

# Influence of Calcination Conditions on Structural and Solid-State Kinetic Properties of Iron Oxidic Species Supported on SBA-15

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Iron oxidic species supported on silica SBA-15 were synthesized with various iron loadings using two different Fe<sup>III</sup> precursors. The effect of varying powder layer thickness during calcination on structural and solid-state kinetic properties of Fe<sub>x</sub>O<sub>y</sub>/SBA-15 samples was investigated. Calcination was conducted in thin (0.3 cm) or thick (1.3 cm) powder layer. Structural characterization of resulting Fe<sub>x</sub>O<sub>y</sub>/SBA-15 samples was performed by nitrogen physisorption, X-ray diffraction, and DR-UV/Vis spectroscopy. Thick powder layer during calcination induced an increased species size independent of the precursor. However, a significantly more pronounced influence of calcination mode on species size was observed for the Fe<sup>III</sup> nitrate precursor

compared to the Fe<sup>III</sup> citrate precursor. Temperature-programmed reduction (TPR) experiments revealed distinct differences in reducibility and reduction mechanism dependent on calcination mode. Thick layer calcination of the samples obtained from Fe<sup>III</sup> nitrate precursor resulted in more pronounced changes in TPR profiles compared to samples obtained from Fe<sup>III</sup> citrate precursor. TPR traces were analyzed by model-dependent Coats-Redfern method and model-independent Kissinger method. Differences in solid-state kinetic properties of Fe<sub>x</sub>O<sub>y</sub>/SBA-15 samples dependent on powder layer thickness during calcination correlated with differences in iron oxidic species size.

## 1. Introduction

In catalysis research, revealing reliable structure-activity correlations requires reducing chemical and structural complexity of metal oxide catalysts. Therefore, dispersing metal oxides on well-defined support materials has been shown to result in suitable model systems.<sup>[1]</sup> Ordered mesoporous silica materials, e.g. SBA-15 or MCM-41,<sup>[2,3]</sup> ordered mesoporous carbon, e.g. CMK-3,<sup>[4,5]</sup> and alumina oxides<sup>[6,7]</sup> are among the most commonly applied and investigated support materials. Moreover, MgO, TiO<sub>2</sub>, ZrO<sub>2</sub> or zeolites are applied as high surface support materials in heterogeneous catalysis.<sup>[8–11]</sup> Supporting metal oxides on high surface materials can achieve highly dispersed and well-separated catalytically active sites. A further advantage is the higher thermal stability of particular metal oxide structures on support materials.<sup>[8,10,11]</sup> Dependent on the support material, metal oxides exhibit significant differences in electronic and chemical properties compared to bulk materials. Various synthesis procedures for dispersing active iron oxide species on suitable support materials have been described in

the literature. However, it remains challenging to achieve well-dispersed and small or even isolated supported iron species.<sup>[12]</sup>

Catalytic activity of supported metal oxide catalysts is influenced particularly by support material properties such as acidity and pore structure,<sup>[1,9,13]</sup> size and dispersion of catalytically active sites,<sup>[4,6,12,14,15]</sup> metal precursor,<sup>[4,6,12,16,17]</sup> and calcination conditions.<sup>[7,18]</sup> Therefore, varying only selected parameters during synthesis appears preferable for deducing reliable structure-activity correlations.<sup>[1,4,18]</sup> Iron-containing catalysts are active in various reactions, such as Fischer-Tropsch synthesis, Friedel-Crafts alkylations, NO<sub>x</sub> removal, and selective oxidation reactions.<sup>[4,7,17,19]</sup> Previously, investigations of iron-containing catalysts were reported regarding the correlation between iron species size, precursor and promotor effect, as well as calcination temperature and catalytic activity.<sup>[4,6,7,15,16,20]</sup> Al-Fatesh et al.<sup>[7]</sup> revealed a distinct effect of calcination temperature on catalytic activity of Fe/Al<sub>2</sub>O<sub>3</sub> catalysts for catalytic methane decomposition (CMD). Fe/Al<sub>2</sub>O<sub>3</sub> samples calcined at lower temperatures were reported to show higher reducibility and higher activity than samples calcined at higher temperature. Torres Galvis et al.<sup>[6]</sup> investigated the effect of precursors on catalytic performance of Fe/α-Al<sub>2</sub>O<sub>3</sub> catalysts for Fischer-Tropsch synthesis of lower olefins (FTO). They showed an impact of the precursor on both dispersion of iron species and resulting iron species size. Significant precursor-dependent differences in catalytic activity resulted only from iron loadings of 5 wt % or 10 wt %. These differences in FTO selectivity were attributed to different aggregation of iron species. Influencing the dispersion of iron species of FeO<sub>x</sub>/SiO<sub>2</sub> catalysts by various synthesis methods were reported by Arena et al.<sup>[15]</sup> and He et al.<sup>[14]</sup> Arena et al.<sup>[15]</sup> showed an enhanced MPO (selective oxidation of methane to formaldehyde) performance for low-loaded FeO<sub>x</sub>/

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SiO<sub>2</sub> catalysts obtained by adsorption/precipitation method by improving the dispersion of active sites. The increased activity in MPO reported by He et al.<sup>[14]</sup> was also attributed to higher dispersion accompanied by higher amount of isolated iron species which was achieved by sol-gel synthesis. For supported copper oxide particles, an influence of calcination mode, i.e. thickness of powder layer during calcination, has been revealed by Koch et al.<sup>[18]</sup> They reported a distinct effect of thick layer calcination on size and electronic structure of copper oxides. Thick layer calcination was associated with an increased copper particle size compared to thin layer calcination and a decreased reducibility.

Investigations of structure-activity correlations in heterogeneous catalysis are frequently performed using time-resolved measurements under non-isothermal conditions. Hence, additional solid-state kinetic analysis of experimental data measured under these conditions may be helpful in corroborating correlations of structure and function of heterogeneous catalysts.<sup>[21]</sup> Applicability of solid-state kinetic analysis to supported iron species on mesoporous silica SBA-15 was recently reported.<sup>[17]</sup> The study showed that solid-state kinetic analysis can corroborate conventional characterization of supported systems. Here, the influence of varying powder layer thickness during calcination on structural and solid-state kinetic properties of supported iron oxidic species was investigated. In addition to conventional characterization, solid-state kinetic analysis was applied to elucidate correlations between iron loading, Fe<sup>III</sup> precursor, calcination mode, and reducibility.

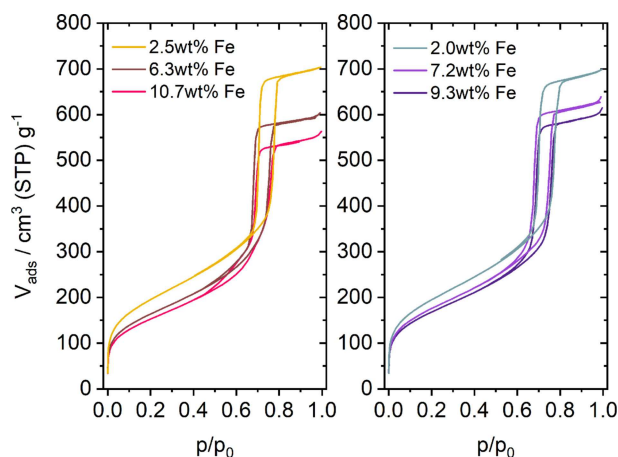
## 2. Results and Discussion

### 2.1. Sample Characterization

#### 2.1.1. Nitrogen Physisorption Measurements

Surface properties and pore structure of Fe<sub>x</sub>O<sub>y</sub>/SBA-15\_Th samples were determined from nitrogen physisorption measurements. Similar to SBA-15 support material, Fe<sub>x</sub>O<sub>y</sub>/SBA-15 samples obtained from thin layer calcination and thick layer calcination exhibited type IV nitrogen adsorption/desorption isotherms indicating mesoporous materials.<sup>[17,22,23]</sup> Figure 1 depicts physisorption isotherms of citrate\_Th and nitrate\_Th samples. Independent of the precursor, adsorption and desorption branches were nearly parallel at the hysteresis loop as expected for regularly shaped pores. Hysteresis loops of Fe<sub>x</sub>O<sub>y</sub>/SBA-15\_Th samples were identified being of type H1 according to IUPAC.<sup>[23]</sup>

A decrease in specific surface area with increasing iron loading was recently reported for Fe<sub>x</sub>O<sub>y</sub>/SBA-15 samples obtained from thin layer calcination.<sup>[17]</sup> For citrate samples, specific surface area decreased from 725.2 to 605.7 m<sup>2</sup>g<sup>-1</sup> with increasing iron loading from 2.5 to 10.7 wt%, while for nitrate samples specific surface area decreased from 703.0 to 633.1 m<sup>2</sup>g<sup>-1</sup> with increasing iron loading from 2.0 to 9.3 wt%. Specific surface area of Fe<sub>x</sub>O<sub>y</sub>/SBA-15\_Th samples decreased further compared to corresponding thin layer calcined samples



**Figure 1.** N<sub>2</sub> adsorption/desorption isotherms of Fe<sub>x</sub>O<sub>y</sub>/SBA-15\_Th samples. Left: Citrate\_Th samples. Right: Nitrate\_Th samples

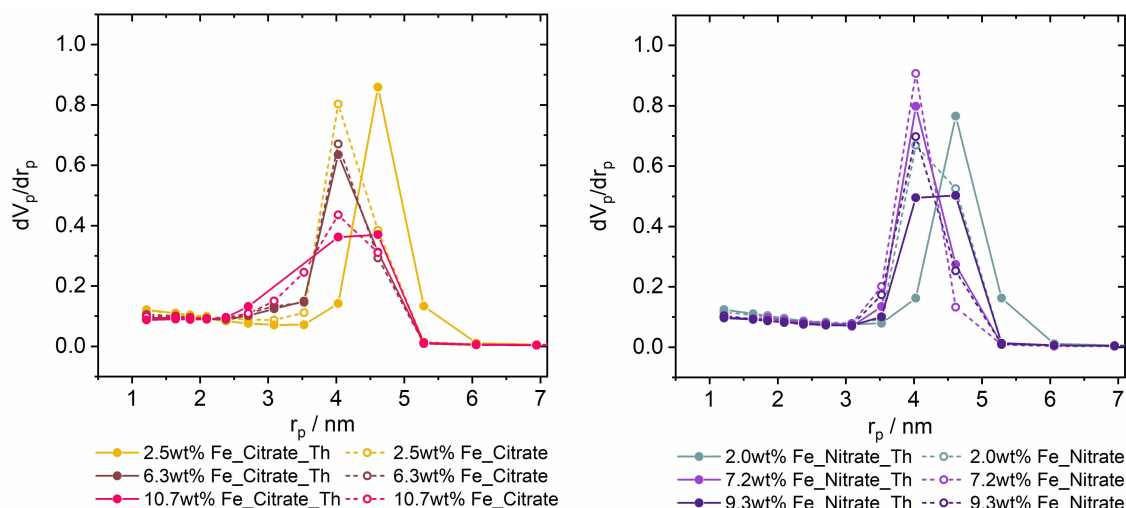
(Table 1). Pore size distributions were calculated by BJH method and revealed a narrow pore size distribution for all Fe<sub>x</sub>O<sub>y</sub>/SBA-15 samples independent of both precursor and calcination mode. Pore size distributions of Fe<sub>x</sub>O<sub>y</sub>/SBA-15\_Th samples compared to corresponding thin layer calcined samples are depicted in Figure 2. The most pronounced influence of thick layer calcination was observed for the lowest loaded citrate and nitrate sample. Narrow pore size distribution of these samples was shifted to larger pore diameters after thick layer calcination. This shift amounted to 1.16 nm.

Additionally, pore volume,  $V_{pore}$ , was determined and summarized in Table 1. Thick layer calcination induced a decrease in pore volume compared to thin layer calcination. Conversely, 7.2 wt% Fe\_Nitrate\_Th and 9.3 wt% Fe\_Nitrate\_Th showed a slight increase in  $V_{pore}$ . For Fe<sub>x</sub>O<sub>y</sub>/SBA-15\_Th samples, the decrease in specific surface area together with the decrease in pore volume with increasing iron loading indicated the presence of iron oxidic species in the mesopores of SBA-15.<sup>[20,22]</sup> Despite a slightly increased  $V_{pore}$  indicating some mesopores might remain unfilled, iron oxidic species being mainly located in the mesopores of SBA-15 seemed also likely for 7.2 wt% Fe\_Nitrate\_Th and 9.3 wt% Fe\_Nitrate\_Th.

**Table 1.** Specific surface area,  $a_{s,BET}$ , and pore volume,  $V_{pore}$ , of Fe<sub>x</sub>O<sub>y</sub>/SBA-15\_Th samples. Differences between Fe<sub>x</sub>O<sub>y</sub>/SBA-15\_Th and corresponding Fe<sub>x</sub>O<sub>y</sub>/SBA-15 samples are denoted as  $\Delta$  values.<sup>[a]</sup>

	$a_{s,BET}/$ m <sup>2</sup> g <sup>-1</sup> [b]	$\Delta a_{s,BET}/$ m <sup>2</sup> g <sup>-1</sup>	$V_{pore}/$ cm <sup>3</sup> g <sup>-1</sup> [c]	$\Delta V_{pore}/$ cm <sup>3</sup> g <sup>-1</sup>
2.5 wt% Fe_Citrate_Th	700.0 ± 0.7	-25.5	1.087 ± 0.001	-0.025
6.3 wt% Fe_Citrate_Th	592.6 ± 0.6	-58.3	0.933 ± 0.001	-0.035
10.7 wt% Fe_Citrate_Th	550.2 ± 0.6	-55.5	0.865 ± 0.001	-0.033
2.0 wt% Fe_Nitrate_Th	701.7 ± 0.7	-1.3	1.079 ± 0.001	-0.017
7.2 wt% Fe_Nitrate_Th	633.4 ± 0.6	-14.4	0.987 ± 0.001	0.016
9.3 wt% Fe_Nitrate_Th	606.0 ± 0.7	-27.1	0.943 ± 0.001	0.004

[a] Measurement errors according to standard deviation determined from multiple measurements. [b] Specific surface area,  $a_{s,BET}$ , was calculated in the relative pressure range,  $p/p_0$ , of 0.05–0.26. [c] Pore volume,  $V_{pore}$ , is based on relative pressure,  $p/p_0$ , of 0.99.



**Figure 2.** Left: Pore radius distribution of citrate\_Th and corresponding citrate samples calculated by BJH method. Right: Pore radius distribution of nitrate\_Th and corresponding nitrate samples calculated by BJH method.

Ratio of mesopore surface area,  $a_{\text{pore}}$ , calculated by BJH method<sup>[24]</sup> and specific surface area,  $a_{\text{s,BET}}$ , calculated by BET method,<sup>[25]</sup> was used for estimating the contribution of micropores to the entire surface area of SBA-15.<sup>[18,26]</sup> However, ratio of  $a_{\text{pore}}/a_{\text{s,BET}}$  cannot be equated with an absolute value for the degree of micropore filling. Furthermore, the effect of powder layer thickness during calcination on ratio of  $a_{\text{pore}}/a_{\text{s,BET}}$  was determined by calculating the difference between  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  and  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples (Table 2). Thick layer calcination induced an increased ratio of  $a_{\text{pore}}/a_{\text{s,BET}}$ , except for 2.0 wt%  $\text{Fe\_Nitrate\_Th}$  and 2.5 wt%  $\text{Fe\_Citrate\_Th}$ . These lowest loaded  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  samples possessed the same ratio of  $a_{\text{pore}}/a_{\text{s,BET}}$ , which was slightly decreased compared to that observed for corresponding  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples. Accordingly, thick layer calcination of lowest loaded samples correlated with an increased contribution of micropores to entire surface area, and hence, a lower degree of micropore filling. For iron loadings higher than 2.5 wt%, citrate\_Th samples showed higher ratios of  $a_{\text{pore}}/a_{\text{s,BET}}$  compared to nitrate\_Th samples with similar iron loading. Apparently, using the citrate precursor resulted in

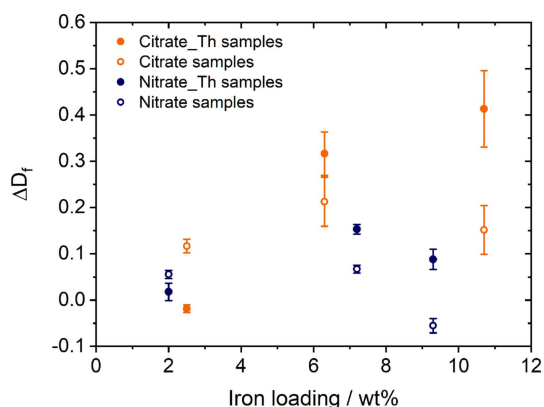
stronger interactions between SBA-15 and  $\text{Fe}^{\text{III}}$  atoms of the precursor, and hence, in higher amounts of micropore filling, independent of layer thickness during calcination. This was ascribed to the more pronounced chelating effect the citrate precursor. Moreover,  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  samples showed a precursor-dependent trend in ratio of  $a_{\text{pore}}/a_{\text{s,BET}}$  as function of iron loading. For citrate\_Th samples, increasing the iron loading correlated with an increasing ratio of  $a_{\text{pore}}/a_{\text{s,BET}}$ . Conversely, for nitrate\_Th samples, ratio of  $a_{\text{pore}}/a_{\text{s,BET}}$  only increased up to 7.2 wt% iron, but decreased with further increasing iron loading. Influence of thick layer calcination on contribution of micropores to entire surface area was more pronounced for the citrate precursor.

In addition to BET and BJH method, modified FHH method was applied for analyzing nitrogen physisorption data of  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  samples. Resulting fractal dimension  $D_f$  was used as a measure of the roughness of the surface of SBA-15.<sup>[26,27]</sup> For  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples, as well as SBA-15, the fractal dimension was recently reported ranging between 2 and 3, indicating a rough surface of the support material.<sup>[17]</sup>  $\Delta D_f$  values were calculated as difference between  $D_f$  values of SBA-15 and those of  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  samples for determining the influence of supported iron oxidic species on surface roughness of the support material (Table 2). In contrast to thin layer calcined  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples, thick layer calcined  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples possessed significantly higher differences in fractal dimension  $\Delta D_f$ . Only for the lowest loaded nitrate and citrate sample  $\Delta D_f$  values decreased due to thick layer calcination indicating an increased SBA-15 surface roughness (Table 2, Figure 3). This increased surface roughness complied with the decreased ratio of  $a_{\text{pore}}/a_{\text{s,BET}}$ . For iron loadings higher than 2.5 wt%, thick layer calcination induced significantly higher  $\Delta D_f$  values compared to thin layer calcination, and hence, a smoother SBA-15 surface. A smoothing of SBA-15 surface for  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  samples agreed with an increased degree of micropore filling. This was induced by higher aggregated and less dispersed iron oxidic

**Table 2.** Contribution of micropores to entire surface area and surface roughness for  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$ . Differences between  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  and corresponding  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples are denoted as  $\Delta$  values.

	$a_{\text{pore}}/a_{\text{s,BET}}$ <sup>[a]</sup>	$\Delta(a_{\text{pore}}/a_{\text{s,BET}})$	$\Delta D_f$ <sup>[b]</sup>	$\Delta(\Delta D_f)$
2.5 wt% $\text{Fe\_Citrate\_Th}$	0.86	-0.02	$-0.02 \pm 0.02$	-0.14
6.3 wt% $\text{Fe\_Citrate\_Th}$	0.94	0.05	$0.32 \pm 0.05$	0.11
10.7 wt% $\text{Fe\_Citrate\_Th}$	0.95	0.04	$0.41 \pm 0.08$	0.26
2.0 wt% $\text{Fe\_Nitrate\_Th}$	0.86	-0.02	$0.02 \pm 0.02$	-0.04
7.2 wt% $\text{Fe\_Nitrate\_Th}$	0.90	0.02	$0.20 \pm 0.01$	0.13
9.3 wt% $\text{Fe\_Nitrate\_Th}$	0.88	0.02	$0.10 \pm 0.02$	0.16

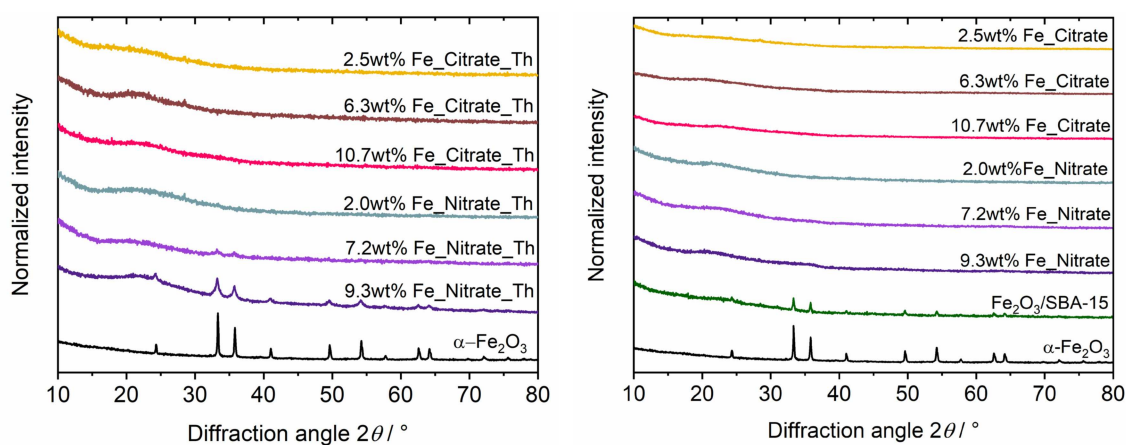
[a] Ratio of mesopore surface area,  $a_{\text{pore}}$ , and specific surface area,  $a_{\text{s,BET}}$ , as measure of micropore contribution to the entire surface of SBA-15. [b] Differences in fractal dimension,  $\Delta D_f$ , between SBA-15 and corresponding  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  samples as measure of the roughness of the surface.



**Figure 3.** Differences in fractal dimension,  $\Delta D_f$ , between SBA-15 support material and corresponding  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  and  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples, dependent on precursor and iron loading.

species of  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  samples. Moreover, compared to those of the nitrate\_Th samples, the surface of SBA-15 of the citrate\_Th samples were smoother. Whereas  $\Delta D_f$  of the citrate\_Th samples increased with increasing iron loading, those of the nitrate\_Th samples increased up to 7.2 wt% iron and subsequently decreased for the highest loaded nitrate\_Th sample (Table 2, Figure 3). This decrease in  $\Delta D_f$  for 9.3 wt%  $\text{Fe\_Nitrate\_Th}$  was correlated with both significantly increased iron oxidic species size and increased amount of crystalline  $\alpha\text{-Fe}_2\text{O}_3$  for this sample (DR-UV/Vis, XRD). Such an increased iron oxidic species size agreed with the lowest pore volume for sample 9.3 wt%  $\text{Fe\_Nitrate\_Th}$ .

As reported for  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples obtained from thin layer calcination,<sup>[17]</sup> precursor-dependent differences in surface roughness of the support material of  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  samples may be explained by different strengths of chelating effect of the two  $\text{Fe}^{\text{III}}$  precursors. However, thick layer calcination enhanced the aggregation and reduced the dispersion of iron oxidic species.



**Figure 4.** Left: Wide-angle X-ray diffraction patterns of  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  samples and crystalline  $\alpha\text{-Fe}_2\text{O}_3$ . Right: Wide-angle X-ray diffraction patterns of  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples, the mechanical mixture, and crystalline  $\alpha\text{-Fe}_2\text{O}_3$ .

### 2.1.2. X-Ray Diffraction

Figure 4 depicts wide angle X-ray diffraction patterns of  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples for both calcination modes. For all  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  as well as for all  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples, a broad diffraction peak at  $23^\circ 2\theta$ , was observed, corresponding to the amorphous silica structure of SBA-15.<sup>[14]</sup> XRD patterns of all citrate samples originating from either thin layer calcination or thick layer calcination, showed no further diffraction peaks. This was indicative of only small and highly dispersed iron oxidic species being present in citrate samples independent of powder layer thickness during calcination. XRD patterns of  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples originating from nitrate samples calcined in thin layer also showed no further diffraction peaks indicative of no long-range ordered phases. Conversely, XRD pattern of 9.3 wt%  $\text{Fe\_Nitrate\_Th}$  showed small diffraction peaks of crystalline  $\alpha\text{-Fe}_2\text{O}_3$ . Furthermore, for 7.2 wt%  $\text{Fe\_Nitrate\_Th}$ , two main diffraction peaks of  $\alpha\text{-Fe}_2\text{O}_3$  were discernible, while 2.0 wt%  $\text{Fe\_Nitrate\_Th}$  showed no further diffraction peaks. Accordingly, using the nitrate precursor in thick layer calcination for iron loadings higher than 2.0 wt% induced significantly larger and less dispersed iron oxidic species on SBA-15 compared to those obtained from citrate precursor.

Small angle XRD patterns of  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  samples exhibited three characteristic diffraction peaks, (10 l), (11 l), and (20 l), corresponding to the two-dimensional hexagonal symmetry of SBA-15 (Figure 5).<sup>[2,28]</sup> Hence, as already reported for thin layer calcined  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples,<sup>[17]</sup> SBA-15 structure remained during synthesis with calcination in thick powder layer.

### 2.1.3. Diffuse Reflectance UV/Vis Spectroscopy

Figure 6 depicts DR-UV/Vis edge energies as function of iron loading of  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  samples, together with those of corresponding  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples and that of the mechanical mixture,  $\text{Fe}_2\text{O}_3/\text{SBA-15}$ . Values of the DR-UV/Vis edge energy can be used for estimating relative metal oxide particle sizes. Both size and dispersion of transition metal oxides influence the



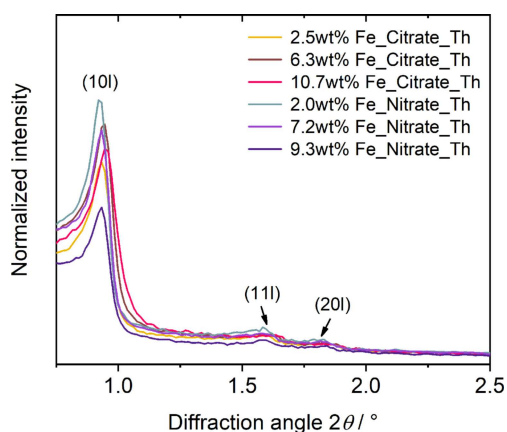


Figure 5. Small-angle X-ray diffraction patterns of  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  samples.

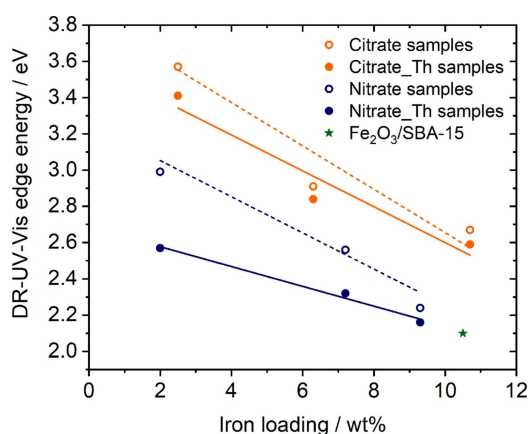


Figure 6. DR-UV/Vis edge energy of  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$ , corresponding  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples, and the mechanical mixture  $\text{Fe}_2\text{O}_3/\text{SBA-15}$  as function of iron loading. Error bars are smaller than the symbols.

position of the edge energy.<sup>[29]</sup> Edge energy values were determined from DR-UV/Vis spectra of  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  samples according to Weber.<sup>[29]</sup> All samples possessed edge energy values higher than that of crystalline  $\alpha\text{-Fe}_2\text{O}_3$  (2.10 eV), as observed for the mechanical mixture. Hence, for all  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  samples, iron oxidic species on SBA-15 were smaller than crystallites in  $\alpha\text{-Fe}_2\text{O}_3$  (average size of  $\sim 32$  nm). Furthermore, edge energies of  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  samples were lower than 4.68 eV being the edge energy of isolated tetrahedrally coordinated  $\text{Fe}^{3+}$  in Fe-MFI zeolite ( $\text{Si}/\text{Fe}=64$ ).<sup>[30]</sup> As third reference,  $\text{Fe}^{\text{III}}$  nitrate precursor consisting of isolated octahedrally coordinated  $\text{Fe}^{3+}$  species was used and edge energy was determined to 3.53 eV. Except for 2.5 wt%  $\text{Fe\_Citrate\_Th}$ , all  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  samples possessed edge energy values lower than 3.53 eV. Thus, supported iron oxidic species were not only larger than isolated tetrahedrally coordinated  $\text{Fe}^{3+}$  species, but also larger than isolated octahedrally coordinated  $\text{Fe}^{3+}$  species, except for 2.5 wt%  $\text{Fe\_Citrate\_Th}$ .

A decrease in edge energy with increasing iron loading for all  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples independent of precursor and powder layer thickness during calcination correlated with an increasing iron oxidic species size. Furthermore, higher edge energies of

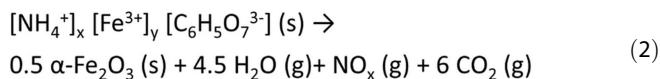
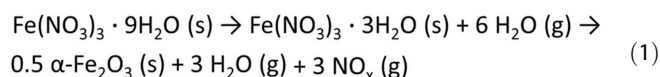
citrate samples compared to those of nitrate samples for both calcination modes indicated smaller iron oxidic species resulting from citrate precursor. Comparing differences in edge energies between  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  and  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples revealed a more pronounced influence of powder layer thickness during calcination for the nitrate precursor. Additionally, decreasing iron loading correlated with an increasing difference in edge energy values between  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  and corresponding  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  sample. Hence, thick layer calcination induced a stronger increase in iron oxidic species size with decreasing iron loading. Independent of the precursor, thick layer calcination yielded higher aggregated and larger iron oxidic species on SBA-15 support material compared to thin layer calcination.

## 2.2. Correlation Between $\text{Fe}_x\text{O}_y$ Species Size and Powder Layer Thickness During Calcination

$\text{Fe}_x\text{O}_y$  species size of all  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples was increased after thick layer calcination. During thick layer calcination, retention time of gaseous decomposition products of the  $\text{Fe}^{\text{III}}$  precursors was extended compared to thin layer calcination. Accordingly, a higher concentration of these gaseous decomposition products in the powder layer resulted during calcination. Due to this higher concentration of gaseous decomposition products of the precursors, gas phase during calcination became relevant. Conversely, for thin layer calcination, influence of changing gas phase was negligible due to the fast removal of gaseous decomposition products of the precursors. Moreover, the effect of powder layer thickness during calcination on  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples was dependent on the precursor. The nitrate precursor induced a more pronounced  $\text{Fe}_x\text{O}_y$  species growth during thick layer calcination compared to the citrate precursor. In principle, three effects, i.e. composition of the gas phase, concentration of gaseous decomposition products, and dispersion of the  $\text{Fe}^{\text{III}}$  ions, might be relevant during thick layer calcination for precursor-dependent differences in resulting iron oxidic species size. In the following, it will be evaluated which of these three effects was decisive for the precursor-dependent differences in  $\text{Fe}_x\text{O}_y$  species size of  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  samples.

As first effect, the composition of the gas atmosphere might influence the  $\text{Fe}_x\text{O}_y$  species growth. For the nitrate precursor,  $\text{Fe}^{\text{III}}$  nitrate nonahydrate, thermal decomposition during calcination yielded nitrogen oxides and  $\text{H}_2\text{O}$  as gaseous decomposition products (Eq. (1),<sup>[31]</sup>). Conversely, thermal decomposition of the citrate precursor,  $(\text{NH}_4, \text{Fe}^{\text{III}})$  citrate, resulted in nitrogen oxides,  $\text{H}_2\text{O}$ , and  $\text{CO}_2$  as gaseous decomposition products (Eq. (2),<sup>[31]</sup>). For both precursors, nitrogen oxides and  $\text{H}_2\text{O}$  were observed. Therefore, these same gaseous decomposition products cannot induce the precursor-dependent differences in iron oxidic species size. Consequently,  $\text{CO}_2$  was the only difference in gas phase composition. Hence, only  $\text{CO}_2$  could induce the smaller and less aggregated  $\text{Fe}_x\text{O}_y$  species of the citrate\_Th samples. However, it appeared more reasonable that another effect significantly influenced iron oxidic species growth. Nevertheless, a possible influence of different compositions of the gas

atmosphere on resulting iron oxidic species could not be excluded.



As second effect, the concentration of gaseous decomposition products, and consequently a shift of the equilibrium during thermal decomposition of the precursors, was considered. Thermal decomposition of the precursors during calcination in thick powder layer may be described as heterogeneous equilibrium reaction. The extended retention time of the gaseous decomposition products during thick layer calcination shifted the equilibrium to the side of the educts, according to Le Chatelier's principle. This induced an increased decomposition temperature, and consequently, enhanced iron oxidic species growth and agglomeration. Compared to the nitrate precursor, thermal decomposition of the citrate precursor yielded higher concentrations of gaseous decomposition products (Eq. (1) and Eq. (2)). Accordingly, thick layer calcination of citrate samples induced a more pronounced shift of the equilibrium to the side of the educts. Therefore, a more pronounced iron oxidic species growth would be expected for the citrate samples compared to the nitrate samples. However, this was not observed. Quite the opposite, the nitrate precursor induced a more pronounced  $\text{Fe}_x\text{O}_y$  species growth during thick layer calcination compared to the citrate precursor. Hence, an effect of the concentration of gaseous decomposition products cannot induce the precursor-dependent differences in  $\text{Fe}_x\text{O}_y$  species size. However, the increased  $\text{Fe}_x\text{O}_y$  species size of all  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples due to thick layer calcination can be explained based on this effect.

As third effect, the dispersion of the  $\text{Fe}^{\text{III}}$  ions was considered. A higher dispersion of  $\text{Fe}^{\text{III}}$  ions hindered  $\text{Fe}_x\text{O}_y$  species growth. Due to the different strengths of chelating effect of the two precursors,<sup>[17]</sup> dispersion of  $\text{Fe}^{\text{III}}$  ions varied dependent on the precursor. The citrate precursor possessing a more pronounced chelating effect, induced higher dispersed and encapsulated  $\text{Fe}^{\text{III}}$  ions before calcination. Therefore,  $\text{Fe}^{\text{III}}$  ions of the citrate precursor were too far away from each other which hindered aggregation during thick layer calcination. Accordingly,  $\text{Fe}_x\text{O}_y$  species growth and aggregation of citrate\_Th samples was less pronounced compared to that of nitrate\_Th samples. Apparently, this effect was stronger than that of the concentration of gaseous decomposition products during thermal decomposition of the precursors. Hence, the dispersion of the  $\text{Fe}^{\text{III}}$  ions was decisive for the precursor-dependent differences in  $\text{Fe}_x\text{O}_y$  species size of  $\text{Fe}_x\text{O}_y/\text{SBA-15}$ \_Th samples.

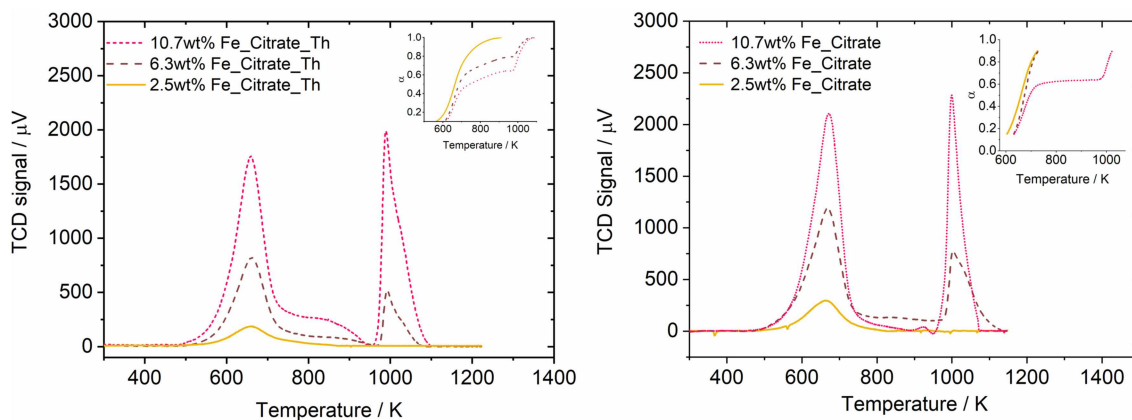
Besides  $\text{Fe}^{\text{III}}$  precursor, iron loading affected the influence of powder layer thickness during calcination on resulting iron oxidic species. Independent of the precursor, lowest loaded  $\text{Fe}_x\text{O}_y/\text{SBA-15}$ \_Th samples showed the most increased iron

oxidic species size compared to corresponding  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples. This iron loading-dependent influence on  $\text{Fe}_x\text{O}_y$  species growth and aggregation was surprising. Since all above described effects were precursor-dependent, none of them could be assigned to the most increased  $\text{Fe}_x\text{O}_y$  species size of lowest loaded  $\text{Fe}_x\text{O}_y/\text{SBA-15}$ \_Th samples. Apparently, the extended retention time of gaseous decomposition products was more influential for low iron loadings up to 2.5 wt%. A possible explanation might be a dependence of the retention time of gaseous decomposition products during calcination on the amount of precursor molecules, and therefore, on iron loading. At low amounts of precursor molecules, retention time was significantly shorter compared to that for higher amounts of precursor molecules. The difference in retention time of gaseous decomposition products between thick and thin layer calcination was presumably higher for low amounts of precursor molecules. Consequently, a more enhanced iron oxidic species growth resulted for lowest loaded  $\text{Fe}_x\text{O}_y/\text{SBA-15}$ \_Th samples.

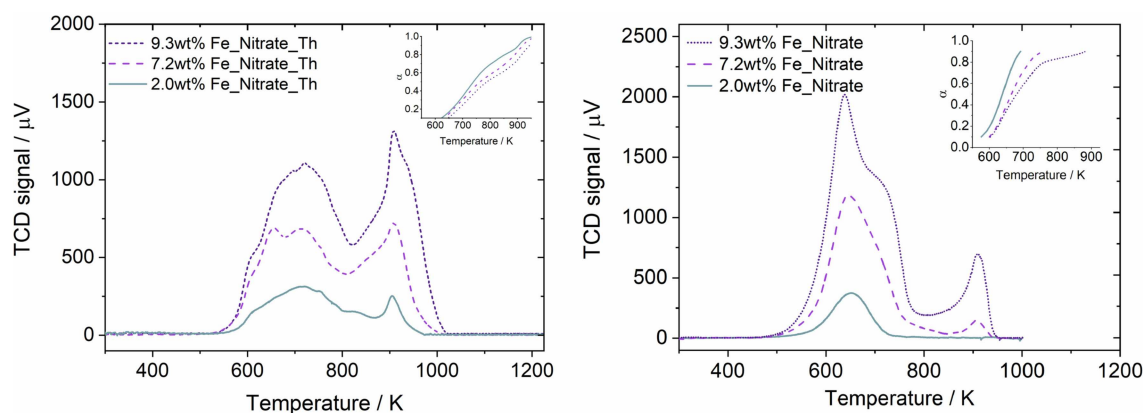
### 2.3. Reducibility of $\text{Fe}_x\text{O}_y/\text{SBA-15}$ \_Th Samples

TPR traces of  $\text{Fe}_x\text{O}_y/\text{SBA-15}$ \_Th samples measured during reduction with  $\text{H}_2$  at a heating rate of 10 K/min are depicted in Figures 7 and 8. Differences in reduction profiles of citrate\_Th compared to citrate samples were only minor (Figure 7). Lowest loaded citrate\_Th sample possessed one single reduction peak indicating a single-step reduction mechanism. The reduction peak of this citrate\_Th sample was slightly broadened compared to that of the citrate sample. Higher loaded citrate\_Th samples showed a two-step reduction mechanism (Figure 7, left). For all citrate\_Th samples, a slight shift of the first TPR maximum towards lower temperatures compared to corresponding citrate samples was observed. This shift of the first TPR maximum indicated a better reducibility of the citrate samples obtained by thick layer calcination. According to literature,<sup>[14,15,22]</sup> reduction of isolated  $\text{Fe}^{3+}$  sites supported on mesoporous  $\text{SiO}_2$  occurs at higher temperatures than reduction of  $\text{Fe}_x\text{O}_y$  oligomers (e.g. TPR maximum centered at 780 K for a sample with 0.05 wt% iron loading consisting mainly of isolated  $\text{Fe}^{3+}$  sites was shifted to 640 K as iron loading rose to 0.08 wt% and amount of  $\text{Fe}_x\text{O}_y$  oligomers increased). Therefore, improved reducibility of citrate\_Th samples was attributed to higher amounts of  $\text{Fe}_x\text{O}_y$  oligomers as well as higher aggregated iron oxidic species induced by thick layer calcination.

In contrast to citrate\_Th, nitrate\_Th samples showed a more pronounced influence of powder layer thickness during calcination on reduction mechanism. TPR traces of nitrate\_Th samples are depicted in Figure 8, left. While lowest loaded nitrate sample possessed a single-step reduction mechanism (Figure 8, right), corresponding nitrate\_Th sample possessed a two-step reduction mechanism. Thick layer calcination of the higher loaded nitrate samples also induced an increasing complexity of the reduction mechanism. TPR traces of 7.2 wt%  $\text{Fe}$ \_Nitrate\_Th and 9.3 wt%  $\text{Fe}$ \_Nitrate\_Th showed a multi-step reduction mechanism with less resolved reduction peaks in the lower



**Figure 7.** Left: TPR traces citrate\_Th samples measured in 5% H<sub>2</sub> in 95% argon at 10 K/min. Inset depicts reduction degree traces with increasing iron loading from left to right. Right: TPR traces citrate samples measured in 5% H<sub>2</sub> in 95% argon at 10 K/min. Inset depicts reduction degree traces with increasing iron loading from left to right.



**Figure 8.** Left: TPR traces nitrate\_Th samples measured in 5% H<sub>2</sub> in 95% argon at 10 K/min. Inset depicts reduction degree traces with increasing iron loading from left to right. Right: TPR traces nitrate samples measured in 5% H<sub>2</sub> in 95% argon at 10 K/min. Inset depicts reduction degree traces with increasing iron loading from left to right.

temperature range. For nitrate\_Th samples, a shift of the first TPR maximum to higher temperatures was observed. Interestingly, thick layer calcination of nitrate samples induced an opposite trend compared to that observed for thin layer calcination. For nitrate samples obtained from thin layer calcination, a better reducibility was observed with increasing iron loading<sup>[17]</sup> and therefore increasing amount of Fe<sub>x</sub>O<sub>y</sub> oligomers.<sup>[14,15,22]</sup> Conversely, the shift of the TPR maxima to higher temperatures for the nitrate\_Th samples (Figure 8) indicated a better reducibility of less aggregated iron species. This shift of the first TPR maximum for the nitrate\_Th samples was probably induced by an increasing amount of crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with increasing iron loading. For crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, increasing particle size correlates with a hindered reducibility.<sup>[14,15,32]</sup> In addition to the shift of the TPR maxima, a significant broadening of the first reduction peak for nitrate\_Th samples was observed. This broadening was attributed to both broadened size distribution of iron oxidic species and bulk diffusion limitation due to higher amounts of crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.<sup>[14]</sup> This coincided with the increasing iron species size (Figure 6) and increasing amount of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> giving rise to X-ray

diffraction peaks (Figure 4) with increasing iron loading of the nitrate\_Th samples. Moreover, the shift of the TPR maxima induced by thick layer calcination mode compared to thin layer calcination mode was larger for nitrate samples than for citrate samples. This larger shift of the TPR maxima also indicated a more distinct effect of powder layer thickness during calcination on Fe<sub>x</sub>O<sub>y</sub>/SBA-15 samples obtained from Fe<sup>III</sup> nitrate precursor.

#### 2.4. Reduction Kinetics under Non-Isothermal Conditions

As previously reported,<sup>[17]</sup> solid-state kinetic analysis can be successfully applied to supported systems and, therefore, constitutes an additional analysis method to obtain information on supported species. Prior to applying model-independent and model-dependent solid-state kinetic analysis methods, reduction degree  $\alpha$  traces were extracted by integration of TPR traces of all Fe<sub>x</sub>O<sub>y</sub>/SBA-15\_Th samples. Resulted  $\alpha$  traces are depicted in the inset in Figure 7 and Figure 8 for citrate\_Th and nitrate\_Th samples, respectively.

### 2.4.1. Kissinger Method

Model-independent Kissinger method yields a single apparent activation energy ( $E_a$ ) of rate-determining step during reduction of  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  samples. By depicting  $\ln[\beta/T_m^2]$  as function of  $1/T_m$ , apparent activation energy of the reduction of  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  was calculated from the slope of the resulting straight line.<sup>[17,33,34]</sup> In order to enable comparison of  $E_a$  for all samples despite differing TPR traces,  $T_m$  corresponded to the first maximum of the TPR traces (Figures 7–8).

Apparent activation energies for  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  samples, corresponding  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples, and the mechanical mixture are summarized in Table 3. As already observed for  $\text{Fe}_x\text{O}_y/\text{SBA-15}$ ,  $\text{Fe}^{\text{III}}$  precursor significantly influenced reducibility, and hence, apparent activation energy of rate-determining step in reduction of  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  samples.<sup>[17]</sup> Highest apparent activation energy of rate-determining step in reduction resulted for lowest loaded nitrate\_Th sample. Increasing iron loading within the nitrate\_Th samples correlated with a decreasing apparent activation energy of reduction. A correlation between increasing iron loading, i.e. increasing species size, and decreasing  $E_a$ , i.e. better reducibility, was already reported for nitrate samples obtained by thin layer calcination.<sup>[17]</sup> Higher loaded nitrate\_Th samples, 7.2 wt%  $\text{Fe\_Nitrate\_Th}$  and 9.3 wt%  $\text{Fe\_Nitrate\_Th}$ , exhibited the same value of  $E_a$  within experimental errors as the mechanical mixture of  $\alpha\text{-Fe}_2\text{O}_3$  and SBA-15. This might be indicative of a similar size of iron oxidic species. Similarities in iron oxidic species size were corroborated by results from DR-UV/Vis spectroscopy and XRD. 7.2 wt%  $\text{Fe\_Nitrate\_Th}$  and 9.3 wt%  $\text{Fe\_Nitrate\_Th}$  possessed a DR-UV/Vis edge energy of 2.3 respectively 2.2 eV, being similar to that of  $\text{Fe}_2\text{O}_3/\text{SBA-15}$  (2.1 eV) (Figure 6). Furthermore, these samples showed XRD peaks corresponding to crystalline  $\alpha\text{-Fe}_2\text{O}_3$  (Figure 4). Accordingly, increasing amount of crystalline  $\alpha\text{-Fe}_2\text{O}_3$  agreed with the decrease in  $E_a$  for higher loaded nitrate\_Th samples. The highest apparent activation energy of 2.0 wt%  $\text{Fe\_Nitrate\_Th}$  coincided with the most distinct broadening of the first TPR peak (Figure 8). Thick layer calcination of the lowest loaded nitrate sample affected the most pronounced difference in iron oxidic species size. For this sample, increased species size, broadened species size distribution, and hence, increased complexity of the reduction mechanism were

**Table 3.** Apparent activation energy,  $E_a$ , of rate-determining step in reduction of  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$ , corresponding  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples, and the mechanical mixture  $\text{Fe}_2\text{O}_3/\text{SBA-15}$ .<sup>[a]</sup>

	$E_a/\text{kJ mol}^{-1}$	
	Thick layer calcined	Thin layer calcined
2.5 wt% $\text{Fe\_Citrate}$	$76 \pm 7$	$39 \pm 8$
6.3 wt% $\text{Fe\_Citrate}$	$102 \pm 8$	$113 \pm 8$
10.7 wt% $\text{Fe\_Citrate}$	$88 \pm 8$	$104 \pm 8$
2.0 wt% $\text{Fe\_Nitrate}$	$130 \pm 3$	$88 \pm 8$
7.2 wt% $\text{Fe\_Nitrate}$	$69 \pm 5$	$84 \pm 1$
9.3 wt% $\text{Fe\_Nitrate}$	$70 \pm 5$	$62 \pm 8$
$\text{Fe}_2\text{O}_3/\text{SBA-15}$		$59 \pm 7$

[a]  $E_a$  values were determined by Kissinger method and reduction was conducted in 5%  $\text{H}_2$  in argon.

observed. Conversely, using the citrate precursor in thick layer calcination yielded highest apparent activation energy in reduction for highest loaded samples, while lowest loaded citrate\_Th sample possessed lowest  $E_a$ . Furthermore, values of  $E_a$  for citrate\_Th samples were higher compared to those of nitrate\_Th samples for iron loadings higher than 2.5 wt%. This was indicative of a precursor-dependent trend in apparent activation energy as function of iron loading for  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  samples, as already observed for  $\text{Fe}_x\text{O}_y/\text{SBA-15}$ .<sup>[17]</sup>

For lowest loaded  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$  samples, the most pronounced influence of powder layer thickness during calcination on apparent activation energy in reduction was observed (Figure 9). A significant increase in apparent activation energy of the reduction of 2.5 wt%  $\text{Fe\_Citrate\_Th}$  and 2.0 wt%  $\text{Fe\_Nitrate\_Th}$ , compared to corresponding  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples, was observed. This might be induced by a broadened species size distribution, being reflected in the broadening of the first TPR maxima. Accordingly, reduction of iron oxidic species with different sizes, ascribed to the first TPR peak, was more difficult compared to that of iron oxidic species with a narrow species size distribution. This yielded an increased apparent activation energy.

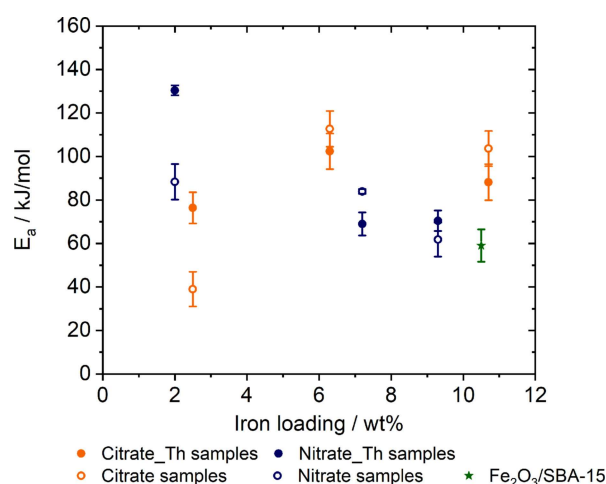
### 2.4.2. Coats-Redfern Method

Model-dependent Coats-Redfern analysis<sup>[34,35]</sup> was applied for providing a complementary analysis method of the non-isothermal kinetic data.

The Coats-Redfern method is based on:

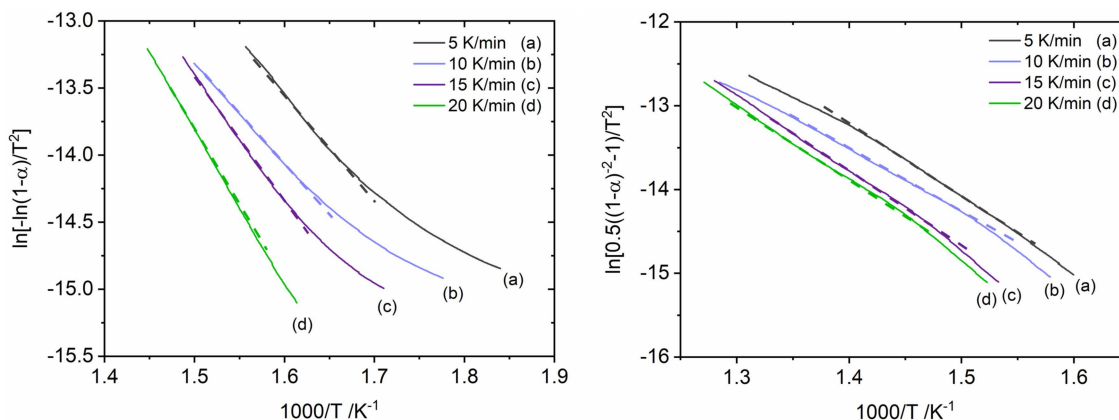
$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E_a} \left[1 - \left(\frac{2RT}{E_a}\right)\right]\right) - \frac{E_a}{RT}, \quad (3)$$

with integral solid-state reaction model  $g(\alpha)$ , temperature  $T$ , heating rate  $\beta$ , apparent activation energy of rate-determining



**Figure 9.** Apparent activation energy,  $E_a$ , of rate-determining step in reduction (5%  $\text{H}_2$  in argon) determined by Kissinger method for  $\text{Fe}_x\text{O}_y/\text{SBA-15\_Th}$ , corresponding  $\text{Fe}_x\text{O}_y/\text{SBA-15}$  samples, and the mechanical mixture as function of iron loading.





**Figure 10.** Linear ranges of reduction degree  $\alpha$  curves using the F1 solid-state reaction model for sample 2.5 wt% Fe\_Citrate\_Th (left, straight lines) and those using the F3 solid-state reaction model for sample 7.2 wt% Fe\_Nitrate\_Th (right, straight lines). Reduction was conducted in 5% H<sub>2</sub> in argon. Dashed lines: Linear regressions. Linear fitting ranges were determined by investigating the effect of extending the fitting borders on corresponding standard derivation. Hence, maximal linear ranges coinciding with good standard derivations were considered.

step  $E_{ar}$ , gas constant  $R$ , and pre-exponential (frequency) factor  $A$ .<sup>[34,35]</sup> Only for suitable solid-state reaction models, depicting  $\ln[g(\alpha)/T^2]$  as function of reciprocal temperature yields straight lines. Apparent activation energies can be obtained from the slope of resulting straight lines.<sup>[34,35]</sup> Only solid-state reaction models,  $g(\alpha)$ , resulting in similar apparent activation energies as obtained from model-independent Kissinger method as well as good linear regressions were selected for further analysis.

For all citrate\_Th samples, F1, D2, A3, and R2 solid-state reaction models revealed wide linear ranges by plotting  $\ln[g(\alpha)/T^2]$  as function of reciprocal temperature. Linear ranges of reduction degree  $\alpha$  curves using the F1 solid-state reaction model for 2.5 wt% Fe\_Citrate\_Th are depicted in Figure 10, left. As observed for 2.5 wt% Fe\_Citrate,<sup>[17]</sup> apparent activation energies at different heating rates for diffusion and Avrami-Erofeyev reaction models, i.e. D2 and A3 reaction models, were significantly higher or lower compared to the results of Kissinger method. Hence, neither the D2 nor the A3 solid-state reaction model were considered for further analysis. The R2 reaction model is denoted geometrical contraction model. For reactions described by the R2 model, nucleation occurs on the surface of the cylindrical crystal and the decreasing interface area between reactant and product phase during reaction determines the reaction rate.<sup>[34]</sup> This concept appeared hardly applicable to citrate\_Th samples with small and dispersed iron oxidic species located in the pore system of SBA-15. For the F1 solid-state reaction model, not only values of apparent activation energy agreed with those obtained from Kissinger method, but also underlying concept was well applicable to small and dispersed iron oxidic species of citrate\_Th samples. Consequently, the F1, Mampel, model was chosen as suitable solid-state reaction model for 2.5 wt% Fe\_Citrate\_Th and all other citrate\_Th samples. For citrate samples, thick layer calcination did not lead to a change in suitable solid-state reaction model.

For lowest loaded nitrate\_Th sample, analysis procedure according to Coats-Redfern method also resulted in F1 solid-

state reaction model being suitable for describing the reduction. Hence, thick layer calcination of 2.0 wt% Fe\_Nitrate induced no change in suitable solid-state reaction model.<sup>[17]</sup>

Here, assuming order-based reaction models as suitable reaction models seemed reasonable regarding the underlying assumptions of these reaction models. Order-based reaction models are considered as the simplest solid-state reaction models. Furthermore, these reaction models are similar to those used in homogeneous kinetics.<sup>[17,34,36]</sup> For homogeneous kinetics, weakly interacting ions in solution are described. There, the reaction rate of order-based reaction models is proportional to the concentration of active sites. Solid-state reactions described by a first-order model start with a large number of nucleation sites resulting in fast nucleation. Similar to Fe<sub>x</sub>O<sub>y</sub>/SBA-15 samples calcined in thin layers,<sup>[17]</sup> reduction of citrate\_Th samples and lowest loaded nitrate\_Th sample was described by a first-order reaction model. Thus, reduction of these samples was neither inhibited by an increasing product layer nor by limited mobility of reactants. Despite an increased iron species size obtained by thick layer calcination compared to thin layer calcination, Fe<sup>III</sup> species of citrate\_Th and 2.0 wt% Fe\_Nitrate\_Th still constituted very small nucleation sites.

Conversely, for higher loaded nitrate\_Th samples, F1, D1, R3, and F3 solid-state reaction models revealed wide linear ranges by plotting  $\ln[g(\alpha)/T^2]$  as function of reciprocal temperature. Linear ranges of reduction degree  $\alpha$  curves using the F3 solid-state reaction model for 7.2 wt% Fe\_Nitrate\_Th are depicted in Figure 10, right. Apparent activation energies for solid-state reaction models F1, D1, R3, and F3 obtained from the slope of resulting straight lines are given in Table 4.

For the D1 solid-state reaction model, apparent activation energies of reduction at different heating rates were significantly higher compared to the result from Kissinger method. Consequently, the D1 was not further considered as suitable reaction model for the reduction of 7.2 wt% Fe\_Nitrate\_Th. Moreover, the F1 solid-state reaction model yielded significantly lower values of apparent activation energy compared to that

**Table 4.** Apparent activation energy,  $E_a$ , of reduction of 7.2 wt% Fe\_Nitrate\_Th depending on the applied solid-state reaction model.<sup>[a]</sup>

Heating rate/ K min <sup>-1</sup>	$E_a$ /kJ mol <sup>-1</sup>			
	D1	R3	F1	F3
5	122.4 ± 0.3	59.1 ± 0.2	58.8 ± 0.1	74.2 ± 0.1
10	135.9 ± 0.6	66.7 ± 0.3	58.6 ± 0.4	68.5 ± 0.2
15	141.0 ± 0.8	69.0 ± 0.4	64.7 ± 0.3	77.2 ± 0.2
20	144.2 ± 0.9	74.6 ± 0.3	59.1 ± 0.3	75.8 ± 0.2

[a] Reduction was conducted in 5% H<sub>2</sub> in argon at various heating rates.

resulted from model-independent solid-state kinetic analysis method. This indicated that thick layer calcination of 7.2 wt% Fe\_Nitrate induced a change in suitable solid-state reaction model. Therefore, first-order reaction model, F1, was no longer suitable for describing the reduction of 7.2 wt% Fe\_Nitrate\_Th. Apparent activation energies which resulted from the R3 reaction model were also lower than that from Kissinger method. Besides lower values of apparent activation energy, R3 reaction model appeared hardly applicable to the reduction of 7.2 wt% Fe\_Nitrate\_Th regarding the underlying assumptions of this reaction model. The R3 reaction model is described as contracting sphere model. Accordingly, nucleation occurs rapidly on the surface of the particles. Geometrical contraction models (R) assume a reaction interface progressing towards the center of the crystal particle during reaction.<sup>[34]</sup> However, Fe<sup>III</sup> species in 7.2 wt% Fe\_Nitrate\_Th were small and located in the pore system of SBA-15. Only a minor fraction of higher aggregated iron oxidic species and crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was observed for this sample, excluding the R3 as suitable reaction model. Consequently, third-order, F3, solid-state reaction model was chosen as suitable reaction model for the reduction of 7.2 wt% Fe\_Nitrate\_Th. Analysis procedure for 9.3 wt% Fe\_Nitrate\_Th also resulted in F3 reaction model being suitable for describing the reduction mechanism of this sample. The increased reaction order for higher loaded nitrate\_Th samples was correlated with an increased amount of higher aggregated iron oxidic species and the presence of a minor fraction of crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Figure 4). For the mechanical mixture Fe<sub>2</sub>O<sub>3</sub>/SBA-15, reaction model R3 was recently shown to be suitable.<sup>[17]</sup> This was consistent with crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles mixed with SBA-15.

## 2.5. Correlation of Structural and Solid-State Kinetic Properties

Similar to Fe<sub>x</sub>O<sub>y</sub>/SBA-15 samples obtained from thin layer calcination,<sup>[17]</sup> results from sample characterization agreed well with those from solid-state kinetic analysis for Fe<sub>x</sub>O<sub>y</sub>/SBA-15 samples obtained from thick layer calcination. Thick layer calcination induced an increased iron oxidic species size due to an extended retention time of gaseous decomposition products of the precursors during synthesis of Fe<sub>x</sub>O<sub>y</sub>/SBA-15\_Th. Compared to Fe<sup>III</sup> ions of the citrate precursor, those of the nitrate precursor were less dispersed before calcination. This yielded a more pronounced Fe<sub>x</sub>O<sub>y</sub> species growth and aggregation for

nitrate\_Th compared to citrate\_Th samples. This increased iron oxidic species size of nitrate\_Th samples correlated with lower values of apparent activation energy of reduction for iron loadings higher than 2.5 wt% compared to citrate\_Th samples (Table 3). Furthermore, within the nitrate\_Th samples, increasing iron oxidic species size and increasing amount of higher aggregated iron oxidic species with increasing iron loading induced a decreasing apparent activation energy of reduction. Besides, increased amount of crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> for 7.2 wt% Fe\_Nitrate\_Th and 9.3 wt% Fe\_Nitrate\_Th coincided with values of apparent activation energy in reduction similar to that of the mechanical mixture, Fe<sub>2</sub>O<sub>3</sub>/SBA-15. Moreover, results from Coats-Redfern method agreed with those from structural characterization. For higher loaded nitrate\_Th samples, significantly increased iron oxidic species size correlated with an increased reaction-order of suitable solid-state reaction model (F3).

Compared to nitrate\_Th samples, for citrate\_Th samples, the influence of powder layer thickness during calcination on structural and solid-state kinetic properties was less pronounced. Despite increased iron oxidic species size due to thick layer calcination, resulting iron oxidic species remained significantly smaller and higher dispersed compared to those obtained from nitrate precursor. Moreover, citrate\_Th samples with iron loadings higher than 2.5 wt% showed a more pronounced micropore filling, and therefore, a smoother SBA-15 surface compared to corresponding nitrate\_Th samples. This was indicative of stronger interactions between iron oxidic species and SBA-15, which were induced by the more pronounced chelating effect of the citrate precursor during synthesis of Fe<sub>x</sub>O<sub>y</sub>/SBA-15\_Th samples. These stronger interactions between iron oxidic species and SBA-15 coincided with the higher values of apparent activation energy in reduction of citrate\_Th samples. Smaller iron oxidic species of citrate\_Th compared to nitrate\_Th samples yielded first-order, F1, solid-state reaction model being suitable to describe the reduction.

Lowest loaded nitrate\_Th sample, 2.0 wt% Fe\_Nitrate\_Th, consisting of similar iron oxidic species as citrate\_Th samples, showed analogous results in solid-state kinetic analysis as citrate\_Th samples. Precursor-dependent differences in reducibility and solid-state kinetic properties of Fe<sub>x</sub>O<sub>y</sub>/SBA-15\_Th samples were predominantly correlated with precursor-dependent differences in resulting iron oxidic species size.

Thick layer calcination of lowest loaded samples induced the most distinct increase in iron oxidic species size and broadened species size distribution. This was ascribed to the highest difference in retention time of gaseous decomposition products between thick and thin layer calcination for lowest iron loadings. These differences in structural characteristics were reflected in the significantly increased apparent activation energy in reduction determined by Kissinger method for 2.5 wt% Fe\_Citrate\_Th and 2.0 wt% Fe\_Nitrate\_Th.

### 3. Conclusion

Iron oxidic species supported on silica SBA-15 were synthesized with iron loadings ranging between 2.0 wt% and 10.7 wt% using two different Fe<sup>III</sup> precursors (Fe<sup>III</sup> nitrate nonahydrate, (NH<sub>4</sub>)<sub>2</sub>Fe<sup>III</sup> citrate). Calcination was conducted in either thin (0.3 cm) or thick (1.3 cm) powder layer. Varying powder layer thickness during calcination significantly influenced structural and solid-state kinetic properties of Fe<sub>x</sub>O<sub>y</sub>/SBA-15 samples. Additionally, the magnitude of the influence of powder layer thickness during calcination was dependent on both Fe<sup>III</sup> precursor and iron loading. Structural characterization of Fe<sub>x</sub>O<sub>y</sub>/SBA-15\_Th samples confirmed iron oxidic species being successfully located in the pore system of SBA-15. Thick layer calcination induced an enhanced iron oxidic species growth and resulting iron oxidic species were larger compared to those obtained from thin layer calcination. This yielded an increased degree of micropore filling and a smoother SBA-15 surface for iron loadings higher than 2.5 wt%. Precursor-dependent differences in iron oxidic species growth during thick layer calcination were induced by different strengths of chelating effect of the Fe<sup>III</sup> precursors. Only for nitrate\_Th samples with iron loadings higher than 2.0 wt%, significant amounts of higher aggregated Fe<sub>x</sub>O<sub>y</sub> and small α-Fe<sub>2</sub>O<sub>3</sub> particles were observed. For all other Fe<sub>x</sub>O<sub>y</sub>/SBA-15\_Th samples, long-range ordering was excluded. Differences in solid-state kinetic properties of Fe<sub>x</sub>O<sub>y</sub>/SBA-15 catalysts dependent on powder layer thickness during calcination correlated with differences in iron oxidic species size.

## Experimental Section

### Sample Preparation

Mesoporous silica SBA-15 was prepared according to Zhao et al.<sup>[2]</sup> The surfactant, Pluronic® P123, was dissolved in a mixture of deionized water and HCl (37%) and the reaction mixture was stirred at 308 K for 24 h. Tetraethylorthosilicate (TEOS) was added to the solution and the reaction mixture was stirred at 308 K for 24 h. Subsequently, the solution was hydrothermally treated in pressure-resistant bottles at 388 K for 24 h. The product was filtered, washed with a mixture of deionized water and ethanol (20:1), air-dried, and calcined. Calcination was carried out in three steps. (I) 378 K for 135 min, (II) 453 K for 3 h, and (III) 873 K for 5 h. The heating rate was kept at 1 K/min. Iron oxides supported on SBA-15 were prepared by incipient wetness technique. Therefore, an aqueous solution of (NH<sub>4</sub>)<sub>2</sub>Fe<sup>III</sup> citrate or Fe<sup>III</sup> nitrate nonahydrate was used.

After drying in air for 24 h, calcination was carried out at 723 K for 2 h in either thin or thick powder layer. In this work, regular calcination mode of Fe<sub>x</sub>O<sub>y</sub>/SBA-15 samples was thin powder layer calcination, whereby powder layer thickness was 0.3 cm. Conversely, for thick powder layer calcination, powder layer thickness was 1.3 cm. Samples calcined in thick powder layer were denoted with the ending "\_Th" to clarify the different powder layer thickness during calcination compared to corresponding Fe<sub>x</sub>O<sub>y</sub>/SBA-15 samples. Moreover, Fe<sub>x</sub>O<sub>y</sub>/SBA-15 samples were denoted as citrate or nitrate samples dependent on used precursor. Accordingly, Fe<sub>x</sub>O<sub>y</sub>/SBA-15 samples calcined in thick powder layer obtained from citrate precursor were denoted citrate\_Th samples and those

obtained from nitrate precursor nitrate\_Th samples. The prepared mechanical mixture of α-Fe<sub>2</sub>O<sub>3</sub> and SBA-15 (10.5 wt% Fe) was denoted Fe<sub>2</sub>O<sub>3</sub>/SBA-15.

After synthesis of Fe<sub>x</sub>O<sub>y</sub>/SBA-15\_Th samples, iron loadings were confirmed by X-ray fluorescence analysis. Furthermore, CHN analysis was performed to confirm a complete decomposition of the precursors. According to the iron loading and the Fe<sup>III</sup> precursor, samples were denoted 2.5 wt% Fe\_Citrate, 6.3 wt% Fe\_Citrate, 10.7 wt% Fe\_Citrate, 2.0 wt% Fe\_Nitrate, 7.2 wt% Fe\_Nitrate, and 9.3 wt% Fe\_Nitrate.

### Sample Characterization

#### X-Ray Fluorescence Analysis

Quantitative analysis of the metal oxide loadings on SBA-15 was conducted by X-ray fluorescence spectroscopy using an AXIOS X-ray spectrometer (2.4 kW model, PANalytical), equipped with a Rh K<sub>α</sub> X-ray source, a gas flow detector, and a scintillation detector. Prior to measurements, samples were mixed with wax (Hoechst wax C micropowder, Merck), ratio 1:1, and pressed into pellets of 13 mm diameter. Quantification was performed by standardless analysis using the software package SuperQ5 (PANalytical).

#### CHN Elemental Analysis

Elemental contents of C, H, and N were determined using a Thermo FlashEA 1112 Organic Elemental Analyzer (ThermoFisher Scientific) with CHNS–O configuration.

#### Nitrogen Physisorption

Nitrogen adsorption/desorption isotherms were measured at 77 K using a BELSORP Mini II (BEL Inc. Japan). Prior to measurements, the samples were pre-treated under reduced pressure (10<sup>-2</sup> kPa) at 368 K for 35 min and kept under the same pressure at 448 K for 15 h (BELPREP II vac).

#### Powder X-Ray Diffraction

Powder X-ray diffraction patterns were obtained using an X'Pert PRO diffractometer (PANalytical, 40 kV, 40 mA) in theta/theta geometry equipped with a solid-state multi-channel detector (PIXel). Cu K<sub>α</sub> radiation was used. Wide-angle diffraction scans were conducted in reflection mode. Small-angle diffraction patterns were measured in transmission mode from 0.4° through 6° 2θ in steps of 0.013° 2θ with a sampling time of 90 s/step.

#### Diffuse Reflectance UV/Vis Spectroscopy

Diffuse reflectance UV/Vis (DR-UV/Vis) spectroscopy was conducted on a two-beam spectrometer (V-670, Jasco) using a barium sulfate coated integration sphere. (Scan speed 100 nm/min, slit width 5.0 nm (UV/Vis) and 20.0 nm (NIR), and spectral region 220–2000 nm). SBA-15 was used as white standard for all samples.

#### Temperature-Programmed Reduction

Temperature-programmed reduction (TPR) was performed using a BELCAT\_B (BEL Inc. Japan). Samples were placed on silica wool in a silica glass tube reactor. Evolving water was trapped using a molecular sieve (4 Å). Gas mixture consisted of 5% H<sub>2</sub> in 95% Ar

with a total gas flow of 40 ml/min. Heating rates used were 5, 10, 15, and 20 K/min to 1223 K. A constant initial sample weight of 0.03 g was used and H<sub>2</sub> consumption was continuously monitored by a thermal conductivity detector.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** Fe<sup>III</sup> precursors · Kinetics · Particle size · Powder layer thickness · Reduction

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