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In-Situ Formation of Fe Nanoparticles from FeOOH Nanosheets on γ -Al₂O₃ as Efficient Catalysts for Ammonia Synthesis

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Supporting Information

ABSTRACT: The preparation process of industrial Fe-based catalysts for ammonia synthesis involves energy-intense and sophisticated treatments. It is thus highly desirable to develop new catalysts with sufficient catalytic performance within smart and more economic approaches. Herein, γ -Al₂O₃-supported FeOOH nanosheets are employed for the first time as ammonia synthesis catalysts. To monitor the potential of these new materials, unsupported FeOOH and Kpromoted catalysts are additionally investigated for comparison. While no activity is observed from the unsupported catalyst, the activity of γ -Al₂O₃-supported catalysts shows an inverse relationship with respect to the amount of Fe. Upon correlation of the catalytic performance with the final state of catalysts, the activity is closely related to the particle size of metallic Fe. Higher activity and lower apparent activation energy can be reached for smaller nanoparticles that are likely to contain more



step-kink structures serving as active sites. The best catalytic performance is obtained for a K-promoted catalyst which shows an activity about 18 times higher compared to that of the corresponding unpromoted one (at 425 $^{\circ}$ C). We conclude that, in addition to the nanostructured character of the Fe, the modifications of its electronic and surface structures induced by the K-promoter are responsible for this enhanced activity.

KEYWORDS: Ammonia synthesis, FeOOH nanosheets, Fe nanoparticles, K-promoter, Al₂O₃, Steps and kinks

INTRODUCTION

Ammonia production from its elements is one of the greatest successes in chemical industry.^{1,2} As an important material, ammonia has been widely used as a precursor for fertilizers and nitrogenous compounds.³ Because of its high hydrogen density and easy liquefaction for storage and transportation, ammonia has additionally been recommended as a promising alternative for chemical hydrogen storage.4-6 Industrially, ammonia is produced by the well-established Haber-Bosch process by using fused Fe-based catalysts operating at high temperatures and pressures.^{7,8} The technical Fe-based catalysts are a mixture of Fe₃O₄ and a series of irreducible oxides (Al₂O₃, K₂O, CaO, etc.) acting as promoters.^{9–11} Although the catalysts have been well-optimized and show advantages such as long lifetime and sufficient activity, use of high temperature (ca. 2000 K)¹² and the sophisticated procedure makes the catalyst preparation a time- and high-energy-consuming process. It is thus highly desirable to develop new catalysts with comparable activity and stability that can be prepared applying smarter and more economic methods.^{13,7}

Attributed to the recent breakthrough in materials science, state-of-the-art two-dimensional (2D) nanomaterials together

with novel preparation strategies bring new excitement to heterogeneous catalysis.^{15–18} Ultrathin nanosheets usually show high surface areas and abundant active sites due to their atomic thickness, making them promising candidates as either catalysts or catalyst precursors for various catalytic reactions.¹⁹ In our previous work we have prepared a series of 2D transition metal hydroxides including Ni(OH)₂, Co(OH)₂, and FeOOH nanosheets through a simple solution approach.¹⁸ The synthesis is performed at room temperature and can be easily scaled up, which is very promising for future industrial applications.

In this work, we have improved our previous method and report, for the first time, the successful synthesis of a series of γ -Al₂O₃-supported FeOOH ultrathin nanosheets and investigation of them as catalysts for the ammonia synthesis. Systematical characterizations, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spec-

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Figure 1. (a) XRD patterns of the unsupported FeOOH, γ -Al₂O₃-supported FeOOH catalysts, and commercial γ -Al₂O₃; (b) Zoom-in XRD patterns of FeOOH/Al₂O₃ (25% Fe) and FeOOH–K/Al₂O₃ (25% Fe) between 29° and 38°.

troscopy (XPS), N₂-physisorption, and temperature-programmed reduction (TPR) have been carried out to study the nature of the catalysts. Further, the impact of the promoters on the current catalyst system is examined by introducing additional potassium (K). All catalysts, including the unsupported FeOOH nanosheets, γ -Al₂O₃-supported FeOOH with different Fe-loadings, and a K-promoted catalyst, have been tested for ammonia synthesis after in-situ activation.

EXPERIMENTAL SECTION

Chemicals. All chemicals were of analytical grade and used as received. FeSO₄·7H₂O and NaBH₄ were purchased from Applichem GmbH (Darmstadt, Germany). Cetyltrimethylammonium bromide (CTAB) was purchased from Sigma-Aldrich. γ -Al₂O₃ was bought from Alfa Aesar. K₂CO₃ was purchased from Merck (Darmstadt, Germany).

Synthesis of FeOOH Nanosheets. Ultrathin FeOOH nanosheets were synthesized by a method similar to what we report in our previous work published elsewhere.¹⁸ Specifically, 4.2 g of FeSO₄: $7H_2O$ and 1.8 g of CTAB were first dissolved in 500 mL of distilled water. The solution was then added with 20 mL (4 M) of freshly prepared NaBH₄ solution. Within 5 min, the color of the solution would turn black. Afterward, the solution mixture was stirred in the open air for 24 h at room temperature. The product was collected by centrifugation, washed with distilled water and ethanol several times, and finally dried at 60 °C.

Synthesis of FeOOH/Al₂O₃ (x% Fe). γ -Al₂O₃-supported FeOOH nanosheets with different Fe-loadings (x% Fe) were synthesized through modifying the above-described method (x% stands for the nominal weight loading of Fe in the reduced catalysts; x = 5, 15, 25). In detail, we mixed 4.2 g of FeSO₄·7H₂O, 1.8 g of CTAB, and a certain amount of γ -Al₂O₃ (16.0 g for 5% Fe, 4.8 g for 15% Fe, and 2.5 g for 25% Fe) with 500 mL of distilled water. Then, the solution was added with 20 mL (4 M) of freshly prepared NaBH₄ solution. The color of the solution turns black within 5 min. The mixture was stirred in the open air at room temperature for 24 h. The product was collected by centrifugation, washed with distilled water and ethanol several times, and finally dried at 60 °C.

Synthesis of FeOOH–K/Al₂O₃ (25% Fe). The nominal weight loading of K in the reduced catalyst is 5%. The K-promoter was introduced into FeOOH/Al₂O₃ (25% Fe) by impregnation of K₂CO₃ solution on 2 g of FeOOH/Al₂O₃ (25% Fe). The impregnating solution was prepared by dissolving 154 mg of K₂CO₃ in 15 mL of distilled water. After impregnation, the as-obtained slurry was stirred at room temperature until most of the water had evaporated. Finally, the product was dried at 60 $^\circ \rm C$ in air.

Characterization. Powder XRD measurements were performed on a Bruker D8 Advance reflection diffractometer equipped with a LynxEye energy-discriminating position-sensitive detector (1D-PSD) using Cu K α_{1+2} radiation. The composition of each sample was determined by using an X-ray fluorescence (XRF) of a Bruker P4 engine. The BET surface area (S_{BET}) of all the samples was determined by a volumetric N₂-physisorption setup (Autosorb-6B, Quantachrome) at 77 K. TPR measurements of the samples were conducted in a fixed-bed reactor by heating the samples in 5% H_2/Ar (80 mL min⁻¹) at a linear heating rate of 6 °C min⁻¹ to 800 °C. XPS spectra were recorded using non-mono-chromatized Mg K α (1253.6 eV) excitation and a hemispherical analyzer (Phoibos 150, SPECS). The binding energy scale was calibrated by the standard Au $4f_{7/2}$ and Cu $2p_{3/2}$ procedure. SEM characterization was carried out by a Hitachi S-4800 SEM instrument equipped with a field emission gun. TEM images, high-resolution TEM (HRTEM) images, annular dark-field scanning TEM (ADF-STEM) images, and energy-dispersive X-ray spectroscopy (EDX) elemental maps were acquired on an aberration-corrected JEOL JEM-ARM200F transmission electron microscope operated at 200 kV. The microscope is equipped with a high-angle Silicon Drift EDX detector with a detection area of 100 mm². The TEM sample of used K-promoted catalyst was prepared in a glovebox and transferred directly to the TEM machine without air contact by a Gatan vacuum transfer holder. For the reduction behavior study, a series of reduced samples were obtained by heating the corresponding parent samples in 5% H₂/Ar (80 mL min⁻¹) at a linear heating rate of 6 $^\circ$ C min⁻¹ to different temperatures (300, 400, 500, 600, 700, and 800 °C).

NH₃ synthesis reactions were tested in a fixed-bed flow reactor. The powders of the catalysts were pressed into pellets and sieved into grains with a size fraction of 250–355 μ m. Prior to the activity tests, 1 g of sieved catalysts (diluted with 1 g of SiC) was loaded into the reactor and reduced in-situ at 500 °C (1 °C min⁻¹) for 14–16 h in 75% H₂/N₂ (440 N mL min⁻¹). After completion of the reduction, the pressure was raised to 90 bar while the temperature was kept at 500 °C. Then, the total flow rate of 75% N₂/H₂ was adjusted to 200 N mL min⁻¹, keeping the temperature constant for 10 h. Reaction temperatures were varied between 325 and 475 °C in 25 °C steps (1 °C min⁻¹). The produced NH₃ was monitored quantitatively by an online IR detector (Emerson X-stream). Only the data points between the detection limit of the IR detector and 10% of the thermodynamic equilibrium were taken into account to calculate the apparent activation energy.



Figure 2. (a) Fe 2p and (b) O 1s XPS spectra of the unsupported FeOOH. (c) Simulated crystal structure of δ -FeOOH according to ref 27. An octahedral cell of oxygen with Fe in its center is emphasized by dark red sticks at the bottom left.

RESULTS AND DISCUSSION

Basic Properties of the Catalysts. The phase composition investigated by powder XRD is illustrated in Figure 1a. The XRD patterns of the unsupported FeOOH show two main reflections centered at 35° and 63° (2 θ) respectively, which can be assigned to 100 and 110 reflections of hexagonal δ -FeOOH (ICDD PDF-2 77-0247, space group *P*3*m*1, *a* = 2.95 Å, *c* = 4.53 Å). Disappearance of the characteristic 112 reflection at 53.8° (2 θ) indicates that a preferred orientation exists in the synthesized δ -FeOOH.²⁰⁻²² For γ -Al₂O₃-supported FeOOH samples, in addition to the aforementioned peaks from δ -FeOOH, several new reflections appear, which can be associated with the structures of γ -Al₂O₃ (ICDD PDF-2 10-0425) and γ-AlOOH (ICDD PDF-2 17-0940). These new reflections become more pronounced with the decrease of Feloading. The γ -AlOOH phase was not formed during the sample preparation, but exists already in the commercial γ -Al₂O₃ powder in the first place, as made evident in Figure 1a. This phase is thermally unstable, and will decompose at an elevated temperature back to γ -Al₂O₃ (Figure S1a).²³ In an attempt to show the potential of this new class of supported nanosheet catalysts, K-promoter was additionally added as K_2CO_3 by a typical wet impregnation method. As shown in Figure 1b, XRD measurement reveals an additional peak at 30.9° (2 θ , marked with *), which is considerably due to the formation of KHCO₃ through the following pathway:^{12,24}

In the promoted sample, the 100 reflection of FeOOH becomes sharper, which is a strong indication for an increased crystallite size. This is in line with previous reports that addition of K can facilitate the growth of FeOOH, leading to a larger crystallite size.^{25,26} For analysis of the chemical state of the elements within the FeOOH, an XPS measurement was performed. The Fe 2p core levels shown in Figure 2a clearly demonstrate that there is no lower oxidation state of Fe present except for Fe³⁺. The peak centered at 712.1 eV along with the small satellite at 720.5 eV could be assigned to $Fe^{3+} 2p_{3/2}$, while the peak centered at 725.9 eV could be attributed to $Fe^{3+} 2p_{1/2}$. For the O 1s, the XPS spectra shown in Figure 2b reveal the existence of three kinds of O, which are in different chemical environments. The peak at 533.0 eV corresponds to the O from the H₂O molecules absorbed on the surface. Two other lowbinding-energy components located at 531.9 and 530.5 eV are the O in the hydroxide-like environment (OH) and the O in the oxide-like environment (lat-O), respectively. Quantitative evaluation shows the OH/lat-O ratio of 44.6:42.5 (Table S1). This is identical with the stoichiometry in the layered structure of δ -FeOOH depicted in Figure 2c, where one side of each layer is terminated by OH, and the other side is terminated by lat-O.²⁷ Additionally, the XPS characterization reveals the existence of B (Table S1, probably in the form of H_3BO_3) which was used for controlling the formation of the 2D structure during fabrication.¹⁸ Nevertheless, B species were completely removed during the activation and/or catalytic process of the catalysts (Figure S14).

The morphologies of all supported catalysts together with free-standing FeOOH and commercial γ -Al₂O₃ powder were investigated by SEM. Figures S2a and S1b show SEM images of FeOOH and γ -Al₂O₃, respectively. One can observe that the FeOOH has a sheetlike structure with a size up to hundreds of nanometers. In comparison, the commercial γ -Al₂O₃ shows much smaller sizes, from several tens of nanometers to 100 nm. It is later made evident by TEM characterization that the γ -Al₂O₃ displays a platelike morphology. The SEM images of γ -Al₂O₃-supported FeOOH with different loadings are shown in Figure S2b-d. The samples show a very good homogeneity. With an increase of the Fe-loading, the nanosheet structures are more highly populated. Additionally, we find that the freestanding FeOOH nanosheets show larger sizes compared to those in the supported samples. This is likely due to the inclusion of γ -Al₂O₃, which inhibits the growth of nanosheets from the coalescence. The loading amount of Fe on the supported samples was determined by XRF. The values derived from XRF are quite close to the nominal values, as exhibited in Table 1 (shown in parentheses). To further analyze the

Table 1. Physical Properties of the As-Prepared Catalysts

sample	Fe-loading ^a (wt %)	K-loading ^a (wt %)	$\overset{S_{BET}}{(m^2 \ g^{-1})}$
γ-Al ₂ O ₃ support			70.7
FeOOH			145.2
FeOOH/Al ₂ O ₃ (25% Fe)	24.7 (25)		94.6
FeOOH/Al ₂ O ₃ (15% Fe)	17.8 (15)		76.9
FeOOH/Al ₂ O ₃ (5% Fe)	5.5 (5)		73.8
FeOOH-K/Al ₂ O ₃ (25% Fe)	21.8 (25)	4.9 (5)	50.4

^{*a*}Fe and K contents are calculated in the reduced state.

morphology of the samples, TEM characterization was applied. The TEM image shown in Figure S3a indicates that the FeOOH has a flexible 2D morphology with lateral size of several micrometers and a measured thickness of ca. 2-3 nm. Figure 3a and Figure S3b,c show TEM images of γ -Al₂O₃supported FeOOH with different Fe-loadings. Again, a clear trend is revealed that with the increased Fe-loading more nanosheet structures are present, which coincides with the SEM observation. The TEM characterization also indicates that the γ -Al₂O₃ has a platelike morphology. The fine structure of the catalysts is analyzed by HRTEM. As shown in Figure 3b, the FeOOH shows well-resolved lattice fringes with a measured *d*spacing of 2.6 Å, corresponding to (100) planes of FeOOH. It was further revealed by fast Fourier transform (FFT) pattern that the domain is single-crystalline and is preferentially oriented along the [001] direction. It is thus considered that the absence of a characteristic 112 peak in the XRD pattern of FeOOH is associated with a preferred orientation of nanosheets and their ultrathin nature. Figure 3c shows an HRTEM image of the γ -Al₂O₃ support. The marked lattice fringes with an interplanar distance of about 2 Å indeed fit to the (004) planes of γ -Alto the (004) planes of γ -Al₂O₃. We additionally performed EDX analysis on the promoted sample to examine the distribution of K. Figure 3d shows an ADF-STEM image of the promoted FeOOH-K/Al₂O₃ (25% Fe) sample. The corresponding summarized EDX spectrum and EDX elemental maps are shown in Figure 3e-i. One can see that, in addition to the elements of Fe, O, and Al that originate from FeOOH nanosheets and the γ -Al₂O₃ support, K is clearly detected in the promoted sample (C and Cu originate from the TEM grid). Interestingly, Fe and K maps exhibit a similar distribution with synchronized intensity, which strongly suggests that the K



Figure 3. (a) TEM image of FeOOH/Al₂O₃ (25% Fe). (b, c) HRTEM images of the FeOOH nanosheet and Al₂O₃ support; insets show FFTs of the images. (d–i) ADF-STEM image of FeOOH–K/Al₂O₃ (25% Fe), the corresponding summarized EDX spectrum, and EDX elemental maps of Fe, K, Al, and O.



Figure 4. (a) TPR profiles of the (green, red, blue) supported, (black) promoted, and (purple) unsupported FeOOH catalysts. (b) Intergraded TPR profiles normalized to time-fractions $(t/t_{a=0.5})$. (c) Enlarged portion of marked region in part b.

adsorbs favorably on the surface of FeOOH nanosheets, perfectly distributed on the catalytically active part (Fecontaining part).

N₂ adsorption-desorption measurements were conducted to explore the texture characteristics and pore size distribution of the catalysts. According to IUPAC classification,²⁸ all tested samples exhibit a type-IV isotherm with an H3-type hysteresis loop except for the promoted sample, which likely has an H1 and H3 hybrid hysteresis loop (Figure S4a). Presence of the H3-type hysteresis loop implies that the samples contain slitshaped mesopores due to aggregates of platelike particles.^{28,29} The free-standing FeOOH nanosheets show the highest surface area $(145.2 \text{ m}^2 \text{ g}^{-1})$ among all the samples. The smallest surface area is measured for the γ -Al₂O₃ support, which is 70.7 m² g⁻¹. For the supported samples (except for the promoted one), their surface areas are positively correlated with the Fe-loadings, as listed in Table 1. After the introduction of K-promoter, the pore system changes significantly. For example, the promoted sample does not exhibit typical H3 but rather exhibits an H1 and H3 hybrid hysteresis. Also, the pore size distribution becomes narrow compared to those of the unpromoted ones (Figure S4b). These results suggest a conversion of the pore type from slit-shaped pores to more uniform mesoporous textures after K addition.²⁸ It has been revealed through EDX elemental maps that the K absorbs preferentially on the FeOOH nanosheets, which may lead to partial blocking of slit pores and generation of a more uniform mesoporous structure. The substantial decrease of the surface area for the promoted sample serves as additional evidence for the above findings.

Reduction Behavior of the Catalysts. Numerous studies have made evident that the activation process of catalysts is highly relevant to the formation of catalytically active α -Fe (also termed as "ammonia iron").³⁰ For a further understanding of reduction behavior prior to the catalytic reaction, TPR measurements were performed up to 800 °C with a linear heating rate of 6 °C min⁻¹ in 5% H₂/Ar. The reduction profiles of the catalysts are shown in Figure 4. Our results clearly reveal that the reduction behavior of FeOOH can be greatly influenced by the presence of the γ -Al₂O₃ support and Kpromoter. For example, the reduction of unsupported FeOOH starts with a slow H_2 consumption from 300 to 450 °C, followed by a fast consumption from 450 to 640 °C. When γ -Al₂O₃ was included, the reduction starts already strongly at 330 °C because of the distribution on the support. The main reduction event begins at ca. 500 °C and reaches higher temperatures for lower FeOOH-loadings. Moreover, the reduction peaks are more distinguishable as an indication for rather separated reduction stages. The reduction temperature is further increased when K was introduced to the system. The reduction stops at around 750 °C, which is about 50 °C higher compared to the unpromoted catalysts. The increased reduction temperature after K-promotion is ascribed to the coverage of K on FeOOH (see Figure 3f,g), which sticks strongly to the oxide part of the nanosheets and partially blocks the access of H₂ to FeOOH. For more insight about the reduction behavior of the catalysts, the integrated TPR profiles and normalized time fractions of integrated TPR curves (α plots) are displayed in Figure S5 and Figure 4b, respectively. One can clearly see the described temperature shifts of the TPR profiles among different catalysts, where, i.e., the reduction of the supported 25% FeOOH catalyst starts at the lowest temperature and the 25% FeOOH with K-promoter at the highest temperature (Figure S5). Additionally, a clear trend in the changes of the shape and inclination of the reduction profiles is observed (Figure 4b and enlarged Figure 4c), which gives further information on the reaction mechanism of the samples. The catalyst with 5% FeOOH-loading shows a pronounced shoulder, which fades gradually in the response to the increased loading of Fe. This shoulder serves as indication for the strength of the metal-support interaction and a delayed reduction. With 25% loading, the shoulder is very weak and vanishes for the corresponding promoted one,



Figure 5. (a) Rate of NH₃ synthesis normalized by mass of Fe. (b) Arrhenius plots over the Al₂O₃-supported catalysts with or without K-promoter.

suggesting again a slightly different reduction mechanism of the K-containing catalyst, already indicated by the shift to higher temperatures (Figure 4a and Figure S5). Moreover, the promoted catalyst displays a much sharper profile in comparison to the unpromoted one. The sharpest profile is obtained for the unsupported FeOOH catalyst, which clearly emphasizes the autocatalytic character of this reduction. However, the TPR curves clearly separate the impacts of the support and the promoter on the reduction behavior of the FeOOH catalysts.

Ex-situ XRD measurements were also performed to monitor the reduction behavior of FeOOH in different catalysts (Figure S6). It is revealed that the transformation from FeOOH to metallic Fe within this sample series passes through similar steps, i.e., δ -FeOOH $\rightarrow \alpha$ -Fe₂O₃ \rightarrow Fe₃O₄ \rightarrow (vonsenite, hulsite) \rightarrow FeO \rightarrow (γ -Fe) \rightarrow α -Fe. The phases of vonsenite, hulsite, and γ -Fe were not clearly shown in the supported catalysts at high temperature, which is probably due to the still XRD amorphous character of these phases and/or their low content. Additionally, strong reflections from the γ -Al₂O₃ support can hinder the detection of minor phases. Comparison of XRD patterns further emphasizes that the temperature region of each reduction step differs among the catalysts, which is in agreement with the TPR curves. The reduction of Fe₃O₄ occurs between 300 and 700 °C for the supported catalysts (Figure S6b,c), whereas it becomes more narrow (from 300 to 600 °C) for the unsupported and promoted catalysts (Figure S6a,d). Moreover, the FeO phase starts to appear between 500 and 600 °C in the unsupported catalysts (Figure S6a). It is, however, shifted to lower temperatures (400-500 °C) in the case of the supported and promoted catalysts (Figure S6b-d). These results again demonstrate the significant effect of γ -Al₂O₃ support and K-promoter in modifying the reduction behavior of FeOOH nanosheets. With an increase of the temperature to 800 °C, only α -Fe was detected in all catalysts except for the promoted one in which the γ -Fe was still present.

The catalytic activity in ammonia synthesis was evaluated for all Fe-based catalysts. Prior to ammonia synthesis, all catalysts were activated in-situ at 500 °C and 4 bar in a stoichiometric gas mixture of $3H_2/N_2$. While the supported catalysts show activity already at this moderate pressure (Figure S7), no detectable amount of NH₃ was produced during the entire activation process for the unsupported catalyst. The catalyst promoted by K shows the highest activity, suggesting the

importance of K as a promoter also for this new class of catalysts. It is additionally shown that the K-promoted catalyst needs 10 h longer to reach a stable performance during the activation procedure compared to the unpromoted ones (Figure S7). This can be explained by the intimate contact between K and Fe, which hinders the formation of active α -Fe and is again in agreement with our TPR results. After the activation process, the pressure in the reactor was elevated to 90 bar. It was accompanied by a strong increase in the product formation of NH₃, as shown in Figure S8. To reach a steady state situation, the reaction conditions during the first 10 h of TOS (time-on-stream) were kept constant. For calculation of the apparent activation energy (E_a) for each catalyst, the NH₃ effluent mole fractions in steady state at various temperatures under 90 bar were determined (Figure S9a). As references, the mole fractions of NH₃ at the thermodynamic equilibrium and an industrial reference catalyst are plotted (Figure S9a). All tested catalysts showed stable NH₃ activities at each temperature. For the FeOOH/Al₂O₃ (5% Fe) and the FeOOH-K/ Al₂O₃ (25% Fe), an additional stability test at 425 °C was performed. Since Fe is the active part of the catalysts, the reaction rate is thus normalized by the Fe mass and compared as a function of their Fe-loading, as exhibited in Figure 5a (see a comparison of the catalyst mass-based results in Figure S9b). As such, the activity of the supported catalysts (unpromoted) follows an order of FeOOH/Al₂O₃ (25% Fe) < FeOOH/Al₂O₃ $(15\% \text{ Fe}) < \text{FeOOH}/\text{Al}_2\text{O}_3$ (5% Fe). An inverse correlation between the activity and the Fe-loading is thus revealed. The E_{2} of supported catalysts, calculated on the basis of the slope of the corresponding Arrhenius plots, is accordingly shown in Figure 5b. The FeOOH/Al₂O₃ (25% Fe) catalyst shows the highest E, value of 123 kJ mol⁻¹. It decreases to 111 and 100 kJ mol⁻¹ with decreased Fe-loading (15% and 5% Fe). The decrease in E_a indicates that, with a lower Fe-loading, the nature of the active site also changes. As a consequence, it is very unlikely that the increase in activity with a decrease of the Feloading is only due to dispersion effects (Table S3). These findings are further supported by calculating the E_a based on the turnover frequencies (TOFs), which give identical values (Figure S15). The best catalytic performance is obtained from the promoted catalyst, which shows not only the highest activity (18 times more active compared to that of the corresponding unpromoted catalyst at 425 °C), but also the lowest activation energy (97 kJ mol⁻¹). These results are in

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Figure 6. XRD patterns of the spent catalysts after ammonia synthesis. (a) Fe-loading series with 100% (without support) and 25%, 15%, and 5% on γ -Al₂O₃. Zoom-in of the corresponding XRD patterns near the (b) 110 and (c) 211 reflection. (d) K-promoted catalyst and the corresponding unpromoted one (both with 25% Fe-loading). Zoom-in of the corresponding XRD patterns near the (e) 110 and (f) 211 reflection.

good agreement with the literature values for the E_a , which also show a large impact of the promoters (Table S2): A decrease from 143 to 104 kJ mol⁻¹ for Ba as promoter and, for a multipromoted commercial reference, 70 kJ mol⁻¹. In addition, the E_a of Al₂O₃-promoted Fe catalyst is given with 96 kJ mol⁻¹, in very good accordance with our measurement.^{11,31}

In ammonia synthesis, experiments and calculations have already demonstrated that, i.e., steps and defects on metallic surfaces act as active sites, strongly making evident the structure-sensitive character of ammonia catalysts.^{32–37} For investigation of the relationship between activity and state of the catalysts in our system, XRD and TEM were employed to characterize the spent catalysts in terms of their size, shape, composition, and structure. Figure 6 shows the XRD data of the spent catalysts. Analyzing the diffraction patterns reveals for the complete sample series that α -Fe is formed during the catalytic process. The patterns in Figure 6a,d clearly show the 110, 200, and 211 reflections of α -Fe centered at 44.7°, 65.0°, and 82.3° (2 θ), respectively. The widths of these characteristic peaks increase with a decrease of Fe-loading (see Figure 6b,c for 110 and 211 reflections, respectively), which is a clear indication for

smaller crystallite sizes. The splitting of the 211 peak is due to the radiation doublet (K α_1 and K α_2). On the basis of the full pattern fit results, the volume-weighted Fe domain size values $(L_{vol}$ -IB) for each catalyst is listed as insets of Figure 6a,d. As expected, the unsupported catalyst shows the biggest domain sizes of 87 nm. The smallest domain sizes of 8 nm are obtained for the catalyst with the lowest Fe-loading (inset of Figure 6a). For a better fit, quality of the unsupported sample strain is included, monitoring the impact of bulk defects (Figure S13). For the fit of the γ -Al₂O₃-supported Fe nanoparticles, no strain is needed, indicating fewer or no bulk defects. The addition of K shows no significant influence on the domain size. In addition, the profiles of the 110 and 211 reflections are almost identical (Figure 6e,f and inset of Figure 6d). This integral information makes evident the negligible influence of K on the bulk properties of the catalyst. The surface defects are invisible by XRD.

Figure 7a-d shows annular dark-field scanning TEM (ADF-STEM) images of the spent catalysts with different Fe-loadings (unpromoted). For enhancement of the visualization of catalytic particles over the support, the particles are colorized

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Figure 7. ADF-STEM images of (a-d) spent catalysts with decreased Fe-loading and (e-h) corresponding particle size distribution of Fe. (i) ADF-STEM image of K-promoted catalyst after reaction and (j-m) EDX elemental maps of Al, O, Fe, and K. Inset of part i shows the corresponding particle size distribution of Fe. (n) HRTEM image and FFT pattern of an Fe nanoparticle of the K-promoted catalyst after catalysis.

blue (the original pictures are provided in Figure S10). A clear trend is observed for the size of the Fe particles, which shrinks with a decrease in Fe-loading. This is confirmed by the particle size distributions shown in Figure 7e-h. The correlation shown above agrees well with the data extracted by XRD analysis (see inset of Figure 6a). In addition to the varied particle size, the shape of the particles differs as well between supported and unsupported catalysts. For example, the unsupported catalyst shows mostly cubic particles with smooth, well-ordered surfaces (Figure S11c,d). In comparison, the supported catalysts exhibit mainly irregular-shaped particles with stepped surfaces after catalytic reaction (Figure 7n, and Figures S11a,b and S12). These results strongly emphasize that the activity of the unpromoted catalysts correlates inversely with the size of the Fe particles, meaning that smaller particles with more surface defects have a higher activity. With respect to the discussed structure sensitivity of ammonia catalysts, these surface steps and kinks of Fe are most likely the active sites for ammonia synthesis. Since small particles have a higher density of stepkink surfaces serving as active centers (Figure S11b,d), an improved activity and distinct structure-activity correlation is observed. This is again in perfect agreement with the calculated E_{av} which decreases from 123 to 100 kJ mol⁻¹ with lower loadings and more defective particles. Additionally, this correlates with the trends of the α -plots (Figure 4b,c), which show a pronounced shoulder at 5% FeOOH-loading (indicating a strong metal—support interaction). In contrast, driven by thermodynamics to minimize the surface energy, active steps and kinks are largely reduced for big particles; thus a smaller reaction rate is resulted.

The K-promoted catalyst shows by far the best catalytic performance. Since the Fe mass in the promoted and the corresponding unpromoted samples is similar, the enormous improvement of the catalytic activity is obviously due to the promotion effect of K. It is well-accepted that K serves as an electronic promoter for ammonia synthesis and effectively modifies the electronic structure of the metal and coadsorbed molecules, i.e., increases the rate of the dinitrogen dissociation.^{30,38–41} The EDX elemental mapping results (Figure 7l,m) reveal that the K sticks almost exclusively on the surface of Fe. Because of this intimate contact between K and Fe, a strong metal-promoter interaction is likely to be induced, thus giving rise to the enhanced catalytic activity of the promoted catalyst. Moreover, in the current system K is found to have additional influences on the structure of Fe.⁴² TEM analysis shows more irregular nanoparticles present in the promoted catalyst

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compared with the corresponding unpromoted catalyst (25% Fe). As such, higher densities of step-kink surfaces are induced, which, in turn, leads to a higher activity of the promoted catalyst. In summary, our results suggest that K acts not only as an electronic promoter (the major effect) but also as a structural one. This leads to the formation of more active sites through affecting the size and the surface of the Fe nanoparticles.⁴² Both effects take place and result in the lowest E_a (97 kJ mol⁻¹) and highest reaction rates. Since, i.e., the Feloading in the promoted catalyst has not yet been optimized, it is highly possible that a further enhanced catalytic performance will be obtained.

CONCLUSION

In summary, a new class of Fe-based catalysts, including unsupported FeOOH, γ -Al₂O₃-supported FeOOH with different Fe-loadings, and a K-promoted catalyst, has been prepared, systematically characterized before (XRD, XPS, BET, SEM, TPR, and TEM/EDX) and after (XRD and TEM) reaction in ammonia synthesis. A clear relationship between the particle size in the spent catalysts and the catalytic activity has been established for the unpromoted catalyst series. The smaller particles exhibit a higher density of step-kink surfaces probably acting as active sites. Thus, an improved catalytic activity is observed. This seems also to correlate with the α -plots of the integrated TPR curves, which show a profile dependence of the FeOOH-loading and the metal-support interaction. In contrast, the catalytically active step-kink surfaces will be largely reduced or even vanish for larger particles, resulting in smaller reaction rates. The best catalytic performance is obtained for a K-promoted catalyst. In addition to its dominating electronic promotion, K serves as a structure promoter for the formation of more active sites by modifying the surface structure of Fe. Our results open up a new pathway for a simple and energy-saving preparation of efficient nanostructured Fe-based catalysts for ammonia synthesis. In addition, our findings provide important insights into the understanding of the promotion effect and the structureactivity relation for this reaction.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b02812.

XRD patterns, SEM images, surface composition, TEM images, N₂ adsorption–desorption isotherms, pore size distributions, integrated TPR curves, ex-situ XRD results, activation data, stepwise catalytic tests, long-term stability results, TOFs, activation energy of unsupported and γ -Al₂O₃-supported catalysts, ADF-STEM images, HRTEM images, EDX spectra, and XRD fitting results of the spent catalysts (PDF)

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Notes

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REFERENCES

(1) Schlögl, R. Catalytic Synthesis of Ammonia—A "Never-Ending Story"? Angew. Chem., Int. Ed. 2003, 42, 2004–2008.

(2) Erisman, J. W.; Sutton, M. A.; Galloway, J.; Klimont, Z.; Winiwarter, W. How a century of ammonia synthesis changed the world. *Nat. Geosci.* **2008**, *1*, 636–639.

(3) Appl, M. Ammonia, 1. Introduction. In Ullmann's Encyclopedia of Industrial Chemistry; Wiley-VCH Verlag GmbH & Co. KGaA, 2000.

(4) US Department of Energy. Potential Roles of Ammonia in a Hydrogen Economy—A Study of Issues Related to the Use Ammonia for On-Board Vehicular Hydrogen Storage. https://energy.gov/sites/prod/ files/2015/01/f19/fcto_nh3_h2_storage_white_paper_2006.pdf (accessed 2006).

(5) Klerke, A.; Christensen, C. H.; Norskov, J. K.; Vegge, T. Ammonia for hydrogen storage: challenges and opportunities. *J. Mater. Chem.* **2008**, *18*, 2304–2310.

(6) Schuth, F.; Palkovits, R.; Schlogl, R.; Su, D. S. Ammonia as a possible element in an energy infrastructure: catalysts for ammonia decomposition. *Energy Environ. Sci.* **2012**, *5*, 6278–6289.

(7) Appl, M. Ammonia, 2. Production Processes. In Ullmann's Encyclopedia of Industrial Chemistry; Wiley-VCH Verlag GmbH & Co. KGaA, 2000.

(8) Kitano, M.; Inoue, Y.; Yamazaki, Y.; Hayashi, F.; Kanbara, S.; Matsuishi, S.; Yokoyama, T.; Kim, S.-W.; Hara, M.; Hosono, H. Ammonia synthesis using a stable electride as an electron donor and reversible hydrogen store. *Nat. Chem.* **2012**, *4*, 934–940.

(9) Jedynak, A.; Szmigiel, D.; Raróg, W.; Zieliński, J.; Pielaszek, J.; Dłużewski, P.; Kowalczyk, Z. Potassium-Promoted Carbon-Based Iron Catalyst for Ammonia Synthesis. Effect of Fe Dispersion. *Catal. Lett.* **2002**, *81*, 213–218.

(10) Rayment, T.; Schlogl, R.; Thomas, J. M.; Ertl, G. Structure of the ammonia synthesis catalyst. *Nature* **1985**, *315*, 311–313.

(11) Pernicone, N.; Ferrero, F.; Rossetti, I.; Forni, L.; Canton, P.; Riello, P.; Fagherazzi, G.; Signoretto, M.; Pinna, F. Wustite as a new precursor of industrial ammonia synthesis catalysts. *Appl. Catal., A* **2003**, 251, 121–129.

(12) Schlögl, R. Preparation and Activation of the Technical Ammonia Synthesis Catalyst. In *Catalytic Ammonia Synthesis: Fundamentals and Practice;* Jennings, J. R., Ed.; Springer US: Boston, MA, 1991.

(13) Sustainable Ammonia Synthesis—Exploring the scientific challenges associated with discovering alternative, sustainable processes for ammonia production. DOE Roundtable Report; US Department of Energy, Office of Science: Dulles, VA, 2016; https://science.energy.gov/ ~/media/bes/pdf/reports/2016/SustainableAmmoniaReport.pdf.

(14) Kandemir, T.; Schuster, M. E.; Senyshyn, A.; Behrens, M.; Schlögl, R. The Haber–Bosch Process Revisited: On the Real Structure and Stability of "Ammonia Iron" under Working Conditions. *Angew. Chem., Int. Ed.* **2013**, *52*, 12723–12726.

(15) Sun, Y.; Lei, F.; Gao, S.; Pan, B.; Zhou, J.; Xie, Y. Atomically Thin Tin Dioxide Sheets for Efficient Catalytic Oxidation of Carbon Monoxide. *Angew. Chem., Int. Ed.* **2013**, *52*, 10569–10572.

(16) Sun, Y.; Liu, Q.; Gao, S.; Cheng, H.; Lei, F.; Sun, Z.; Jiang, Y.; Su, H.; Wei, S.; Xie, Y. Pits confined in ultrathin cerium(IV) oxide for studying catalytic centers in carbon monoxide oxidation. *Nat. Commun.* **2013**, *4*, 2899.

(17) Sun, Y.; Gao, S.; Lei, F.; Xie, Y. Atomically-thin two-dimensional sheets for understanding active sites in catalysis. *Chem. Soc. Rev.* **2015**, 44, 623–636.

ACS Sustainable Chemistry & Engineering

(18) Fan, H.; Huang, X.; Shang, L.; Cao, Y.; Zhao, Y.; Wu, L.-Z.; Tung, C.-H.; Yin, Y.; Zhang, T. Controllable Synthesis of Ultrathin Transition-Metal Hydroxide Nanosheets and their Extended Composite Nanostructures for Enhanced Catalytic Activity in the Heck Reaction. *Angew. Chem., Int. Ed.* **2016**, *55*, 2167–2170.

(19) Bai, S.; Xiong, Y. Recent Advances in Two-Dimensional Nanostructures for Catalysis Applications. *Sci. Adv. Mater.* 2015, 7, 2168–2181.

(20) Chen, H.; Zhang, F.; Fu, S.; Duan, X. In Situ Microstructure Control of Oriented Layered Double Hydroxide Monolayer Films with Curved Hexagonal Crystals as Superhydrophobic Materials. *Adv. Mater.* **2006**, *18*, 3089–3093.

(21) Gao, S.; Sun, Y.; Lei, F.; Liang, L.; Liu, J.; Bi, W.; Pan, B.; Xie, Y. Ultrahigh Energy Density Realized by a Single-Layer β -Co(OH)2 All-Solid-State Asymmetric Supercapacitor. *Angew. Chem., Int. Ed.* **2014**, 53, 12789–12793.

(22) Zhang, Q.; Zhang, C.; Liang, J.; Yin, P.; Tian, Y. Orthorhombic α -NiOOH Nanosheet Arrays: Phase Conversion and Efficient Bifunctional Electrocatalysts for Full Water Splitting. ACS Sustainable Chem. Eng. **2017**, *5*, 3808–3818.

(23) Rozita, Y.; Brydson, R.; Comyn, T. P.; Scott, A. J.; Hammond, C.; Brown, A.; Chauruka, S.; Hassanpour, A.; Young, N. P.; Kirkland, A. I.; Sawada, H.; Smith, R. I. A Study of Commercial Nanoparticulate *γ*-Al2O3 Catalyst Supports. *ChemCatChem* **2013**, *5*, 2695–2706.

(24) Herzog, B.; Herein, D.; Schlögl, R. In situ X-ray powder diffraction analysis of the microstructure of activated iron catalysts for ammonia synthesis. *Appl. Catal., A* **1996**, *141*, 71–104.

(25) Dry, M. E.; Oosthuizen, G. J. The correlation between catalyst surface basicity and hydrocarbon selectivity in the Fischer–Tropsch synthesis. *J. Catal.* **1968**, *11*, 18–24.

(26) Yang, Y.; Xiang, H.-W.; Xu, Y.-Y.; Bai, L.; Li, Y.-W. Effect of potassium promoter on precipitated iron-manganese catalyst for Fischer–Tropsch synthesis. *Appl. Catal., A* **2004**, *266*, 181–194.

(27) Patrat, G.; de Bergevin, F.; Pernet, M.; Joubert, J. C. Structure locale de δ -FeOOH. Acta Crystallogr., Sect. B: Struct. Sci. **1983**, B39, 165–170.

(28) Sing, K. S.W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquerol, J.; Siemieniewska, T. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure Appl. Chem.* **1985**, *57*, 603–619.

(29) Ortega, K. F.; Rein, D.; Lüttmann, C.; Heese, J.; Özcan, F.; Heidelmann, M.; Folke, J.; Kähler, K.; Schlögl, R.; Behrens, M. Ammonia Decomposition and Synthesis over Multinary Magnesioferrites: Promotional Effect of Ga on Fe Catalysts for the Decomposition Reaction. *ChemCatChem* **2017**, *9*, 659–671.

(30) Schlögl, R. Ammonia Synthesis. In *Handbook of Heterogeneous Catalysis*; Wiley-VCH Verlag GmbH & Co. KGaA, 2008.

(31) Hagen, S.; Barfod, R.; Fehrmann, R.; Jacobsen, C. J. H.; Teunissen, H. T.; Chorkendorff, I. Ammonia synthesis with bariumpromoted iron-cobalt alloys supported on carbon. *J. Catal.* **2003**, *214*, 327–335.

(32) Falicov, L. M.; Somorjai, G. A. Correlation between catalytic activity and bonding and coordination number of atoms and molecules on transition metal surfaces: Theory and experimental evidence. *Proc. Natl. Acad. Sci. U. S. A.* **1985**, *82*, 2207–2211.

(33) Dahl, S.; Logadottir, A.; Egeberg, R. C.; Larsen, J. H.; Chorkendorff, I.; Törnqvist, E.; Nørskov, J. K. Role of Steps in N2 Activation on Ru(0001). *Phys. Rev. Lett.* **1999**, *83*, 1814–1817.

(34) Hammer, B.; Nørskov, J. K. Theoretical surface science and catalysis—calculations and concepts. *Adv. Catal.* **2000**, *45*, 71–129.

(35) Egeberg, R. C.; Dahl, S.; Logadottir, A.; Larsen, J. H.; Nørskov, J. K.; Chorkendorff, I. N2 dissociation on Fe(110) and Fe/Ru(0001): what is the role of steps? *Surf. Sci.* **2001**, *491*, 183–194.

(36) Norskov, J. K.; Bligaard, T.; Hvolbaek, B.; Abild-Pedersen, F.; Chorkendorff, I.; Christensen, C. H. The nature of the active site in heterogeneous metal catalysis. *Chem. Soc. Rev.* **2008**, *37*, 2163–2171.

(37) Vojvodic, A.; Medford, A. J.; Studt, F.; Abild-Pedersen, F.; Khan, T. S.; Bligaard, T.; Nørskov, J. K. Exploring the limits: A low-pressure, low-temperature Haber-Bosch process. Chem. Phys. Lett. 2014, 598, 108-112.

(38) Bare, S. R.; Strongin, D. R.; Somorjai, G. A. Ammonia synthesis over iron single-crystal catalysts: the effects of alumina and potassium. *J. Phys. Chem.* **1986**, *90*, 4726–4729.

(39) Strongin, D. R.; Somorjai, G. A. The effects of potassium on ammonia synthesis over iron single-crystal surfaces. *J. Catal.* **1988**, *109*, 51–60.

(40) Strongin, D. R.; Somorjai, G. A. On the rate enhancement of ammonia synthesis over iron single crystals by coadsorption of aluminum oxide with potassium. *Catal. Lett.* **1988**, *1*, 61–66.

(41) Strongin, D. R.; Somorjai, G. A. A Surface Science and Catalytic Study of the Effects of Aluminum Oxide and Potassium on the Ammonia Synthesis Over Iron Single-Crystal Surfaces. In *Catalytic Ammonia Synthesis: Fundamentals and Practice*; Jennings, J. R., Ed.; Springer US: Boston, MA, 1991.

(42) Huo, C.-F.; Wu, B.-S.; Gao, P.; Yang, Y.; Li, Y.-W.; Jiao, H. The Mechanism of Potassium Promoter: Enhancing the Stability of Active Surfaces. *Angew. Chem., Int. Ed.* **2011**, *50*, 7403–7406.