Activity and Structural Changes of Fe-based Catalysts
during CO₂ Hydrogenation towards CH₄ – A Mini Review

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Heterogeneous iron catalysts are active in the hydrogenation of carbon oxides and are widely investigated for the production of long-chained hydrocarbons according to the Fischer-Tropsch synthesis. Moreover, high selectivity of light hydrocarbons, such as CH₄, also occurs strongly depending on reaction conditions and catalyst formulations. As a consequence, Fe catalysts reveal promising methanation activity as referred to the traditional Ni catalysts. Additionally, Fe catalysts also benefit from their low price and toxicological harmlessness. However, the dynamic behavior of iron upon CO₂ hydrogenation is not yet unraveled unambiguously including phase transformations, structural changes and participation of carbon species formed. The present review highlights these complex processes of Fe catalysts with special focus on the methanation of CO₂. Additionally, different analytical tools useful for ex situ and in situ studies are critically evaluated.

1. Introduction

Within the last decades, the production of synthetic natural gas (SNG) gains increasing importance. In the so-called Power-to-Gas (PtG) process, renewable electricity is used for the formation of “green” H₂ by the electrolysis of water. Subsequently, H₂ is converted into CH₄ which can be easily stored and transported in the existing natural gas grid. As a result, SNG represents a suitable energy carrier for the chemical storage of excess electricity. Using abundant CO₂ as the carbon source, methanation additionally contributes to the reduction of greenhouse gas emissions.[1]

Nickel was recognized as an active material for CO methanation since the pioneering studies of Sabatier and Senderens in 1902.[2] Moreover, other group 8–10 metals, most notably Ru, Rh, Co and Fe, are now known to be active in methanation as well.[3] However, mainly Ni catalysts are investigated in the methanation of CO and CO₂, due to their high activity and selectivity towards CH₄, as well as their moderate prices compared to that of Ru. A summary on the structure and composition of Ni as well as noble metal based methanation catalysts is given in the review article from Wang et al.[4] However, one of the drawbacks of traditional Ni catalysts is their toxicity, which necessitates special recovery techniques for spent catalysts.[5] Furthermore, the formation of highly toxic and volatile nickel carboxyls can lead to catalyst deactivation by loss of the active metal or decrease in the active surface area known as carbonyl-induced particle sintering.[6] Besides, sinter effects of the support also cause deactivation of Ni catalysts under harsh hydrothermal conditions upon methanation.[7]

Fe based catalysts are known to be active in syngas reactions, for example in the synthesis of NH₃ as well as production of hydrocarbons by the Fischer-Tropsch synthesis.[8,9] Moreover, iron oxides catalyze the water-gas shift reaction (WGS).[10] But, only little is known on the efficient formation of CH₄ during CO₂ hydrogenation using Fe catalysts. Basically, clear conclusions are difficult, since a broad product spectrum is formed under H₂/CO₂ syngas conditions including CO, CH₄, higher alkanes and olefins as well as alcohols. Moreover, Fe catalysts are characterized by complex structural changes in H₂/CO₂ atmosphere impeding the identification of active species.

In this mini-review, the CO₂ methanation activity of Fe catalysts is highlighted describing the effect of temperature, pressure, H₂/CO₂ ratio as well as space velocity. Furthermore, an overview of structure as well as phase transformations under syngas conditions and their role in methanation is presented. These findings are complemented by the evaluation of suitable analytical techniques in order to characterize Fe catalysts for the hydrogenation of CO₂.

2. CO₂ methanation activity of Fe catalysts

Methanation of CO₂ [Eq. (1)] and CO [Eq. (2)] are highly exothermic and the total number of molecules decreases upon reaction. Therefore, low temperatures and high pressures are thermodynamically favorable. Both methanation reactions are connected by the WGS reaction [Eq. (3)], which can influence the gas composition during methanation. A detailed thermodynamic investigation was presented by Gao et al.[11]

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\begin{align*}
\text{CO}_2 + 4\text{H}_2 & \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta_{\text{r}}H^\circ = -165 \text{kJ/mol} \quad (1) \\
\text{CO} + 3\text{H}_2 & \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \quad \Delta_{\text{r}}H^\circ = -206 \text{kJ/mol} \quad (2) \\
\text{CO} + \text{H}_2\text{O} & \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad \Delta_{\text{r}}H^\circ = -41 \text{kJ/mol} \quad (3)
\end{align*}
\]

The influence of temperature, pressure, molar H₂/CO₂ ratio and space velocity on the CO₂ conversion (X(CO₂)) as well as CH₄ yield (Y(CH₄)) during CO₂ hydrogenation on bare iron oxide precursors is shown in Figure 1. The data are mainly taken from studies on the CO₂-based Fischer-Tropsch synthesis,[12–22] whereas the samples are activated by H₂ before the catalytic investigations. The CO₂ conversion tends to increase with rising temperature when keeping the pressure (1 bar) as well as the molar H₂/CO₂ ratio (4) constant. However, the CO₂ conversion is always below the thermodynamic limit, which amounts to 97% at 250°C and 71% at 500°C. The CH₄ yield is also significantly lower than the thermodynamic one, while a maximum of 10% is found at 400°C for 1 bar and molar H₂/CO₂ ratio of 4.[19] Higher methanation activity reasonably appears at decreasing space velocity.
Moreover, the influence of reactor pressure is evaluated between 1 and 25 bar, while a temperature range of 300 to 320°C and a molar H₂/CO ratio of 4 according to the stoichiometry (Eq. 1) are studied. With rising pressure the CH₄ yield firstly increases and subsequently declines again for pressures above ca. 10 to 15 bar. This effect is mainly ascribed to the favored formation of higher hydrocarbons according to the Fischer-Tropsch synthesis. A similar behavior is found for the space velocity indicating reduced CH₄ formation below ca. 0.5 l/g/h. In line with the influence of reactor pressure, high residence time of CO₂ and H₂ in the catalyst bed enhances the chain growth of the hydrocarbons. Also, a slight decrease in CO₂ conversion with rising pressure is found in the range of 0.5 to 1.0 l/g/h (Figure 1), which is ascribed to condensation of higher hydrocarbons in the pores of the Fe catalysts limiting the gas diffusion.²³

Furthermore, high molar H₂/CO₂ ratios are beneficial for pronounced CO₂ conversion as well as CH₄ yield. Excess of H₂ increases the thermodynamic CH₄ yield and accelerates the methanation. In particular, inclining H₂ partial pressure enhances the hydrogenation of reactive surface carbon species towards CH₄.²⁴ Also, it is assumed, that oxidation of active iron carbide phases by CO₂ and H₂O into less reactive FeOₓ is suppressed at high partial pressure of H₂.²⁵ Generally, substantial CH₄ yield is reported for elevated temperatures above 400°C, pressures in the range of 15 bar and high molar H₂/CO₂ ratios, e.g. Y(CH₄) = 34% at 400°C, 15 bar, molar H₂/CO ratio of 6 and 1.14 l/g/h, whereas the CH₄ selectivity is 50% only.²⁶ Furthermore, in a recent study demonstrates a maximum CH₄ yield of 81% (X(CO₂) = 85%) using a bare α-Fe₃O₄ pre-exposed to H₂.²⁷ Note that CO significantly appears as side product, while C₂-C₄ hydrocarbons are formed in minor abundance only; corresponding methanation conditions are referred to a stoichiometric H₂/CO₂ ratio, 400°C, 15 bar and 8.3 l/g/h. Additionally, Yoshida et al.²⁸ showed CH₄ yields about 60 to 70% on partially H₂-reduced FeOₓ. However, direct comparison of this result with above-mentioned studies is difficult, since the reaction is performed at 300°C and 1 bar as batch process with high residence time of about 30 min.

Furthermore, supported Fe catalysts are also investigated for CO₂ hydrogenation. Jun et al.²⁹ reported on increasing CH₄ yield from 2 (X(CO₂) = 7%) to 5 (X(CO₂) = 16%) and 9% (X(CO₂) = 23%) when conducting the CO₂ hydrogenation at 300°C, 10 bar, a molar H₂/CO₂ ratio of 3 and 1.9 l/g/h taking SiO₂, TiO₂- and Al₂O₃-carriers loaded with 0.25% Fe. Suo et al.³⁰ indicated more pronounced CH₄ formation on Fe/TiO₂ (5 wt.% Fe) as compared to a corresponding Al₂O₃-supported sample. Moreover, Fe catalysts supported by carbon nanotubes achieve CH₄ yields up to 10% at 360°C, 25 bar, a molar H₂/CO ratio of 3 and 50 l/g/h.³¹ Contrary, maximum CH₄ yield of 4% is obtained at 300°C, 10 bar and a molar H₂/CO₂ ratio of 3 using a Fe-loaded HY zeolite.²¹

The effect of different promotors on activity and selectivity of Fe catalysts in CO₂ hydrogenation was systematically evaluated to enhance the yield of selected hydrocarbon products. Fe based Fischer-Tropsch catalysts usually imply K₂O, which enhances the CO₂ adsorption while reducing the adsorption capacity of H₂. Consequently, production of higher hydrocarbons as well as olefins is increased.³² Addition of potassium should therefore be avoided for efficient CH₄ formation upon CO₂ hydrogenation. Similar effects concerning the increase in the average molecular weight of hydrocarbon products is reported for Cu.³³ Moreover, Prasad et al.³⁴ show increased CO₂ chemisorption and CH₄ yield, when promoting a Fe catalyst with V, Cr, Mn or Zn. Moreover, Al, Ce, Sm and Mg are also identified as suitable promotors for Fe catalysts. For instance, doping an active α-Fe₃O₄ precursor with 2 wt.% Mg leads to an increase in the CH₄ yield from 3% to 8% upon CO₂ methanation at 400°C, 8 bar and a molar H₂/CO₂ ratio of 4 (150 l/g/h).³⁵

Finally, it is stated in the literature, that the introduction of Fe into conventional Ni catalysts enhances activity and stability during CO₂ hydrogenation. An increase in CO₂ conversion (71%) and CH₄ selectivity (98%) is found, when the CO₂ methanation is performed at 360°C and 6 bar on a Ni₃Fe/Al₂O₃ catalyst as...
compared to Ni/Al₂O₃ (CO₂ conversion: 51%, CH₄ selectivity: 91%). Also, no deactivation is observed for Ni₃Fe/Al₂O₃ during 40 h syngas exposure, while the bare Ni catalysts exhibit a decrease in CO₂ conversion from 51 to 47%.[32]

3. Structural changes of Fe catalysts during CO₂ hydrogenation and correlation with activity

While Fe-based catalyst precursors are mainly present in oxidic state, strong structural changes and phase transformation occur under syngas conditions. Iron oxides, metallic iron and iron carbides are found to coexist. Carbonaceous species formed on the catalyst crucially influence the activity as well. They are generally differentiated between adsorbed atomic carbon (Cₐ), polymeric surface carbon (Cβ), iron carbides (Cγ) and graphitic carbon deposition (Cδ).[7,33] The highly dynamic nature of Fe catalyst in CO₂/H₂ exposure is exceptional as compared to other transition metals, e.g. Ni. Typically, iron carbides are originated from activation and CO₂ hydrogenation including θ-Fe₃C, χ-Fe₅C₂ and Fe₇C₃. These carbides reveal stable structures, in which the carbon atoms are located in trigonal prismatic interstices. Moreover, metastable carbides such as ε-Fe₅C and ε'-Feₓ₂C were recently reported revealing carbon atoms in

Figure 1. Effect of temperature, pressure, molar H₂/CO₂ ratio and space velocity on CO₂ conversion (left) and CH₄ yield (right) during the CO₂ hydrogenation using bare iron oxide precursor catalysts.[12–22]
octahedral interstices.\(^{34,35}\) Also, un-stoichiometric carbides (Fe,C) formed from \(\alpha\)-Fe and iron carbides are known.\(^{36}\)

The thermodynamic stability of the carbides was investigated in dependency of temperature and gas phase composition.\(^{35}\) Generally, \(\theta\)-Fe,C exists at relatively low concentration of carbon containing gas species, while \(\chi\)-Fe,C\(_2\) and Fe,C\(_3\) appear in the presence of higher carbon amounts. Moreover, \(\chi\)-Fe,C\(_2\) is preferably produced at temperatures around 250°C. Rising temperature consequently leads to the transformation of bulk carbide composition into \(\theta\)-Fe,C as well as Fe,C\(_3\). However, corroboration of thermodynamic trends by experimental tests is rather difficult, since Fe-based catalysts reveal strongly dynamic phase transformation under syngas conditions depending on temperature, gas composition, physical-chemical properties of the samples as well as activation procedure. For example, Lee et al.\(^{35}\) demonstrate rising \(\chi\)-Fe,C\(_2\) proportion from 20 to 63% upon CO hydrogenation at 1 bar and a molar \(H_2/CO\) ratio of 4, when the temperature is increased from 250 to 400°C. But, this trend is contrary to the findings of Smit et al.\(^{34}\) as described above. Additionally, different properties of iron oxide precursors strongly influence CO hydrogenation activity as well as structural changes of the catalysts.\(^{32}\)

Different CH\(_4\) yields are obtained during CO hydrogenation at 300°C and 10 bar on Fe,O\(_2\) catalysts, when varying the preparation method, e.g. precipitation (Y(CH\(_4\)) = 7%) and template-assisted synthesis procedure (Y(CH\(_4\)) = 3%). Also, the spent precipitation catalysts are mainly composed of Fe,O\(_4\) (72%) and a relatively small amount of \(\chi\)-Fe,C\(_2\) (28%), while catalysts prepared by template-assisted technique exhibit iron carbide proportion above 80% under the same conditions. Moreover, it is common, that Fe-based catalysts do not reach stationary performance and composition over long time on stream crucially impeding comparison of different materials. Structural changes of a bare Fe,O\(_2\) catalyst during CO\(_2\) hydrogenation at 300°C, 10 bar and a molar \(H_2/CO\) ratio of 2 occur even after more than 100 h.\(^{36}\) After activation by \(H_2\) at 400°C this catalyst exhibits fast carburization in the initial stage of syngas reaction. Subsequently, the amount of \(\chi\)-Fe,C\(_2\) rises, whereas the \(\theta\)-Fe,C proportion declines. Also, in the first hours of reaction Fe,O\(_4\) appears (ca. 27%). This partial oxidation of the catalyst is generally ascribed to the presence of CO, and H,O (Eq. 1 and 2). Similar findings are observed for CO\(_2\) hydrogenation at 320°C, 1 bar and a molar \(H_2/CO\) ratio of 4 over bare Fe,O\(_2\) catalysts.\(^{36}\) After \(H_2\) pre-exposure, the amounts of \(\theta\)-Fe,C and \(\chi\)-Fe,C\(_2\) continuously increase, while a maximum Fe,O\(_4\) ratio of 34% is found tentatively decreasing with ongoing time on stream.

It is widely assumed, that iron carbides represent active species in the formation of hydrocarbons during CO\(_2\) hydrogenation.\(^{37,38}\) However, no unanimous understanding exists on detailed structure-activity correlations as well as the role of different bulk carbide phases. Some groups also suggest the important participation of surface carbon species (C\(_\text{ad}\) and C\(_\text{de}\)) in the formation of hydrocarbons, while bulk carbide structures mainly act as spectator species.\(^{39,40}\) Niemantsverdriet et al.\(^{40}\) distinguished three reaction models for Fe-based Fischer-Tropsch synthesis, which are basically relevant for the CO\(_2\) hydrogenation on Fe catalysts. In the carbide model, the iron carbide bulk structure of the catalyst determines the number of active surface carbide sites. The competition model assumes surface iron atoms as active sites, which allow dissociative adsorption of CO\(_2\). Subsequently, these surface carbon atoms (C\(_\text{ad}\)) are involved in three different reactions, i.e. diffusion in the bulk and formation of iron carbides, reaction with adsorbed H leading to formation of hydrocarbons as well as polymerization into less reactive bulk carbon species. Finally, in the slow activation model, hydrogenation is supposed to occur at surface complexes consisting of Fe, C and H, while the previous CO adsorption and dissociation is faster than all the following reactions. Typically, initial hydrogenation activity is rather low within this model, since the surface complexes are formed at a slow rate. On the contrary, mechanisms of catalyst deactivation are discussed more consistently. Oxidation of the catalysts towards Fe,O\(_3\) is widely accepted as one of the main deactivation routes of CO\(_2\) hydrogenation. Also, the deposition of less reactive bulk carbon entities (C\(_\text{b}\)) consequently leading to blocking of active surface sites contributes to the catalyst deactivation.\(^{41}\) These carbon moieties are formed by polymerization and agglomeration of surface carbon, especially at high temperatures and long time on stream. Finally, morphological changes also occur under syngas conditions including attrition and break-up of catalyst particles caused by physical stress associated with phase transformation and carbon deposition.\(^{41}\)

4. Characterization of Fe catalysts exposed to syngas

Since the properties of Fe catalysts essentially control the catalytic activity as well as phase transformations upon CO\(_2\) hydrogenation, detailed characterization of spent samples is mandatory for fundamental structure-activity correlations and identification of active species. Due to the variety of structural changes, which take place during the conversion (section 3), complementary characterization methods are needed. Therefore, advantages as well as limitations of the different techniques often used in literature are critically evaluated. Analysis of bulk phase composition is mainly made by X-ray diffraction (XRD) and \(^{57}\)Fe Mössbauer spectroscopy. Usually, Fe catalysts are passivated in situ after CO\(_2\) hydrogenation in order to avoid oxidation of Fe and C species, which are not stable under atmospheric conditions. This is done by introducing small amounts of O\(_2\) (<1 vol.%) in flowing inert gas at room temperature.\(^{42}\) Stable carbides, e.g. \(\theta\)-Fe,C\(_2\), \(\chi\)-Fe,C\(_2\) and Fe,C\(_3\), metallic Fe and Fe,O\(_4\) are easily distinguishable by XRD. Contrary, metastable carbides are difficult to analyze, because they often reveal distorted crystalline structures as well as amorphous entities. Furthermore, relatively small crystallite sizes impede precise identification due to reflex broadening.

Additionally, these carbideic structures are hardly stable under atmospheric conditions, thus requiring in situ XRD analyses. These measurements can be conducted at relevant temperatures as well as elevated pressures.\(^{43,44}\) Indeed, distinct phase
assignment of ε-carbides (ε-Fe2C and ε'-Fe2,3C) is focused in several studies. Simulated XRD patterns of ε-Fe2C and ε'-Fe2,3C provide identical lattice parameters and indicate some differences in the site occupancy of carbon atoms. To overcome this limitation of XRD and to identify amorphous structures as well as small Fe crystallites 57Fe Mössbauer spectroscopy is useful. Simulated Mössbauer spectra of ε-Fe2C consist of only one sextet with magnetic splitting of 18.0 T reflecting uniform chemical environment of the Fe atoms. In contrast to that, ε'-Fe2,3C reveals six sub-bands with hyperfine fields between 17.1 and 25.9 T. Thus, differentiation of these iron carbides is basically feasible. However, the analysis of iron carbide mixtures by 57Fe Mössbauer spectroscopy is often very difficult due to strong overlapping of specific sub-spectra with nearly identical hyperfine fields. This effect is also observed for the sextet of θ-Fe2C with hyperfine field of 20.8 T at room temperature being in a similar range of one of the three sub-bands of γ′-Fe2C2 (21.7 T at room temperature). Table 1 shows the Mossbauer parameters of 15 θ-Fe2C/γ′-Fe2C2 mixtures, which we have prepared by exposing different iron oxide precursors to a mixture of H2 and CO with a molar ratio of 4 at 400°C and 1 bar for 18 h. Differences in isomer shift (δ), quadrupole splitting (ΔEQ) and magnetic splitting (B0) are ascribed to limited resolution of respective spectra during fitting, especially for small sub-bands, as well as small changes in the chemical environment of the Fe atoms.

Moreover, carbide structures with particle sizes below ca. 10 to 13 nm cause typical superparamagnetic duplets in respective Mössbauer spectra. However, the assignment to specific iron carbide phases as well as differentiation of oxidic entities is difficult, since isomer shifts and quadrupole splittings are in a similar range. Therefore, complementary analytical techniques such as carbon content determination, temperature programmed hydrogenation (TPH) and X-ray absorption spectroscopy (XANES, EXAFS) are required. The latter is particularly useful for the ex situ and in situ characterization of amorphous structures towards the oxidation state and coordination of Fe species, consequently complementing XRD analysis. For CO2 hydrogenation on Fe catalysts, this technique is often employed for determination of the carburation degree during activation or syngas reaction as well as the amount of oxidized Fe moieties in the catalysts. One challenge of EXAFS and XANES techniques is the small sample amount, which is necessary for transmission of the X-rays. Therefore, combination with additional in situ techniques and detection of small proportions of gas phase products might become difficult to elucidate structure-activity relations.

For the investigation of structural evolution as well as formation of carbonaceous species, laser Raman spectroscopy (LRS) is a useful method. LRS can also be taken for in situ measurements under typical reaction and activation conditions. One drawback of LRS is the possible catalyst damage or transformation by the power input of the laser. However, this issue can be overcome with certain adjustment of settings such as changing laser frequency, lowering the laser power and measurement time. The lattice vibrational modes of iron carbides are Raman inactive as exemplarily shown for Fe2C. Despite this, LRS is a suitable technique to follow the carburation of Fe catalysts. Taking into consideration carbon-stretching vibrations, disordered sp2-hybridized carbon moieties (D band at 1340 cm−1) and crystalline graphitic entities (G band at 1600 cm−1) are reliably differentiated as shown for syngas exposure of α-Fe2O3 at 450°C. Additionally, formation of Fe2O3 is reflected by the LRS peak at about 660 cm−1. Moreover, carburization of Fe catalysts, e.g. α-Fe2O3, under syngas conditions is qualitatively estimated by the D and G bands. More detailed, both LRS features continuously increase with time on stream after CO/H2 activation, while rise in intensity is less pronounced after CO activation indicating limited carburation of the catalyst. Furthermore, intensity ratio of G and D bands is higher for CO/H2-activated catalyst as compared to CO activation indicating substantial formation of inactive graphite-like carbon species. Additionally, temperature programmed hydrogenation (TPH) is a powerful tool for the characterization of carbonaceous species formed on Fe catalysts during CO2 hydrogenation. After CO2 hydrogenation, respective catalyst is cooled to room temperature in inert gas and then H2 is supplied, while ramping the temperature. In TPH, solid carbon species are hydrogenated to yield CH4. According to the temperature, the CH4 formation is assigned to different carbon entities. CH4 production regimes imply atomic surface carbon (Cα: 270–390°C), polymeric, amorphous carbon entities (Cα: 420–455°C), iron carbides (Cγ: 480–690°C) and less reactive graphitic carbon (Cγ: 600–750°C). However, the TPH profile of γ-Fe2O3 catalyst obtained after CO2 hydrogenation at 400°C and 1 bar for 18 h shows two distinct CH4 peaks at ca. 310 and 470°C (Figure 2). XRD analysis of this catalyst after reaction indicates complete transformation into a mixture of θ-Fe2C and γ′-Fe2C2. When the TPH is stopped after the first CH4 peak, XRD as well as 57Fe Mössbauer spectroscopy both evidence exclusive presence of α-Fe. Hence, the TPH peak ranging from 220 to 400°C is clearly attributed to the complete hydrogenation of the iron carbides. As a consequence, the assignment of the CH4 signals should be made by using accompanying characterization methods, since the TPH profiles also depend on the physical-chemical proper-

### Table 1. 57Mössbauer parameters of 15 θ-Fe2C/γ′-Fe2C2 mixtures prepared from different iron oxide precursors by exposure to H2 and CO2 with a molar ratio of 4 at 400°C and 1 bar for 18 h.

| δ (mm s−1) | ΔEQ (mm s−1) | B0 (T) |
|------------|--------------|--------|
| θ-Fe2C     | γ′-Fe2C2     |        |
| 0.28–0.38  | 0.22–0.31    | 0.14–0.17 |
| 0.24–0.34  | 0.06–0.12    | 0.09–0.16 |
| 0.20–0.30  | 0.03–0.13    | 0.06–0.16 |
| 0.13–0.20  | 0.03–0.13    | 0.03–0.23 |
| 0.23–0.35  | 0.12–0.20    | 0.09–0.16 |
| 0.15–0.26  | 0.10–0.20    | 0.11–0.15 |
| 0.28–0.38  | 0.20–0.32    | 0.15–0.20 |

[a] Measurements were made at ambient conditions and 82 K using a modular 57Fe Mössbauer spectrometer (WissEl) with a 100 mCi 57Co source operated in constant acceleration mode; spectra were fitted using least square procedure assuming Lorentzian peak shape, while respective parameters are reported relative to α-Fe.
The authors declare no conflict of interest.

Keywords: CO₂ · hydrogenation · methanation · iron · catalyst
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