CO₂ Methanation on Fe Catalysts Using Different Structural Concepts

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The hydrogenation of carbon dioxide towards methane and water is evaluated on different types of iron catalysts. The catalysts refer to different structural concepts implying a bare iron oxide, a silica-supported and a core-shell system. Highest CO₂ conversion of about 20 % is achieved with the bulk catalysts and the supported material. However, although revealing reduced CH₄ formation rate, the core-shell catalyst exhibits pronounced resistance against coke formation as well as thermal sintering and particle attrition upon syngas reaction.

Keywords: CO₂ hydrogenation, Coking, Core-shell catalyst, Iron, Methane

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1 Introduction

In heterogeneous catalysis, the design of catalysts as well as their physical-chemical properties crucially influence the activity, selectivity and stability. In dependency of the application and chemical reaction, two different structural types of catalysts are commonly used. On the one hand, there are supported catalysts characterized by high surface area substrates, e.g., binary metal oxides such as Al₂O₃ and TiO₂, onto which the catalytically active species are located, preferably in high dispersion [1]. These catalysts are often prepared by impregnation techniques and are mainly used when expensive precious metals are the active components, e.g., Pt/Al₂O₃ and Pd/Al₂O₃. On the other hand, bulk materials, which exemplarily can be prepared by precipitation and melt flow techniques, are mainly used in non-noble metal catalysis. Prominent examples of this concept are the NH₃ synthesis and CO hydrogenation according to the Fischer-Tropsch synthesis, which are performed on Fe catalysts using bare Fe₂O₃ precursors modified with K₂O, SiO₂ or Al₂O₃ promotors [2, 3]. Furthermore, for CO₂ hydrogenation, e.g., CO₂ methanation \( \text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}; \Delta H^\circ = -165 \text{kJ mol}^{-1} \), supported Fe catalysts are also investigated, particularly in R&D, while Ni-based catalyst systems are commonly used for efficient CH₄ formation during CO₂ hydrogenation [4]. For the supported Fe catalysts, metal loading as well as interactions between support material and Fe entities play an important role for the catalytic activity, selectivity and stability [5–7].

One major challenge in the CO₂ hydrogenation on Fe-based catalysts is their deactivation, which is comprehensively reviewed by de Smit et al. [8]. Loss of catalytic activity over time on stream under syngas conditions is mainly ascribed to oxidation of active carbide phase into magnetite as well as loss of active catalytic surface by sinter effects, formation of volatile carbonyls and deposition of inactive carbon moieties. However, no unanimous understanding exists on the detailed structure of active carbide species (specifically iron carbide bulk phase or surface carbide), due to the highly dynamic and complex structural changes of Fe catalysts during CO₂ hydrogenation. In this context, core-shell catalysts are known to reveal high stability as also proven within this work and are already investigated for esterification [9], ammonia decomposition [10], olefin hydrogenation [11] and Fischer-Tropsch synthesis [12, 13]. Although synthesis of core-shell catalysts is rather complex, unique properties are achieved, e.g., narrow particle size distribution, resulting in outstanding materials for scientific research, as recently shown for methanation [14]. Moreover, changes of particle size and shape can be easily studied by transmission electron microscopy (TEM) since the well-defined core-shell arrangement is stable under reaction conditions [10].

Against this background, the present paper addresses the influence of different structural concepts of Fe catalysts on the CO₂ hydrogenation performance with special focus on coking resistance. More detailed, bare α-Fe₂O₃, silica-supported Fe oxide and a core-shell catalyst with nano-sized Fe cores embedded into a SiO₂ shell were prepared, physically-chemically characterized and tested for CO₂ hydrogenation. The as-prepared and spent samples are characterized by

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X-ray diffraction (XRD), $^{57}\text{Fe}$ Mössbauer spectroscopy, TEM as well as temperature-programmed hydrogenation (TPH) to identify structural evolution under syngas conditions as well as the impact on catalytic performance.

2 Experimental

2.1 Catalyst Preparation

The bare $\alpha$-$\text{Fe}_2\text{O}_3$ sample (> 98 %) was commercially available (Lanxess). Preparation of the supported catalyst was done by incipient wetness impregnation. The amorphous SiO$_2$ carrier was loaded by an aqueous solution of Fe(NO$_3$)$_3$$\cdot$$9\text{H}_2\text{O}$ (Merck) with known concentration such that the solution was completely absorbed resulting in a Fe proportion of 15 wt %. After impregnation, the sample was dried for 1 h at 80°C and subsequently calcined for 2 h in flowing air at 400°C.

The core-shell catalyst was prepared using an adapted reverse microemulsion method [15]. For the oil phase 100 mL cyclohexane (VWR Chemicals, AnalaR NORMAPUR®) was mixed with 34.2 g of polyoxyethylene (10) cetyl ether (Brij® C10, Sigma Aldrich/Merck) and heated to 50°C. Subsequently 5 mL of a 5 mM aqueous FeCl$_3$ solution (Acros Organics, p.a.) was added to the mixture under continuous stirring followed by 3 mL of hydrazine hydrate (aqueous solution, 35 wt %, Sigma Aldrich/Merck). To encapsulate the obtained iron oxide nanoparticles, with an average size of 8 nm as measured by TEM, in silica 21.4 mL tetraethyl orthosilicate (TEOS, Merck) was added to the suspension mentioned above followed by 3 mL of a 5 M aqueous ammonia solution (Carl Roth, 30 wt %, ROTIPURAN®) under stirring for 2 h. Afterwards the microemulsion was destabilized by addition of 2-propanol (VWR Chemicals, technical) and centrifuged at 8000 rpm for 15 min. The obtained particles were washed several times in 2-propanol, dried over night at 80°C and calcined at 420°C for 4 h (ramp 2 K min$^{-1}$). Within this paper, sample codes are used for differentiation of the three catalyst types implying $\alpha$-$\text{Fe}_2\text{O}_3$ for the bulk catalyst, 15Fe/SiO$_2$ for the supported sample and 15Fe@SiO$_2$ for the core-shell system containing 15 wt % Fe as well.

2.2 Catalyst Characterization and CO$_2$ Hydrogenation Tests

The catalysts were physico-chemically characterized by powder X-ray diffraction (PXRD), $^{57}\text{Fe}$ Mössbauer spectroscopy, transmission electron microscopy and temperature programmed hydrogenation. PXRD was performed on a D8 Discover (Bruker-AXS) with Co-Kα radiation (35 kV, 45 mA). The diffractograms were recorded in 2θ mode from 20 to 90° with a step width of 0.06° and a time of 4 s per step. DIFFRAC EVA software (Bruker-AXS) was used for assignment of the reflexes, while quantitative phase composition was evaluated by DIFFRAC TOPAS software (Bruker-AXS) employing standard fitting procedure according to the Rietveld refinement. The crystallite size was estimated using the Scherrer equation.

Investigation of Fe species as well as phase composition was done with $^{57}\text{Fe}$ Mössbauer spectroscopy at ambient conditions using a 100 mCi $^{57}$Co source embedded in a Rh matrix. The spectrometer (WissEl) was operated in constant acceleration mode. Mössbauer spectra were fitted using least square procedure assuming Lorentzian peak shapes, while isomer shift, quadrupole splitting, and hyperfine field are reported relative to $\alpha$-Fe.

Bright field TEM micrographs were taken by a Zeiss TEM 109 equipped with a CCD camera. For sample preparation, a droplet of ethanol (VWR 96 % Ph. Eur.) solution containing the sample powder (ca. 0.5 mg mL$^{-1}$) was deposited on a carbonized Cu grid, followed by evaporation of the ethanol.

For catalytic tests, 200 mg of the as-prepared samples was used taking a grain size of 125 to 250 µm. Respective catalyst was fixed in a glass rube reactor (i.d. 8 mm) with quartz wool, while the temperature was monitored by two K-type thermocouples placed directly in front of and behind the fixed bed. Prior to CO$_2$ hydrogenation, the catalyst was activated in 20 vol % H$_2$ in N$_2$ with a total flow of 500 mL min$^{-1}$ (STP) at 350°C for 3 h representing a typical pretreatment in syngas applications. Subsequently, the reaction temperature of 400°C was adjusted in N$_2$ flow and the hydrogenation was started at 1 bar and a molar H$_2$/CO$_2$ ratio of 4 with a CO$_2$ proportion of 10 vol %. N$_2$ was taken as balance. The reaction conditions are suitable to compare the hydrogenation activity of the different Fe catalysts [16, 17]. The total flow was 500 mL min$^{-1}$ (STP) resulting in a space velocity of ca. 52 000 h$^{-1}$ (69.2 mmol(CO$_2$)/mol(Fe))/s). The reactor effluents were monitored by a hot measuring MultiGas 2030 FTIR spectrometer (MKS Instruments).

TPH analyses were performed for characterization of carbonaceous species formed on the catalysts upon CO$_2$ hydrogenation. For this purpose, respective catalyst was flushed with N$_2$ directly after reaction and was rapidly cooled to room temperature. Subsequently, pure H$_2$ was dosed (200 ml min$^{-1}$), while TPH was started by linearly increasing the temperature to 800°C with a ramp of 5 K min$^{-1}$. As for activity studies, reactor effluents, especially CH$_4$, were analyzed by FTIR.

3 Results and Discussion

The results of PXRD and $^{57}\text{Fe}$ Mössbauer spectroscopic analyses of the as-prepared samples are presented in Fig. 1, whereas derived crystalline phases, crystallite sizes and Mössbauer parameters are summarized in Tab.1. As expected, the PXRD pattern of the bare iron oxide only reveals reflexes, which are attributed to $\alpha$-$\text{Fe}_2\text{O}_3$. Reflexes
related to \( \alpha \)-Fe\(_2\)O\(_3\) are also present in the diffractogram of 15Fe/SiO\(_2\), whereas a relatively broad reflex at ca. 2\( ^\circ \) (2\( \theta \)) including strong reflexes referred to \( \gamma \)-Fe\(_2\)O\(_3\).

The \( ^{57}\)Fe Mössbauer spectrum of 15Fe@SiO\(_2\) shows a duplet with an isomer shift of 0.29 mm s\(^{-1}\) and quadrupole splitting of 0.67 mm s\(^{-1}\), which is interpreted with superparamagnetic Fe\(^{3+}\) species (Fig. 1 right, Tab. 1). It is well known from literature, that iron oxide entities smaller than ca. 13 nm provide such duplet signal [18]. This is also in line with the \( \gamma \)-Fe\(_2\)O\(_3\) crystallite size of 15Fe@SiO\(_2\), which amounts to ca. 6 nm as estimated from Scherrer equation. The average crystallite size of the \( \alpha \)-Fe\(_2\)O\(_3\) entities present in 15Fe/SiO\(_2\) is somewhat higher (ca. 17 nm), while both a superparamagnetic Fe\(^{3+}\) duplet (fraction: 10 \%) and a sextet with hyperfine field of 50.9 T (fraction: 90 \%) appear in the \( ^{57}\)Fe Mössbauer spectrum. The former signal again indicates small iron oxide moieties (< ca. 13 nm), whereas the latter evidences larger \( \alpha \)-Fe\(_2\)O\(_3\) particles (> ca. 13 nm). Consequently, a relatively broad size distribution of the iron oxide entities present in this sample is evident. Finally, the \( ^{57}\)Fe Mössbauer spectrum of the bare iron oxide shows exclusive presence of a sextet associated with \( \alpha \)-Fe\(_2\)O\(_3\) in line with PXRD.

In the CO\(_2\) hydrogenation studies, CH\(_4\) and CO are the only carbon-containing products found in the gas phase. Note that no significant CO\(_2\) conversion is obtained when performing the reaction at the stated conditions without catalyst. For comparison purposes, catalytic activity is expressed in terms of CH\(_4\) and CO reaction rate (molar amount of CH\(_4\) or CO formed per time and total Fe amount present in the catalyst). Interpretation of the time-dependent performance behavior is not addressed in the present paper since this is already topic of previous works and many scientific researches [16, 17, 19, 20]. Instead, a constant reaction time of 17 h was chosen for all samples to compare hydrogenation activity as well as carbon deposits of the Fe-based catalysts (Fig. 2).

The catalytic results show similar CH\(_4\) formation rate for \( \alpha \)-Fe\(_2\)O\(_3\) and 15Fe/SiO\(_2\); the respective CO\(_2\) conversion and CH\(_4\) selectivity for the Fe-based catalysts are shown in Fig. 2 (right). The 15Fe/SiO\(_2\) catalyst achieves the highest CO formation due the reverse water-gas shift reaction (CO\(_2\) + H\(_2\) \( \rightarrow \) CO + H\(_2\)O; \( \Delta H^\circ = 41\) kJ mol\(^{-1}\)). More detailed, the formation rate of CO is more than doubled as compared to the bare \( \alpha \)-Fe\(_2\)O\(_3\) catalyst. CO\(_2\) conversion of the core-shell catalyst is rather small compared to \( \alpha \)-Fe\(_2\)O\(_3\) and 15Fe/SiO\(_2\).

**Table 1.** Fe crystallite phase and average crystallite size \((d_{\text{cryst}})\) derived from PXRD as well as \( ^{57}\)Fe Mössbauer parameters (isomer shift \( \delta \), quadrupole splitting \( \Delta E_Q \) and hyperfine field \( B_{hf} \)) of the as-prepared catalysts.

| Sample    | Fe phase | \( d_{\text{cryst}} \) [nm] | \( \delta \) [mm s\(^{-1}\)] | \( \Delta E_Q \) [mm s\(^{-1}\)] | \( B_{hf} \) [T] | Area ratio [%] | Assignment |
|-----------|----------|-----------------------------|------------------------------|----------------------------------|-----------------|---------------|-------------|
| \( \alpha \)-Fe\(_2\)O\(_3\) | \( \alpha \)-Fe\(_2\)O\(_3\) | 44                           | 0.39                         | -0.22                            | 51.2            | 100           | \( \alpha \)-Fe\(_2\)O\(_3\) |
| 15Fe/SiO\(_2\) | \( \alpha \)-Fe\(_2\)O\(_3\) | 17                           | 0.37                         | -0.22                            | 50.9            | 90            | \( \alpha \)-Fe\(_2\)O\(_3\) |
| 15Fe@SiO\(_2\) | \( \gamma \)-Fe\(_2\)O\(_3\) | 6                            | 0.29                         | 0.67                             |                 | 100           | Fe\(^{3+}\) |

a) derived from XRD results; b) derived from \( ^{57}\)Fe Mössbauer spectroscopy.
mainly ascribed to the low reaction pressure and high space velocity. Also, the methanation activity of the core-shell catalyst is about ten times lower as for \( \alpha \)-\( Fe_2O_3 \). Conventional Ni catalysts reveal selective \( CH_4 \) formation with a \( CO_2 \) conversion of about 91\% representing the thermodynamically maximum \( CH_4 \) yield at the reaction conditions investigated in this work (400 °C and 1 bar) [4, 21]. However, despite their high \( CH_4 \) formation rates, \( \alpha \)-\( Fe_2O_3 \) and 15Fe/SiO\(_2\) exhibit a clear pressure increase in front of the catalyst bed during syngas reaction amounting to approx. 0.8 and 0.4 bar after 17 h of reaction, respectively. This blocking of the catalyst bed is related to the formation of solid carbon deposition on the catalyst upon \( CO_2 \) hydrogenation. Contrary, no rise in pressure occurs in the investigation with 15Fe@SiO\(_2\).

The amount of carbon species present on the catalysts is quantified by TPH (Fig. 3), where solid carbon is exclusively converted into \( CH_4 \) at different temperatures. It was recently reported that TPH traces below 400 °C, which are obtained for bare iron oxide catalysts directly after \( CO_2 \) hydrogenation, are mainly associated with iron carbide entities, while \( CH_4 \) signals at higher temperatures correspond to coke-like deposits [16]. This assignment is also confirmed by the amount of \( CH_4 \) released between 220 and 350 °C during TPH of \( \alpha \)-\( Fe_2O_3 \) (0.91 mmol), which is in line with the carbon amount of a Fe\(_2C\)/Fe\(_5C_2\) mixture representing typical iron carbides in \( CO_2 \) hydrogenation (the carbon amount of bare Fe\(_2C\) and Fe\(_5C_2\) based on 2.50 mmol Fe used in the TPH tests amounts to 0.83 and 1.00 mmol, respectively) [7]. Therefore, the bulk carbon deposition leading to catalyst blocking are calculated by integration of respective TPH curves above 400 °C (Fig. 3).

The calculated carbon amounts correlate well with the stated pressure increase during the reaction. Moreover, formation of carbonaceous bulk structures with very low reactivity (TPH signal above 600 °C) are found for 15Fe/SiO\(_2\), potentially contributing to the relatively high pressure rise although the quantity of carbon deposits is only one tenth (1.30 mmol) as compared to the bare \( \alpha \)-\( Fe_2O_3 \) catalyst (12.3 mmol). These carbonaceous entities might result from strong interactions with the support material [22]. Moreover, carbon depositions are drastically suppressed for the core-shell catalyst (0.04 mmol), which is also confirmed by the TEM micrographs of the spent samples shown in Fig. 4.

Beside the absence of any detectable bulk carbon deposits on 15Fe@SiO\(_2\), the core-shell structure is intact during reaction without thermal sintering. In contrast, particle break up and attrition is observed for the spent \( \alpha \)-\( Fe_2O_3 \) sample consequently leading to limited stability of bare iron oxide catalysts in \( CO_2 \) hydrogenation [23]. Also, significant bright regions are found in the spent \( \alpha \)-\( Fe_2O_3 \) sample very likely associated with carbon-rich structures surrounding the heavier iron carbide particles (darker regions in respective TEM micrograph). It is assumed that the SiO\(_2\) shell efficiently hinders the accumulation of solid carbon on the catalyst. Moreover, the amount of iron carbides is significantly lower for 15Fe@SiO\(_2\) as compared to 15Fe/SiO\(_2\) and \( \alpha \)-\( Fe_2O_3 \) as proven by TPH (Fig. 3), potentially resulting in a reduced methanation activity. It is known from literature that carbide entities play a crucial role in the formation of hydrocarbons during \( CO_x \) hydrogenation [19]. Moreover, we showed recently that the carburization behavior of Fe-based catalysts during \( CO_2 \) hydrogenation strongly depends on particle size, while larger Fe entities exhibit faster carbon deposition [17]. This is in line with the increasing average crystallite size according to the ranking: 15Fe@SiO\(_2\) (6 nm) < 15Fe/SiO\(_2\) (17 nm) < \( \alpha \)-\( Fe_2O_3 \) (44 nm).
Furthermore, it is noteworthy that the amount of carbon deposits on the core–shell catalyst is ca. 300 times smaller compared to the bare $\alpha$-Fe$_2$O$_3$ catalyst and still 32 times lower than the impregnated Fe catalyst while the activity is only reduced by factor 12. The high stability of 15Fe@SiO$_2$ is summarized in Fig. 5 showing the ratio of total CH$_4$ amount as well as the amount of solid carbon deposited on the catalyst both formed during 17 h of CO$_2$ hydrogenation. However, it has to be stated that the methanation activity of the core-shell catalyst needs to be improved. This can be done by increasing the iron carbide proportion in the catalyst, e.g., by using a suitable activation procedure with CO consequently leading to efficient carburization of the catalyst. Finally, conventional Ni catalysts achieve drastically higher CH$_4$ yield close to the thermodynamic equilibrium amounting to ca. 85% at 400°C and 1 bar.

![Figure 5. Ratio of total CH$_4$ amount and the amount of carbonaceous deposits on the Fe-based catalysts both formed during CO$_2$ hydrogenation for 17 h at 400°C and 1 bar.](image)

### 4 Summary

In the present paper, CO$_2$ hydrogenation on Fe-based catalysts using different structural concepts (bare iron oxide, a silica-supported sample and a core-shell system) are investigated. The bare iron oxide catalyst as well as the impregnated sample show relatively high activity at 400°C and 1 bar, but also reveal strong deposition of carbonaceous species. Although revealing lower CH$_4$ formation rates, the stability of the core-shell catalyst is drastically higher. Beside reduced formation of carbon deposits, no significant change in particle size and shape upon syngas reaction is found. The gap in catalytic activity might be overcome by increased catalyst amount used in CO$_2$ hydrogenation, which is currently investigating. Also, the influence of technically relevant promotor metals as well as suitable activation methods need to be evaluated.

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