4 Experimental Results and Discussion

#### 4.1 Commercial Steam Reforming Catalyst

The "effective" performance of the catalyst for RWGS was measured using particles with 3 mm diameter. The influence of temperature on conversion of CO₂ and selectivities to CO and CH₄ are illustrated in Fig. 3.

For the given conditions, CO₂ equilibrium conversion was nearly reached. The selectivity to CH₄ and CO corresponded to thermodynamic equilibrium and, therefore, CO was exclusively yielded for temperatures above 800°C. Thus, the catalyst seems suitable for the considered process.

#### 4.2 Catalyst Stability

For industrial implementation, the catalyst’s stability is crucial and was examined by experiments with around 20 h time-on-stream. Only a small amount of the crushed catalyst and a short residence time of about 1 ms, respectively, were used in order to reach a conversion significantly below equilibrium, and to suppress mass transport effects as far as possible. Fig. 4 shows the result of three experiments in a temperature range from 700°C to 900°C. The catalyst is stable at 900°C, but catalyst deactivation is visible at 800°C and is even more pronounced at 700°C. However, after about 12 h time-on-stream, the reactor was cooled down to the former temperature and again the initial CO₂ conversion was reached. So deactivation at 700°C and 800°C is reversible, and sintering and poisoning can be excluded as deactivation mechanism. With regard to thermodynamics (see Fig 2 b), catalyst deactivation caused by carbon formation on the catalyst surface seems most likely.

To proof whether carbon formation occurs, experiments in a range of 700°C to 900°C were done with 22 h time-on-stream. The carbon then burned off and, based on the gas analysis (CO, CO₂), the amount of coke was calculated (Fig. 5). The amount of carbon was very low with 0.48–0.53 mg C per g of catalyst and did not alter significantly with temperature. Nevertheless, the influence of the carbon load on the catalytic activity is more pronounced at lower temperatures. Even if likely to occur at high temperatures, further irreversible deactivation mechanisms, such as catalyst sintering, were not observed. This fact seems evident as the commercial steam reforming catalyst is designed for high temperatures of at least 800°C. However, as the catalyst is stable for technical temperatures of about 900°C, catalyst deactivation should not be a problem in technical application.
4.3 Modeling of Kinetic Data

To study the influence of the catalyst particle’s diameter on the kinetics, experiments with either commercial (cylinders, $3 \times 3$ mm) or crushed particles ($60–150$ mm) were performed. In addition, simulations were conducted based on the presented model. In order to achieve a CO$_2$ conversion below thermodynamic equilibrium, very low residence times of 1–1.4 ms were applied. Fig. 6 summarizes the results for the crushed (a) and technical catalyst particles (b).

With increasing temperature, the CO$_2$ conversion on the crushed catalyst exceeds the conversion on the 3-mm particles more and more, e.g., at 900°C by a factor of around 3, which obviously results from mass transport limitations. In both cases, the simulation matches the experimental data. At a higher, but still rather short residence time of about 20 ms, equilibrium is always reached for the crushed particles; for 3-mm particles, equilibrium is only reached at temperatures above 900°C (Fig. 7). Again, the agreement of measurements and calculation is very satisfactory.
To elucidate whether and to what extent internal and/or external mass transport limits the effective kinetics, the overall efficiency (Eq. (31)) and the pore efficiency only (Eq. (18)) were calculated for different particle diameters at 700 °C and 900 °C (Fig. 8).

The deviation between pore efficiency only and overall efficiency at both temperatures is rather small, which indicates that the effective rate is mainly influenced by internal mass transport limitations; external mass transport is therefore rather fast. This behavior is explained by different diffusivities. Internal mass transport is determined by the pore diffusivity (Eq. (28)) and external mass transport by molecular diffusivity. For the given reaction conditions, the pore diffusion coefficient of CO₂ is by about one order of magnitude smaller than the molecular diffusion coefficient, which is the result of the mean pore diameter of 150 nm and the strong influence of Knudsen diffusion, respectively (Fig. 9).

Summing up, for technically relevant conditions, the effective rate is strongly influenced by pore diffusion. For the given particle size of 3 mm, the pore diffusion effectiveness factor is only 10% at 900 °C; see Fig. 8.

5 Considerations with Regard to a Technical Application of the RWGS Process

For a technical application of the endothermic RWGS process, basically two parameters, the applied pressure and temperature (profile) in the reactor, will deviate from lab-scale experiments. For a technical process, elevated pressures may be advantageous as the downstream FTS unit is typically run at 30 bar. In this work, a steel tube reactor, made from 1.4876 high-temperature steel, was used for selected lab-scale experiments at 30 bar. However, as the steel contained about 30% Ni, the wall catalyzed the RWGS. At 780 °C, about 65% of the CO₂ equilibrium conversion was already reached without the Ni catalyst ($t_\text{empty tube} = 1.5$ s, $u_s = 0.2$ m s⁻¹); thus, further kinetic experiments were pointless. With regard to a larger technical reactor, the wall effect is much less relevant as the ratio of wall surface area to reactor volume decreases with increasing reactor diameter ($A_\text{reactor wall}/V_\text{reactor} = 4/d_\text{reactor}$). For example, for a technical reactor diameter of 1 m, the $A$-to-$V$-ratio would drop from 400 m⁻¹ (lab-scale with 1 cm diameter) to only 4 m⁻¹.

Hence, as no experimental data for the RWGS kinetics at elevated pressures could be achieved with the available equipment, only an estimation of the influence of pressure on the effective rate is offered here. The calculations are based on the intrinsic kinetics measured at 1 bar and the modeled influence of pore and external diffusion at higher pressures and thus may deviate from reality. Fig. 10 illustrates the influence of pressure on the pore and overall effectiveness factor at 900 °C.

As expected, both efficiency factors decrease with pressure as the molecular diffusivity declines with pressure. The influence of external mass transport rises resulting from the decreasing molecular CO₂ diffusivity. For a reactor pressure of 30 bar, the overall efficiency drops to about 2%, and the external mass transport then even dominates the effective kinetics.

With regard to temperature, the lab-scale reactor showed an almost isothermal temperature profile. For a technical application, the construction of an isothermal reactor is difficult as the reactor would have to be heated externally. Therefore, stage-wise adiabatic operation with intermediate heating of the gas is an option. The adiabatic decline in temperature to reach
(almost) equilibrium conversion (in each stage) was estimated by a simple heat balance of the RWGS:

\[
\Delta T_{ad} = \frac{\Delta R H_{X_{CO2, equi}}}{4 c_p}
\]  

(33)

The factor 4 in Eq. (33) results from the assumed H2-to-CO2-ratio of 3. Tab. 4 indicates that an industrial RWGS reactor should at least consist of two adiabatic stages to achieve a sufficiently high CO2 conversion of about 80 %.

**Table 4.** Adiabatic reactor temperature for equilibrium conversion of CO2 (\(p = 1 \text{ bar}, \text{H}_2:\text{CO}_2 = 3:1\)).

<table>
<thead>
<tr>
<th>Stage</th>
<th>(T_{in} [^\circ C])</th>
<th>(T_{out} [^\circ C])</th>
<th>(X_{CO2, equi} [%])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>900</td>
<td>753</td>
<td>71</td>
</tr>
<tr>
<td>2</td>
<td>900</td>
<td>884</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>900</td>
<td>896</td>
<td>79</td>
</tr>
</tbody>
</table>

### 6 Summary

This work shows that a commercial steam reforming Ni catalyst is able to catalyze the RWGS reaction very effectively. The CO2 equilibrium conversion of 80 % at 900 °C is almost achieved within a short residence time of less than 100 ms. Long-term experiments proof the catalyst's stability at 900 °C, while carbon formation on the catalyst at lower temperatures leads to (reversible) catalyst deactivation. The intrinsic kinetics was determined and a simulation model for the effective kinetics derived and validated by the experimental data with varying catalyst particle size. For a technical catalyst with a diameter of several millimeters, mass transport effects have a strong influence on the rate; the effectiveness factor at 900 °C is then about 10 % at 1 bar, mainly because of pore diffusion, and only 2 % at an elevated pressure of 30 bar, then almost equally to the result of internal and external mass transfer limitations. Due to the endothermal character of the RWGS reaction, a fixed-bed reactor with at least two adiabatic stages with intermediate heating seems to be a promising concept.

The authors have declared no conflict of interest.

### Symbols used

- \(A_m\): external surface area (catalyst)
- \(c_{i, b}\): concentration in the bulk phase
- \(c_{i, equi}\): concentration for the thermodynamic equilibrium
- \(c_{i, s}\): concentration on the catalyst surface
- \(c_p\): heat capacity
- \(d_p\): particle diameter
- \(d_{p, eq}\): pore diameter
- \(D_i\): diffusivity

### Greek letters

- \(\beta_{CO2}\): mass transport coefficient
- \(\epsilon_p\): porosity of particle
- \(\epsilon_{bed}\): porosity of the catalyst bed
- \(\eta_{pore}\): pore efficiency
- \(\eta_{overall}\): overall efficiency
- \(\psi_{reversible}\): reversible Thiele modulus
- \(\nu_g\): gas viscosity
- \(\rho_g\): gas density
- \(\rho_p\): density of particle
- \(\rho_{bed}\): density of catalyst bed
- \(\tau\): residence time
- \(\tau_p\): tortuosity of particle
- \(\Delta R H_i\): reaction enthalpy

### Abbreviations

- BET: Brunauer-Emmett-Teller
- FTS: Fischer-Tropsch synthesis
- Re: Reynolds
- RWGS: reverse water-gas shift
- Sc: Schmidt number
- Sh: Sherwood number
- Shp: Sherwood for particles
- WGS: water-gas shift
References


