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Article

In situ preparation of mesoporous Fe/TiO₂ catalyst using Pluronic F127-assisted sol-gel process for mid-temperature NH₃ selective catalytic reduction

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ABSTRACT

An Fe/TiO₂ catalyst with uniform mesopores was synthesized using Pluronic F127 as a structure-directing agent. This catalyst was used for selective catalytic reduction of NO with NH₃. The catalytic activity and resistance to H₂O and SO₂ of Fe/TiO₂ prepared by a template method were better than those of catalysts synthesized using impregnation and coprecipitation. The samples were characterized using N₂-physisorption, transmission electron microscopy, ultraviolet-visible spectroscopy, X-ray photoelectron spectroscopy, and in situ diffuse reflectance infrared Fourier-transform spectroscopy. The results showed that Pluronic F127 acted as a structural and chemical promoter; it not only promoted the formation of a uniform mesoporous structure, leading to a higher surface area, but also improved dispersion of the active phase. In addition, the larger number of Lewis acidic sites, indicated by the presence of coordinated NH₃ species (1188 cm⁻¹) and the N–H stretching modes of coordinated NH₃ (3242 and 3388 cm⁻¹), were beneficial to mid-temperature selective catalytic reduction reactions.

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1. Introduction

Atmospheric contaminant elimination has become an important research topic in recent years. NO_x emissions from mobile and stationary sources are major air pollutants and pose serious threats to the environment because they can cause acid rain, photochemical smog, and ozone depletion [1]. Selective catalytic reduction (SCR) with NH₃ is one of the most promising techniques for reducing NO_x emissions from stationary sources. The main commercial industrial catalysts currently available for this process are V₂O₅/TiO₂ modified with WO₃ or MoO₃ [2,3]. However, they have drawbacks such as low N₂ selectivity,

a narrow temperature window (300–400 °C), and the toxicity of V species to humans [4]. The development of novel SCR catalysts to replace conventional V-based catalysts has therefore been widely investigated.

In recent years, the use of Fe-based catalysts, which have the advantages of low cost, high chemical stability, and non-toxicity, in SCR reactions has attracted much attention [5–8]. In particular, supported Fe/TiO₂ catalysts have been well studied because of their excellent catalytic activities at mid-high temperatures (200–400 °C) in SCR reactions [9,10]. It has been suggested that the multiple valence states of iron oxides can provide active redox components. Anatase TiO₂ is re-

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garded as one of the best supports for SCR catalysts because (1) active components can be well dispersed on the TiO₂ surface [11–14], (2) electron excitation and charge transfer from TiO₂ to the active components can occur [13,15,16], and (3) the anti-SO₂ performance of TiO₂ is better than those of other supports [12,17,18].

Several methods have been developed for synthesizing supported Fe/TiO₂ catalysts. Alves et al. [19] reported that Fe/TiO₂ prepared by solution impregnation showed high activity at temperatures lower than 450 °C and pointed out that interactions occurred between iron(III) oxide and TiO₂. Coprecipitation is another common technique for synthesizing supported Fe/TiO₂ catalysts [9,20,21]. Some studies have shown that this method can provide large specific surface areas, and this is beneficial to SCR reactions [12]. However, Wachs et al. [22] argued that the higher activities of coprecipitated catalysts were the result of new sites associated with surface defects on the TiO₂ support rather than the higher surface area. In addition, a sol-gel method using butyl titanate as the Ti source was used to synthesize an Fe/TiO₂ catalyst [23]. In this method, doping ions were incorporated into the TiO₂ lattice, resulting in lattice defects and improved catalytic activity [24].

Recently, methods for the preparation of mesoporous, high-surface-area materials using structure-directing agents have been reported. Organic molecules such as surfactants (e.g. Pluronic P123 and F127) are used as templating agents to adjust the pore structures of the catalysts [25–27]. The majority of SCR catalysts are oxides of transition metals, e.g. Ti, Fe, Mn, and Ce. During precursor drying and calcination, the tension in the pores increases, causing pores to collapse. A surfactant can reduce the interfacial energy and decrease capillary stress, ultimately enabling the production of mesoporous catalysts with high surface areas and stable pore structures. Surfactants should therefore be good promoters for the preparation of SCR catalysts. In this work, Fe/TiO₂ catalysts were synthesized using a sol-gel process assisted by an anionic surfactant, namely Pluronic F127. For comparison, catalysts were also synthesized using impregnation and coprecipitation. The effects of the preparation process on the catalyst properties were studied using the Brunauer-Emmett-Teller (BET) method, transmission electron microscopy (TEM), ultraviolet-visible (UV-vis) spectroscopy, X-ray photoelectron spectroscopy (XPS), and H₂ temperature-programmed reduction (H₂-TPR). The effects of the synthetic method on the SCR reaction mechanism were also investigated using in situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS).

2. Experimental

2.1. Chemicals

The triblock copolymer surfactant Pluronic F127 (poly(ethylene oxide)-(polypropylene oxide)-poly(ethylene oxide)), tetraethyl titanate (TBOT), Fe(NO₃)₃·9H₂O, and TiOSO₄·2H₂O were purchased from Sigma-Aldrich (USA). Analytical-grade anhydrous ethanol (>99.7%), CH₃COOH (36%–38%), and NH₃·H₂O (25%–28%) were used.

2.2. Catalyst synthesis

Fe/TiO₂ was prepared using an F127-assisted sol-gel process. In a typical preparation, F127 (0.4 mmol) was added to sufficient anhydrous ethanol and the solution was heated gently until the F127 was completely dissolved. Then certain amounts of TBOT and CH₃COOH were dissolved in the F127 solution under vigorous stirring for 30 min, giving a transparent yellow solution. Fe(NO₃)₃·9H₂O solution was then added drop-wise to the solution under continuous stirring. The molar ratios of the components in the mixture were TBOT:F127:CH₃COOH:Fe(NO₃)₃·9H₂O = 1:0.004:0.7:0.14. The mixture was stirred for 2 h and then kept at room temperature for about 3 d to form a gel. The gel was dried in an oven at 110 °C for 12 h, and then calcined in air at 450 °C for 3 h. The obtained sample was denoted by Fe/TiO₂(t). The nominal loading of Fe in the catalyst was 10 wt% (Fe/TiO₂ = 10 wt%, the same below).

For comparison, supported Fe/TiO₂ catalysts were also prepared using wet impregnation and coprecipitation methods. In the impregnation method, anatase TiO₂ (Hehai Technology Company, China) was impregnated with an appropriate amount of Fe(NO₃)₃·9H₂O solution. After stirring for 30 min, the mixture was dried overnight at 110 °C and then calcined at 450 °C in air for 3 h. In the coprecipitation method, TiOSO₄·2H₂O was used as a TiO₂ precursor. Certain amounts of Fe(NO₃)₃·9H₂O and TiOSO₄·2H₂O were completely dissolved in deionized water (80 mL). Aqueous NH₃ was added to the solution under vigorous stirring until it was completely deposited. The obtained precipitate was removed by filtration, washed several times with deionized water, and dried at 110 °C overnight. The catalyst was obtained by calcination at 450 °C in air for 3 h. The Fe/TiO₂ catalysts prepared by impregnation and coprecipitation were denoted by Fe/TiO₂(i) and Fe/TiO₂(c), respectively.

2.3. Catalyst evaluation

The samples activities were evaluated using a fixed-bed reactor under a simulated flue gas containing 200 ppm NO, 200 ppm NH₃, 80 ppm SO₂ (when used), 5 vol% H₂O (when used), 5 vol% O₂, and balance N₂. The quartz tube diameter was 8 mm. The total gas flow rate was maintained at 400 cm³/min over 2.0 g of 40–60 mesh catalyst, corresponding to a gas hourly space velocity (GHSV) of 12 000 h⁻¹. The reaction temperature was controlled using a programmable temperature controller with a K-type thermocouple inserted into the catalyst bed. The NO_x concentrations at the reactor inlet and outlet were determined continuously using a flue gas analyser (KM9106 Quintox, Kane International Limited).

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

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

2.4. Catalyst characterization

The specific surface area was determined by the BET method using N₂ adsorption at -196 °C (Micromeritics ASAP 2020).

The pore size distribution was calculated using the Barrett–Joyner–Halenda (BJH) method. Samples were degassed at 200 °C for 2 h prior to measurements.

TEM images were obtained using a JEM-2010 instrument operated at 200 kV.

UV-vis diffuse reflectance spectroscopy was performed using a Shimadzu UV-3600 spectrophotometer. BaSO₄ was used as the reference material and spectra were recorded in the range 200–900 nm.

Raman spectroscopy was performed using a Horiba Labram instrument at a laser wavelength of 514.5 nm. The spectra were recorded from 200 to 1000 cm⁻¹ with a resolution of 1 cm⁻¹.

XPS was performed using a Kratos XSAM 800 electron spectrometer fitted with an Al K_α source (1486.6 eV). All binding energies were calibrated using the C 1s core level at 284.8 eV as an internal standard.

NH₃ temperature-programmed desorption (NH₃-TPD) was performed at a total flow rate of 50 mL/min. Before the experiments, the samples were pretreated in N₂ at 300 °C for 1 h. NH₃ adsorption was performed at 180 °C. Desorption was achieved by heating the samples from 120 to 600 °C; NH₃ was continuously monitored using a portable FT-IR gas analyser.

H₂-TPR was performed (Micromeritics Autochem 2920) using 100 mg of catalyst in a quartz U-tube under a mixture of 5 vol% H₂ and N₂. The total flow rate was 50 mL/min and the heating rate was 10 °C/min. Prior to the experiments, each sample was pretreated in pure N₂ at 300 °C for 1 h.

In situ DRIFT spectra were recorded from 800 to 4000 cm⁻¹ at a resolution of 8 cm⁻¹ with 100 scans in Kubelka–Munk mode, using a Bruker Tensor 27 FT-IR spectrometer equipped with a mercury cadmium telluride detector. Prior to each experiment, the sample was pretreated in pure N₂ at 300 °C for 1 h to eliminate physically adsorbed water and other impurities. The sample background spectrum at each target temperature was recorded during cooling. After cooling to room temperature, the sample was exposed to a controlled stream of 200 ppm NH₃ or 200 ppm NO + O₂ and balance N₂ at 100 mL/min for 1 h. After purging with purified N₂ for 30 min, desorption spectra were obtained at various target temperatures by subtraction of the corresponding background reference.

3. Results and discussion

3.1. Catalytic performance evaluation

Fig. 1 shows the NH₃-SCR performance of the samples synthesized using different methods as a function of temperature from 90 to 300 °C. NO conversion increased significantly across the entire temperature range, in the order Fe/TiO₂(t) > Fe/TiO₂(i) > Fe/TiO₂(c). Although nearly 100% NO conversion was achieved on all catalysts at 300 °C, the activities in the temperature window 180–250 °C (medium temperature zone) greatly differed. Fe/TiO₂(t) gave the best performance and nearly 90% NO was removed at 180 °C, whereas only 46% and 18% NO were removed using Fe/TiO₂(i) and Fe/TiO₂(c), respectively. Fig. 2 shows the N₂ selectivities of the samples. In the mid-temperature range, the N₂ selectivities of the three

Fig. 1. NH₃-SCR performance over various Fe/TiO₂ catalysts. Reaction conditions: N₂ balance, [NO] = [NH₃] = 200 ppm, [O₂] = 5 vol%, GHSV = 12000 h⁻¹.

Fig. 2. N₂ selectivities over various Fe/TiO₂ catalysts. Reaction conditions: N₂ balance, [NO] = [NH₃] = 200 ppm, [O₂] = 5 vol%, GHSV = 12000 h⁻¹.

samples were greater than 90% and the N₂ selectivity of Fe/TiO₂(t) was slightly higher than those of the other two samples. All the results indicate that the method used to synthesize Fe/TiO₂ greatly influenced the mid-temperature activity and N₂ selectivity. This is investigated in detail in the following sections.

3.2. Structure and morphology

The structural properties of the prepared catalysts were investigated using N₂ adsorption–desorption isotherms. The results are shown in Fig. 3 and the BET surface areas, pore volumes, and average pore diameters are listed in Table 1. Fe/TiO₂(t) had the largest specific surface areas (112.40 m²/g) and gave a type-IV isotherm with an H1 hysteresis loop, indicating that mesopores with a narrow size distribution were formed during synthesis. The corresponding pore size distribution curves (insets in Fig. 3) show that Fe/TiO₂(t) consisted of uniform mesopores (5.3 nm). Fe/TiO₂(c) also gave a typical type-IV isotherm, but the quantity adsorbed was much lower than in the case of Fe/TiO₂(t) because of the smaller pore volume (0.13 cm³/g), which significantly reduced the specific sur-

Fig. 3. N₂ adsorption-desorption isotherms and BJH pore size distribution curves (inset) for various Fe/TiO₂ catalysts. (a) Fe/TiO₂(t); (b) Fe/TiO₂(i); (c) Fe/TiO₂(c).

Table 1

Textural properties of samples.

Catalyst	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)
Fe/TiO ₂ (t)	112.40	0.22	6.21
Fe/TiO ₂ (i)	87.78	0.29	14.27
Fe/TiO ₂ (c)	72.49	0.13	8.29

face area. Fe/TiO₂(i) gave a type-II isotherm, suggesting the presence of both mesopores and some macropores, therefore the average pore size of Fe/TiO₂(i) was much larger than those of the other catalysts, leading to a small specific surface area. These results show that the synthetic method had important effects on the structural properties of Fe/TiO₂.

The samples were also investigated using high-resolution TEM. The images in Fig. 4 show that the primary particle sizes of Fe/TiO₂(t), Fe/TiO₂(i), and Fe/TiO₂(c) were about 10, 11, and 15 nm, respectively. For Fe/TiO₂(t), clear lattice fringes (0.352 nm) were observed on the catalyst surface, corre-

sponding to the (101) crystal phase of anatase TiO₂. However, unlike Fe/TiO₂(i) and Fe/TiO₂(c), Fe₂O₃ was not directly detected on the Fe/TiO₂(t) surface, although the presence of Fe was confirmed using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Table 2). These results show that the particles of Fe species were better dispersed on the Fe/TiO₂(t) surface, and this promotes the SCR reaction.

3.3. UV-vis and Raman spectra

The characteristic absorption peaks in the UV-vis spectra (Fig. 5) can be used to confirm the presence and the charges of transition-metal ions. Anatase TiO₂ showed a clear O²⁻ → Ti⁴⁺ charge-transfer band centred at 256 nm. Generally, Fe₂O₃ shows a broad absorption peak at around 533 nm, attributed to *d-d* absorption of Fe(III) [28]. The TiO₂ absorption band broadened when Fe was introduced, possibly because of interactions between Fe and Ti resulting from incorporation of Fe into the TiO₂ lattice [24]. The absorption band shifted by about 40 nm in the Fe/TiO₂(t) and Fe/TiO₂(c) spectra, indicating

Fig. 4. TEM and high-resolution TEM images of various Fe/TiO₂ catalysts. (a1, a2) Fe/TiO₂(t); (b1, b2) Fe/TiO₂(i); (c1, c2) Fe/TiO₂(c).

Table 2

Total loadings and surface chemical compositions of catalysts.

Catalyst	Mass fraction of Fe by ICP (%)	Surface atomic content by XPS (%)			
		Fe	O	Ti	O _α /(O _α +O _β)
Fe/TiO ₂ (t)	8.6	10.0	64.2	25.8	27.4
Fe/TiO ₂ (i)	8.5	14.5	64.0	21.5	21.1
Fe/TiO ₂ (c)	8.8	10.7	63.8	25.6	16.8

Fig. 5. UV-vis spectra of various Fe/TiO₂ catalysts.

stronger interactions in these two samples. Bond energy changes or charge transfer caused by interactions generate defects, producing more active sites. Interactions between Fe and Ti were also identified using Raman spectroscopy (Fig. 6). The Raman spectrum of anatase TiO₂ has three major bands, at around 403, 519, and 640 cm⁻¹ [29]. Among the three samples, the Fe/TiO₂(t) catalyst showed the largest red shift to a lower wavenumber of the peak at 393 cm⁻¹, suggesting strong interactions between Fe and Ti; this is consistent with the UV-vis results.

Fig. 6. Raman spectra of various Fe/TiO₂ catalysts.

3.4. XPS analysis

The elementary oxidation states and surface compositions of the different catalysts were investigated using XPS; the Fe 2p and O 1s spectra are shown in Fig. 7. The surface atomic concentrations and concentrations obtained using ICP-AES are shown in Table 2. Fig. 7(a) shows that the Fe 2p spectra of the three samples were approximately the same. Clear peaks corresponding to Fe³⁺ were observed at 710.8 eV (Fe 2p_{3/2}), 725.1 eV (Fe 2p_{3/2}), and 710.8 eV (Fe 2p_{3/2} satellite peak); however, no peaks at 715 eV, attributable to the Fe²⁺ shakeup satellite, were detected, implying that the predominant Fe species in all the catalysts was Fe³⁺ [20,30]. Table 2 shows that Fe/TiO₂(i) had the highest surface atomic Fe concentration among the samples. This could be the result of aggregation of Fe atoms on the catalyst surface layer, which would severely disrupt dispersion of the active components, and reduce the catalytic activity. The ICP-AES results (Table 2) show that the Fe contents on all the catalysts were almost the same, implying that the impact of Fe loading on the SCR activity could be ignored.

Fig. 7. XPS spectra of various Fe/TiO₂ catalysts. (a) Fe 2p; (b) O 1s.

The O 1s XPS spectrum was fitted with two peaks and the results after deconvolution are shown in Fig. 7(b). The peak located at 529.2–529.7 eV corresponds to lattice oxygen (denoted by O_{β}). The peak centred at 531.1–531.5 eV is ascribed to surface adsorbed oxygen (denoted by O_{α}). The relative concentration ratios, i.e. $O_{\alpha}/(O_{\alpha} + O_{\beta})$, were 27.4%, 21.1%, and 16.8% for Fe/TiO₂(t), Fe/TiO₂(i), and Fe/TiO₂(c), respectively. The surface active adsorbed oxygen could enhance the oxidation of NO to NO₂, resulting in a fast SCR reaction ($\text{NO} + \text{NO}_2 + 2\text{NH}_3 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$) [31]. The UV-vis and Raman spectra and catalytic performance suggest that a high concentration of surface adsorbed oxygen derived from defects could partly explain the high catalytic activity of Fe/TiO₂(t).

3.5. NH₃-TPD analysis

The adsorption of NH₃ on the catalyst surfaces at 180 °C was investigated using NH₃-TPD; the results are shown in Fig. 8. One broad desorption peak spanning the temperature range 200–400 °C was observed for all three samples. This peak is attributed to NH₃ desorption from weak and medium acidic sites. For the Fe/TiO₂(t) catalyst, the peak intensity increased sharply with increasing desorption temperature; the peak was most intense at 305 °C, and the intensity was twice that of the peak for Fe/TiO₂(c). In addition, the area under the peak, which represents the quantity of chemisorbed NH₃ molecules, showed that the NH₃ adsorption capacities followed the order Fe/TiO₂(t) > Fe/TiO₂(i) > Fe/TiO₂(c). A combination of the BET and NH₃-TPD results shows that the large specific surface area and optimal pore structure of Fe/TiO₂(t) helped to increase the number of acidic sites for NH₃ adsorption, and the improved NH₃ adsorption capacity greatly benefited the SCR reaction.

3.6. Reduction properties (H₂-TPR)

The reducibility, which is an important factor in NH₃-SCR, can be determined using H₂-TPR. Fig. 9 shows that all the three samples showed clear H₂ consumption below 500 °C, namely at 388 °C for Fe/TiO₂(t), 431 °C for Fe/TiO₂(i), and 447 °C for Fe/TiO₂(c). This is ascribed to the reduction of Fe₂O₃ to Fe₃O₄

Fig. 8. NH₃-TPD curves for various catalysts.

Fig. 9. H₂-TPR profiles of various Fe/TiO₂ catalysts.

[19]. It is worth noting that the Fe₂O₃ to Fe₃O₄ reduction peak in the case of Fe/TiO₂(t) was at a lower temperature (388 °C) than those for the other samples, indicating that the interactions between ions and Ti species in the template method enhanced the redox properties of the catalyst. Two reduction peaks, at around 524/587 °C and 710/761 °C, assigned to reduction of Fe₃O₄ to FeO and FeO to Fe, respectively, were also observed for the samples. The initial reduction temperatures for the samples differed from each other. In general, the initial reduction temperature reflects the redox capability of the catalyst, and a lower temperature indicates a stronger redox capability. It can therefore be concluded that the order of the catalyst reducibilities was Fe/TiO₂(t) > Fe/TiO₂(c) > Fe/TiO₂(i). The enhanced redox properties of the catalysts are one possible reason for their excellent activities [32].

3.7. Coadsorption of NO + O₂

The adsorption of NO + O₂ over the catalysts at various temperatures was investigated using in situ DRIFTS; the spectra are shown in Fig. 10. The results show that the methods used to synthesize the catalysts significantly affected NO adsorption and states. DRIFT spectra for NO adsorption on the three samples were recorded to clarify the NO species adsorbed on the different samples; the spectra are shown in Fig. 10(a). Fe/TiO₂(i) showed the fewest bands for NO adsorption, with only four peaks, because it gave the weakest interactions between the active component and the support. Strong peaks were observed at 1184 (NO⁻ species) and 1461 cm⁻¹ (monodentate nitrate), and weak peaks were observed at 1603 (gaseous NO₂ molecules) and 1668 cm⁻¹ (bridged nitrate) [25,33,34]. It is worth noting that these peaks, except the one corresponding to NO⁻ species (1184 cm⁻¹), gradually disappeared with increasing temperature from 50 to 150 °C (Fig. 10(c)), suggesting low thermal stability of the adsorption bands. More nitrate species were formed on Fe/TiO₂(c) than on Fe/TiO₂(i). Fig. 10(d) shows that the peak at 1642 cm⁻¹, attributed to the asymmetric frequency of gaseous NO₂ molecules, disappeared at 200 °C [33,35]. The peak at 1251 cm⁻¹ was assigned to unstable bridged nitrate, which was only pre-

Fig. 10. In situ DRIFT spectra for NO + O₂ adsorption at different temperatures on various Fe/TiO₂ catalysts (a), Fe/TiO₂(t) (b), Fe/TiO₂(i) (c), and Fe/TiO₂(c) (d).

sent at low temperatures. After this peak vanished, M-NO₂ compounds (1346 cm⁻¹) appeared with increasing temperature, implying that the stable bridged nitrates were transformed into M-NO₂ compounds on the surface of the coprecipitated catalyst [34]. The band at 1471 cm⁻¹ can be attributed to monodentate nitrate because it disappeared at around 150 °C [34,36]. The two bands at 1187 and 1133 cm⁻¹ are assigned to NO species and NO²⁻ species, respectively [33]. It is worth noting that as the temperature increased the bands at 1346 and 1187 cm⁻¹ red shifted, indicating that the corresponding species were unstable. For Fe/TiO₂(t), unlike the other two catalysts, high-intensity bands for adsorption of bridged nitrate (1241 cm⁻¹), bidentate nitrate (1578 cm⁻¹), and gaseous NO₂ molecules (1603 cm⁻¹) were observed at 50 °C (Fig. 10(a)). Fig. 10(b) shows that as the temperature increased, the bands for monodentate nitrate at 1289 and 1479 cm⁻¹ vanished at 150 °C and the intensities of the other peaks decreased slowly, implying that the nitrate species on Fe/TiO₂(t) were more stable than those on Fe/TiO₂(i) and Fe/TiO₂(c). Chen et al. [25] reported that bridged and bidentate nitrates could react with preadsorbed NH₄⁺ or NH₃ to produce more reactive intermediates, thereby accelerating the standard SCR reaction (2NO + 2NH₃ +

1/2O₂ → 2N₂ + 3H₂O). It was also reported that NO₂ improves the SCR activity via the fast SCR reaction (NO + NO₂(a) + 2NH₃(a) → 2N₂ + 3H₂O) [37]. The oxidation of NO to NO₂ is therefore generally accepted as being an important step in enhancing the SCR reaction. The addition of F127 promoted NO oxidation to NO₂, possibly because high dispersion of the active component enables combination of more NO₂ species, producing more monodentate nitrate species (Fe-O-NO₂). The results show that a larger number of interactions assisted NO oxidation and further improved the catalytic activity.

3.8. Surface acidities (in situ DRIFTS of NH₃ adsorption)

Chemisorption of NH₃ can be used to investigate the surface acidity of a supported Fe/TiO₂ catalyst; this is another important factor in its catalytic performance in NH₃-SCR [38,39]. The DRIFT spectra of NH₃ adsorption over the three catalysts are shown in Fig. 11. The three samples showed various bands in the ranges 1000–1700 and 3000–3500 cm⁻¹. The bands at 1435–1450 and 1658–1670 cm⁻¹ correspond to the symmetric and asymmetric bending vibrations, respectively, of NH₄⁺ chemisorbed on Brönsted acidic sites [5,40]. The peaks at

Fig. 11. In situ DRIFT spectra of NH_3 adsorption at different temperatures on various Fe/TiO_2 catalysts (a), $\text{Fe}/\text{TiO}_2(\text{t})$ (b), $\text{Fe}/\text{TiO}_2(\text{i})$ (c), and $\text{Fe}/\text{TiO}_2(\text{c})$ (d).

around 1180 and 1610 cm^{-1} are assigned to the symmetric and asymmetric bending vibrations, respectively, of surface NH_3 chemisorbed on Lewis acidic sites [40,41]. The band at 1340 cm^{-1} is attributed to bending vibrations of NH_3 coordinated to one type of Lewis acidic site [42]. The N–H stretching modes of NH_3 coordinated to Lewis acidic sites are observed at 3157, 3230–3250, and 3372–3392 cm^{-1} [2,12,43], and the N–H stretching modes of NH_4^+ bound to Brönsted acidic sites vibrate at 3083 cm^{-1} [40].

Only weak Lewis acidic sites are present on TiO_2 and the addition of metal oxides introduces Brönsted acidic sites [44]. Fig. 11(a) suggests that both Brönsted and Lewis acidic sites were present on the catalyst surfaces. It should be noted that the intensities of the bands for NH_4^+ chemisorbed on Brönsted acidic sites (1435–1450 and 1658–1670 cm^{-1}) decreased significantly with increasing temperature over the range 50–150 $^{\circ}\text{C}$ as a result of decomposition and desorption. When the temperature exceeded 150 $^{\circ}\text{C}$, the Brönsted acid signals almost disappeared for all the samples, but the intensities of the bands for coordinated NH_3 on Lewis acidic sites (1188/1184/1181, 1340, and 1610 cm^{-1}) were little changed. These results imply that the Lewis acidic sites were more stable than the Brönsted acidic sites. Fig. 11(a) shows that the adsorption of NH_3 species on the sample surfaces differed greatly at 50 $^{\circ}\text{C}$. There were

more Lewis acidic sites on the surface of $\text{Fe}/\text{TiO}_2(\text{t})$ than on $\text{Fe}/\text{TiO}_2(\text{i})$ and $\text{Fe}/\text{TiO}_2(\text{c})$, shown by the band intensities for coordinated NH_3 (1188 cm^{-1}) and the bending vibration of N–H bonds (3242 cm^{-1}). The reason could be related to the synthetic process. (1) In the template method, the active component was encapsulated by the template, i.e. F127, and the number of Lewis acidic sites increased during template calcination [45]. (2) In the coprecipitation method, the active component was primarily covered with hydroxyl groups $[\text{TiO}(\text{OH})_2/\text{Fe}(\text{OH})_3]$, therefore more Brönsted acidic sites were generated from the residual hydroxyl group after calcination, identified by the strong band near 1658 cm^{-1} . In the NH_3 -SCR reaction, Lewis acidic sites are more important than Brönsted acidic sites [46], resulting in a better catalytic performance by $\text{Fe}/\text{TiO}_2(\text{t})$. In addition, it is worth noting that a band at 1553 cm^{-1} , attributed to amide species ($-\text{NH}_2$), was observed for $\text{Fe}/\text{TiO}_2(\text{i})$. As the temperature increased, the intensity of $-\text{NH}_2$ band decreased rapidly. A new peak at 1590 cm^{-1} was detected, which could be attributed to intermediates ($-\text{NH}_2$, $-\text{NH}$, and $-\text{N}$) formed during NH_3 oxidation, which mechanistic studies have been shown to be unnecessary for, but have a positive effect on, the NH_3 -SCR reaction [40]. In addition, for the coprecipitated catalyst, a clear peak was observed at 1341 cm^{-1} ; it could be related to sulfur species remaining in the catalyst.

Fig. 12. Effects of H₂O and SO₂ on NO conversions over various catalysts at 210 °C. Reaction conditions: N₂ balance, [NO] = [NH₃] = 200 ppm, [O₂] = 5 vol%, [SO₂] = 80 ppm (when used), 5 vol% H₂O (when used), GHSV = 12000 h⁻¹.

3.9. Resistance to H₂O and SO₂ poisoning

Flue gas usually contains some SO₂ and H₂O, therefore the resistances to SO₂ and H₂O of the catalysts were examined at 210 °C. Fig. 12 shows that the NO conversions over Fe/TiO₂(i) and Fe/TiO₂(c) declined sharply when SO₂ and H₂O were introduced. The NO conversions of these two samples decreased by about 40% in the first 5 h, and only achieved 38% and 5%, respectively. In comparison, the NO conversion over Fe/TiO₂(t) decreased slightly, and was still higher than 70% after the first 5 h. Moreover, in the following 7 h, the NO conversion over Fe/TiO₂(t) remained stable and changed little. We suggest that there are two main reasons for deactivation of the catalyst by H₂O and SO₂: (1) deposition of sulfate species on the catalyst surface, blocking the active sites; and (2) sulfation of the active component by SO₂, making it inactive in the SCR reaction. The large specific surface area and well-developed pore structure of Fe/TiO₂(t) could slow the deposition of sulfate species, facilitating reactant transportation and improving its resistance against H₂O and SO₂.

4. Conclusions

The effects of the methods used to prepare Fe/TiO₂ catalysts on the morphological structure, surface chemical properties, and catalytic performances in the SCR of NO by NH₃ were compared. The results show that the catalyst prepared using a template method, i.e. Fe/TiO₂(t), had the highest specific surface area and largest concentration of pore size distribution, and showed the best SCR activity. The characterization results suggest that the Fe/TiO₂(t) catalyst had the highest concentration of surface adsorbed oxygen (O_α) and the strongest interactions between the active component and the support; this enhanced the oxidation of NO to NO₂ and improved the fast SCR reaction (NO + NO₂ + 2NH₃ → 2N₂ + 3H₂O). Moreover, in situ DRIFTS showed that NO + O₂ adsorption was most stable on Fe/TiO₂(t), because the intensities of the peaks at 1241 cm⁻¹ (bridged nitrate), 1578 cm⁻¹ (bidentate nitrate), and 1603 cm⁻¹

(gaseous NO₂ molecules) were still high at 200 °C, whereas the peaks in the spectra for Fe/TiO₂(i) and Fe/TiO₂(c) almost disappeared. The Fe/TiO₂(t) catalyst therefore had excellent SCR activity. In addition, the large NH₃ adsorption capacity, shown by the intensity of the peak at 1188 cm⁻¹ (coordinated NH₃ species), and the presence of Lewis acidic sites, shown by the strong N–H stretching modes of coordinated NH₃ (3242 and 3388 cm⁻¹), played a crucial role in the NH₃-SCR reaction.

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Graphical Abstract

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In situ preparation of mesoporous Fe/TiO₂ catalyst using Pluronic F127-assisted sol-gel process for mid-temperature NH₃ selective catalytic reduction

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The Fe-TiO₂ catalyst synthesized by a F127-assisted process showed the uniform mesopore structure, the strong interaction between Fe and Ti, and the excellent SCR activity in mid-temperature region with the comparison of catalysts prepared by traditional impregnation and coprecipitation methods.

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F127辅助制备介孔Fe/TiO₂催化剂用于中温NH₃选择性催化还原反应

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摘要: NO_x是大气污染物的重要组成部分, 能够造成酸雨、光化学烟雾和臭氧层破坏等一系列环境问题, 严重危害人类健康。选择性催化还原(SCR)是控制NO_x排放的主要技术, 当前工业上普遍采用的是钒钛催化剂, 然而该催化剂活性温度窗口较窄(300–400 °C), N₂选择性较低, 而且钒物种本身有毒。因此开发新型SCR催化剂成为研究热点。

Fe/TiO₂催化剂具有稳定的化学性质, 环境污染少且价格低廉, 近年来受到广泛关注。为了提高Fe/TiO₂催化活性, 人们采用了各种不同的制备方法。本文以F127作为结构导向剂, 结合溶胶-凝胶法原位合成了具有介孔结构、工作温度在150–300 °C的Fe/TiO₂脱硝催化剂, 并与普通浸渍法和共沉淀法制备的催化剂进行了对比。利用N₂吸附脱附、紫外-可见光谱、X射线电子能谱、NH₃程序升温脱附和原位红外光谱等技术研究了制备方法对Fe/TiO₂催化剂物理结构及脱硝性能的影响。结果表明, 相较于浸渍法和共沉淀法, 模板法制备的催化剂具有较高的脱硝效率和抗H₂O和SO₂性能。作为结构导向剂,

F127能够诱导催化剂形成均匀的介孔结构,有利于提高催化剂比表面积,促进反应物分子的扩散和转移,从而提高催化剂脱硝效率。

进一步研究发现,模板法能够明显促进活性组分Fe物种的分散和NH₃吸附,载体与活性组分具有较强的相互作用,因而有利于催化剂产生较多的活性位。结合XPS结果,较多的活性位点有利于表面吸附氧(O_a)在催化剂表面的吸附。O_a有利于NO到NO₂的转化,从而促进快速SCR反应: $\text{NO} + \text{NO}_2 + 2\text{NH}_3 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$ 。通过原位红外机理分析证明,吸附在模板法制备的催化剂表面的NO物种具有较强的稳定性,当温度超过200 °C时,仍然保持一定的吸附强度;吸附NH₃红外结果表明, Lewis酸性位比Brønsted酸性位具有更强的稳定性,当温度超过150 °C仍然具有较强的Lewis酸吸附。催化剂表面稳定的NO物种和Lewis酸位上强的NH₃吸附是催化剂催化活性增加的重要原因。

关键词: Fe/TiO₂; 介孔结构; 相互作用; 中温氨选择催化还原

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