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Article

Comprehensive understanding of the superior performance of Sm-modified Fe₂O₃ catalysts with regard to NO conversion and H₂O/SO₂ resistance in the NH₃-SCR reaction

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ABSTRACT

Sm-doped Fe₂O₃ catalysts, with a homogeneous distribution of Sm in Fe₂O₃ nanoparticles, were synthesized using a citric acid-assisted sol-gel method. Kinetic studies show that the reaction rate for NO_x reduction using the optimal catalyst (0.06 mol% doping of Sm in Fe₂O₃) was nearly 11 times higher than that for pure Fe₂O₃, when calculated based on specific surface area. Furthermore, the Fe_{0.94}Sm_{0.06}O_x catalyst maintains > 83% NO_x conversion for 168 h at a high space velocity in the presence of SO₂ and H₂O at 250 °C. A substantial amount of surface-adsorbed oxygen was generated on the surface of Fe_{0.94}Sm_{0.06}O_x, which promoted NO oxidation and the subsequent fast reaction between NO_x and NH₃. The adsorption and activation of NH₃ was also enhanced by Sm doping. In addition, Sm doping facilitated the decomposition of NH₄HSO₄ on the surface of Fe_{0.94}Sm_{0.06}O_x, resulting in its high activity and stability in the presence of SO₂ + H₂O.

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1. Introduction

Nitrogen oxides (NO_x) produced from stationary and mobile sources are one of the primary environmental pollutants. They can cause environmental problems, such as acid rain, photochemical smog, and the greenhouse effect, which seriously endanger human health [1,2]. The selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) in oxygen-rich conditions is considered the most effective technology to control NO_x emissions

[3–5]. However, there are also several disadvantages of commercial V₂O₅-WO₃/TiO₂ catalysts, including weak low temperature catalytic activity, a relatively narrow operation temperature window (300–400 °C), and the toxicity of vanadium species expelled as hazardous wastes, that limit the further application of NH₃-SCR [3,6–8]. Therefore, it is necessary to develop vanadium-free and environmentally benign catalysts for low temperature NH₃-SCR reactions.

In recent years, other metal oxides, including Mn, Fe, Co, and

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Cu oxides, were employed to prepare deNO_x catalysts [9–11]. Yan *et al.* [9] reported that the MnFeO_x catalyst showed promising NH₃-SCR activity in the 80–200 °C temperature range because of the strong interaction between Mn and Fe. Meng *et al.* [10] developed spinel-structured CoMnO_x catalysts, with a high ability of adsorption of NO_x and improved redox properties, that showed high NH₃-SCR activity. Ali *et al.* [11] prepared a series of CuNbO_x catalysts and performed complete NO conversion at 180–330 °C owing to the abundant acid sites in the catalysts. Among the metal oxides, iron oxide-based catalysts have attracted significant attention due to their many advantages, such as adequate redox properties between Fe³⁺ and Fe²⁺ and low cost [12–14]. However, their narrow operating temperature window, fewer acid sites, and low activity restrict their applications. Thus, the introduction of a second element, such as Ti or W, to overcome their shortcomings has been widely performed in previous studies [15–17]. Liu *et al.* [15] prepared FeTiO_x catalysts and systematically investigated the microstructure, structure-activity relationship, and reaction mechanism of the NH₃-SCR reaction. Yang *et al.* [16] synthesized FeTiO_x catalysts exhibiting remarkable NH₃-SCR activity and H₂O and/or SO₂ resistance at 300–400 °C using a co-precipitation method. Wang *et al.* [17] reported a W-doped Fe₂O₃ catalyst with an octahedral [FeO₆]/[WO₃] structure, which could provide Brønsted acid sites for high NO conversion.

As mentioned above, Fe-based catalysts have been widely studied. However, the problems of relatively low activity and poor long-time H₂O and SO₂ resistance at low temperatures persist. Thus, further exploration of Fe-based catalysts is necessary. As is well known, rare-earth metals with adequate redox properties, appropriate surface acidities, and excellent oxygen storage-release ability have been used in many NH₃-SCR catalysts [6,7,18,19]. In particular, recent studies suggest that Sm-doped metal oxide catalysts exhibit significant catalytic activity and SO₂/H₂O resistance. Meng *et al.* [20] found that a Sm-doped MnO_x catalyst showed considerable SO₂ tolerance and suggested that the incorporation of Sm could weaken the interaction of SO₂ with the active sites. Our previous work also suggested that Sm doping is a useful strategy to enhance the activity and SO₂ durability of a catalyst, which is very important for practical applications [21,22]. In this study, considering the good SO₂ tolerance of both Fe and Sm, a series of Sm-doped Fe₂O₃ catalysts were synthesized using a citric acid method. Various characterization techniques were employed to study the effects of Sm doping on the NH₃-SCR activity and H₂O/SO₂ resistance of the catalysts. Furthermore, the interaction mechanisms of NH₃ and NO + O₂ with the surfaces of the catalysts and the SO₂ resistance performance of the catalysts were deeply investigated. The main purpose of this work is as follows. Firstly, it focuses on revealing the relationships between the surface physicochemical properties and the activities of the catalysts, e.g., the influences of Sm doping on the redox properties and surface acidity of catalysts. Secondly, it aims to gain insight into the superior H₂O/SO₂ resistance of the Fe_{0.94}Sm_{0.06}O_x catalysts for the NH₃-SCR reaction. We hope that this work will provide guidance for designing Fe-based catalysts

and promote their application in the near future.

2. Experimental

2.1. Catalyst preparation

The Fe_{0.94}Sm_{0.06}O_x catalysts were prepared using a citric acid method. Calculated amounts of Fe(NO₃)₃·9H₂O and Sm(NO₃)₃·6H₂O were dissolved in deionized water and stirred for 0.5 h. Then, citric acid was added to the solution under stirring for 0.5 h (the molar ratio of citric acid to metal ion was 1). The mixed solution was heated to 80 °C, where it was maintained for 5 h under stirring. Afterward, the as-formed gel was dried at 110 °C overnight in an oven. Finally, the samples were calcined at 500 °C for 4 h in air.

The Fe₂O₃ and Fe_{0.94}Sm_{0.06}O_x catalysts tested after the NH₃-SCR reaction in the presence of H₂O and SO₂ for 168 h are denoted as Fe₂O₃-U and Fe_{0.94}Sm_{0.06}O_x-U, respectively. The 5 wt% NH₄HSO₄/Fe₂O₃ and NH₄HSO₄/Fe_{0.94}Sm_{0.06}O_x samples were prepared by an impregnation method, and the obtained samples are labeled as Fe₂O₃-N and Fe_{0.94}Sm_{0.06}O_x-N. A Fe_{0.94}Sm_{0.06}O_x sample prepared via a co-precipitation method, using Fe(NO₃)₃·9H₂O and Sm(NO₃)₃·6H₂O as precursors and an ammonia solution (25 wt%) as the precipitant, was synthesized for comparison, and is denoted as Fe_{0.94}Sm_{0.06}O_x-CP (The specific synthesis method for Fe_{0.94}Sm_{0.06}O_x-CP is provided in the Supplementary Material).

2.2. Catalyst characterization and DFT calculations

X-ray powder diffraction (XRD) patterns were recorded by a Philips X'pert Pro diffractometer with Cu K_α (40 kV, 100 mA) radiation (λ = 0.15406 nm). The data of 2θ from 10° to 80° were obtained with a scanning speed of 2° min⁻¹. A micromeritics ASAP-2020 apparatus was used to measure the N₂ adsorption-desorption isotherms. The specific surface areas of the catalysts were calculated using the Brunauer-Emmett-Teller (BET) method at 77 K by N₂ adsorption. Electron paramagnetic resonance (EPR) signals were recorded on a Bruker A300-10/12/S-LC spectrometer. Inductively coupled plasma-optical emission spectrometry (ICP-OES) was performed on a Thermo Scientific iCAP 7000 apparatus to determine the actual concentration of the elements in the samples. A JEOL 2100 F microscope operating at an acceleration voltage of 200 kV was used for the high-resolution transmission electron microscopy (HR-TEM) and scanning-transmission mode (STEM) images. STEM images were collected using a high-angle annular dark field detector (HAADF). The PHI 5000 Versa Probe system was used to conduct the X-ray photoelectron spectroscopy (XPS) measurements with monochromatic Al K_α radiation (1486.6 eV, 15 kW). The binding energies were calibrated using the C 1s peak (284.6 eV) as a reference. Thermogravimetry (TG) measurements of the samples were performed on a STA6000 at a heating rate of 10 °C min⁻¹ in a high-purity N₂ flow.

H₂ temperature programmed reduction (H₂-TPR) analysis was performed on a Pantech Instruments Finedorb-3010

chemisorption analyzer using a 7 vol% H₂/Ar mixture as the reducing agent. Before the H₂/Ar mixture stream was introduced, 10 mg of each sample was heated at 200 °C for 1 h in a N₂ stream. H₂-TPR was started from room temperature and the temperature was increased to 900 °C at a rate of 10 °C min⁻¹. NH₃ temperature programmed desorption (NH₃-TPD) experiments were performed on a multifunction chemisorption analyzer with a quartz U-tube reactor with a TCD. First, 50 mg of each sample was heated at 350 °C for 1 h in a N₂ stream. Then, the samples were exposed to NH₃/N₂ for 1 h at room temperature until the adsorption was saturated. Subsequently, the samples were flushed with N₂ at 100 °C for 1 h to remove weakly adsorbed NH₃. Finally, the temperature was raised to 600 °C at a rate of 10 °C min⁻¹.

The *in situ* DRIFTS were performed on a Nicolet iS50 FT-IR spectrometer with an MCT/B detector and a reaction cell with ZnSe windows. The sample was pretreated at 400 °C for 1 h in a N₂ stream and then cooled to 50 °C. The background spectra were collected during the cooling process. The concentrations of different gases were as follows: 500 × 10⁻⁶ NH₃, 500 × 10⁻⁶ NO, 5 vol% O₂, and 200 × 10⁻⁶ SO₂; the concentrations were balanced with N₂ at a 100 ml min⁻¹ flow rate.

All the density functional theory (DFT) calculations were carried out using the Perdew-Burke-Ernzerhof (PBE) functional with the Vienna Ab initio Simulation Package (VASP) version 5.3.5 [23]. The kinetic energy cut-offs were 400 eV for the geometry optimization and 500 eV for the electronic structure calculations. The DFT+U method can describe the electron correlation in transition metal atoms and their oxide systems, such as Fe₂O₃. U values of 4.0 and 8.0 eV were employed to model the *d* orbital of Fe and *f* orbital of Sm, respectively, which correspond exceptionally with experimental data [21,22,24]. The convergence accuracies of the energy values and atomic force were set as 1 × 10⁻⁵ a.u. and 0.02 eV Å⁻¹, respectively. The α-Fe₂O₃ (001) surface was selected for the calculations.

2.3. Catalytic performance test

The catalytic activity and N₂ selectivity were investigated

with a reaction gas composition of 500 × 10⁻⁶ NH₃, 500 × 10⁻⁶ NO, 5 vol% O₂, 200 × 10⁻⁶ SO₂, and 5 vol% H₂O and balanced with N₂ on a fixed bed. The gas hourly space velocity (GHSV) was 60000 or 90000 h⁻¹. The concentrations of NO_x, NH₃, NO₂, and N₂O were detected by a Thermo Fisher iS10 FT-IR spectrometer. The NO_x conversion and N₂ selectivity were calculated as:

$$\text{NO}_x \text{ conversion (\%)} = \frac{[\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}}}{[\text{NO}_x]_{\text{in}}} \times 100\%$$

$$\text{N}_2 \text{ selectivity (\%)} = \frac{[\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}} - 2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}} \times 100\%$$

3. Results and discussion

3.1. Catalytic performance

The NH₃-SCR activities and N₂ selectivities of the catalysts as a function of reaction temperature are displayed in Fig. 1(a) and Fig. S1. The results show that the NO_x conversion and N₂ selectivity of Fe₂O₃ are relatively low. Only ~70% NO_x conversion is achieved at 275–300 °C. The pure Sm₂O₃ is inactive in the whole operation temperature window and shows very low activity for NO_x conversion. Interestingly, the NO_x conversion and N₂ selectivity of all the catalysts improve sharply after adding Sm into Fe₂O₃. As the amount of Sm increases, the deNO_x efficiency of the Fe_ySm_xO_z catalyst exhibits a volcano-type tendency. The Fe_{0.94}Sm_{0.06}O_x shows the best NO_x conversion (> 95%) and N₂ selectivity (> 93%) in a wide operation temperature range (175–325 °C).

The composition of industrial exhaust is usually complex and includes significant amounts of SO₂ and H₂O, which will deactivate the deNO_x catalyst. Therefore, high SO₂ and H₂O durability is required for a potential catalyst. The influence of SO₂ and H₂O + SO₂ on the NO_x conversion of Fe₂O₃ and Fe_{0.94}Sm_{0.06}O_x catalysts at 250 °C was investigated and is shown in Fig. S2 and Fig. 1(b). As shown in Fig. S2, when 200 × 10⁻⁶ SO₂ is added into the feed gas at 250 °C, a drop in NO_x conversion of approximately 19% occurs over Fe₂O₃, which decreases

Fig. 1. NO_x conversion of the synthesized catalysts as a function of reaction temperature (a) and the influence of 200 × 10⁻⁶ SO₂ and 5 vol% H₂O on Fe_{0.94}Sm_{0.06}O_x for the NH₃-SCR reaction at 250 °C (b).

from 53% to 34%. After cutting off the SO_2 , the NO_x conversion over Fe_2O_3 does not completely recover. However, the NO_x conversion over $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ retains about 95% efficiency and recovers to $\sim 100\%$ after the SO_2 is cut-off.

The influences of both H_2O and SO_2 on Fe_2O_3 and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ were also studied, as shown in Fig. 1(b). When 5% H_2O is introduced into the simulated flue gas, a drop in the NO_x conversion over both the catalysts can be observed, which is $\sim 13\%$ for Fe_2O_3 and $\sim 5\%$ for $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ ($\text{GHSV} = 60000 \text{ h}^{-1}$). The decrease in activity may be due to the competitive adsorption of H_2O gas with NH_3/NO on the active sites [25]. The activities of the catalysts remain unchanged over the next 24 h, suggesting that the catalysts cannot be deactivated by H_2O at 250°C . After $200 \times 10^{-6} \text{ SO}_2$ is introduced into the feed gas simultaneously, the NO_x conversions of the catalysts further decrease to $\sim 31\%$ and $\sim 87\%$ for Fe_2O_3 and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$, respectively. It is notable that the NO_x conversion of $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ remains above $\sim 85\%$ for more than 168 h under this condition. Moreover, it can even maintain an NO_x conversion of $\sim 83\%$ at $\text{GHSV} = 90000 \text{ h}^{-1}$. It is well known that the H_2O and SO_2 durability is the most important property for practical $\text{NH}_3\text{-SCR}$ applications to eliminate NO_x . Therefore, this catalyst is very promising for industrial applications. It is also noted that the activity of Fe_2O_3 remains at $\sim 21\%$ for more than 168 h at 250°C , suggesting that the pure Fe_2O_3 also shows a strong ability to resist SO_2 and H_2O . After SO_2 and H_2O are cut off, the NO_x conversion over $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ rapidly recovers to 100%, indicating that the sulfates formed on the surface of $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ have minimal effect on its activity in the present condition. However, the activity of Fe_2O_3 only recovers to 35%, which may be due to the deposition of NH_4HSO_4 on the surface of the catalyst [26]. The influence of the calcination temperature on the activity of $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ was studied and is shown in Fig. S3. The activity of the catalyst first improves and then decreases with increasing calcination temperature. The catalyst calcinated at 500°C shows the best activity and the broadest temperature window among the catalysts.

To investigate the intrinsic activity of the catalysts, steady-state kinetics studies were performed for Fe_2O_3 and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$. The reaction rates and apparent activation energies (E_a) of Fe_2O_3 and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ are calculated and shown

in Fig. 2 and Table S1. As shown in Fig. 2(a), the reaction rates calculated based on the specific surface area (R_s) increase with increasing temperature. The reaction rates of $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ are 6–11 times higher than those of Fe_2O_3 . In addition, the practical application of the catalysts is also always evaluated by the mass of the catalysts. The reaction rates calculated based on mass of catalyst (R_m) are shown in Fig. 2(b). The R_m values of $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ are 20–37 times higher than those of Fe_2O_3 , suggesting that $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ is much more efficient than pure Fe_2O_3 . Fig. 2(c) shows the E_a of Fe_2O_3 and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$. The results suggest $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ has a lower E_a than that of Fe_2O_3 , which is in accordance with the $\text{NH}_3\text{-SCR}$ performance of the catalysts.

3.2. Textural properties, surface compositions, and chemical states of the catalysts

The N_2 adsorption-desorption isotherms of the synthesized catalysts are shown in Fig. S4. The BET surface areas are summarized in Table S2. All the catalysts except pure Sm_2O_3 show type IV isotherms with hysteresis loops at a high relative pressure, suggesting the presence of mesopores [27]. In addition, it can be seen that the BET surface areas of the catalysts first increase with increasing Sm content and then decrease when the content of Sm is higher than 0.06. The $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ catalyst shows the highest BET surface area. ICP-OES was measured to detect the molar ratio of Fe/Sm in the $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x\text{-CP}$ and $\text{Fe}_y\text{Sm}_z\text{O}_x$ catalysts. As shown in Table S3, the final molar ratios of Fe/Sm correspond well to the initial feed ratios, suggesting that the synthetic method used to create the catalysts in this work has minimal effect on the molar ratio.

Fig. 3 shows the XRD patterns of a series of Fe_2O_3 and $\text{Fe}_y\text{Sm}_z\text{O}_x$ catalysts. It is apparent that the characteristic peaks of Fe_2O_3 correspond well to the standard card of $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS: 33-0664). With the increase of Sm content, the intensities of all diffraction peaks become weaker, suggesting a low crystallization of the $\text{Fe}_y\text{Sm}_z\text{O}_x$ catalysts. No diffraction peaks corresponding to Sm can be observed, and a low intensity diffraction peak assigned to $\gamma\text{-Fe}_2\text{O}_3$ is detected at 30.24° and 43.28° , which means that doping with Sm may induce the transformation of the crystalline phase from $\alpha\text{-Fe}_2\text{O}_3$ to

Fig. 2. Reaction rates based on the specific area (a), mass (b), and apparent activation energies (c) of the $\text{NH}_3\text{-SCR}$ reactions over the Fe_2O_3 and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ catalysts.

Fig. 3. XRD patterns of the synthesized catalysts.

γ -Fe₂O₃. The magnetic characteristics of the Fe_ySm_zO_x catalysts further imply the partial phase transformation of α -Fe₂O₃ to γ -Fe₂O₃. To exclude the effects of the crystalline phase on the catalytic activity of NO_x conversion, the NH₃-SCR activity of γ -Fe₂O₃ was also tested. As shown in Fig. S5, the NO_x conversion activity of γ -Fe₂O₃ is almost equal to that of α -Fe₂O₃, and it is also much lower than that of Fe_{0.94}Sm_{0.06}O_x. Thus, there is no appreciable relationship between the crystalline phase and NO_x conversion activity of the catalysts in this work.

The morphologies of Fe₂O₃ and Fe_{0.94}Sm_{0.06}O_x were observed by TEM and HR-TEM (Fig. 4). As shown in the TEM results, the crystal size of Fe₂O₃ is larger than 70 nm, and the particles aggregate significantly (Fig. 4(a)). After the addition of Sm, the particles are more well-dispersed than in the Fe₂O₃ sample, and the size of most of the particles decreases to below 15 nm (Fig. 4(c)). The HR-TEM results show that the crystallization of Fe₂O₃ is better than that of Fe_{0.94}Sm_{0.06}O_x, and the interplanar distance of catalysts can be observed. As seen in Fig. 4(b), the lattice fringes with interplanar distances of 0.226 and 0.250 nm (inset of Fig. 4(b)) are indexed to the (006) and (110) facets, respectively [28], which suggest that the Fe₂O₃ particles

may expose the (001) and (110) facets. Similar lattice fringes can also be observed in Fe_{0.94}Sm_{0.06}O_x (Figs. 4(d)), which suggests the exposed plane was not affected by the Sm doping of Fe₂O₃. The HAADF image and EDS mappings of the Fe_{0.94}Sm_{0.06}O_x catalyst are displayed in Figs. 4(e)–(h), and the results suggest that Sm is highly dispersed in the catalyst. The results verified that the metallic element can be well distributed into Fe₂O₃ by the citric acid method. In addition, the Fe_{0.94}Sm_{0.06}O_x-CP catalyst prepared by the co-precipitation method has also been investigated by TEM, HR-TEM, and HAADF, and the images and EDS mappings are shown in Fig. S6. Fig. S6(a) and Fig. S6(b) suggest that the most of the Fe_{0.94}Sm_{0.06}O_x-CP particles are smaller than 10 nm. The EDS mappings (Figs. S6(d)–(f)) suggest that Sm is also well dispersed in the Fe_{0.94}Sm_{0.06}O_x-CP catalyst. However, the HR-TEM image (Fig. S6(a)) shows that the lattice fringes of Fe_{0.94}Sm_{0.06}O_x-CP are difficult to discern, suggesting a bad crystallization, which may be one of the reasons for its lower activity compared with the catalysts prepared by the citric acid method.

XPS was performed to investigate the surface composition and elemental valence states of the Fe₂O₃ and Fe_ySm_zO_x catalysts, and the results are shown in Fig. 5 and Table 1 (also in Fig. S7 and Table S4 in the Supplementary Material). As shown in Fig. 5(a), the peaks at 710.0–712.5 eV are ascribed to Fe 2p_{3/2}, and the peaks at 723.0–724.0 eV are attributed to Fe 2p_{1/2}. The XPS profiles were deconvoluted by the Gaussian-Lorentz function. The Fe 2p_{3/2} peak can be fitted to two different peaks at 710.2 and 712.1 eV, which are assigned to Fe²⁺ and Fe³⁺, respectively. In addition, the peak at 718.5 eV is the satellite peak of Fe₂O₃ [29,30]. Fig. 5(b) displays the XPS results of Sm 3d_{5/2}. The Sm 3d_{5/2} peaks can be fitted to two peaks; the binding energies centered at ~1083.3 and ~1080.1 eV are assigned to Sm³⁺ and Sm²⁺, respectively [22,31]. The areas of the Fe³⁺, Fe²⁺, Sm³⁺, and Sm²⁺ peaks are integrated, and the ratios of Fe³⁺/Fe²⁺ and Sm³⁺/Sm²⁺ for Fe₂O₃ and Fe_{0.94}Sm_{0.06}O_x are listed in Table 1. As can be seen, after the Sm doping of Fe₂O₃, the ratio of Fe³⁺/Fe²⁺ increases from 1.03 (Fe₂O₃) to 1.65 (Fe_{0.94}Sm_{0.06}O_x). Meanwhile, the ratio of Sm³⁺/Sm²⁺ decreases from 2.50 (Sm₂O₃) to 2.20 (Fe_{0.94}Sm_{0.06}O_x). These results reveal

Fig. 4. TEM images of Fe₂O₃ (a) and Fe_{0.94}Sm_{0.06}O_x (c), HR-TEM images of Fe₂O₃ (b) and Fe_{0.94}Sm_{0.06}O_x (d), and HAADF image (e) and EDS mappings (f–h) of Fe_{0.94}Sm_{0.06}O_x.

Fig. 5. XPS spectra of α -Fe₂O₃, Fe_{0.94}Sm_{0.06}O_x, and Sm₂O₃ over the Fe 2p (a), Sm 3d (b), and O 1s (c) spectral regions.

that the valence state of Fe increases and the valence state of Sm decreases, which suggests that the electrons will redistribute and that Sm doping increases the valence state of Fe during the preparation of the catalysts. DFT calculations were performed to further support the experimental results. The Sm-doped Fe₂O₃ model is shown in Fig. 6, and the differential charge densities are calculated using the following equation (1):

$$\rho_{\text{diff}} = \rho_{\text{FeSmO}} - (\rho_{\text{FeO}} + \rho_{\text{Sm}}). \quad (1)$$

Fig. 6(b) and Fig. 6(d) show that the electron density around the Fe atoms decreases after Sm doping, suggesting that electrons redistribute in the Sm-doped Fe₂O₃ catalyst. The increased amount of Fe³⁺ may promote the oxidation of NH₃ into NH₂, which is an important intermediate product in the NH₃-SCR reaction [21,22].

Fig. 5(c) and Fig. S7(c) show the O 1s spectra; the binding energy at 530.8 eV corresponds to surface-adsorbed oxygen (denoted O_α), and the binding energies at 529.4–529.6 eV are attributed to the lattice oxygen (denoted O_β) [31–34]. O_α is generally considered to be very active due to its higher mobility compared with O_β in the oxidation reaction [25,35]. The ratio O_α/(O_α + O_β) is listed in Table 1 and Table S4. The amount of O_α increases remarkably after the Sm doping of α -Fe₂O₃, and the highest O_α content is 50.8% for the Fe_{0.94}Sm_{0.06}O_x sample. The high O_α content enhances the oxidation of NO into NO₂ and the further “fast SCR” process [36], which could be one of the reasons for the good activity of Fe_{0.94}Sm_{0.06}O_x.

Table 1

Surface compositions of the Fe₂O₃, Sm₂O₃ and Fe_{0.94}Sm_{0.06}O_x catalysts.

Sample	Fe ³⁺ /Fe ²⁺	Sm ³⁺ /Sm ²⁺	O _α /(O _α + O _β) (%)
Fe ₂ O ₃	1.03	—	43.7
Sm ₂ O ₃	—	2.50	—
Fe _{0.94} Sm _{0.06} O _x	1.65	2.20	50.8
Fe ₂ O ₃ -U	1.84	—	53.6
Fe _{0.94} Sm _{0.06} O _x -U	3.04	2.00	58.7

3.3. Reduction properties and surface acidities

3.3.1. Reduction properties of the catalysts

H₂-TPR was used to characterize the reduction properties of catalysts, and the profiles of the Fe_ySm_zO_x catalysts are shown in Fig. S8. For Sm₂O₃, there are no distinct reduction peaks at 100–900 °C except for a weak peak at 685 °C, indicating that Sm₂O₃ cannot be significantly reduced at relatively low temperatures (< 500 °C). The profile of the Fe₂O₃ sample exhibits three major reduction peaks at ~384, 587, and 711 °C, which are associated, respectively, with successive reductions of Fe₂O₃ → Fe₃O₄ → FeO → Fe [25,34,37]. Corresponding with the reaction temperature window, the H₂-TPR profiles of the Fe_ySm_zO_x samples at 200–400 °C are presented in Fig. 7(a) and discussed in detail. As can be seen, a new peak appears at ~322

Fig. 6. Optimized Sm-doped Fe₂O₃ (001) model from the DFT calculations: (a) top view and (c) side view. Differential charge densities of the Sm-doped Fe₂O₃ (001) model: (b) top view and (d) side view. The blue and yellow colors indicate the loss and gain of electrons, respectively.

Fig. 7. (a) H₂-TPR profiles of the synthesized catalysts at 200–400 °C; (b) the relationship between the numbers of different acid sites and NO conversion.

°C after doping Fe₂O₃ with Sm, which is attributed to the reduction of the surface-adsorbed oxygen [15]. When the Sm content is lower than 0.06, the reduction temperature of the surface-adsorbed oxygen is almost constant. After integrating the area under the peaks (Table 2), it can be observed that the area increases with the Sm content (Sm < 0.06), which suggests that more surface-adsorbed oxygen will be produced by a higher Sm doping. More surface-adsorbed oxygen is beneficial for NO oxidation [36]. The NO oxidation reaction was performed to support this hypothesis. As shown in Fig. S9, the catalytic efficiency of Fe_{0.94}Sm_{0.06}O_x for the conversion of NO into NO₂ is higher than that of Fe₂O₃ in the whole temperature range. However, further increasing the Sm content (Sm > 0.06) shifts the peak at ~322 °C to a higher temperature, suggesting that the reducibility of the catalysts deteriorates. Similarly, the peak attributed to the reduction of Fe₂O₃ at ~384 °C shifts to a higher temperature when the Sm content is higher than 0.06. Thus, when the Sm content is higher than 0.06, the poor redox properties of the catalysts are responsible for the lower activity.

3.3.2. Surface acidities of the catalysts

Surface acidity is one of the key factors for catalysts of the NH₃-SCR reaction. NH₃-TPD was performed to study the surface acidity of the catalysts. Fig. S10 shows the NH₃-TPD profiles of the Fe₂Sm_xO_x catalysts. The peaks α (~98 °C), β (188 °C)

and γ (~287 °C) are attributed to physically adsorbed NH₃ and chemically adsorbed NH₃ at weak and mid-strong acid sites, respectively [37,38]. The δ peak (410–460 °C) is significant (for Sm > 0.08) and is assigned to the chemically adsorbed NH₃ at strong acid sites [25]. The integrated peak areas of each acid site are listed in Table S5. It is evident that the numbers of different surface acid sites increase remarkably after Sm doping of Fe₂O₃. In addition, when the Sm content is higher than 0.08, the numbers of weak and mid-strong acid sites decrease while the number of strong acid sites increases, suggesting that the acid sites become significantly stronger with more Sm doping. Fig. 7(b) shows the relationship between the numbers of different kinds of acid sites (or the activities of catalysts) and the Sm content. The number of weak and mid-strong acid sites follows the same order as the activity of the catalysts: Fe_{0.94}Sm_{0.06}O_x > Fe_{0.96}Sm_{0.04}O_x > Fe_{0.92}Sm_{0.08}O_x > Fe_{0.90}Sm_{0.10}O_x > Fe_{0.98}Sm_{0.02}O_x > Fe₂O₃. This suggests that the weak and mid-strong acid sites may play a crucial role in NH₃-SCR activity, and thus Fe_{0.94}Sm_{0.06}O_x, possessing the most weak and mid-strong acid sites, shows the best activity. The number of weak and mid-strong acid sites may also determine the NH₃-SCR activity at different temperatures. When the Sm content is too high, the strength of acidity is too strong for the reaction to proceed, i.e., the NH₃ adsorbed on the strong acidic sites is unfavorable for the NH₃-SCR reaction, which is in accordance with previously reported results [39,40].

Table 2

Peak area of the samples at different reduction temperatures.

Sample	Peak area (a.u.)	
	~322 °C	~384 °C
Fe ₂ O ₃	—	582.0
Fe _{0.98} Sm _{0.02} O _x	87.9	278.1
Fe _{0.96} Sm _{0.04} O _x	186.5	86.3
Fe _{0.94} Sm _{0.06} O _x	268.0	122.4
Fe _{0.92} Sm _{0.08} O _x	284.9	96.2
Fe _{0.90} Sm _{0.10} O _x	154.6	104.7

3.4. Interaction mechanisms of NH₃ and NO + O₂ with the surfaces of the catalysts

3.4.1. In situ DRIFTS of NH₃ adsorption-desorption on the catalysts

The *in situ* DRIFTS spectra of NH₃ adsorption-desorption over the Fe₂O₃, Sm₂O₃, and Fe_{0.94}Sm_{0.06}O_x catalysts as the temperature increases from 50 to 350 °C are shown in Fig. 8. The three bands appearing at 1599 (δ_{as}), 1143 (δ_s) and 1223 cm⁻¹

Fig. 8. *In situ* DRIFTS spectra of NH_3 adsorption-desorption over the Fe_2O_3 (a), Sm_2O_3 (b), and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ (c) catalysts; *in situ* DRIFTS spectra of $\text{NO} + \text{O}_2$ adsorption-desorption over the Fe_2O_3 (d), Sm_2O_3 (e), and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ (f) catalysts as the temperature increases from 50 to 350 °C.

(δ_s) at 50 °C on the Fe_2O_3 catalyst (Fig. 8(a)) correspond to coordinated NH_3 molecules bonded to Lewis acid sites. No bands corresponding to the vibration of ionic NH_4^+ can be detected, which suggests that there are minimal Brönsted acid sites [17,36,41]. The adsorption of NH_3 on the surface of Sm_2O_3 is much lower than that on Fe_2O_3 (Fig. 8(b)) and only the bands of coordinated NH_3 appear, at 1620 (δ_{as}) and 1128 cm^{-1} (δ_s) [21,26]. The coordinated NH_3 bands for both the Fe_2O_3 and Sm_2O_3 catalysts weaken with increasing temperature, and nearly disappear at 275 °C. However, the NH_3 bands over $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ are very strong. As shown in Fig. 8(c), bands corresponding to both the coordinated NH_3 groups (δ_s at 1163 and 1285 cm^{-1} , and δ_{as} at 1600 cm^{-1}) bonded to Lewis acid sites and the ionic NH_4^+ groups (δ_{as} at 1427 cm^{-1} and δ_s at 1349 cm^{-1}) bonded to Brönsted acid sites can be observed [15,25,42,43]. The significant increase of both acid sites can be explained as follows. The TEM results (Fig. 4) suggested that the crystal size of $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ is much lower than that of Fe_2O_3 due to the Sm doping. There are more coordinatively unsaturated cations, i.e., oxygen defects, on these small nanoparticles, which has been proven by the EPR results (Fig. S11). The new Lewis acid sites are generated from these cations. In addition, some defects may be filled with surface oxygen, and the protons required for charge neutrality form Brönsted acid sites, which is similar to zeolite catalysts [44]. When the temperature increases from 50 to 350 °C, the symmetric N–H bending vibration of the coordinated NH_3 groups shifts from 1163 to 1199 cm^{-1} . The reason for this shift is that hydrogen bonds form between chemically adsorbed NH_3 at low temperatures and break at high temperatures due to NH_3 desorption [21,45]. The bands assigned to ionic NH_4^+ groups gradually become weaker with increasing temperature and disappear at ~200 °C. However, the bands corresponding to coordinated NH_3 groups still exist at 350 °C, which indicates that the coordinated NH_3 groups bonded to Lewis acid sites are more stable. Combined with the NH_3 -TPD results, it can be concluded that the weak acid sites should be attributed to Brönsted acids and the mid-strong and strong acid sites should be attributed to Lewis acids. Compared with

the Fe_2O_3 and Sm_2O_3 catalysts, the adsorption of coordinated NH_3 on the surface of $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ is much stronger, which may play a major role in NH_3 -SCR at high temperature (> 200 °C). Therefore, the NO_x conversions of the Fe_2O_3 and Sm_2O_3 catalysts are very poor in the high temperature range due to their small number of Lewis acid sites. In addition, it has been reported that Brönsted acid sites have an important effect on the activity at low temperatures (< 200 °C) [21,46,47]. Among the three catalysts, the number of Brönsted acid sites in the $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ sample is much higher than that in the other two samples, which should lead to a high NO_x conversion activity except for the poor redox properties at low temperatures.

In addition, a band at 1562 cm^{-1} , assigned to NH_2 adsorbed on the Lewis acid sites, is observed on $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$; it is generated by the oxidation of adsorbed NH_3 [32,48]. However, it is not observed on the Fe_2O_3 and Sm_2O_3 samples. These results suggest that the Sm doping of Fe_2O_3 improves the redox properties and that it is beneficial for the activation of NH_3 to generate NH_2 . The NH_2 can react with NO , producing N_2 at low temperatures, which further promotes the NH_3 -SCR reaction, as shown in following equation: $\text{NH}_2 + \text{NO} \rightarrow \text{NH}_2\text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O}$ [21]. Thus, the de NO_x efficiency and N_2 selectivity of the $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ catalyst are good at low temperatures.

3.4.2. *In situ* DRIFTS of $\text{NO} + \text{O}_2$ adsorption-desorption on the catalysts

The *in situ* DRIFTS spectra of $\text{NO} + \text{O}_2$ adsorption-desorption over the Fe_2O_3 , Sm_2O_3 , and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ catalysts are shown in Fig. 8 and Fig. S12. For Fe_2O_3 (Fig. 8(d)), the bands corresponding to adsorbed NO_2 (1610 cm^{-1}), bidentate nitrate (1567 cm^{-1}), monodentate nitrate (1282 cm^{-1}), bridged nitrate (1238 cm^{-1}), bridged nitrite (1206 cm^{-1}), and linear nitrite (1002 cm^{-1}) can be observed [9,17,21,49,50]. As the temperature increases from 50 to 350 °C, the adsorbed NO_2 , bidentate nitrate, and bridged nitrate are all relative stable, and they all still exist even at 350 °C. The bands of adsorbed monodentate nitrate and linear nitrite become weaker with increasing temperature, suggesting that they are unstable and will desorb or

transform into the other nitrate/nitrite species. Accordingly, it should be noted that the bridged nitrite band gets stronger with increasing temperature, which suggests that they may be generated from monodentate nitrate and linear nitrite. For the Sm_2O_3 sample (Fig. 8(e)), there are fewer adsorbed NO_x species than those for the Fe_2O_3 catalyst. Only bidentate nitrate (1600 cm^{-1}), bridged nitrite (1206 cm^{-1}), and linear nitrite (1013 cm^{-1}) can be observed, suggesting that the adsorption of NO_x species on the surface of Sm_2O_3 is weak. Furthermore, it should be noted that almost no adsorbed NO_2 can be detected, suggesting that there is minimal oxidation of NO into NO_2 on the Sm_2O_3 surface. The NO_x species on the surface of the $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ catalyst (Fig. 8(f)) are similar to those of Fe_2O_3 . All the nitrate/nitrite species observed on Fe_2O_3 can also be observed on $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$, and the intensity of all the bands is stronger, which suggests that the NO_x adsorption capacity is enhanced due to the addition of Sm.

3.4.3. *In situ* DRIFTS of the interaction between $\text{NO} + \text{O}_2$ and adsorbed NH_3 on Fe_2O_3 and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$

NH_3 adsorption on the catalysts was first carried out for 1 h followed by N_2 purging at 200°C . Then, $\text{NO} + \text{O}_2$ was introduced to react with the adsorbed NH_3 , and the spectra were recorded as a function of time, as shown in Fig. 9(a) and Fig. 9(b). The bands corresponding to coordinated NH_3 ($3400\text{--}3100$, 1599 , and 1223 cm^{-1}) can be observed (Fig. 9(a)). After $\text{NO} + \text{O}_2$ was introduced into the IR cell, the coordinated

NH_3 was rapidly consumed, and the corresponding bands disappeared after 5 min, which suggests that coordinated NH_3 can react with NO_x in the SCR reaction. After the pre-adsorbed NH_3 was completely consumed, the adsorbed NO_x species, including NO_2 (1605 cm^{-1}), bidentate nitrate (1554 cm^{-1}), bridged nitrate (1246 cm^{-1}), and bridged nitrite (1215 cm^{-1}), could be detected. The reaction between $\text{NO} + \text{O}_2$ and adsorbed NH_3 on the $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ catalyst was also studied using *in situ* DRIFT spectra, as shown in Fig. 9(b). The spectra are similar to those of Fe_2O_3 except for the appearance of the NH_2 band (1562 cm^{-1}) [32,48]. After 5 min, the coordinated NH_3 and NH_2 completely disappear from the surface of $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$, suggesting that both of them act as a reducer in the SCR reaction. These results suggest the Eley-Rideal (E-R) mechanism can occur on the surface of the Fe_2O_3 and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ catalysts.

3.4.4. *In situ* DRIFTS spectra of the interaction between NH_3 and adsorbed $\text{NO} + \text{O}_2$ on Fe_2O_3 and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$

The interactions between pre-adsorbed NO_x species and NH_3 on the surface of the Fe_2O_3 and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ catalysts were also investigated, and the results are shown in Fig. 9(c) and Fig. 9(d). Regarding Fe_2O_3 , adsorbed NO_2 (1610 cm^{-1}), bidentate nitrate (1557 cm^{-1}), monodentate nitrate (1282 cm^{-1}), bridged nitrate (1238 cm^{-1}), bridged nitrite (1206 cm^{-1}), and linear nitrite (1002 cm^{-1}) cover the surface of the catalyst. The NO_2 reacts rapidly with the injected NH_3 and disappears, and the monodentate nitrate also disappears after 5 min. However,

Fig. 9. *In situ* DRIFTS spectra of the interaction between $\text{NO} + \text{O}_2$ and adsorbed NH_3 over the Fe_2O_3 (a) and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ (b) catalysts; *in situ* DRIFTS spectra of the interaction between NH_3 and adsorbed $\text{NO} + \text{O}_2$ over the Fe_2O_3 (c) and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ (d) catalysts at 200°C as a function of time.

most adsorbed NO_x species, including the bidentate nitrate, bridged nitrate, bridged nitrite, and linear nitrite, are inactive and still exist after 60 min. After 5 min, the coordinated NH_3 ($3400\text{--}3100$, 1599 , and 1244 cm^{-1}) and ionic NH_4^+ (1350 cm^{-1}) appear. These results suggest that the adsorbed NO_x and NH_3 can coexist on the surface of the catalyst. All the peaks of the adsorbed NO_x species and NH_3 of Fe_2O_3 can be found in the spectra of $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$, and the spectra of the two catalysts show nearly the same variation. In addition, NH_2 is observed at 1562 cm^{-1} for the $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ sample. These results suggest that the reactions between NH_3 and the pre-adsorbed NO_x species are rare and further support the notion that the NH_3 -SCR reaction proceeds primarily in accordance with the E-R mechanism.

In summary, it can be concluded from the *in situ* DRIFTS results that the reaction pathways on the two catalysts are almost the same. However, the activation of NH_3 is easier on the surface of $\text{Fe}_y\text{Sm}_z\text{O}_x$, which further improves the catalytic activity. It has been reported that NH_2 is generated from the oxidative hydrogen abstraction of NH_3 by metal ions in the catalyst [48]. Thus, the improvement in the NH_3 activation ability should be responsible for the good NH_3 activation ability of the Sm-doped Fe_2O_3 catalyst.

3.5. SO_2 resistance of the catalysts

3.5.1. TG characterization

To study the surface species formed by the NH_3 -SCR reaction with SO_2 and H_2O , TG characterization of fresh and used Fe_2O_3 and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ catalysts was performed, and the curves are shown in Fig. 10. Compared with the fresh catalysts, there is significantly more mass loss for the used catalysts, which indicates the formation of sulfate species during the testing of the $\text{SO}_2 + \text{H}_2\text{O}$ process. As can be seen, the weight losses of the catalysts can be divided into three steps. Step I ($50\text{--}200\text{ }^\circ\text{C}$) is assigned to the loss of adsorbed H_2O . Step II ($200\text{--}500\text{ }^\circ\text{C}$) is mainly related to the decomposition of the $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 generated by the NH_3 -SCR reaction [22]. For the Fe_2O_3 -U sample, the weight loss in step II is $\sim 0.33\%$, whereas it is $\sim 0.69\%$ for the $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ -U sample. This result suggests that the amount of

$(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 formed on $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ -U is higher than that on Fe_2O_3 -U, which should be attributed to the high surface area of $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$. It has been reported that $\text{Fe}_2(\text{SO}_4)_3$ starts to decompose at about $500\text{ }^\circ\text{C}$ and that $\text{Sm}_2(\text{SO}_4)_3$ will decompose above $700\text{ }^\circ\text{C}$ [22]. Therefore, step III ($500\text{--}850\text{ }^\circ\text{C}$) is assigned to the decomposition of $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Sm}_2(\text{SO}_4)_3$. Thus, both $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 and metal sulfate species can be formed on the surface of catalyst.

3.5.2. BET, XPS, and HAADF images and corresponding EDS mappings of the used catalysts

The BET surface area of the used catalysts decreases markedly due to the formation of the sulfate species on the surface of the catalysts, as can be seen in Table S2. The decrease in the surface area (ΔA) of $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ -U (32.8%) is slightly higher than that of Fe_2O_3 -U (26.2%), indicating that more sulfate species form on the surface of $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ -U. The XPS spectra of Fe_2O_3 -U and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ -U are shown in Fig. 11, and the values of $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{O}_\alpha/(\text{O}_\alpha + \text{O}_\beta)$ are listed in Table 1. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios of the Fe_2O_3 -U and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ -U samples are higher than those of the fresh samples, which indicates that SO_2 may react with Fe^{2+} via the following reaction: $2\text{Fe}^{2+} + \text{SO}_2 + \text{O}_2 \rightarrow 2\text{Fe}^{3+} + \text{SO}_4^{2-}$ [22]. Furthermore, there is more O_α on the used catalysts, which should be due to the formation of sulfates on the surfaces of the used catalysts [22,26]. S $2p$ spectra are presented in Fig. 11(d); the binding energies at 168.5 and 169.5 eV correspond to $\text{S}^{6+} 2p_{3/2}$ and $2p_{1/2}$, respectively, indicating that sulfates formed on both $\alpha\text{-Fe}_2\text{O}_3$ -U and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ -U [26]. The HAADF image and the corresponding EDS mappings of Fe_2O_3 -U and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ -U are displayed in Figs. 12(a)–(i). No significant change in morphology can be observed for either catalyst after 168 h of NH_3 -SCR reaction. Furthermore, S was detected on the surface of both Fe_2O_3 -U and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ -U.

3.5.3. *In situ* DRIFTS of $\text{SO}_2 + \text{O}_2$ adsorption on Fe_2O_3 and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$

The *in situ* DRIFTS spectra of $\text{SO}_2 + \text{O}_2$ adsorbed on the catalysts at $250\text{ }^\circ\text{C}$ as a function of time were collected to investigate the sulfate species on the surfaces of the catalysts, as shown in Fig. 13. For Fe_2O_3 (Fig. 13(a)), bands at 1364 ($\text{S}=\text{O}$), 1307 ($\text{S}-\text{O}$), and 1080 cm^{-1} ($\text{S}-\text{O}$) are observed, which can be

Fig. 10. TG curves of the Fe_2O_3 (a) and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ (b) catalysts.

Fig. 11. XPS spectra of α - Fe_2O_3 -U and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ -U over the Fe 2p, Sm 3d, O 1s, and S 2p spectral regions.

Fig. 12. HAADF image and EDS mappings of Fe_2O_3 -U (a–d) and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ -U (e–i).

attributed to the formation of surface sulfate species [26]. The band at 1459 cm^{-1} is assigned to SO_3 [30]. The band at 1158 cm^{-1} is ascribed to the formation of bulk-like sulfate species [51]. The band at 1620 cm^{-1} is assigned to H_2O , which is due to the reaction between SO_2 and the surface basic hydroxyls [51]. For $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$, only four bands at 1620, 1439, 1158, and 1057 cm^{-1} (which grow in intensity over time) can be observed

(Fig. 13(b)), which are attributed to H_2O , SO_3 , bulk-like sulfate species, and surface sulfate species, respectively. These results show that bulk-like sulfate species can form on the surface of both catalysts.

According to previous studies, there are two pathways for SO_2 deactivation on catalysts. First, SO_2 can react with H_2O and NH_3 to form NH_4HSO_4 , which will block the active sites. Second,

Fig. 13. *In situ* DRIFTS $\text{SO}_2 + \text{O}_2$ adsorption spectra over Fe_2O_3 (a) and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ (b) at 250 °C as a function of time.

SO_2 can directly react with surface metal oxides to form stable metal sulfates, which also deactivate the active sites of catalysts [52,53]. To further investigate the surface deactivation effect of NH_4HSO_4 on the NH_3 -SCR activities, 5 wt% NH_4HSO_4 was loaded onto Fe_2O_3 and $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$. As shown in Fig. S13, NH_4HSO_4 has almost no effect on the NH_3 -SCR activities above 250 °C for $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$, which demonstrates that NH_4HSO_4 can decompose above 250 °C. In contrast, the activity of Fe_2O_3 -N is lower than that of fresh Fe_2O_3 at 250 °C, suggesting that the NH_4HSO_4 cannot decompose completely on the Fe_2O_3 surface at this temperature. In addition, to investigate the effect of surface metal sulfation of the catalysts on the NH_3 -SCR reaction, the samples were pretreated with $\text{SO}_2 + \text{O}_2$ (250 °C, $1000 \times 10^{-6} \text{ SO}_2$, 5 vol% O_2 , 1 h) before testing their activity. As shown in Fig. S14, the activity of $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ decreases slightly above 250 °C. However, it is interesting that the activity of Fe_2O_3 pretreated by $\text{SO}_2 + \text{O}_2$ is even higher than that of fresh Fe_2O_3 above 250 °C. These results reveal that while Fe_2O_3 itself shows a strong resistance to metal sulfation, it is difficult to decompose the NH_4HSO_4 that forms on its surface at relatively low temperatures. After doping Fe_2O_3 with Sm, the decomposition temperature of NH_4HSO_4 decreases, and many more active sites are exposed to participate in the reaction. Thus, although the surface metal sulfation of Sm-doped Fe_2O_3 is slightly stronger than that of Fe_2O_3 , both catalysts maintain high activity in the presence of $\text{SO}_2 + \text{H}_2\text{O}$ for a long time. Furthermore, after $\text{SO}_2 + \text{H}_2\text{O}$ is cut off, the NO_x conversion of $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ rapidly recovers to 100% after a 168 h test, which suggests that the decrease in the activity is more probably induced by compete adsorption between the $\text{SO}_2 + \text{H}_2\text{O}$ and reactants rather than chemical deactivation of the catalyst.

4. Conclusions

The Sm doping of Fe_2O_3 catalysts significantly improves their NH_3 -SCR reactivity, and they show remarkable $\text{SO}_2 + \text{H}_2\text{O}$ resistance with regard to the NH_3 -SCR reaction. The $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ catalyst maintains more than 83% NO_x conversion for 168 h in the presence of $200 \times 10^{-6} \text{ SO}_2$ and 5 vol% H_2O at 250 °C. The $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ particles are much better dispersed than those of Fe_2O_3 due to the addition of Sm, and the Sm is well dispersed in the $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ catalyst. Additional Fe^{3+} is generated by Sm doping, which promotes the oxidation

of NH_3 into NH_2 , an important intermediate in the NH_3 -SCR reaction. Additional surface-adsorbed oxygen on $\text{Fe}_{0.94}\text{Sm}_{0.06}\text{O}_x$ is generated by the addition of Sm, which is beneficial for NO oxidation and a subsequent fast reaction. The adsorption and activation ability of NH_3 is enhanced by Sm doping, which also enhances the activity. The NH_4HSO_4 formed on the surface of Fe_2O_3 during the reaction does not decompose easily. Thus, the activity decreases and is not recovered, even after SO_2 and H_2O are cut off at 250 °C. After Sm doping, NH_4HSO_4 decomposes more easily, which results in a high $\text{SO}_2 + \text{H}_2\text{O}$ resistance.

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Graphical Abstract

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Comprehensive understanding of the superior performance of Sm-modified Fe_2O_3 catalysts with regard to NO conversion and $\text{H}_2\text{O}/\text{SO}_2$ resistance in the NH_3 -SCR reaction

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Sm-doping of Fe_2O_3 provides excellent $\text{SO}_2 + \text{H}_2\text{O}$ resistance for the NH_3 -SCR reaction at low temperatures by accelerating the decomposition of NH_4HSO_4 on the surface of the catalyst.

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Sm掺杂对Fe₂O₃催化剂NH₃-SCR反应活性及抗水抗硫性作用

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摘要: 氮氧化物(NO_x)是主要的环境污染物之一, 会造成酸雨、光化学烟雾和温室效应等环境问题。氨选择性催化还原(NH₃-SCR)技术是目前控制NO_x排放的最有效技术。其中, Fe₂O₃催化剂因其良好的抗硫性和低廉的成本而受到广泛关注, 有望用作NO_x消除催化剂, 但是它的低温还原性差、脱硝效率低等缺点限制了其应用。近期研究表明, 钐掺杂金属氧化物可以调节其表面酸碱性及氧化还原性, 可有效提高氧化物催化剂的脱硝效率和抗水抗硫性能。因此, 将铁、钐二者优势结合, 为合成一种低温、高效、环境友好型脱硝催化剂提供了可能。本文通过柠檬酸辅助的溶胶凝胶法合成了一系列钐均匀掺杂入Fe₂O₃纳米颗粒的复合氧化物脱硝催化剂, 采用X射线光电子能谱(XPS), 氢气程序升温还原(H₂-TPR), 氨气程序升温脱附(NH₃-TPD)以及原位漫反射红外光谱(*in situ* DRIFTS)等方法研究了钐的掺杂对铁基催化剂脱硝效率和抗水抗硫性的影响, 旨在揭示催化剂表面物理化学性质和催化活性之间的关系。

通过活性测试发现, 钐的掺杂可以使Fe_{0.94}Sm_{0.06}O_x催化剂在175–325 °C时实现>95%的脱硝效率和>93%的N₂选择性。动力学测试研究表明, 当基于催化剂的比表面积计算时, Fe_{0.94}Sm_{0.06}O_x催化剂的脱硝效率是纯Fe₂O₃催化剂的11倍; 基于质量计算时则为37倍。此外, 250 °C时抗水抗硫测试结果显示, Fe_{0.94}Sm_{0.06}O_x催化剂可以在通入200 × 10⁻⁶ SO₂ + 5 vol% H₂O, 空速为90000 h⁻¹时脱硝效率保持83%达168小时, 并且在切断H₂O和SO₂后, 该催化剂的脱硝效率可以很快完全恢复。XPS和H₂-TPR结果表明, 钐的掺杂使Fe_{0.94}Sm_{0.06}O_x催化剂的表面产生了大量的表面吸附氧, 从而促进了NO的氧化以及快速NH₃-SCR反应的进行。NH₃-TPD与原位DRIFTS结果表明, 钐的掺杂增强了催化剂的表面酸性, 有效地提高了NH₃的吸附和活化能力, 进而提高了催化剂的脱硝效率。另外, 钐的掺杂还可以促使NH₄HSO₄在Fe_{0.94}Sm_{0.06}O_x催化剂表面较低温度下的分解, 从而使催化剂具有很好的抗水抗硫性能。

关键词: 氨选择性催化还原; NO_x消除; 钐掺杂Fe₂O₃催化剂; 抗水抗硫性能; 168小时测试

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