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Article

Performances of $\text{CuSO}_4/\text{TiO}_2$ catalysts in selective catalytic reduction of NO_x by NH_3

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ABSTRACT

A series of $\text{CuSO}_4/\text{TiO}_2$ catalysts were prepared using a wet impregnation method. The activity of each sample in the selective catalytic reduction of NO by NH_3 (NH_3 -SCR) was determined. The effects of SO_2 and H_2O , and their combined effect, on the activity were examined at 340 °C for 24 h. The catalysts were characterized using N_2 adsorption-desorption, X-ray diffraction, X-ray photoelectron spectroscopy, temperature-programmed reduction of H_2 (H_2 -TPR), temperature-programmed desorption of NH_3 (NH_3 -TPD), and in situ diffuse-reflectance infrared Fourier-transform spectroscopy (DRIFTS). The $\text{CuSO}_4/\text{TiO}_2$ catalysts had good activities, with low production of N_2O above 340 °C. SO_2 or a combination of SO_2 and H_2O had little effect on the activity, and H_2O caused only a slight decrease in activity during the experimental period. The NH_3 -TPD and H_2 -TPR results showed that CuSO_4 increased the amounts of acid sites and adsorbed oxygen on the catalyst. In situ DRIFTS showed that the NH_3 -SCR reaction on the $\text{CuSO}_4/\text{TiO}_2$ catalysts followed an Eley-Rideal mechanism. The reaction of gaseous NO with NH_3 adsorbed on Lewis acid sites to form N_2 and H_2O could be the main reaction pathway, and oxygen adsorption might favor this process.

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1. Introduction

Nitrogen oxides (NO_x), which are emitted from combustion of fossil fuels, are a major cause of air pollution, and can cause phenomena such as photochemical smog, acid rain, and ozone depletion [1]. Selective catalytic reduction with NH_3 (NH_3 -SCR) is an efficient method for abating NO_x from stationary sources and is widely used in coal- or biomass-fired power plants. The catalyst is important in SCR and $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ is a popular commercial SCR catalyst. $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ is excellent for NO_x abatement, but V_2O_5 is toxic, and the catalyst causes extensive oxidation of SO_2 to SO_3 [2]. Much effort has therefore been made to develop new SCR catalysts [3,4].

SO_2 is present in the flue gas from coal-fired power plants, therefore sulfur tolerance is an important index for SCR catalysts. Under the SCR conditions, SO_2 and O_2 react with oxides to form thermodynamically stable sulfate phases. These cover the catalyst surface and reduce the number of active sites for the SCR reaction, causing deactivation of the SCR catalyst [5]. For example, Ce/TiO_2 has excellent activity in NH_3 -SCR, but when SO_2 is added to the reaction, $\text{Ce}(\text{SO}_4)_2$ and $\text{Ce}_2(\text{SO}_4)_3$ formation significantly decreases the activity [6]. $\text{MnO}_x/\text{Al}_2\text{O}_3$ shows high activity and selectivity in NH_3 -SCR at 110–350 °C, but MnO_x is converted to MnSO_4 in the presence of SO_2 , resulting in catalyst deactivation [7]. Al_2O_3 , which has a high specific surface area, is a popular catalyst carrier, but it can react with SO_2 and O_2 to

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form $\text{Al}_2(\text{SO}_4)_3$; this greatly decreases the specific surface area and causes significant catalyst deactivation [8,9]. In our recent research, we found that sulfation promoted the activity of commercial $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$, which has been deactivated by K, by increasing the number of acid sites on the deactivated catalyst [10]. The sulfation of a $\text{CuO}/\text{Al}_2\text{O}_3$ catalyst sorbent for a short time promotes SCR activity at high temperatures ($> 300^\circ\text{C}$) [11]. Sulfate catalysts may therefore be promising for use in $\text{NH}_3\text{-SCR}$ and may have high sulfur tolerance and low toxicity. However, research on the use of sulfate catalysts in $\text{NH}_3\text{-SCR}$ is limited. Ma et al. [12] found that an $\text{Fe}_2(\text{SO}_4)_3/\text{TiO}_2$ catalyst had excellent activity and low N_2O selectivity in $\text{NH}_3\text{-SCR}$ at $350\text{--}450^\circ\text{C}$, and displayed high sulfur and H_2O tolerance. Pietrogioacomi et al. [13] found that a $\text{CuSO}_4/\text{ZrO}_2$ catalyst showed good activity in $\text{NH}_3\text{-SCR}$, but the temperature window was narrow and the sulfur tolerance was unknown. It is still important to investigate sulfate catalysts for $\text{NH}_3\text{-SCR}$.

Because of its high specific surface area and high tolerance of SO_2 , TiO_2 (anatase) is commonly used as a support in SCR catalysts [14,15]. In this study, a series of $\text{CuSO}_4/\text{TiO}_2$ catalysts were prepared. Their activities and tolerance of SO_2 and H_2O were tested. The catalysts were characterized using N_2 adsorption-desorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature-programmed reduction of H_2 ($\text{H}_2\text{-TPR}$), and temperature-programmed desorption of NH_3 ($\text{NH}_3\text{-TPD}$). The $\text{NH}_3\text{-SCR}$ reaction mechanism on $\text{CuSO}_4/\text{TiO}_2$ was investigated using *in situ* diffuse-reflectance infrared Fourier-transform spectroscopy (DRIFTS).

2. Experimental

2.1. Catalyst preparation

$\text{CuSO}_4/\text{TiO}_2$ catalysts were prepared using a wet impregnation method. TiO_2 (anatase, T104937-100g, Aladdin, China) was pretreated at 300°C in air for 3 h and then cooled to room temperature in a desiccator. Solutions containing 1, 2, and 4 wt% CuSO_4 (AR; 100 mL) were prepared. TiO_2 (3.0 g) was added to the solution and the mixture was stirred at 40°C for 1 h. The mixed solution was filtered and the residue was dried at 60°C for 30 min and then at 120°C for 2 h. The catalyst was calcined at 500°C in air for 5 h. Samples are denoted by $x\text{CuTi}$, where x is the concentration of CuSO_4 solution.

2.2. Activity measurements

The catalytic activity was evaluated using a fixed-bed quartz reactor ($\Phi 10\text{ mm} \times 600\text{ mm}$). The catalyst sample (20–40 mesh) was placed in the middle of the reactor. The total gas flow rate was 1250 mL/min and the gas consisted of NO (0.05%), NH_3 (0.05%), SO_2 (0.15%, when used), H_2O (5%, when used), and O_2 (4%) in N_2 . The concentrations of O_2 , NO , and NO_2 were determined using a flue gas analyzer (T-350, Testo Company, Germany) and N_2O was detected using gas chromatography (7890A, Agilent Technologies, USA). The NO_x conversion (x) is defined by

$$x = (\text{C}_{\text{NO}_x,\text{in}} - \text{C}_{\text{NO}_x,\text{out}}) / \text{C}_{\text{NO}_x,\text{in}} \times 100\% \quad (1)$$

where $\text{C}_{\text{NO}_x,\text{in}}$ and $\text{C}_{\text{NO}_x,\text{out}}$ are the NO_x ($\text{NO} + \text{NO}_2$) concentrations of the gas stream at the inlet and outlet, respectively, of the reactor.

2.3. Catalyst characterization

N_2 adsorption-desorption was performed at -196°C using a NOVA 2000e surface area and pore size analyzer (Quantachrome, USA). The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method and the pore size distribution was obtained using the Barrett–Joyner–Halenda method. Powdered samples were examined by XRD (X'Pert Pro diffractometer, PANalytical B.V., The Netherlands) using $\text{Cu K}\alpha$ radiation. XPS was performed using an ESCALAB 250 spectrometer (Thermo Fisher Scientific Company, USA). $\text{H}_2\text{-TPR}$ was performed using a Quantachrome ChemBET-3000 TPR-TPD chemisorption analyzer. The sample (50 mg) was preheated under a stream of He at 500°C for 1 h and then cooled to 100°C . The temperature was progressively increased to 600°C at $10^\circ\text{C}/\text{min}$ in a stream of 5% H_2/Ar and the thermal conductivity detector signal was recorded. $\text{NH}_3\text{-TPD}$ was performed using the same instrument; NH_3 was detected using mass spectrometry (MS; DYCOR LC-D100, Ametek Company, USA). A sample (50 mg) was preheated under a stream of He at 500°C for 1 h and then cooled to 50°C . The gas flow was changed to 5% NH_3/Ar for 30 min, and then the sample was purged with He at 100°C for 1 h to remove weakly adsorbed NH_3 . The temperature was progressively increased to 600°C at $10^\circ\text{C}/\text{min}$.

2.4. In situ DRIFTS

In situ DRIFTS was performed using a Bruker Vertex 70 infrared spectrometer with KBr optics and a mercury cadmium telluride detector cooled by liquid N_2 . The DRIFTS reaction cell (Harrick Scientific) was fitted with KBr windows and a heating cartridge that enabled the sample to be heated to 500°C . For NH_3 or $\text{NO} + \text{O}_2$ adsorption, the powdered sample was preheated in the reaction cell at 500°C for 1 h under a N_2 flow (50 mL/min), and then cooled to 80, 180, 280, and 380°C . The background spectrum was recorded at the corresponding temperature. The sample was exposed to 0.3% NH_3/N_2 or 0.3% $\text{NO} + 4.0\%$ O_2/N_2 for 15 min and then purged with N_2 for 15 min. DRIFTS was then performed. All spectra were recorded at a resolution of 4 cm^{-1} by accumulating 100 scans.

In situ DRIFTS of $\text{NO} + \text{O}_2$ on a catalyst sample pretreated with NH_3 was also performed. The catalyst sample was first preheated at 500°C for 1 h in N_2 , and cooled to 380°C ; the background spectrum was then recorded. The sample was exposed to 0.3% NH_3/N_2 for 15 min and then purged with N_2 for 15 min. Then 0.3% $\text{NO} + 4\%$ O_2/N_2 was imported and spectra were recorded at 3, 5, 10, 15, and 20 min.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1. N₂ adsorption-desorption isotherms and pore size distributions (insert) for 0CuTi, 1CuTi, 2CuTi, and 4CuTi samples.

The N₂ adsorption-desorption isotherms and pore size distributions for all the samples are shown in Fig. 1. The isotherms show that pure TiO₂ is significantly mesoporous [16]. The isotherms did not change significantly after TiO₂ impregnation with various CuSO₄ solutions, suggesting that CuSO₄ did not noticeably affect the carrier pore structure. The pore size distributions support this conclusion. Fig. 1 shows that all the samples had similar pore size distributions, with a peak at around 4.7 nm. The specific surface areas (A_{BET}), total pore volumes (V_{p}), and average pore radii (r_{A}) of the samples are shown in Table 1. The specific surface area decreased slightly, and the average pore radius increased slightly, with increasing CuSO₄ concentration.

The XRD patterns of all the samples are shown in Fig. 2. Pure TiO₂ had diffraction peaks at $2\theta = 25.3^\circ, 36.9^\circ, 37.9^\circ, 38.6^\circ, 48.0^\circ, 53.9^\circ, 55.0^\circ, 62.8^\circ, 69.0^\circ, 70.3^\circ$, and 75.1° , corresponding to anatase (PDF 03-065-5714); anatase was therefore the main phase of the carrier. The anatase diffraction peaks were retained after TiO₂ impregnation with CuSO₄ solutions, suggesting that CuSO₄ was well dispersed on the carrier or the CuSO₄ concentration was lower than the limit of detection.

The O 1s, Cu 2p, and S 2p XPS profiles for the 0CuTi and 4CuTi samples are shown in Fig. 3. Two main oxygen species were detected in pure TiO₂, i.e., lattice oxygen, at 529.6 eV, and adsorbed oxygen, at 530.8 eV [17]. Lattice oxygen predominated and the ratio of adsorbed oxygen to lattice oxygen was about 0.41:1. Lattice oxygen and adsorbed oxygen were also present in the 4CuTi sample. The amount of adsorbed oxygen was higher in the 4CuTi sample than in pure TiO₂. The ratio of

Fig. 2. XRD patterns for 0CuTi, 1CuTi, 2CuTi, and 4CuTi samples.

adsorbed oxygen to lattice oxygen increased to 1.50:1, suggesting that the presence of CuSO₄ greatly increased the amount of adsorbed oxygen in the catalyst. Fig. 3 shows that no distinct peak from Cu atoms was observed at 945.0–925.0 eV for the 0CuTi sample. However, a peak at 932.0 eV was observed for the 4CuTi sample, suggesting that Cu atoms were loaded on the support and mainly present as Cu²⁺ [18]. The same trend was observed for S atoms. A peak at 168.2 eV, assigned to SO₄²⁻, was detected for the 4CuTi sample [19].

The catalyst surface reducibility has an important effect on the activity in the NH₃-SCR reaction [20]. The surface reducibility of each catalyst sample was determined using H₂-TPR; the results are shown in Fig. 4(a). No significant peak was observed

Fig. 3. O 1s, Cu 2p, and S 2p XPS spectra for 0CuTi and 4CuTi samples.

Table 1

Specific surface areas, total pore volumes, and average pore radii of samples

Samples	A_{BET} (m ² /g)	V_{p}^* (cm ³ /g)	r_{A} (nm)
0CuTi	56.6	0.2311	8.17
1CuTi	54.3	0.2196	8.15
2CuTi	54.0	0.2201	8.16
4CuTi	52.9	0.2369	8.96

* Obtained at $p/p_0 = 0.99$.

Fig. 4. H₂-TPR profiles (a) and release of SO₂ (b) during H₂-TPR for different samples.

for pure TiO₂. Large reduction peaks were observed for the catalysts obtained by TiO₂ impregnation with CuSO₄ solutions. The reduction peaks were located at about 520 °C for 1CuTi and 500 °C for 2CuTi. This suggests that the surface reducibility increased with increasing CuSO₄ concentration. The reduction peak is assigned to sulfate reduction [12], i.e., $\text{CuSO}_4 + 2\text{H}_2 \rightarrow \text{Cu} + 2\text{H}_2\text{O} + \text{SO}_2$. The amount of SO₂ produced during H₂-TPR was determined using MS ($m/e = 64$); the results are shown in Fig. 4(b). As the figure shows, the SO₂ peak was consistent with the reduction peak. However, two reduction peaks were observed for the 4CuTi sample, at about 350 and 490 °C. Fig. 4(b) shows that the latter peak can be assigned to reduction of surface sulfate. The former peak can be assigned to reduction of surface-adsorbed oxygen. It is concluded that CuSO₄ increases the amount of oxygen adsorbed on the catalyst; this is consistent with the XPS results. H₂S was also detected by MS ($m/e = 34$) during H₂-TPR, but the amount was few; this is consistent with the results of previous research [21].

It has been reported that NH₃ adsorption on acid sites of catalysts is an important step in the NH₃-SCR reaction [10,22]. NH₃ is first adsorbed on Brønsted or Lewis acid sites to form NH₄⁺ or coordinated NH₃, and then reacts with gaseous or adsorbed nitric oxides to form N₂ and H₂O [15,22,23]. The effect of CuSO₄ on the catalyst acid sites was investigated using NH₃-TPD; the results are shown in Fig. 5. A broad peak from about 200 to 500 °C was observed for pure TiO₂. After CuSO₄ was loaded on the support, the onset temperature for NH₃ de-

Fig. 5. NH₃-TPD profiles for various catalysts.

sorption dropped to about 150 °C and the intensity of the NH₃ desorption peak clearly increased, suggesting that CuSO₄ increased the amount of acid sites on the catalyst.

3.2. NH₃-SCR performance

The catalytic performances of the samples are shown in Fig. 6(a). Pure TiO₂ had the poorest activity. The NO_x conversion increased from 11.8% to 32.7% when the temperature was increased from 300 to 450 °C for the 0CuTi sample. The activities of the CuSO₄/TiO₂ samples were significantly higher than that of pure TiO₂. The catalytic activity increased with increas-

Fig. 6. (a) Activities of CuSO₄/TiO₂ and VWTi catalysts (GHSV = 50000 h⁻¹) and (b) effect of GHSV on 4CuTi activity.

Fig. 7. Effects of SO_2 and/or H_2O on activity of 4CuTi sample. Reaction conditions: 0.05% NO , 0.05% NH_3 , 4% O_2 , 0.15% SO_2 (when used) and 5% H_2O (when used) in N_2 , 340 °C, 50000 h^{-1} .

ing CuSO_4 concentration, i.e., the 4CuTi sample had the highest activity. The activity of a commercial SCR catalyst was tested under the same conditions; the results are also shown in Fig. 6(a). The activity of the 4CuTi sample was similar to that of the commercial catalyst, and the NO_x conversion was higher than 94% when the temperature was higher than 340 °C. However, the 4CuTi activity was lower than that of the commercial catalyst below 340 °C. The 4CuTi activity therefore still needs to be improved, especially at temperatures below 340 °C. The influence of the gas hourly space velocity (GHSV) on the 4CuTi activity is shown in Fig. 6(b). The GHSV had little effect on the sample activity at temperatures above 340 °C. However, the activity decreased significantly at temperatures lower than 340 °C. N_2O is the main byproduct of NH_3 -SCR; data on N_2O production are also shown in Fig. 6(a). N_2O production with 4CuTi was lower than that with VWTi. The effect of SO_2 or H_2O on the 4CuTi activity was investigated by adding 0.15% SO_2 or 5.0% H_2O to the reactor for about 24 h at 340 °C; the results are shown in Fig. 7. 4CuTi showed a high tolerance of SO_2 , and SO_2 had little influence on the sample activity during the experimental period. After addition of 5.0% H_2O , the 4CuTi activity decreased slightly; the NO_x conversion was still higher than

93% when the sample was exposed to H_2O for about 24 h. The combined effect of H_2O and SO_2 on the 4CuTi activity was also examined; the results are shown in Fig. 7. A combination of H_2O and SO_2 had little influence on the activity of the catalyst. It is concluded that the samples had a high tolerance of SO_2 and H_2O , in accordance with previous results [12].

3.3. In situ DRIFTS

DRIFT spectra obtained after adsorption of NH_3 on 4CuTi at different temperatures are shown in Fig. 8(a). Bands at 1243, 1307, 1357, 1593, 1665, 3160, 3263, and 3350 cm^{-1} and a broad band at 1390–1529 cm^{-1} were detected after treatment of the catalyst with NH_3/N_2 for 15 min and purging with N_2 for 15 min at 80 °C. The band at 1665 cm^{-1} and the broad band at 1390–1529 cm^{-1} are assigned to NH_4^+ formed by NH_3 protonation on Brönsted acid sites [10,24]. The bands at 1243, 1307, and 1593 cm^{-1} are assigned to NH_3 adsorbed on Lewis acid sites [24]. The band at 1357 cm^{-1} is assigned to $-\text{NH}_2$ wagging [10]. The bands at 3350, 3263, and 3160 cm^{-1} are assigned to coordinated NH_3 adsorbed on Lewis acid sites [25]. The bands moved to slightly higher wavenumbers with increasing temperature. The intensities of the band at 1665 cm^{-1} and the broad band at 1390–1529 cm^{-1} decreased significantly at 280 °C, and they almost disappeared at 380 °C, suggesting that NH_4^+ on Brönsted acid sites was unstable. However, the bands assigned to NH_3 adsorbed on Lewis acid sites were still present at 380 °C, suggesting that NH_3 adsorbed on Lewis acid sites was more stable. It is concluded that at high temperatures NH_3 was mainly adsorbed on Lewis acid sites in 4CuTi.

The spectra for $\text{NO} + \text{O}_2$ adsorption on 4CuTi at different temperatures are shown in Fig. 8(b). Bands at 1243, 1285, 1358, 1514, 1549, 1585, and 1613 cm^{-1} were observed at 80 °C. Bands at 1650–1500 cm^{-1} are widely accepted to arise from surface nitrate or nitro species adsorbed primarily on transition-metal active sites of catalysts [26]. The bands at 1613 and 1243 cm^{-1} can be assigned to bridging nitrates [27], and those at 1585 and 1549 cm^{-1} can be assigned to bidentate nitrate [25,27]. The bands at 1358 cm^{-1} can be assigned to $\nu_{\text{asym}}(\text{NO}_2)$

Fig. 8. In situ DRIFT spectra of 4CuTi samples (a) treated with 0.3% NH_3/N_2 for 15 min and purged with N_2 for 15 min at 80, 180, 280, and 380 °C; (b) Treated with 0.3% NO and 4% O_2 for 15 min and purged with N_2 for 15 min at 80, 180, 280, and 380 °C; (c) Pretreated with 0.3% NH_3 and exposed to 0.3% $\text{NO} + 4\%$ O_2 for various times at 380 °C.

of chelated nitrito surface species [28] and those at 1514 and 1285 cm^{-1} can be assigned to monodentate nitrate [27]. When the temperature was increased to 180 $^{\circ}\text{C}$, the bands at 1285 and 1514 cm^{-1} disappeared, suggesting that surface monodentate nitrate was unstable. The other bands were still detected at 180 and 280 $^{\circ}\text{C}$. However, all the bands almost disappeared at 380 $^{\circ}\text{C}$, suggesting that little NO was adsorbed on the surface at high temperatures. This suggests that NO cannot form stable intermediates that could participate in the SCR reaction at high temperatures.

In situ DRIFT spectra of NO + O₂ on a catalyst sample pretreated with NH₃ at 380 $^{\circ}\text{C}$ are shown in Fig. 8(c). After NO + O₂ was introduced, the intensities of the bands assigned to NH₃ adsorbed on Lewis acid sites decreased greatly, suggesting that NH₃ adsorbed on the catalyst reacted with NO + O₂. The changes in the –NH region support this conclusion. It seems that some nitrates were formed on the catalyst surface, but the adsorption was unstable. When the supply of NO + O₂ was stopped, the bands disappeared. It can be concluded that the reaction mainly occurred between NH₃ adsorbed on Lewis acid sites and gaseous NO; this is different from the mechanism involved for the V₂O₅-WO₃/TiO₂ catalyst. Most researchers agree that with the V₂O₅-WO₃/TiO₂ catalyst, NH₃ is first adsorbed on Brönsted acid sites as NH₄⁺ and then takes part in the reaction [22]. The SCR reaction on CuSO₄/TiO₂ could follow the Eley–Rideal mechanism, and reaction of gaseous NO with NH₃ adsorbed on Lewis acid sites to form N₂ and H₂O could be the main reaction pathway. The XPS and H₂-TPR results show that CuSO₄ increased the amount of oxygen adsorbed on the catalyst surface. The adsorbed oxygen might favor the reaction of NH₃ adsorbed on Lewis acid sites with gaseous NO.

4. Conclusions

CuSO₄/TiO₂ catalysts showed excellent activities in the NH₃-SCR reaction at temperatures higher than 340 $^{\circ}\text{C}$ and a

high tolerance of SO₂ or H₂O. These are promising NH₃-SCR catalysts for use in coal-fired power plants. The NH₃-SCR reaction on CuSO₄/TiO₂ could follow the Eley–Rideal mechanism. Unlike the case for a V₂O₅-WO₃/TiO₂ catalyst, the reaction of gaseous NO with NH₃ adsorbed on Lewis acid sites to form N₂ and H₂O could be the main reaction pathway on CuSO₄/TiO₂ catalysts. CuSO₄ increases the amounts of acid sites and adsorbed oxygen on the catalysts, and the adsorbed oxygen could promote the NH₃-SCR reaction on Lewis acid sites.

References

- [1] M. F. Fu, C. T. Li, P. Lu, L. Qu, M. Y. Zhang, Y. Zhou, M. G. Yu, Y. Fang, *Catal. Sci. Technol.*, **2014**, 4, 14.
- [2] Y. Peng, J. H. Li, W. B. Shi, J. X. Xu, J. M. Hao, *Environ. Sci. Technol.*, **2012**, 46, 12623.
- [3] X. Y. Shi, H. He, L. J. Xie, *Chin. J. Catal.*, **2015**, 36, 649.
- [4] G. X. Wu, J. Li, Z. T. Fang, L. Lan, R. Wang, M. C. Gong, Y. Q. Chen, *Catal. Commun.*, **2015**, 64, 75.
- [5] Z. M. Liu, J. H. Li, A. S. M. Junaid, *Catal. Today*, **2010**, 153, 95.
- [6] W. Q. Xu, H. He, Y. B. Yu, *J. Phys. Chem. C*, **2009**, 113, 4426.
- [7] W. S. Kijlstra, M. Biervliet, E. K. Poels, A. Bliet, *Appl. Catal. B*, **1998**, 16, 327.
- [8] F. C. Galisteo, R. Mariscal, M. L. Granados, J. L. G. Fierro, P. Brettes, O. Salas, *Environ. Sci. Technol.*, **2005**, 39, 3844.
- [9] Y. K. Yu, C. He, J. S. Chen, L. Q. Yin, T. X. Qiu, X. R. Meng, *Catal. Commun.*, **2013**, 39, 78.
- [10] Y. K. Yu, J. X. Wang, J. S. Chen, X. R. Meng, Y. T. Chen, C. He, *Ind. Eng. Chem. Res.*, **2014**, 53, 16229.
- [11] G. Y. Xie, Z. Y. Liu, Z. P. Zhu, Q. Y. Liu, J. Ge, Z. G. Huang, *J. Catal.*, **2004**, 224, 42.
- [12] L. Ma, J. H. Li, R. Ke, L. X. Fu, *J. Phys. Chem. C*, **2011**, 115, 7603.
- [13] D. Pietroggiacomini, D. Sannino, A. Magliano, P. Ciambelli, S. Tuti, V. Indovina, *Appl. Catal. B*, **2002**, 36, 217.
- [14] L. Pang, C. Fan, L. N. Shao, J. X. Yi, X. Cai, J. Wang, M. Kang, T. Li, *Chin. J. Catal.*, **2014**, 35, 2020.
- [15] G. Busca, L. Lietti, G. Ramis, F. Berti, *Appl. Catal. B*, **1998**, 18, 1.
- [16] G. Z. Liu, G. L. Zhao, F. X. Meng, S. D. Qu, W. Li, X. W. Zhang, *Energy*

Graphical Abstract

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Performances of CuSO₄/TiO₂ catalyst in selective catalytic reduction of NO_x by NH₃

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CuSO₄ increased the activities of catalysts for the selective catalytic reduction of NO by NH₃. A CuSO₄/TiO₂ catalyst had high tolerance of H₂O and SO₂.

- Fuels*, **2012**, 26, 1220.
- [17] X. L. Tang, F. Y. Gao, Y. Xiang, H. H. Yi, S. Z. Zhao, *Catal. Commun.*, **2015**, 64, 12.
- [18] D. Lopez, R. Buitrago, A. Sepulveda-Escribano, F. Rodriguez-Reinoso, F. Mondragon, *J. Phys. Chem. C*, **2008**, 112, 15335.
- [19] S. Kato, Y. Hirano, M. Iwata, T. Sano, K. Takeuchi, S. Matsuzawa, *Appl. Catal. B*, **2005**, 57, 109.
- [20] Y. Peng, J. H. Li, W. Z. Si, J. M. Luo, Y. Wang, J. Fu, X. Li, J. Crittenden, J. M. Hao, *Appl. Catal. B*, **2015**, 168, 195.
- [21] L. K. Boudali, A. Ghorbel, P. Grange, *Appl. Catal. A*, **2006**, 305, 7.
- [22] N. Y. Topsøe, *Science*, **1994**, 265, 1217.
- [23] G. Ramis, G. Busca, F. Bregani, P. Forzatti, *Appl. Catal.*, **1990**, 64, 259.
- [24] D. A. Pena, B. S. Uphade, P. G. Smirniotis, *J. Catal.*, **2004**, 221, 421.
- [25] L. Chen, Z. C. Si, X. D. Wu, D. Weng, *ACS Appl. Mater. Interf.*, **2014**, 6, 8134.
- [26] D. Wang, L. Zhang, K. Kamasamudram, W. S. Epling, *ACS Catal.*, **2013**, 3, 871.
- [27] L. Q. Nguyen, C. Salim, H. Hinode, *Appl. Catal. B*, **2010**, 96, 299.
- [28] M. A. Debeila, N. J. Coville, M. S. Scurrell, G. R. Hearne, *Catal. Today*, **2002**, 72, 79.

CuSO₄/TiO₂催化剂在氨选择性催化还原氮氧化物反应中的性能

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摘要: 氮氧化物(NO_x)是主要的大气污染物之一。氨气选择性催化还原法(NH₃-SCR)是目前去除固定源排放的氮氧化物的最有效方法, 被广泛用于燃煤或者生物质的火电厂中。催化剂是NH₃-SCR法的核心, 其中V₂O₅-WO₃/TiO₂催化剂是主要的商业SCR催化剂; 但是V₂O₅有毒, 对环境的影响很大; 另外, 该催化剂具有较高的SO₂氧化性能。因而研究者一直在探索新型的SCR催化剂。SO₂是燃煤电厂烟气中的典型气体之一, 所以抗硫性能是催化剂的一个重要指标。在SCR反应条件下, SO₂和O₂容易与氧化物催化剂发生反应生成稳定性较高的硫酸盐, 覆盖在催化剂表面而引起催化剂失活。但已有研究发现, 硫化会提高K中毒后的V₂O₅-WO₃/TiO₂催化剂的活性。并且, 短时间的硫化可以明显提高CuO/Al₂O₃的NH₃-SCR活性。硫酸盐催化剂或许具有较低毒性和较高抗硫性能, 应该是一种有前景的SCR催化剂。本文以商业纳米TiO₂为载体, 采用湿式浸渍法制备了一系列的CuSO₄/TiO₂催化剂。在自制的活性评价装置上测试了样品的NH₃-SCR活性并且在340 °C下连续24 h测试了SO₂、水蒸气及两者共同作用对催化剂活性的影响。使用N₂等温吸附-脱附、X射线衍射(XRD)、X射线光电子能谱(XPS)、H₂程序升温还原(H₂-TPR)和NH₃程序升温脱附(NH₃-TPD)对催化剂进行了表征。另外, 采用原位红外漫反射光谱研究了CuSO₄/TiO₂催化剂上的NH₃-SCR反应过程。

N₂等温吸附-脱附结果表明, 负载的CuSO₄没有明显改变载体的孔结构。而XRD结果仅显示锐钛矿TiO₂的衍射峰, 说明CuSO₄在载体上有较好的分散度或者CuSO₄的含量低于检测限。XPS结果显示, 催化剂中的铜主要以Cu²⁺形式存在, 硫主要以SO₄²⁻形式存在, 而氧主要以晶格氧和吸附氧两种形式存在, 并且CuSO₄的存在会增加催化剂中吸附氧的含量。H₂-TPR结果表明, 随着CuSO₄含量的增加, 催化剂的氧化还原能力逐渐增强。NH₃-TPD结果表明, 催化剂表面的酸性位数目随着样品中CuSO₄含量的增加而增加。

纯TiO₂的NH₃-SCR活性很差, 当温度从300 °C增加到450 °C时, 最高NO_x转化率仅为32.7%。但当CuSO₄负载到TiO₂上以后, 催化剂活性明显提高。在反应温度高于340 °C时, CuSO₄/TiO₂催化剂的NO_x转化率在94%以上, 与商业V₂O₅-WO₃/TiO₂催化剂相当, 并且其N₂O生成量低于商业催化剂。不过, 当温度低于340 °C时, CuSO₄/TiO₂催化剂的NO_x转化率明显低于商业催化剂, 说明CuSO₄/TiO₂催化剂的活性仍有待改善。连续24 h测试了SO₂、水蒸气及两者的共同作用对CuSO₄/TiO₂催化剂活性的影响。结果显示, 单独的水蒸气会导致活性轻微下降, 但SO₂以及两者共同存在时对催化剂的活性基本没有影响。CuSO₄/TiO₂催化剂的NH₃吸附红外光谱表明, 催化剂上存在Lewis和Brønsted两种酸性位, 但Brønsted酸性位上的NH₄⁺稳定性较差, 280 °C时即基本消失。在高温时, NH₃主要吸附在Lewis酸性位上且CuSO₄/TiO₂催化剂对NO_x的吸附能力较差, 红外光谱未检测到NO_x的吸附峰。380 °C下, 当NO和O₂通入预吸附NH₃的催化剂样品时, 属于Lewis酸性位上NH₃的红外峰明显下降, 说明Lewis酸性位上吸附的NH₃参与了反应。

CuSO₄/TiO₂显示出高的抗硫抗水性能和比较好的NH₃-SCR活性, 应该是一种有应用前景的SCR催化剂。CuSO₄可以增加催化剂的酸性位数目和吸附氧量。根据原位红外漫反射结果, CuSO₄/TiO₂上的SCR反应遵循Eley-Rideal机理。气相的NO与吸附在Lewis酸性位上的NH₃反应生成N₂和H₂O或许是主要的反应途径, 并且吸附氧可能会促进这个过程。

关键词: 选择性催化还原; 硫酸铜; 活性; Eley-Rideal机理; 路易斯酸性位

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