

Size-Dependent Activity of Iron Nanoparticles in Both Thermal and Plasma Driven Catalytic Ammonia Decomposition

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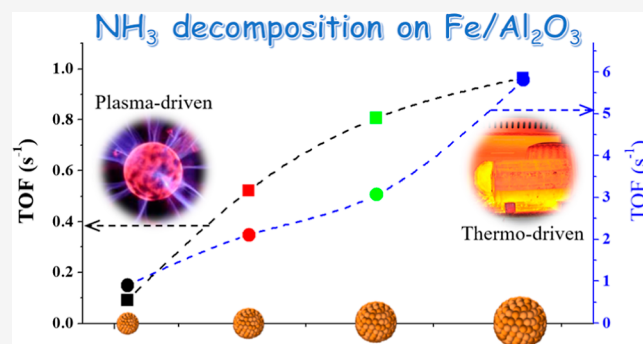


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Supporting Information

ABSTRACT: Water-dispersible Fe_3O_4 nanoparticles with diameters of 4.2 ± 0.6 , 6.1 ± 0.8 , 8.1 ± 1 , and 10.4 ± 1 nm were prepared through the polyol method and employed as the precursors of $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ catalysts to study the size-dependent activity. We identified that the activity of the catalysts in NH_3 decomposition (driven by both thermal and dielectric barrier discharge plasma) increased with increasing Fe_3O_4 particle size. The turnover frequencies (TOFs) were increased from 0.9 to 5.8 s^{-1} with an increasing Fe_3O_4 precursor size from 4.2 to 10.4 nm during the thermocatalytic decomposition. A quite similar “particle size effect” was also observed for the plasma catalytic decomposition, although lower TOF was observed. Additionally, reaction-induced catalyst reconstruction was identified during the early-stage of the catalytic decomposition and can be attributed to the nitridation of FeO_x to Fe_xN . Our results provide new evidence for the “structure-sensitivity” of the catalytic NH_3 decomposition.



INTRODUCTION

Heterogeneous catalysis by nanosized transition metal particles has, frequently, been found to be “structure-sensitive”.^{1–3} The specific reaction rates and selectivities are sensitive (either increase or decrease) to the metal particle size, leading to the significant “particle size effect”.^{4–10} Therefore, understanding the size-reactivity relationship is critical to the “structure-sensitive” heterogeneous catalytic processes. Various synthesis strategies have been developed for the preparation of nanoparticles with uniform sizes and morphologies,¹¹ based on which many studies were performed to understand the nature of the size and morphology effect.¹²

An intriguing example of “structure-sensitivity” is identified in the conventional ammonia synthesis (known as the Haber–Bosch process: fixing N_2 and H_2 to produce NH_3),¹³ which has been verified by several pioneers in the field of heterogeneous catalysis during the 1970s–1980s.¹⁴ For example, Dumesic and Boudart identified that the turnover frequency (TOF) (referred to as “turnover number” in their original paper) of the small Fe particles is an order of magnitude smaller than that for larger particles.¹⁵ According to Ertl and co-workers, nitrogen adsorption on well-defined Fe single-crystal surfaces demonstrated a strongly anisotropic nature.¹⁶ The Fe(111) plane, due to the presence of exposed seven-coordinated Fe atoms on the surface, has been found to be the most active plane for nitrogen dissociation.¹⁷ The same conclusion was also addressed by Somorjai and co-workers,¹⁸ where an activity ratio of 418:25:1 was found for the Fe(111), Fe(100), and Fe(110) planes, respectively.^{18,19} Besides the commercial Fe-

based catalysts, other catalysts, such as Mo_2N ,²⁰ Re,²¹ and Ru,^{22,23} also demonstrated the same “structure-sensitivity”. For example, Volpe and Boudart identified that the turnover rates of ammonia synthesis on Mo_2N decreased by a factor of 25 as the particle size decreased from 12 to 3 nm.²⁰ The Somorjai group found that, for the Rhenium catalyst, the reactivity ratio for the Re(0001), Re(1010), Re(1120), and Re(1121) crystal faces was 1:94:920:2820, respectively.²¹

As the reverse process of ammonia synthesis, ammonia decomposition has recently received increasing attention because NH_3 has been considered a promising H_2 carrier.²⁴ Ammonia has a high volumetric ($121 \text{ kg H}_2/\text{m}^3$) and gravimetric (17.75 wt %) hydrogen capacity and can be readily liquefied at a mild pressure of ~ 8 bar at room temperature, giving rise to an energy density of 4.25 kW h/L . Therefore, NH_3 decomposition has been extensively studied for CO_x -free H_2 production recently.^{25–29} Quite similar to NH_3 synthesis, the “structure-sensitivity” has also been identified for NH_3 decomposition over the Ni,^{30,31} Ir,³² Ru,³³ and Pt³⁴ catalysts. With the Ni-based catalysts, the first-principles calculation suggested that the energy barrier of

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associative desorption of N on the stepped Ni(211) is 1.1 eV higher than that on the closed-packed Ni(111).³⁰ Consequently, the turnover rates increased with increasing Ni particle size.³⁰ Nonetheless, a similar “particle size”/“structure-sensitivity” effect for NH₃ decomposition over the Fe-based catalyst has not been systematically elucidated.³⁵ Noteworthy, most of the current studies on NH₃ decomposition focus on the thermocatalytic process, which requires a temperature of up to 550 °C.³⁵ At low temperatures, the recombinative desorption of nitrogen (N_{ad}) from the catalyst surface is significantly inhibited.³⁶ While plasma driven catalysis has been proposed to assist the decomposition of NH₃,³⁷ the influence of particle size on the activity has not been studied.

Recently, we developed a continuous growth method to synthesize water-dispersible iron oxide nanoparticles with precisely controlled sizes.^{38,39} In this method, the nanoparticles with increasing sizes could be synthesized, under the same reaction conditions (temperature and solvent), by repeatedly adding the reactant for additional growth. The reaction provides ideal nanoparticles to study the size-dependent behavior for the “structure-sensitivity”. In this paper, a series of water-dispersible Fe₃O₄ nanoparticles with narrow size distributions were synthesized and employed as the precursors of Fe₃O₄/Al₂O₃ catalysts to study the size-dependent activity. With Fe₃O₄ particle sizes of 4.2 ± 0.6, 6.1 ± 0.8, 8.1 ± 1, and 10.4 ± 1 nm prepared, we will demonstrate the influence of particle size on the activity of both thermal and plasma driven catalytic NH₃ decomposition. Specifically, we show that the TOF increases with increasing Fe₃O₄ particle size. Noteworthy, the Fe₃O₄ nanoparticles on the Al₂O₃ support were partially reduced to FeO_x during activation in H₂ (10%) and transformed into Fe_xN during the early-stage of the reaction.

■ EXPERIMENTAL SECTION

Synthesis of Fe₃O₄ Nanoparticles. The iron oxide nanoparticles were synthesized through the polyol method according to our previous studies.^{38,39} Typically, iron(III) acetylacetonate (Fe(acac)₃) (88 mg, 0.25 mmol) was first mixed with diethylene glycols (DEG) (2.5 mL) in a three-necked flask under argon to obtain solution A (0.1 mmol Fe/mL). In another flask, Fe(acac)₃ (211 mg, 0.6 mmol) was mixed with DEG (6 mL) to obtain solution B (0.1 mmol Fe/mL). The obtained solutions (A and B) were heated to 120 °C for an hour. Then, solution B was kept at 70 °C for later use. Solution A was further heated slowly (heating rate of 2.5 °C/min) to the desired temperature for 2 h for the first growth. After that, solution B (2.5 mL, 0.25 mmol) was added to react for another 2 h, as the second growth. The solution B was added repeatedly to synthesize iron oxide nanoparticles with desired sizes. The samples were mixed with MilliQ water and purified by centrifugal filtration (Amicon, 30 K). After being repeated three times, the final products were dispersed in MilliQ water for further use.

Preparation of Fe₃O₄/Al₂O₃. Fe₃O₄/Al₂O₃ catalysts were prepared through impregnation of the as-synthesized Fe₃O₄ nanoparticles (in aqueous) on the γ-Al₂O₃ support (Inframat Advanced Materials: Product #26N-0801G), which has an average particle size of 20–50 nm and BET surface area >150 m²/g. Before impregnation, the Al₂O₃ support was first calcined at 550 °C for 12 h in a muffle furnace. Typically, the appropriate amounts of the as-synthesized Fe₃O₄ nanoparticles (~5 mg Fe in water) were diluted to around 5 mL and added to 0.5 g of Al₂O₃. The obtained slurry was then

sonicated for 10 min before being transferred to a rotary evaporator to remove water under a vacuum of 150 mbar at 65 °C. The obtained sample was dried under air at 100 °C overnight and then calcined at 450 °C for 4 h (to remove trace DEG) in a tube furnace at a ramp of 5 °C/min under 100 mL/min of dry air. The Fe loadings according to the ICP-MS were 0.7, 0.46, 0.46, and 0.35 wt % for the Fe₃O₄ with particle sizes of 4.2 ± 0.6, 6.1 ± 0.8, 8.1 ± 1, and 10.4 ± 1 nm, respectively.

Catalyst Characterization. Transmission electron microscopy (TEM) images and STEM–EDX chemical mapping of the activated catalysts were obtained using a JEOL 2100TEM (accelerating voltage 200 kV) equipped with a Gatan camera. The diluted sample in isopropanol was cast on FCF300-CU (Electron Microscopy Science) 300 mesh carbon-coated copper grid and allowed to dry at room temperature overnight. The size analysis from TEM images was performed using ImageJ software (version 1.52a) by taking the average size of 100 particles.

The X-ray photoelectron spectroscopy (XPS) analysis was carried out with a Scienta Omicron ESCA 2SR XPS system equipped with a flood source charge neutralizer. The powder samples were pressed into thin pellets, fixed on the sample stage with double-sided carbon tape, and then loaded into the loadlock chamber and pumped until the vacuum was below 5 × 10^{−7} mbar before they were transferred into the sample analysis chamber. The XPS spectra were collected with a Mono Al Kα X-ray source (1486.6 eV) at a power of 450 W, and the pressure in the analysis chamber was maintained below 5 × 10^{−9} mbar. Source and analyzer angle is fixed at 54.7°, and the take-off angle is fixed at 90°. A wide region survey scan and high-resolution core-level scans of all elements of the sample were recorded and calibrated with respect to the C 1s at 284.8 eV.

Thermocatalytic NH₃ Decomposition. The thermocatalytic testing was performed in a “U-shape” quartz reactor [with a volume of 2 mL (id Φ = 1/2”)] connected to a home-built gas supply manifold allowing the transient analysis. For all catalytic tests, 0.05 g of the Fe₃O₄/Al₂O₃ catalysts was used. The samples were pre-treated in 10% H₂/Ar (30 mL/min) at 600 °C (ramp: 10 °C/min) for 1 h. Then, the spectra of pure Ar (30 mL/min) and the mixture of NH₃/Ar (Ar: 10 mL/min and NH₃: 20 mL/min) were collected for mass spectrometer calibration by the external standard method. The reactions were performed at 600 °C under atmospheric pressure at a gas hourly space velocity (GHSV) of 600 mL/g/min. The early-stage catalytic performance was obtained by switching the reactor inlet from Ar to NH₃/Ar, and the back-transient was obtained by switching the influent gas from NH₃/Ar back to inert (Ar). The reactor effluent was measured by the online Agilent 5973 MS (equipped with MS Sensor 2.0 software, Diablo Analytical, Inc.). The *m/z* = 16, 28, and 40 for NH₃, N₂, and Ar, respectively, were monitored continuously.

Plasma Catalytic NH₃ Decomposition. The plasma catalytic testing was performed in a coaxial dielectric barrier discharge (DBD) reactor consisting of a quartz tube with an inner diameter of 4 mm and an outer diameter of 1/4”. A scheme of the reactor system is shown in Figure S1a. Specifically, a 6 cm long stainless steel mesh (20 mesh) is employed as the outer electrode and wrapped tight around the quartz tube. A 1/16” tungsten electrode is inserted at the center of the reactor and act as the inner electrode. The discharge volume of the DBD reactor is 0.64 cm³ without a

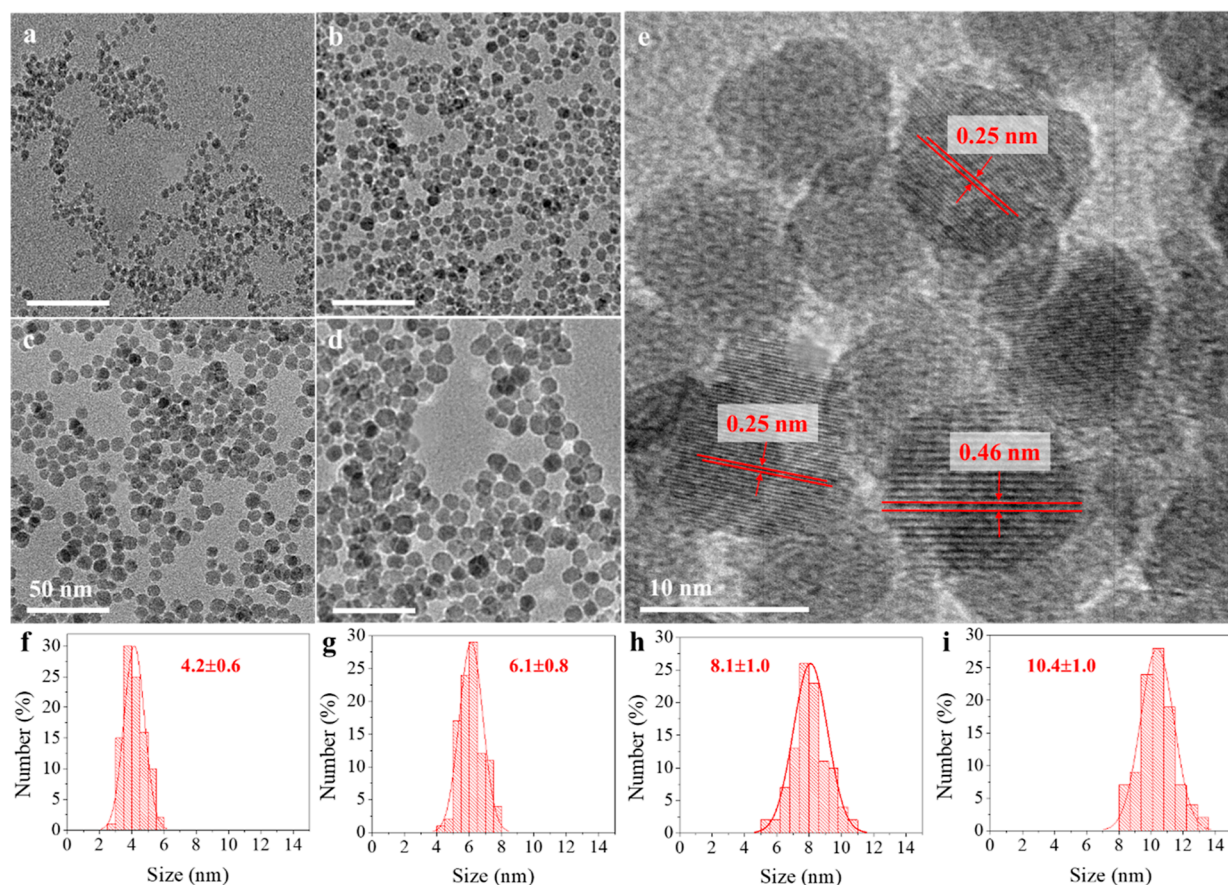


Figure 1. HRTEM images of the as-synthesized Fe_3O_4 nanoparticles (a–e) and the size distribution histogram (f–i).

catalyst. The DBD plasma was generated using a PMV500 high voltage AC power source with an applied voltage of 10 kV and a frequency of around 24 kHz. The applied voltage was measured using an oscilloscope (Tetronix MDO32 3-BW-100) connected to a high voltage probe (1000:1, Tektronix P6015A), and the gas voltage was measured across a 10 nF capacitor by the same oscilloscope with TPP0250 voltage probe. The power input of the plasma (around 11 W) was measured based on the area inside the charge–voltage (Q – V) Lissajous curves.⁴⁰

During the plasma catalytic testing, a 0.1 g catalyst was loaded into the plasma reactor (see Figure S1b for the details). The reaction was performed under ambient conditions at a total flow rate of 30 mL/min (NH_3 20 mL/min and Ar 10 mL/min), which provided a specific energy input (SEI) of 22 J/cm³. The plasma reactor outlet was measured directly by the same Agilent 5973 MS.

TOF Evaluation. The apparent TOF was calculated based on the total surface area per gram of Fe nanoparticles, which can be calculated from

$$S = \frac{6}{\rho\phi}$$

where ρ is the bulk density of Fe ($7.89 \times 10^6 \text{ m}^3/\text{g}$) and ϕ is the diameter of the particles after catalysis (similar to the Fe_3O_4 precursor according to the TEM of the used samples).

A surface area of 0.0613 nm^2 per iron atom was used for TOF calculation, corresponding to ~ 16 Fe atoms per nm^2 .¹⁰ The TOF is calculated from

$$\text{TOF} = \frac{r \times 6.13 \times 10^{-20} \times N_a}{S}$$

where r is the reaction rate ($\text{mol}_{\text{NH}_3}/\text{g}_{\text{Fe}}/\text{min}$) and N_a is the Avogadro constant.

Although the reduced Fe nanoparticles were transformed into Fe_xN during the reaction, the nitridation decreases simultaneously the bulk density ρ (increases the total surface area S) and site density (increases the surface area per iron atom). Therefore, estimating the TOF based on Fe could only introduce a negligible error.

RESULTS AND DISCUSSION

Design and Synthesis of $\text{Fe}/\text{Al}_2\text{O}_3$ Catalysts with Different Fe Sizes. The $\text{Fe}/\text{Al}_2\text{O}_3$ catalysts (with different Fe sizes ranging from 4–11 nm) employed for NH_3 decomposition were prepared using the water-dispersible Fe_3O_4 nanoparticles as the precursor. The Fe_3O_4 nanoparticles were introduced into the $\gamma\text{-Al}_2\text{O}_3$ support through impregnation under sonication using water as the solvent. To obtain water-dispersible Fe_3O_4 nanoparticles with tunable and narrow size distributions, we employed the polyol method.^{38,39} The strategy is based on the thermal decomposition of the $\text{Fe}(\text{acac})_3$ precursor in the DEGs. The particle size was tuned by a stepwise growth. With such a synthesis strategy, four samples of Fe_3O_4 nanoparticles with different sizes were prepared. The representative TEM images of the Fe_3O_4 nanoparticles and their corresponding size distribution histogram are shown in Figure 1a–d and f–i, respectively. It is seen that water-dispersible Fe_3O_4 nanoparticles with sizes of $4.2 \pm$

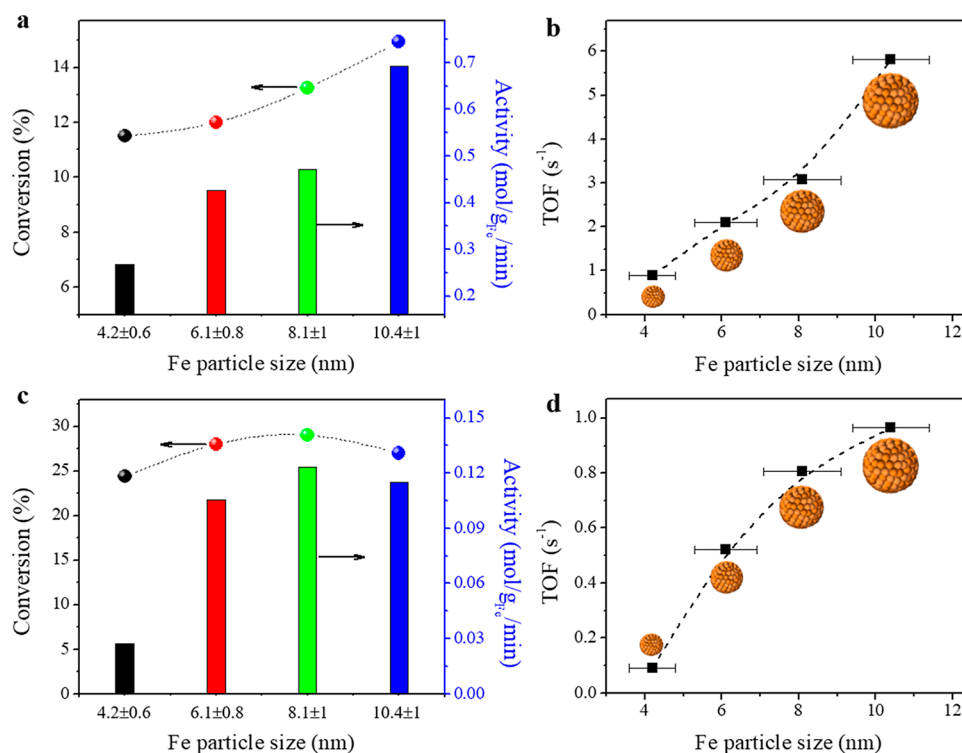


Figure 2. Influence of Fe₃O₄ nanoparticle size on the catalytic activity of NH₃ decomposition. (a,b) Conversion, specific activity, and TOF during the thermocatalytic reaction at 600 °C. (c,d) Conversion, specific activity, and TOF during plasma catalytic reaction without external heating.

0.6, 6.1 ± 0.8, 8.1 ± 1, and 10.4 ± 1 nm were successfully synthesized. Specifically, the Fe₃O₄ nanoparticles show spheric morphology and quite narrow size distributions (deviation ≤ 1 nm statistically). The size and morphology of the nanoparticles on the Al₂O₃ support are almost unchanged after the reaction (vide infra). The selected high-resolution transmission electron microscopy (HRTEM) image of the nanoparticles is shown in Figure 1e. The measured lattice distance of the majority of the nanoparticles is around 0.25 nm, which corresponds to the (311) plane of the Fe₃O₄ crystalline phase. The identification of the (311) plane from the HRTEM is consistent with the XRD pattern of the Fe₃O₄ nanoparticles,³⁸ where the (311) plane was found to be the most intense diffraction peak (JCPDS no. 03-0863). The measured lattice distance around 0.46 nm was also identified by the HRTEM, which can be assigned to the (111) plane of the Fe₃O₄ crystalline.

Size-Dependent Activity in Thermocatalytic NH₃ Decomposition. The catalytic performance of the Fe₃O₄/Al₂O₃ catalysts (with different Fe₃O₄ nanoparticle sizes) in thermocatalytic NH₃ decomposition is shown in Figure 2a,b. As shown in Figure 2a (left axis), during the thermocatalytic NH₃ decomposition at 600 °C, NH₃ conversion between 11.5–15% was obtained over the Fe₃O₄/Al₂O₃ catalysts. It is seen that NH₃ conversion increases with increasing Fe₃O₄ nanoparticles size. Noteworthy, the Al₂O₃ used in this study is almost inactive for the thermocatalytic NH₃ decomposition under the investigated conditions (see Figure S2). Therefore, the NH₃ conversion was converted into mass-specific activity (per gram of Fe). As shown in Figure 2a: right axis, the specific activity increased from 0.27 to 0.69 mol_{NH₃}/g_{Fe}/min with increasing Fe₃O₄ nanoparticles size from 4.2 to 10.4 nm. The specific activity over the present Fe/Al₂O₃ catalysts is significantly higher than that of the Fe/CNFs reported in the literature (the activity of the Fe/CNFs catalyst was estimated

to be ~0.14 mol_{NH₃}/g_{Fe}/min).³⁵ In the literature, the particle size of the Fe species was found to be 40–300 nm.³⁵ We expect that the present catalysts demonstrated a higher mass-specific activity due to the rationally designed Fe₃O₄ nanoparticles at the relatively smaller size range.

The mass-specific activities were further converted into TOFs for a better demonstration of the “particle size effect”. TOF values were calculated using simple geometric arguments for spherical particle shapes and a surface iron density of 0.0613 nm⁻² corresponding to ~16 atoms of Fe nm⁻².¹⁰ It must be noted that the Fe₃O₄ nanoparticles were partially reduced to FeO_x during H₂ pre-treatment and converted into Fe_xN during the reaction (vide infra), which could lead to TOF values deviation slightly from that obtained based on Fe⁰. The TOF values (see Figure 2b) were increased from 0.9 to 5.8 s⁻¹ with an increasing Fe₃O₄ nanoparticles size from 4.2 to 10.4 nm. We expect that the TOF could further increase with increasing Fe₃O₄ nanoparticle size. For example, the TOF estimated from the literature³⁵ is around 9 s⁻¹ when the average particle size is around 100 nm. Nonetheless, the mass-specific activity must be decreased at a larger particle size due to the loss of total metal surface area per gram of nanoparticles.

Size-Dependent Activity in Plasma Catalytic NH₃ Decomposition. The integration of DBD non-thermal plasma (NTP) with heterogeneous catalytic processes is an emerging technology for low-temperature chemical transformations.⁴⁰ Therefore, unlike the thermocatalytic NH₃ decomposition which requires a reaction temperature up to 600 °C, the plasma catalytic reaction was performed under “ambient conditions” (without external heat supply). The temperature of the reactor is around 200 °C (measured by attaching a thermocouple to the outer electrode right after the shutdown of plasma) with the applied power of plasma. The electrical signals of the applied discharge in the mixing of NH₃

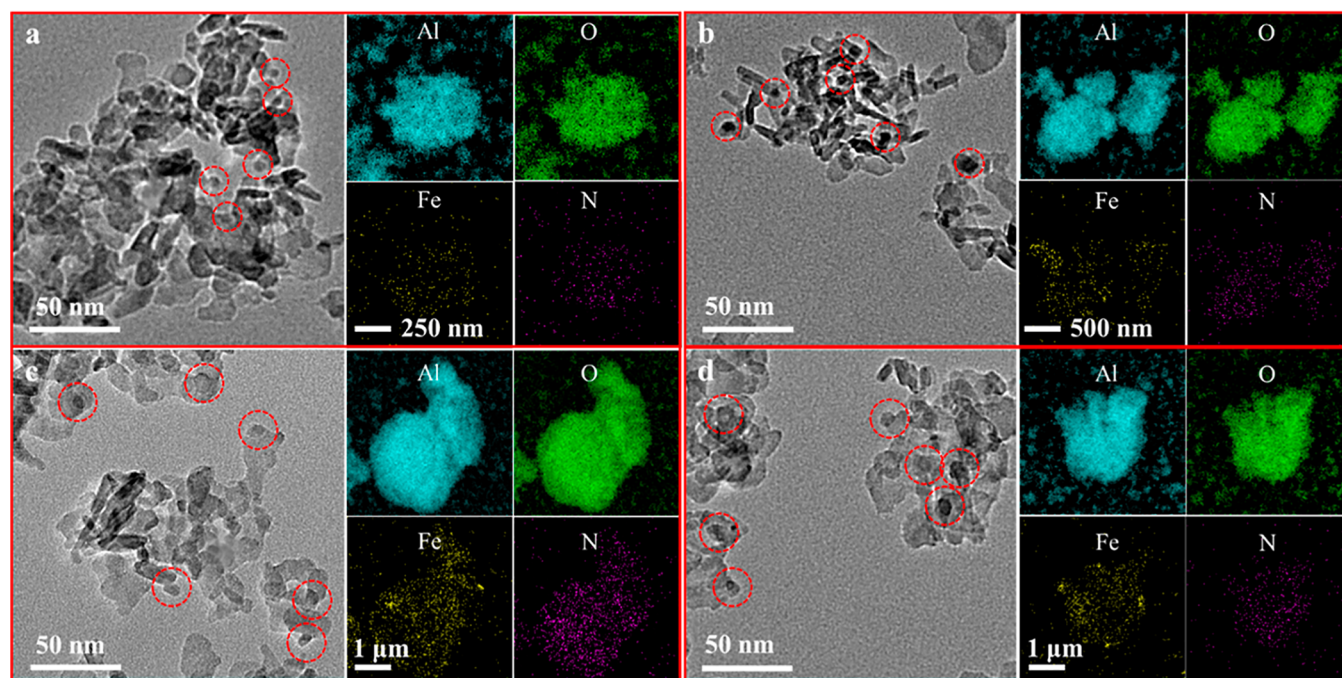


Figure 3. TEM and STEM–EDS images of the $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ catalysts after NH_3 decomposition at 600 °C for 1 h. (a) Fe_3O_4 (4.2 nm), (b) Fe_3O_4 (6.1 nm), (c) Fe_3O_4 (8.1 nm), and (d) Fe_3O_4 (10.4 nm).

and Ar with $\text{Fe}/\text{Al}_2\text{O}_3$ catalyst are shown in Figure S3a, and the Q – V Lissajous curve of the discharge is shown in Figure S3b. It is seen that the shape of the Lissajous curve is between a parallelogram and oval shape, which is a typical discharge behavior in the presence of catalytic material. The power deposition from the applied voltage was calculated based on the area of the Lissajous curve, and it is 11 W.

The activity of plasma driven NH_3 decomposition in terms of conversion, specific activities, and TOF is shown in Figures 2c,d and S4. Unlike the thermocatalytic reaction, during which NH_3 decomposition is negligible over the Al_2O_3 , as shown in Figure S4, the conversion of NH_3 is around 15% without a catalyst (plasma alone) and 22% when packed with Al_2O_3 . Ammonia conversion increased from 22% to a range between 24–29% with the presence of Fe_3O_4 nanoparticles with different sizes. The space-time activity ranges from 200–240 $\mu\text{mol}/\text{min}$, which corresponds to the plasma efficiency of 0.3–0.36 $\text{mmol}_{\text{NH}_3}/\text{kJ}_{\text{plasma}}$. Note that NH_3 conversion/activity over the $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ catalyst increased with increasing Fe_3O_4 particle size from 4.2 to 8.1 nm, which is quite similar to the thermocatalytic reaction. However, NH_3 conversion/activity decreased with a further increase of the Fe_3O_4 size from 8.1 to 10.4 nm.

Considering that the Al_2O_3 -packed plasma reactor shows considerable activity in NH_3 decomposition, the activity attained on the Fe_3O_4 nanoparticles was deconvoluted from the overall activity by subtracting the activity of the plasma packed with Al_2O_3 . As shown in Figure 2c, the mass-specific activity over the Fe nanoparticles ranges from 0.03–0.12 $\text{mol}_{\text{NH}_3}/\text{g}_{\text{Fe}}/\text{min}$, which is about an order of magnitude lower than the thermocatalytic reactions. The same as NH_3 conversion, the mass-specific activity increased with increasing Fe_3O_4 size from 4.2 to 8.1 nm but decreased with further increasing the size to 10.4 nm. Nevertheless, the TOF values (see Figure 2d) were continuously increased from 0.09 to 0.96

s^{-1} with an increasing Fe_3O_4 nanoparticle size from 4.2 to 10.4 nm.

Discussion. The above results demonstrate a significant “particle size effect” in NH_3 decomposition, driven by both heat and DBD plasma, over the $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ catalyst. Generally, the TOF increases with increasing Fe_3O_4 particle size, which is quite similar to the trend observed by Boudart and co-workers in NH_3 synthesis over the Fe and Mo_2N catalysts.^{15,20} Therefore, it might be expected that the relative proportion of sites that have higher activity for NH_3 decomposition would decrease as particle size becomes smaller.¹⁵ Further information about the catalytically active phase will be discussed based on the characterization of the used catalyst as well as the kinetic behavior during the transient experiment. The TEM images and STEM–EDS mappings of the $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ catalysts after thermocatalytic NH_3 decomposition are shown in Figure 3. It is seen from the TEM images that the size of the nanoparticles (highlighted with red circles) was almost not changed after being impregnated to the Al_2O_3 support and subjected to the NH_3 decomposition. Note that the Fe nanoparticles cannot be clearly distinguished from the Al_2O_3 support from the TEM images, which is not a surprise due to the low loading. Nonetheless, from the STEM–EDS mapping, the Fe species were found to distribute among the Al_2O_3 support.

Another piece of important information from the STEM–EDS is the N mapping. It is seen that N is distributed homogeneously with Fe for all of the four catalysts after NH_3 decomposition, indicating that the Fe_3O_4 nanoparticles were transformed into iron nitride (Fe_xN) during the reaction. The formation of Fe_xN was also verified by the XPS spectra of the $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ catalyst after catalysis. As shown in Figure 4, a clear peak of N 1s was observed for all of the used catalysts, which suggested the occurrence of surface nitridation during the NH_3 decomposition. However, the Fe 2p peaks of the fresh and used catalysts reveal a feature dominated by iron oxides at

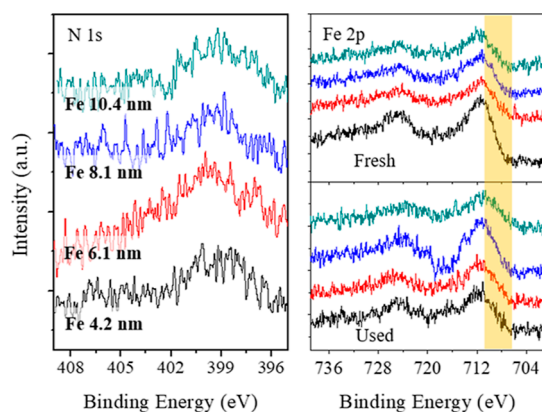


Figure 4. XPS spectra of Fe/Al₂O₃ catalysts with different Fe particle sizes.

a binding energy of 711.5 eV for Fe 2p 3/2 and 724.6 eV for Fe 2p 1/2, indicating that the samples were oxidized during exposure to air. Nonetheless, the peaks of Fe 2p 3/2 for the used catalyst seem broader than the fresh samples, indicating a new peak (at a binding energy of 708 eV for Fe_xN⁴¹) might be deconvoluted [see Figure S5 for the deconvolution of Fe₃O₄ (4.2 nm)/Al₂O₃]. It is seen that while the peak at 708 eV can be deconvoluted for the used Fe₃O₄ (4.2 nm)/Al₂O₃ catalyst, such a peak was absent for the fresh catalyst. Therefore, the Fe 2p XPS spectra once again suggested the presence of the Fe_xN phase, which can be oxidized when exposed to air.

Indeed, the formation of iron nitride was not a surprise during the NH₃ decomposition because of the high N–N recombination barrier (which favors the nitridation).⁴² Back to the early work by Boudart and co-workers,¹⁵ a complete transformation of the metallic iron particles into iron nitride was realized at 670 K under NH₃. Therefore, the actual working catalyst for the NH₃ decomposition must be Fe_xN, although deep nitridation has been found to deactivate the catalyst.³⁷ According to recent work by Lu et al.,⁴³ the highest NH₃ decomposition activity was observed over the Fe/Fe₄N mixing phase. The authors suggested that the deposition of an N on the Fe(100) surface modifies the electronic structure of its surrounding iron atoms, causing a significant reduction of the initial dehydrogenation barrier of NH₃.⁴³

The nitridation of FeO_x nanoparticles during the NH₃ decomposition can be further discussed based on the chemical transient analysis. As shown in Figure 5a, during the early-stage of the NH₃ decomposition, N₂ takes a significantly longer time (>100 s) to reach the steady-state than NH₃ (<15 s). However, such a delay (in reaching the steady-state) was absent during the second circle early-stage (see Figure 5c). Therefore, the results indicated the occurrence of significant reconstruction of the catalytically active sites during the first circle of the transient analysis. Such a reconstruction, according to the XPS and STEM–EDS characterization discussed above, must be associated with the nitridation of the FeO_x nanoparticles. Additionally, a pronounced peak of H₂O was observed during the first circle early-stage transient, indicating that the Fe₃O₄ nanoparticles were partially reduced to FeO_x during the H₂ pre-treatment. After the reaction reaches steady-state, the reactor inlet was switched from NH₃/Ar back to H₂/Ar or Ar, leading to the back-transient behavior of such a catalytic system (see Figure 5b,d). The decay time of N₂ is significantly longer under Ar than that in 10% H₂/Ar, indicating that the

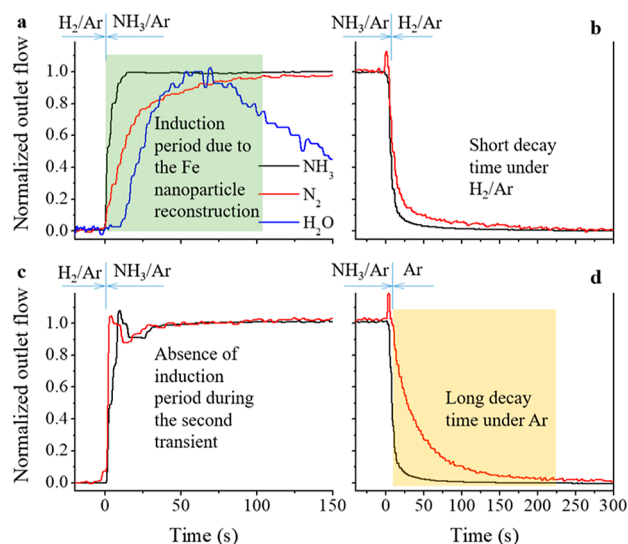


Figure 5. Transient analysis of thermocatalytic NH₃ decomposition over the Fe₃O₄/Al₂O₃ catalyst. (a) Early-stage catalytic behavior after switching the reactor inlet from H₂/Ar to NH₃/Ar; (b) back-transient behavior after switching from NH₃/Ar back to H₂/Ar; (c) second circle early-stage behavior; and (d) back-transient behavior after switching from NH₃/Ar to Ar.

presence of H₂ facilitates the N–N recombination and desorption. With the presence of H₂, Fe_xN can be reduced back to the elemental Fe, consequently, favoring the desorption of the residual N_{ads}.⁴⁴ According to Ganley et al.,⁴⁵ the NH₃ decomposition rate over the Fe is limited by the N–N recombination ($2\text{N}_{(\text{ads})} \rightarrow \text{N}_{2(\text{g})}$).

From a practical point of view, the present study compared the activity of NH₃ decomposition driven by both thermal and DBD plasma. While the thermocatalytic decomposition shows higher TOF, the space-time yield of the present model catalysts remains low due to the lower Fe loading. The plasma-assisted NH₃ decomposition, although showing significantly higher overall activity under “ambient conditions” (without external heat supply), the plasma/catalyst synergy needs to be further optimized in order to increase the energy efficiency. Specifically, the energy efficiency of the plasma during the present study is 1.5–2 mol_{H₂}/kW h, quite similar to that reported by Wang et al. for the plasma NH₃ decomposition over the Fe-based catalyst.³⁷ We expect that the energy efficiency of the plasma catalytic decomposition can be enhanced by increasing the Fe loading, optimizing the ratio between the volumes of plasma to catalysts, and electrode materials, as well as the plasma catalytic reactor optimization. For example, an adiabatic plasma reactor (minimizing the heat loss to the surrounding) could significantly increase the efficiency (results are not shown), because the NH₃ decomposition is an endothermic reaction.

CONCLUSIONS

We demonstrated the presence of the pronounced “particle size effect” in NH₃ decomposition over the Fe₃O₄/Al₂O₃ catalyst and compared the size-dependent activity between the thermocatalytic decomposition and the DBD plasma-assisted decomposition. We synthesized the water-dispersible with narrow size distribution Fe₃O₄ nanoparticles with diameters between 4–11 nm through thermal decomposition of Fe(acac)₃ in the DEGs. Then, the Fe₃O₄/Al₂O₃ model

catalysts with different particle sizes were prepared using the as-synthesized Fe_3O_4 as the precursor. Specifically, the TOF values for the thermal and plasma driven catalytic NH_3 decomposition showed the same trend, namely, the TOF value increases with increasing Fe_3O_4 particle size. The TOF was increased from 0.9 to 5.8 s^{-1} (during the thermocatalytic decomposition) and from 0.09 to 0.96 s^{-1} (during the plasma driven decomposition) with the increase of Fe_3O_4 size from 4.2 to 10.4 nm. We also identified the reaction-induction reconstruction during the early-stage of the thermocatalytic decomposition, which can be attributed to the nitridation of FeO_x to Fe_xN . Such a reconstruction of the catalytically active phase under the reaction conditions has been widely studied for the Fe catalysts during ammonia synthesis and decomposition reactions. The pronounced “particle size effect” demonstrated in this study provided new evidence for the “structure-sensitivity” of the catalytic NH_3 decomposition.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.2c02092>.

Experimental setup for plasma catalytic reaction, electrical signals of plasma, and additional catalytic data (PDF)

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G.C. and J.Q. contributed equally to the experimental work described in this paper.

Notes

The authors declare no competing financial interest.

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