Fe based core–shell model catalysts for the reaction of CO₂ with H₂

Johann Kirchner¹ · Christian Zambrzycki² · Zeynep Baysal¹ · Robert Güttel² · Sven Kureti¹

Received: 16 June 2020 / Accepted: 26 August 2020 / Published online: 7 September 2020
© The Author(s) 2020

Abstract

Fe@SiO₂ core–shell model catalysts were investigated for the conversion of CO₂ and H₂ into CH₄, CO and H₂O. For evaluation of the effect of core size on the catalytic activity, samples with Fe particle sizes of 4, 6 and 8 nm were prepared. Fresh and spent catalysts were thoroughly characterized by X-ray diffraction, ⁵⁷Fe Mössbauer spectroscopy, transmission electron microscopy, temperature programmed hydrogenation and X-ray photoelectron spectroscopy. As a result, the yield of the major product CO as well as CH₄ was increased with Fe core size. Additionally, growing Fe cores led to stronger carburization and higher amount of reactive carbide entities, which drive the CH₄ formation. Finally, formation of inactive bulk carbon deposition is strongly suppressed for the core–shell catalysts in comparison to bulk iron oxide catalysts used for CO₂ hydrogenation.

Keywords Catalyst · Core–shell · Iron · CO₂ hydrogenation · Particle size · Structure–activity correlation

Introduction

Rising emission of greenhouse gases and their impact on global climate increasingly attracts attention on the sustainable utilization of CO₂ [1]. In this context, the hydrogenation of CO₂ is widely considered to yield valuable products like methane

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s11144-020-01859-9>) contains supplementary material, which is available to authorized users.

✉ Sven Kureti
sven.kureti@icc.tu-freiberg.de

¹ Institute of Energy Process Engineering and Chemical Engineering, Chair of Reaction Engineering, Technical University of Freiberg, Fuchsmuehlenweg 9, 09599 Freiberg, Germany

² Institute of Chemical Engineering, Ulm University, Albert-Einstein-Allee 11, 89081 Ulm, Germany

[2, 3], higher hydrocarbons [4–6] and methanol [7, 8]. For the CO₂ based synthesis of hydrocarbons Fe catalysts are known to be effective [6, 9, 10], whereas they undergo complex phase transformations and structural changes upon reaction [9, 11–13]. Catalytic activity is strongly influenced by reduction, oxidation and carburization of bulk Fe phases as well as by different types of carbon entities formed during hydrogenation [14]. The resulting dynamic behavior of the Fe catalysts hinders the unraveling of active sites and the understanding of activation and deactivation processes. These effects and processes occurring during CO₂ methanation on Fe catalysts are highlighted in a recent review article [15]. Furthermore, important structural properties of the catalysts, such as particle and crystallite size often reveal broad distributions, which additionally impede the correlation of structure and activity, particularly for bare Fe catalysts [10]. Finally, iron oxides are also known to catalyze the water gas shift reaction [16].

For investigation of structure–activity relations, nanostructured core–shell catalysts offer unique properties making them suitable as model materials in catalysis research [17, 18]. For instance, changes of size and shape of the active core nanoparticles upon conversion can easily be studied by transmission electron microscopy (TEM), as the core–shell arrangement is well-defined and stable during reaction [19].

Fe based core–shell catalysts are already studied for a broad variety of important catalytic processes, e.g. esterification [20], ammonia decomposition [19], alcohol oxidation [21], olefin hydrogenation [22] and Fischer–Tropsch synthesis [23]. Contrary, no papers are reported so far for the investigation of Fe containing core–shell catalysts in the hydrogenation of CO₂ to CH₄ (CO₂ + 4H₂ ⇌ CH₄ + 2H₂O; ΔH = − 165 kJ mol^{−1}). Additionally, the reverse water gas shift reaction is often reported as a competing reaction of methanation when using Fe catalysts (CO₂ + H₂ ⇌ CO + H₂O; ΔH = 41 kJ mol^{−1}) [11].

In this study, core–shell model catalysts with different sizes of nanoparticulate Fe cores embedded in a SiO₂ shell were prepared and thoroughly characterized. Additionally, the catalysts were tested for the reaction of CO₂ and H₂ with particular focus on the selectivity of CH₄ versus CO as well as the influence of Fe particle size on catalytic activity. For evaluation of structural changes upon the conversion and the effect of Fe core size on catalytic performance, fresh and spent samples were physical-chemically characterized by X-ray diffraction (XRD), ⁵⁷Fe Mössbauer spectroscopy, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) as well as temperature-programmed hydrogenation (TPH). Bare γ-Fe₂O₃, which was recently reported as effective CO₂ methanation catalyst, was taken as a reference sample [10].

Experimental

Preparation of the core–shell catalysts

Spherical silica encapsulated iron catalysts were prepared using an adapted reverse microemulsion method. For the oil phase 100 mL cyclohexane (VWR Chemicals,

AnalaR NORMAPUR[®]) were mixed with 34.2 g of polyoxyethylene (10) cetyl ether (Brij[®] C10, Sigma Aldrich/Merck) in a round-bottom flask and heated to 50 °C. Subsequently, 5 mL of a 1 M aqueous FeCl₃ solution (ACROS Organics, p.a.) were added to the mixture under continuous stirring. After 30 min of homogenization 3 mL of hydrazine hydrate (aqueous solution, 35 wt%, Sigma Aldrich/Merck) were added dropwise and slowly to the solution followed by continuously stirring for 1 h. The color of the solution changed from bright yellow to dark brown which indicates the formation of iron nanoparticles. To encapsulate the obtained iron oxide nanoparticles in silica 21.4 mL tetraethyl orthosilicate (TEOS, Merck, p.a.) was added to the suspension followed by 3 mL of a 5 M aqueous ammonia solution (Carl Roth, 30wt%, ROTIPURAN[®]). This mixture was stirred continuously 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). With defined variation of the surfactant type and SiO₂ precursor it is possible to control Fe particle sizes in a range from 3.5 to 8 nm.

Reaction conditions for catalytic tests

For catalytic tests 200 mg of as-prepared core-shell samples as well as the bare γ -Fe₂O₃ reference was used taking a grain size of 125 to 250 μ m. Grains were made by pressing the powder samples at 0.5 MPa followed by crushing and sieving. Respective catalyst was fixed in a glass tube 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 CO₂ hydrogenation, the catalyst was activated in 20 vol% H₂ in N₂ with a total flow of 500 ml/min (STP) at 350 °C for 3 h. Subsequently, reaction temperature was adjusted in N₂ flow and the hydrogenation was started at 1 bar and a stoichiometric molar H₂/CO₂ ratio of 4 with a CO₂ proportion of 10 vol.%. N₂ was taken as balance. The total flow was 500 ml/min (STP) resulting in a space velocity of ca. 52,000 h⁻¹ (69.2 mmol(CO₂)/mol(Fe)/s).

Catalyst characterization

Powder X-ray diffraction (XRD) was performed on a D8 Discover (Bruker-AXS) with Co K α radiation (35 kV, 45 mA). The diffractograms were recorded in 2 θ mode from 15° to 85° 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.

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

Bright field TEM micrographs were taken by a Zeiss TEM 109 equipped with a CCD camera. For sample preparation for these measurements, a droplet of ethanol (VWR 96% Ph. Eur.) solution containing the sample powder (ca. 0.5 mg/ml) was deposited on a carbonized Cu grid, followed by evaporation of the ethanol.

X-ray photoelectron spectroscopy (XPS) was performed for the core-shell catalysts using an Escalab Xi+ (Thermo Scientific) with Avantage software for data acquisition and analysis. All analyses were carried out under high vacuum conditions (10^{-7} mbar) using monochromatic Al K_{α} radiation. Surface charge was compensated by an electron flood gun. High resolution spectra of Si2p, O1s, C1s and Fe2p were measured with a pass energy of 25 eV.

Results and discussion

Preparation of the spherical encapsulated Fe catalysts was done by microemulsion method as recently published [24] (detailed description in ESI) adjusting a Fe mass fraction of 15 wt% for all samples. The Fe particle size distribution of three different as-prepared core-shell catalysts was obtained from TEM micrographs (Fig. 1, Fig. S1) resulting in average core sizes of 4, 6 and 8 nm, which is expressed by the respective sample codes used within this paper, e.g. Fe(6)@SiO₂ for average core size of 6 nm. The total particle size of all samples amounts to ca. 16 nm leading to a decreasing shell thickness with increase in core size.

Respective XRD patterns reveal a broad reflex at ca. 27° (2 θ) assigned to the amorphous SiO₂ shell, while γ -Fe₂O₃ or Fe₃O₄ represent the major Fe phase (Fig. 2, left). Differentiation of both phases by XRD is rather difficult, since they imply very similar crystalline structures and lattice parameters. However, ⁵⁷Fe Mössbauer spectra excluded Fe₃O₄, since only superparamagnetic high-spin Fe³⁺ species appeared. These entities are reflected by their isomer shift ($\delta=0.29\text{--}0.35$ mm s⁻¹) as well as quadrupole splitting ($\Delta E_Q=0.51\text{--}0.68$ mm s⁻¹) (Fig. 2 right, Table S2) [25, 26].

Fig. 1 TEM micrograph of Fe(8)@SiO₂ (left) and Fe core particle size distribution of the core-shell catalysts (right) each based on analysis of more than 200 particles

Fig. 2 XRD patterns (left) with reflexes assigned to γ -Fe₂O₃ (filled diamond) and SiO₂ (open square) and ⁵⁷Fe Mössbauer spectra (right) at room temperature of the as-prepared core-shell catalysts; (hkl) indices refer to γ -Fe₂O₃

Also, the absence of magnetic coupling, which would produce a sextet pattern, suggests Fe₂O₃ particles smaller than ca. 13 nm [27, 28]. Furthermore, the crystallite size of γ -Fe₂O₃ estimated from Scherrer equation based on the X-ray diffractograms amounts to 4, 5 and 6 nm for Fe(4)@SiO₂, Fe(6)@SiO₂ and Fe(8)@SiO₂, respectively, showing a similar trend as compared to TEM.

Exemplarily, Fig. 3 and Table S3 demonstrates the CO₂ hydrogenation performance of Fe(8)@SiO₂ referring to a gas hourly space velocity of 52,000 h⁻¹, an operation pressure of 1 bar and a stoichiometric H₂/CO₂ ratio. The catalytic tests were performed after H₂ activation and are related to steady-state conditions (detailed reaction conditions in ESI). In the reaction of CO₂ with H₂, CO and CH₄ are the only carbon containing products detected in the gas phase. Catalytic

Fig. 3 Steady-state formation rates of CH₄ and CO taken after syngas exposure for 30 min for different temperatures in conversion of CO₂ and H₂ on Fe(8)@SiO₂ catalyst; conditions: p=1 bar, y(H₂)/y(CO₂)=4, GHSV=52,000 h⁻¹

performance is expressed in terms of reaction rate of CH_4 and CO (molar amount of CH_4 or CO formed per time and total Fe amount). For temperatures between 300 and 550 °C, CO represents the major product, while its formation rate continuously increases with rising temperature. This effect is ascribed to the endothermic reverse water gas shift reaction, which is thermodynamically favored at elevated temperatures. The relatively low CH_4 selectivity (4% at 300 °C and decreasing with inclining temperatures) is attributed to the high space velocity ($52,000 \text{ h}^{-1}$) and atmospheric operation pressure. The rate of CH_4 formation goes through a maximum at 400 °C associated with kinetic limitation at lower temperatures and increasingly accelerating backward reaction at higher temperatures. It has to be stated, that the present work aims to investigate the influence of particle size on the production of CO and CH_4 without optimization of the CH_4 yield. Thus, although relatively small total CO_2 conversions below 6% are achieved, the reaction conditions are suitable for this fundamental approach. Moreover, atmospheric pressure conditions lead to suppression of higher hydrocarbon production thus admitting the methanation as model reaction for CO_2 hydrogenation without chain propagation.

The apparent activation energy of CO_2 conversion on Fe(8)@SiO_2 is estimated as 60 kJ/mol (Fig. S2), which underlines the absence of significant mass transfer limitations. Note that no significant CO_2 consumption is found in hydrogenation on bare SiO_2 clearly showing the catalytic effect of the Fe cores.

The effect of Fe core size on catalytic performance was investigated at 400 °C, since at this temperature Fe(8)@SiO_2 reveals highest methanation efficiency (Fig. 3). As a result, Fig. 4 demonstrates inclining rate of CH_4 and CO formation with increase in size of Fe particles encapsulated inside the SiO_2 shell. For comparison, bare $\gamma\text{-Fe}_2\text{O}_3$ (crystallite size ca. 25 nm; XRD pattern in Fig. S4) shows about 10 times higher CH_4 and 15 times higher CO production rate as referred to the best core-shell catalyst, i.e. Fe(8)@SiO_2 . While CO_2 conversion is generally enhanced for larger Fe particles, the CH_4 selectivity is nearly the same (ca. 3%) for the three investigated core-shell catalysts.

Fig. 4 Steady-state formation rates of CH_4 and CO in conversion of CO_2 and H_2 after 17 h at 400 °C on the core-shell catalysts with different Fe core sizes as well as bare $\gamma\text{-Fe}_2\text{O}_3$ as reference; conditions: $p=1 \text{ bar}$, $y(\text{H}_2)/y(\text{CO}_2)=4$, $\text{GHSV}=52,000 \text{ h}^{-1}$

The TEM images of the samples taken after CO_2 conversion show brighter regions in the inner part of the core–shell structures (Fig. S3). This effect suggests some shrinkage of the cores associated with reduction of the Fe oxide precursor to metallic Fe upon the H_2 activation. This is in line with the higher density of $\alpha\text{-Fe}$ ($\rho = 7.87 \text{ g/cm}^3$) as compared to $\gamma\text{-Fe}_2\text{O}_3$ ($\rho = 4.86 \text{ g/cm}^3$) [29]. Moreover, it is assumed, that the volume reduction does not substantially change by carburization, which partially occurs during CO_2 hydrogenation, e.g. $\rho(\text{Fe}_3\text{C}) = 7.69 \text{ g/cm}^3$. The observed shrinkage also indicates the permeability of the SiO_2 shell, which is crucial for the gas transport to the catalytically active Fe core. Additionally, the TEM images reveal an intact core–shell structure after hydrogenation without any thermal sintering of the Fe cores or appearance of possible coke deposits.

For detailed characterization of carbonaceous species formed during syn-gas reaction, TPH analyses were performed after 17 h time on stream referring to steady-state conditions (Fig. 5). The TPH profiles obtained for the three core–shell catalysts exhibit minor formation of CH_4 in the temperature range from 280 to 400 °C, while a strong CH_4 feature occurs between 420 and 700 °C. In the literature, specific hydrogenation regimes are roughly ascribed to different types of carbon species including adsorbed surface carbon (270–390 °C), polymeric surface carbon (420–460 °C), iron carbides (480–690 °C) and graphitic deposits (above 690 °C) [30]. Based on this assignment, the major CH_4 formation is tentatively referred to carbidic carbon species originated from the carburization of Fe cores upon CO_2 hydrogenation. Carburization is quantitatively checked by integrating the respective TPH signal (400–700 °C) revealing carbon amounts of 22, 35 and 40 μmol for the samples with an average Fe core size of 4, 6 and 8 nm, respectively. From these results it is deduced, that the carburization of the catalysts clearly depends on the Fe core size, i.e. the proportion of carbon increases with the size of the Fe particle. Additionally, the quantitative carbon analyses by TPH imply molar C/Fe ratios below 0.1 for the three catalysts confirming incomplete iron carbide formation. Assuming exclusive formation of Fe_3C , which is

Fig. 5 TPH patterns and respective total carbon amounts of the different core–shell catalyst after CO_2 hydrogenation for 17 h at 400 °C and 1 bar; Fe amount is 535 μmol for all samples

known as preferred carbide phase in hydrogenation of CO_2 under the established conditions [10], the carburization degree of $\text{Fe}(8)@\text{SiO}_2$ is about 20% only.

^{57}Fe Mössbauer spectra of the spent core–shell catalysts (Fig. S5, Table S4) comprise two duplets, respectively, whereas no iron carbide sextets appear. However, iron carbide particles smaller than ca. 10 nm are known to form typical superparamagnetic duplets with isomer shift and quadrupole splitting close to the values of the pronounced duplet ($\delta=0.37\text{--}0.51\text{ mm s}^{-1}$, $\Delta E_Q=0.72\text{--}0.98\text{ mm s}^{-1}$). In the spent samples, the latter features reveal fractions above 65%. Albeit, accurate quantification of superparamagnetic carbide structures is limited, since the Mössbauer parameters of carbidic and oxidic Fe^{3+} duplets are in a similar range and superimposition due to relatively broad line widths cannot be excluded [31]. It may be speculated, that superparamagnetic iron carbide species contribute to this intense duplet, since the quadrupole splitting of the spent samples tentatively increases as compared to the as-prepared catalysts. Also, the calculated Fe_3C amount based on the TPH results generally fits to the relative areas of this duplet (68–87%) corroborating the incomplete carbide formation during CO_2 hydrogenation. Moreover, an additional duplet is found for the spent samples, which is assigned to Fe^{2+} species according to the isomer shift ($\delta=0.83\text{--}1.26\text{ mm s}^{-1}$) and quadrupole splitting ($\Delta E_Q=1.96\text{--}2.27\text{ mm s}^{-1}$). Furthermore, the proportion of Fe^{2+} increases with rising Fe core size from 13% ($\text{Fe}(4)@\text{SiO}_2$) to 27% ($\text{Fe}(6)@\text{SiO}_2$) and finally 32% ($\text{Fe}(8)@\text{SiO}_2$).

Furthermore, no significant differences in the surface compositions of the as-prepared and spent catalysts are observed by XPS considering the quantities of Si, O, C and Fe (Fig. S6). However, molar C and Fe surface fractions are below 1% consequently leading to small intensities in respective spectra. Moreover, the formation of graphitic carbon species during conversion of CO_2 and H_2 is excluded due to the absence of the corresponding peak at ca. 284.5 eV [32]. This corroborates the TEM results, which do not provide indication for carbon deposits. In contrast to that, TPH study of bare $\gamma\text{-Fe}_2\text{O}_3$ performed after the $\text{CO}_2\text{--H}_2$ reaction shows drastic deposition of bulk carbon species (ca. 9100 μmol [10]), which reveals lower hydrogenation activity compared to Fe carbides. However, catalytic activity is higher as referred to the core–shell samples possibly associated with complete carburization of the bulk catalyst. Indeed, faster carburization of bulk relative to nanosized Fe catalysts was recently reported [33].

Using methanation as a key reaction for determination of CO_2 hydrogenation activity, the CH_4 formation rate of the core–shell catalysts is correlated with the amount of carbidic carbon derived from TPH. As a result, Fig. 6 suggests the importance of the abundance of Fe carbides for the methanation of CO_2 . This interpretation is in good agreement with the literature demonstrating carbidic structures as active species in CO_x hydrogenation on Fe catalysts [9, 10].

Conclusion

In summary, core–shell catalysts with defined Fe core sizes were investigated as model catalysts for the conversion of CO_2 with H_2 . The study shows that reverse water gas shift reaction, i.e. production of CO, represents the major pathway with

Fig. 6 Correlation of carbon quantity obtained from TPH and CH_4 formation rate of the core-shell catalysts with different Fe core sizes (the line is just a guide for the eyes)

substantial formation of CH_4 , while higher hydrocarbons are not observed. Due to the synthesis of unique core-shell catalysts with narrow particle size distributions a valid correlation of catalytic performance and catalyst structure (particle size) is obtained. More detailed, rising Fe particle sizes from 4 to 8 nm leads to clear enhancement of the CO and CH_4 formation. Additionally, growing Fe core size results in stronger carburization and active Fe carbide entities, which are responsible for the increasing CH_4 production. Furthermore, the carburization behavior for the core-shell catalysts differ significantly from that of bulk Fe catalysts, as recently reported in our previous work, as well [34]. This observation may be caused by a confinement effect of the encapsulated Fe nanoparticles within a silica shell [35] and requires further research. Despite the focus on fundamental studies in this work, Fe based core-shell catalysts might be of technical relevance, since they do not imply any pronounced susceptibility towards coke deposition as reported for bulk Fe catalysts [10].

Funding Open Access funding provided by Projekt DEAL.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

1. Köne AÇ, Büke T (2010) *Renew Sustain Energy Rev* 14:2906–2915
2. Rönsch S, Schneider J, Matthischke S, Schlüter M, Götz M, Lefebvre J, Prabhakaran P, Bajohr S (2016) *Fuel* 166:276–296
3. Wei W, Jinlong G (2011) *Front Chem Sci Eng* 5:2–10
4. Riedel T, Claeys M, Schulz H, Schaub G, Nam S-S, Jun K-W, Choi M-J, Kishan G, Lee K-W (1999) *Appl Catal A: Gen* 186:201–213
5. Geng S, Jiang F, Xu Y, Liu X (2016) *ChemCatChem* 8:1303–1307
6. Albrecht M, Rodemerck U, Schneider M, Bröring M, Baabe D, Kondratenko EV (2017) *Appl Catal B: Environ* 204:119–126
7. Kiss AA, Pragt JJ, Vos HJ, Bargeman G, de Groot MT (2016) *Chem Eng J* 284:260–269
8. Bukhtiyarova M, Lunkenbein T, Kähler K, Schlögl R (2017) *Catal Lett* 147:416–427
9. de Smit E, Weckhuysen BM (2008) *Chem Soc Rev* 37:2758–2781
10. Kirchner J, Anollec JK, Lösch H, Kureti S (2018) *Appl Catal B: Environ* 223:47–59
11. Lee M-D, Lee J-F, Chang C-S (1990) *J Chem Eng Jpn* 23:130–136
12. Pérez-Alonso FJ, Herranz T, Rojas S, Ojeda M, Lópezranados M, Terreros P, Fierro JLG, Gracia M, Gancedo JR (2007) *Green Chem* 9:663–670
13. Herranz T, Rojas S, Perezalonso F, Ojeda M, Terreros P, Fierro J (2006) *J Catal* 243:199–211
14. Bartholomew CH (2001) *Appl Catal A: Gen* 212:17–60
15. Kirchner J, Baysal Z, Kureti S (2020) *ChemCatChem* 12:981–988
16. Newsome DS (1980) *Catal Rev Sci Eng* 21:275–318
17. Ghosh Chaudhuri R, Paria S (2012) *Chem Rev* 112:2373–2433
18. Zeng B, Hou B, Jia L, Wang J, Chen C, Sun Y, Li D (2013) *ChemCatChem* 5:3794–3801
19. Feyen M, Weidenthaler C, Güttel R, Schlichte K, Holle U, Lu A-H, Schüth F (2011) *Chemistry* 17:598–605
20. Tai Z, Isaacs MA, Durndell LJ, Parlett CM, Lee AF, Wilson K (2018) *Mol Catal* 449:137–141
21. Yao LH, Li YX, Zhao J, Ji WJ, Au CT (2010) *Catal Today* 158:401–408
22. Hudson R, Rivière A, Cirtiu CM, Luska KL, Moores A (2012) *Chem Commun* 48:3360–3362
23. Ni Z, Qin H, Kang S, Bai J, Wang Z, Li Y, Zheng Z, Li X (2018) *J Colloid Interface Sci* 516:16–22
24. Misra A, Zambrycki C, Klokner G, Kotyrbá A, Anjass MH, Castillo IF, Mitchell SG, Güttel R, Streb C (2019) *Angew Chem* 131:1–6
25. Kuzmann E, Nagy S, Vértes A (2003) *Pure Appl Chem* 75:801–858
26. Mercante LA, Melo WWM, Granada M, Troiani HE, Macedo WAA, Ardison JD, Vaz MGF, Novak MA (2012) *J Magn Magn Mater* 324:3029–3033
27. Alfassi ZB (1994) *Chemical analysis by nuclear methods*. Wiley, New York
28. Siddique M, Ahmed E, Butt NM (2010) *Phys B* 405:3964–3967
29. Cornell RM, Schwertmann U (2003) *The iron oxides, structure, properties, reactions, occurrences and uses*. Wiley, Weinheim
30. Xu J, Bartholomew CH (2005) *J Phys Chem B* 109:2392–2403
31. Amelse JA, Butt JB, Schwartz LH (1978) *J Phys Chem* 82:558–563
32. Bonnet F, Ropital F, Lecour P, Espinat D, Huiban Y, Gengembre L, Berthier Y, Marcus P (2002) *Surf Interface Anal* 34:418–422
33. Cheng K, Virginie M, Ordonsky VV, Cordier C, Chernavskii PA, Ivantsov MI, Paul S, Wang Y, Khodakov AY (2015) *J Catal* 328:139–150
34. Kirchner J, Zambrycki C, Kureti S, Güttel R (2020) *Chem Ing Tech* 92:603–607
35. Ilsemann J, Straß-Eifert A, Friedland J, Kiewidt L, Thöming J, Bäumer M, Güttel R (2019) *ChemCatChem* 11:4884–4893

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.