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Selective Catalytic Reduction of $\mathrm{NO_x}$ over Fe/TiO_2 Prepared by F127-Template Method at Mid-Temperature

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Abstract

A series of catalysts based on Fe/TiO_2 were synthesized by template, impregnation, and co-precipitation methods for mid-temperature selective catalytic reduction of NO with NH₃. The samples were characterized by Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), temperature programmed desorption (TPD) and Diffuse reflectance infrared Fourier transform spectra (DRIFTS). Among these catalysts, the sample prepared by template method exhibited the best catalytic performance. Analyses indicated that large specific surface area, good dispersion of active phase, and stronger NH₄⁺ adsorption on Brønsted acid sites might be the main reasons for the high catalytic performance of Fe/TiO_2 prepared by template method.

Keywords: NH₃-SCR; Fe/TiO₂; Template method; Mid-temperature

Introduction

Nitrogen oxides (NO_x), emitted from stationary and mobile sources, is one of the major atmospheric pollutants, which can cause a series of environmental problems such as acid rain, photochemical smog and ozone depletion [1]. Selective catalytic reduction (SCR) of NO with NH₃ is currently proved to be the most commonly and effective technology to remove NO_x in the flue gas from stationary sources. In the technology, V_2O_5/TiO_2 promoted by WO₃ or MoO₃ is the most commercially used catalyst [2], which exhibits excellent catalytic performance within the temperature range of 330-400°C. However, some drawbacks such as a narrow operating temperature window, dust block, heavy metal deactivated, and biological toxicity caused by vanadium species limit its application [3,4]. Hence, lots of efforts have been devoted to develop novel vanadium-free catalysts with the advantages of wide temperature usable range, high catalytic performance and friendly to environment.

In recent years, Fe-based catalysts have attracted great interest for its good catalytic ability in medium temperature, which can be applied to the purification of flue gas at the range of 150-280°C, such as coke oven flue gas, and glass furnace gas. Several Fe-based catalysts have been developed to employ in the application, such as Fe_2O_3 -TiO₂ [5], Fe_2O_3 -Pillared clay catalyst [6], and Fe-ZSM-5 catalyst [7] prepared by solution impregnation [8], co-precipitation [9] and ion-exchange methods [10]. Moreover, to further improve the catalytic activity, metal oxides doping (cerium, copper, manganese and the like) was proposed to modify the Fe-based catalysts [11-13]. Although these catalysts showed high denitration efficiency, the still low mid-temperature catalytic activity, complex and costly preparation methods have hindered their largescale applications.

Template method, as one of the most effective pathways to tune the physical and chemical properties of catalysts, has been used in many catalyst preparation processes. In the processes, template would adjust the pore structure and promote the dispersion extent of active phase [14-16], thereby enhancing the catalytic activity of catalysts. However, much less attention has been focused on template method for the preparation of Fe-based catalysts for SCR at mid-temperature. Anionic surfactant Pluronic F127 is a three-block copolymer and could release anions in aqueous solution [17], which can be an efficient template agent. Therefore, in this work, a novel simple method towards Fe/TiO₂ catalyst with high catalytic activity used for NH₃-SCR in the mid-temperature range (150-280°C) was synthesized by template method using Pluronic F127 (PEO₁₀₀PPO₇₀PEO₁₀₀) as template. For comparison, the catalytic

performance of Fe/TiO₂ catalysts synthesized by impregnation and coprecipitation methods was also evaluated under the same conditions.

Experimental

Catalyst preparation

Template method (t): All chemicals used were analytical grade. Firstly, 0.4 mmol Pluronic F127 was dissolved into 0.1 mol ethanol at room temperature. Secondly, 0.1 mol tetraethyl orthotitanate and 9 ml CH₃COOH were added into the above solution under vigorous stirring until a transparent yellow solution was formed. Thirdly, a solution with 5.8 g Fe(NO₃)₃.9H₂O in 9 ml deionized water was then added. After stirring for 2 h, the resultant was placed at room temperature for 3 days to form a gelatum. Finally, the gelatum was dried at 110°C overnight and calcined at 450°C in air for 3 h at a heating rate of 2°C/ min. Before using, the catalyst (Fe/TiO₂ (t)) was crushed and sieved to 40-60 mesh. The used nominal load of Fe in the catalyst was 10 wt. % (Fe/TiO₂=10 wt. %, the same below).

Impregnation method (i): Iron-doped titania was prepared by an aqueous incipient wetness impregnation method. 0.06 mol TiO₂ was impregnated by equal volume $Fe(NO_3)_3$ solution with 3.6 g of $Fe(NO_3)_3.9H_2O$. After stirring for 2 h at 80°C the sample was dried at 110°C for 6 h and calcined at 50°C in air for 3 h. Finally, the catalyst of $Fe(TiO_2(i))$ was crushed and sieved to 40-60 mesh.

Coprecipitation method (c): Iron-doped titania was also prepared by coprecipitation method. 0.08 mol titanyl sulfate and 4.5 g $Fe(NO_3)_3$,9H₂O were dissolved completely in 80 ml water, and tammonia water was then gradually added to the solution with stirring for 2 h. The obtained product was filtered and washed with deionized water and then dried at 110°C, finally the catalyst of Fe/TiO₂(c) was crushed and sieved to 40-60 mesh.

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Characterization of the sample

The textural structures of the samples were measured by N_2 adsorption at 77 K in a Micromeritics ASAP2020 system. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method, and the pore size distributions were calculated by BJH method.

X-ray diffraction (XRD) was performed to characterize the power by an X-ray diffractometer (D8 ADVANCE), operating at 40 kv and 45 mA using Cu-K_a radiation. Diffraction patterns were recorded over a 2 θ range of 20-80° using a step size of 0.02°.

The morphology of the catalyst was observed by scanning electron microscope (SEM, JSM-7001F, JEOL, and Japan).

Diffuse reflectance infrared Fourier transform spectra (DRIFTS) were collected from 800 to 4000 cm⁻¹ by a Bruker Tensor 27 instrument equipped with a MCT detector. The spectra were obtained at the resolution of 8 cm⁻¹ with 100 scans in Kubelka-Munk mode.

 $\rm NH_3$ temperature programmed desorption ($\rm NH_3-TPD$) experiment was carried out under a total flow rate of 50 ml/min. Before experiment, the samples were pretreated in pure $\rm N_2$ at 300°C for 1 h. $\rm NH_3$ adsorption was performed at 180°C. Desorption was carried out by heating samples from 180°C to 600°C, and the $\rm NH_3$ was continuously monitored using a portable FT-IR gas analyzer.

Catalytic activity test

The activity measurement for the selective catalytic reduction of NO by NH₃ was carried out in a fixed-bed reactor under a simulated flue gas containing 500 ppm NO, 500 ppm NH₃, 6.5% O₂, N₂ balance. The total gas flow rate was maintained at 400 cm³/ min over 2.0 g of the catalyst, corresponding to the GHSV of 12000 h⁻¹. For the reaction, the desired temperature was controlled by a programmable temperature controller. The NO_x concentration at the inlet and outlet of the reactor were analyzed continuously by a flue gas analyzer (KM9106 Quintox, Kane International Limited).

Results and Discussion

SCR activity

Reaction conditions: $[NH_3]=[NO]=500$ ppm, $[O_2]=6$ vol %, N_2 balance, total flow rate=400 ml/min, GHSV=12000 h⁻¹

The SCR performances of synthesized samples for NH₃-SCR as a function of reaction temperature from 120-300°C are presented in Figure 1. The NO conversion of the three catalysts increased with the rise of temperature and followed the order Fe/TiO₂(t)>Fe/TiO₂(i)>Fe/TiO₂(c). Although the highest NO conversion of these three catalysts was observed at 300°C, the Fe/TiO₂(t) showed the best SCR activity, with NO conversion of higher than 90% at the temperature window in the range of 175-300°C. The results indicate that the preparation method of the samples was a crucial factor, and template method is superior to others.

BET analysis

The BET surface area, pore volume, mesopore area and pore size of Fe/TiO_2 catalysts are summarized in Table 1. It could be found that the surface area of $\text{Fe/TiO}_2(t)$ is the largest, and that of $\text{Fe/TiO}_2(c)$ is smallest, and the trend is same with the mesopore area. The pore size distributions are shown in Figure 2, it can be observed that the pore diameter varied among the different samples, and the porosity of Fe/TiO_2 is mainly made up of mesopores. The pore diameter of $\text{Fe/TiO}_2(t)$

mainly distributed at 2-50 nm, and that is why it has the biggest average pore diameter. The most pore size of Fe/TiO₂ (t) and Fe/TiO₂(c) are about 5 nm and 10 nm respectively. While Fe/TiO₂ (t) catalyst shows a relatively larger surface area, which is attribute to the addition of Pluronic F127 that could adjust pore structure [18]. All these results indicated that the textural parameters of Fe/TiO₂ had been greatly influenced by mesopore structures, and optimal pore structure of Fe/TiO₂ could provide larger specific surface area. In addition, it can be noted that the variation of surface area was in consistent with catalytic performance, and that is probably that larger surface area can adsorb more of NH₃, which could facilitate the reaction of NH₃- SCR [19].





Catalysts\	BET surface area	Mesopore A _{BET}	Pore volume	Average pore diameter
	(m² g-¹)	(m² g⁻¹)	(cm³ g-1)	(nm)
$Fe/TiO_2(t)$	122.05	113.83	0.27	8.95
Fe/TiO ₂ (i)	64.15	53.89	0.25	16.21
Fe/TiO ₂ (c)	57.26	46.32	0.05	3.77

Table 1: Textural properties of samples.



XRD and SEM

The XRD patterns of the samples for each method were shown in Figure 3. For all the Fe/TiO₂ samples, the distinctive obvious diffraction peaks around 25°, 38°, 48°, 54° and 62° corresponding to (101), (004), (200), (105) and (204) of crystal phases of anatase TiO₂ (JCPDS 21-1272) were detected. Besides the anatase phase, several diffraction peaks assigned to Fe₂O₃ (JCPDS 33-0664) were also detected in Fe/TiO₂(i) and Fe/TiO₂(c). While, the Fe₂O₃ diffraction peaks could not be detected in the Fe/TiO₂(t) sample, although the Fe contents are same as other samples. The result may be due to the great interaction between TiO₂ and iron oxides, and thus iron oxides could be dispersed well in the Fe/TiO₃(t) sample.

In addition, it is noted that the anatase peaks of Fe/TiO₂(i) were sharper than the other two, indicating that the crystalline degree and size on the sample increased according to Scherrer's formula. The result of SEM (Figure 4) imagine also showed that the agglomeration and sintering of fine particles are existed on the surface of the Fe/TiO₂(i), which could contribute to the increase of grain size. The large particle was not conducive to the dispersion of active phase in the catalyst, thereby leading to a decrease of NO removal efficiency. According to Scherrer's formula, larger half peak width of Fe/TiO₂(t) and Fe/TiO₂(c) implied smaller grain sizes. By comparison, the particle size of Fe/TiO₂(t) is the smallest in these three catalysts which could be also identified by SEM, which was beneficial to SCR process [13].

To investigate the NH₃ adsorption on the catalysts at 180°C, NH₃-TPD analysis was performed and the results were presented in Figure 5. All of the samples exhibited a broad NH₃ desorption peak in the temperature range of 180-450°C, which was attributed to NH₃ desorbed by weak and medium acid sites [20], which implied that the Fe/TiO₂ had both Lewis acid and Brønsted acid. However, the peak areas of various catalysts were extremely different, indicting the different acid-site density or the number of each acid-site [21]. The quantitative estimation of acid sites is shown in Figure 6, and it followed the order Fe/TiO₂(t)>Fe/TiO₂(c)>Fe/TiO₂ (i). It is well know that the chemisorbed NH₃ molecules were crucial roles in the SCR reaction according to Eley-Rideal mechanism [22]. In the case of Fe/TiO₂(t), the peak intensity started to rise at temperature 180°C, and the adsorption capacity was 0.18 mmol/g, which was two times higher than that of Fe/TiO₂(i). It could be attributed to the larger specific surface area, optimal





Figure 4: SEM images of the samples. $\mathbf{a_1}$, $\mathbf{a_2}$: Fe/TiO₂ (t) **b**: Fe/TiO₂ (i) **c**: Fe/TiO₂ (c).



pore structure [14], and the interaction between TiO_2 and iron oxides [9] during calcination process for the removal of template. It is worth noting that the variation of adsorption capacity was not consistent with the catalytic performance, suggesting that there also other factors affecting SCR reaction.

DRIFT studies

To further explore the Brønsted acid and Lewis acid on the surface of the catalysts, NH_3 adsorption was performed with a DRIFT spectrometer at 180°C. NH_3 (500 ppm) was injected firstly for 30 min. After N_2 purging, the adsorbed species were examined as shown in Figure 7. Several bands in the ranges of 1000-1700 cm⁻¹ and 3300-3700 cm⁻¹ were observed over these samples. The bands at 1441 cm⁻¹ and 1640 cm⁻¹ were attributed to the symmetric and asymmetric bending vibration of N-H bond in NH_4^+ chemisorbed on Brønsted acid sites, respectively [23,24]. While the band at 1136 and 1347 cm⁻¹ were the symmetric bending vibrations of N-H bond in coordinate NH_3 chemisorbed on Lewis acid [25]. In the N-H stretching vibration region, bands were found at 3339 and 3452 cm⁻¹. Some negative bands





around 3610 and 3754 cm⁻¹ were also found, which could be assigned to hydroxyl consumption due to the interaction with NH, to form NH⁺ [26,27]. The obtained results also implied that both Lewis acid sites and Brønsted acid sites are existed on the surface of all samples as NH₂-TPD. For Fe/TiO₂(c), few peaks can be detected except an obvious adsorption of the NH₄⁺ (1640 cm⁻¹) corresponding to Brønsted acid sites and this could account for its poor catalytic efficiency. The main reason for this result was possibly related to the small surface area, which leading to the less exposed adsorption sites in the catalyst. In contrast, stable acid sites could be found on Fe/TiO₂(t) and Fe/TiO₂(i), and simultaneously, it seemed that Brønsted acid was stronger than Lewis acid over the both samples, but the activity of Fe/TiO₂(t) with the stronger NH4 adsorbed on the Brønsted acid sites tended to be higher than Fe/TiO₂(i). In addition, the intensity of peaks at 3610 cm^{-1} on $Fe/TiO_2(t)$ increased obviously. The reason may be ascribed to the preparation process: after calcination at 500°C, the template of F127 was turned into gas and exhaust, while the hydroxyl group on isolate active phase was difficult to be removed [14]. It is important to note that a band appeared at 1553 cm⁻¹, which did not belong to Brønsted or Lewis acid sites. Studies [8,25] suggested that it could be attributed to amid (-NH₂) species, which played a key role in SCR reaction, corresponding to the higher catalytic activity of $Fe/TiO_2(t)$ and $Fe/TiO_2(i)$ than $Fe/TiO_2(c)$. In a conclusion, the Brønsted and Lewis acid sites both existed in the samples, but the former is dominant. The stronger Brønsted acid sites should be a mainly reason for the enhanced catalytic activity of $Fe/TiO_2(t)$, especially during mid-temperature.

Conclusion

Catalysts based on Fe/TiO₂ were synthesized by three different methods. Among the catalysts, the Fe/TiO₂ prepared using F127 as template showed excellent catalytic activity for NO removal at med-temperature. About 90% catalytic efficiency could be obtained over Fe/TiO₂ (t). Through the BET, XRD, SEM, TPD and DRIFT characteristic analysis, different physical structure and surface properties over various catalysts were observed. Large specific surface area, good dispersion of of active phase, and stronger NH₄⁺ adsorption assigned to Brønsted acid sites might be the main reasons for the highest catalytic performance of Fe/TiO₂ (t).

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