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Article

Influence of sulfation on CeO₂-ZrO₂ catalysts for NO reduction with NH₃

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ABSTRACT

CeO₂-ZrO₂ (CeZr) and sulfated CeO₂-ZrO₂ (S-CeZr) catalysts were prepared for the selective catalytic reduction of NO with NH₃. The CeZr catalysts exhibited higher activity at low temperatures (< 200 °C) and lower activity at high temperatures (> 200 °C) than the S-CeZr catalysts. The sulfation of CeZr was studied in terms of surface acidity, redox properties and NO adsorption-desorption by temperature-dependent experiments and *in situ* infrared spectroscopy. S-CeZr displayed high concentrations of acidic sites and increased surface acidities, but poor reducibility compared with CeZr. The high acidity of S-CeZr was attributed to the presence of Brønsted acid sites, arising mainly from the surface sulfates. Because the surface was covered with sulfate species, S-CeZr showed lower NO adsorption and weaker oxidation ability than CeZr. The adsorption of NH₃ on the Brønsted acid sites restricted the reaction with NO at low temperatures, but the selective catalytic reduction cycle occurred easily at relatively low temperatures (150 °C), and the weakly bound nitrite was partially activated on the S-CeZr catalyst at relatively high temperatures (300 °C). The catalytic mechanisms for the CeZr and S-CeZr catalysts at 150 and 300 °C were also studied.

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1. Introduction

In light of impending stricter emission standards, attention has been focused on the reduction of NO emissions, which are caused by power plants and diesel vehicles. Selective catalytic reduction (SCR) with NH₃ is one of the most widely adopted technologies for the removal of NO from stationary sources and diesel vehicle exhausts. Commercial V₂O₅-WO₃/TiO₂ catalysts display superior efficiency in NO_x reduction at 300–400 °C, but present some issues, such as the toxicity of vanadium oxides and the formation of N₂O and high concentrations of SO₃ at high temperatures [1–3]. Therefore, the development of new cata-

lysts with low or no vanadia loading is critical for solving the problems mentioned above.

Ceria and ceria-containing materials are an important class of catalyst support and have been widely used as catalysts or structural promoters in heterogeneous catalytic reactions because of their favorable reducibility and remarkable oxygen storage capability [4,5]. CeO₂-WO₃ catalysts have demonstrated favorable SCR activity above 200 °C, even under a space velocity of 500000 h⁻¹, and broadened the activity window relative to that of the commercial catalysts. These catalysts also exhibited higher poisoning resistance towards SO₂ and alkali metals [6–9]. Wang et al. [10] studied a series of CeO₂-ZrO₂ catalysts

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modified with transition metal oxides and found that their excellent redox properties could improve the performance of the SCR reaction. Liu et al. [11] investigated the effect of Ce on the activity and alkali resistance of a V_2O_5 - TiO_2 catalyst, and found that the addition of Ce not only reduced the vanadium loading in V_2O_5 - TiO_2 but also enhanced the activity and alkali resistance of this catalyst. At the same time, a series of MoO_3 -doped CeO_2 - ZrO_2 (CeO_2 - TiO_2) catalysts were studied for use in SCR with NH_3 , and the added MoO_3 was found to significantly enhance the activity of the CeO_2 - ZrO_2 catalyst over a wide temperature range [12].

SO_2 is an inevitable poisoning component in flue gas, and sulfation of SCR catalysts usually occurs when they are used in industry [13–15]. Manganese- and iron-based catalysts commonly suffer from severe deactivation induced by SO_2 [16–18]. However, CeO_2 pretreated with SO_2 was found to exhibit excellent SCR activity; this might be attributed to the sulfation effect [19]. There are three methods for catalyst sulfation: gas-phase, liquid-phase and precursor-sulfate methods. Results of X-ray photoelectron spectroscopy experiments described in the literature [20] and our previous work [16] suggest that only one sulfur species (SO_4^{2-}) is formed on the catalyst surface. However, the sulfation mechanism for ceria-based catalysts and the influence of sulfation on the surface acidity, reducibility and NO adsorption-desorption behavior of the catalysts have not yet been elucidated. In the present paper, the sulfation of CeO_2 - ZrO_2 SCR catalysts was systematically studied, taking into account the adsorbed NH_3 and NO_x species and the redox properties of the catalysts.

2. Experimental

2.1. Catalyst preparation

The CeO_2 - ZrO_2 catalyst was prepared by a homogeneous precipitation method [21]. Ammonium cerium nitrate, zirconium nitrate and excess urea solution were mixed in the desired molar ratio (1:1:20). The resultant solution was heated to boiling with stirring until precipitation was observed. The above mixture was then aged overnight, filtered and washed with deionized water. The precipitate was calcined at 500 °C for 5 h. The resultant powder was denoted as CeZr. To prepare the sulfated CeO_2 - ZrO_2 catalyst, CeZr was immersed in concentrated sulfuric acid (6 mol/L) for 72 h. The catalyst was filtered, washed with deionized water and then calcined at 500 °C for 5 h. The resultant powder was denoted as S-CeZr.

2.2. SCR performance

Activity measurements were carried out in a fixed-bed quartz reactor (inner diameter 5 mm) using 100 mg catalyst (40–60 mesh). The feed gas mixture contained 0.05% NO , 0.05% NH_3 and 3% O_2 , and was balanced with N_2 . The total flow rate of the feed gas was 200 mL/min, and the space velocity was about 120000 mL/(g_{cat}·h). The concentrations of NO , NO_2 and NH_3 were continually monitored by Fourier transform infrared (FTIR) spectroscopy (Gasetm FTIR DX-4000). Activity

data were collected until the reaction reached a steady state after being maintained for 30 min at each temperature point.

2.3. Catalyst characterization

Characterization of the Brunauer-Emmett-Teller (BET) surface areas of the samples was carried out using a Micromeritics ASAP 2020 apparatus. The crystal structure was determined from X-ray diffraction (XRD) measurements (Rigaku, D/MAX 2500 V/PC) from 20° to 80° at a step rate of 10°/min and operated at 50 kV and 200 mA with $Cu K\alpha$ radiation.

Temperature-programmed reduction of H_2 (H_2 -TPR) experiments were performed up to 1000 °C on a chemisorption analyzer (Micromeritics, ChemiSorb 2720 TPx) under 10% H_2 /Ar gas flow (50 mL/min) with a heating rate of 10 °C/min. Temperature-programmed desorption of NO (NO -TPD) experiments were performed in a fixed-bed quartz reactor. Before the test, each sample was pretreated in He at 350 °C for 1 h and the sample was purged under 1000 ppm NO at room temperature. After isothermal desorption under N_2 at 30 °C, the temperature was raised to 630 °C at a rate of 10 °C/min.

In situ IR spectroscopy was recorded using an FTIR spectrometer (Nicolet 6700) equipped with a SMART collector and an MCT detector. The catalyst was loaded into a Harrick IR cell and heated to 350 °C under N_2 at a total flow rate of 100 mL/min. The background spectrum was collected in an atmosphere of flowing N_2 and was subtracted from the spectrum of each sample. The spectra were recorded by accumulating 32 scans. To minimize the influence of absorbance from different samples, the absorbance intensity was set to 3.00 for every sample at 300 °C.

3. Results and discussion

3.1. SCR performance

Fig. 1 illustrates the SCR performance of CeZr and S-CeZr catalysts in terms of NO_x conversion and N_2O formation in the

Fig. 1. SCR performance of CeZr and S-CeZr. Reaction conditions: catalyst = 100 mg, $[NO] = [NH_3] = 500$ ppm, $[O_2] = 3\%$, total flow rate = 200 mL/min, GHSV = 120000 mL/(g_{cat}·h).

temperature range 150–400 °C. Below 200 °C, CeZr presented higher activity than S-CeZr. However, when the temperature was above 200 °C, S-CeZr exhibited considerably greater efficiency in NO_x reduction than did CeZr. Almost 100% NO reduction was achieved between 300 and 350 °C using S-CeZr and a relatively high space velocity of 120000 mL/(g_{cat}·h). When the temperature was higher than 350 °C, both catalysts showed lower activity in the SCR process than they did at lower temperatures. This can be attributed to the oxidation of NH₃ to N₂, N₂O, or NO. Moreover, N₂O was also formed during the reaction. When using the CeZr catalyst, the concentration of N₂O gradually increased from about 4 ppm (this could be a result of error in the equipment) to nearly 10 ppm with increasing temperature. In contrast, for the S-CeZr catalyst, the N₂O concentration remained essentially the same from 150 to 400 °C. These results indicate that the N₂ selectivity of the CeZr catalyst could be improved by sulfation.

To investigate the oxidation of NH₃ and NO using the two catalysts, the concentrations of NH₃, N₂ (calculated from the difference in the NH₃, N₂O and NO concentrations), N₂O and NO during NH₃ oxidation at 400 °C were determined and are provided in Fig. 2(a). The concentration of NO₂ was below 2 ppm. The major product when using the CeZr catalyst was N₂, with minor amounts of N₂O and NO also produced. In contrast, for the S-CeZr catalyst, although a considerable amount of N₂ was obtained, the concentrations of N₂O and NO were less than 10 ppm. Fig. 2(b) presents the NO to NO₂ ratios, indicating the oxidation of NO to NO₂, at 250–350 °C. The S-CeZr catalyst exhibited a lower ability for NO oxidation than did CeZr, and almost 30% of the NO was oxidized to NO₂ at 400 °C. Based on these results, it is proposed that the oxidation ability of CeZr was reduced by sulfation.

3.2. Characterization

The BET surface areas for CeZr and S-CeZr were 93.5 and 66.0 m²/g, respectively. This indicates that sulfation decreased the catalyst surface area. However, considering the higher activity of S-CeZr at higher temperatures, it is evident that the SCR performance was not only determined by surface area, but also by the chemical properties of the catalyst, including re-

Fig. 2. (a) Concentrations of NH₃, N₂, N₂O and NO during NH₃ oxidation with CeZr and S-CeZr at 400 °C; (b) Ratios of NO to NO₂ in the temperature range 250–350 °C.

Fig. 3. XRD patterns of CeZr and S-CeZr.

ducibility, acidity and adsorption/desorption behavior. XRD patterns of the CeZr and S-CeZr samples are shown in Fig. 3. All of the peaks can be attributed to the cubic fluorite phase of CeO₂; however, the crystallinity was not ideal, possibly because of the formation of cerium-zirconium solid. According to these results, sulfation with concentrated sulfuric acid did not damage the CeZr crystal.

Fig. 4 shows the H₂-TPR profiles of the catalysts. The peak centered at 544 °C was assigned to the reduction of surface Ce⁴⁺ to Ce³⁺ in the CeZr catalyst [22,23]. For the S-CeZr sample, a more intense peak was observed at 586 °C. Based on previous studies of the TPR profiles of SO₂-treated catalysts, this peak could be attributed to the overlap of peaks corresponding to the reduction of surface cerium and the decomposition of sulfur [16,24]. Moreover, the initial H₂ consumption (400–450 °C) for CeZr was greater than that for S-CeZr, and the onset temperature was lower for CeZr than for S-CeZr. These results indicate that the reducibility of the CeZr catalyst was reduced after sulfation. This may originate from the tight binding of sulfur to the surface cerium atoms.

3.3. Surface acidity

Fig. 5 shows the NH₃-TPD profiles of CeZr and S-CeZr catalysts in the temperature range 50–600 °C. Only a single peak at

Fig. 4. H₂-TPR profiles of CeZr and S-CeZr.

Fig. 5. NH_3 -TPD profiles of CeZr and S-CeZr catalysts.

150 °C was detected for the CeZr catalyst, and the concentration of NH_3 gradually decreased with increasing temperature. For the S-CeZr catalyst, a broader band was observed at 130–300 °C, and thereafter the NH_3 concentration decreased. These results show that the acidity of the sulfated catalyst was stronger than that of CeZr. Furthermore, the amount of NH_3 desorption was higher for S-CeZr than that for CeZr, especially in the higher temperature region, which indicates that a strong enhancement of the surface acidity occurred on sulfation.

3.4. Adsorbed NO_x species

Fig. 6 displays the NO -TPD profiles of CeZr and S-CeZr. The two intense peaks at 233 and 451 °C were ascribed respectively to the weak and strong adsorption of nitrite or nitrate species on the catalyst surface, especially at basic cerium sites. The two peaks in the NO_2 profile at 215 and 435 °C were assigned to the nitrate species. For the S-CeZr samples, the area under all the peaks was reduced and the spectrum was shifted to the lower temperature region. These results correlated with those from the NO oxidation experiments shown in Fig. 2(b); there was minimal and weak NO adsorption on the surface of the S-CeZr catalyst.

Fig. 6. NO -TPD profiles of CeZr and S-CeZr catalysts.

To further identify the nature and configuration of the surface nitrite and nitrate species, *in situ* IR spectra were recorded for both catalysts during the TPD process and are shown in Fig. 7. Five peaks, at 1213, 1455, 1534, 1560 and 1606 cm^{-1} were observed in the FT-IR spectrum of the CeZr sample at 100 °C. These peaks were attributed to bridged nitrate (1606 cm^{-1}), bidentate nitrate (1560 cm^{-1}) and monodentate nitrate (1534 cm^{-1}) species. The peaks at 1455 and 1213 cm^{-1} were ascribed to bridged and monodentate nitrite species, respectively [25–27]. On increasing the temperature to 300 °C, the intensity of all the peaks was reduced and the peak at 1455 cm^{-1} almost disappeared. At 400 °C, evidence of some adsorbed nitrate species could still be obtained from the spectrum. For the S-CeZr samples, shown in Fig. 7(b), bidentate nitrate species were not observed and only weakly adsorbed bridged and monodentate nitrate species formed on the catalyst. These results suggest that the suppression of NO adsorption by sulfation is mainly

Fig. 7. *In situ* FT-IR spectra of NO desorption on CeZr (a) and S-CeZr (b) catalysts.

Fig. 8. *In situ* sequential FT-IR spectra of the CeZr catalyst at 150 °C (a, b) and 300 °C (c, d) under different conditions. (a, c) The dehydrated catalyst was first treated with NH_3 , then NO and O_2 were added, and finally the NO and O_2 flow was stopped; (b, d) The gases indicated for (a, c) were applied in reverse order.

caused by a decrease in the adsorption of bidentate nitrate species. Sulfation also lowers the number of other NO adsorption sites, and thus reduces the amount of adsorbed bridged nitrate and monodentate nitrite species. With an increase in temperature, the monodentate nitrite species desorbed first from the surface below 300 °C, and only a small proportion of the monodentate nitrate species could be seen in the spectra at higher temperatures.

3.5. Reaction details

Fig. 8(a) shows the *in situ* FT-IR spectra of the CeZr catalyst at 150 °C. At first, peaks corresponding to Lewis and weak Brønsted acid sites could be observed in the spectra. When the sample was purged with NO and O_2 for 3 min, new peaks attributed to monodentate nitrite species appeared in considerable quantities over 20 min. The number of surface acid sites gradually decreased, and at the same time the peak between 1000 and 1250 cm^{-1} disappeared or overlapped with the large band from the monodentate nitrite. The peaks at 1443 cm^{-1} (Brønsted acid sites) and 1602 cm^{-1} (Lewis acid sites) also became weaker during the first 10 min. This indicates that NH_3 , whether adsorbed on Lewis or Brønsted acid sites, is still active at 150 °C. When NH_3 and NO were applied in reverse order

(Fig. 8(b)), newly adsorbed acid sites were observed in the spectrum after 1 min and increased in number with increasing exposure time. However, the pre-adsorbed nitrite and nitrate species were inactive under the NH_3/O_2 gas flow. As discussed above, these species were mainly bound to the cerium atoms, and covered the ceria to some extent. This could have limited the number of surface redox sites supported by the ceria, and led to the suppression of NH_3 activation by the catalyst. This could in turn result in the relatively low SCR activity of the catalysts in the low temperature region.

Fig. 8(c) and (d) show the *in situ* FT-IR spectra for the reaction with the CeZr catalyst at 300 °C. Because of the weak adsorption of the NH_3 molecules on the surface at this temperature, only weak Lewis and Brønsted acid sites could be observed after full pre-adsorption of NH_3 . As soon as NO and O_2 were introduced into the gas flow, considerable amounts of bidentate and monodentate nitrate and nitrite species were bound to the surface and their amount increased as the exposure time was increased up to 10 min. When the gas order was reversed (Fig. 8(d)), a considerable amount of nitrate and nitrite species were observed in the spectrum on application of NO. After introducing NH_3 and O_2 into the gas flow, the peaks attributed to bridged nitrate and bidentate nitrate species decreased in intensity with increasing exposure time, whereas the

Fig. 9. *In situ* sequential FT-IR spectra of the S-CeZr catalyst at 150 °C (a, b) and 300 °C (c, d) under different conditions. (a, c) The dehydrated catalyst was first treated with NH_3 , then NO and O_2 were added, and finally the NO and O_2 flow was stopped; (b, d) The gases indicated for (a, c) were applied in reverse order.

intensities of the monodentate nitrate and nitrite species were almost unchanged after 30 min. These results indicate that some of the adsorbed nitrate species could participate in the SCR reaction with gaseous or weakly adsorbed NH_3 in the relatively high temperature region.

Fig. 9 displays the *in situ* FT-IR spectra for the reaction using the S-CeZr catalyst. Large amounts of Brønsted acid sites and newly formed Lewis acid sites were obtained after NH_3 treatment. However, most of the Brønsted acid sites and the band near 1300 cm^{-1} (Lewis acid sites) were inactive on addition of NO and O_2 at 150 °C, except for the peak centered at 1150 cm^{-1} , which originated from the CeZr catalyst. These results indicate that the newly generated surface acid sites, including both Lewis and Brønsted acid sites, bond so strongly with the surface that they cannot react with gaseous or adsorbed NO_x . Fig. 9(b) shows the *in situ* IR spectra with reversed gas order. At first, some weakly adsorbed NO_x species were observed at 150 °C. When NH_3 and O_2 were introduced into the gas flow, these adsorbed NO_x species disappeared. Thereafter, peaks corresponding to NH_3 bound to the Lewis and Brønsted acid sites appeared and increased in intensity after 3 min.

The *in situ* FT-IR spectra of the S-CeZr catalyst at 300 °C are shown in Fig. 9(c) and (d). After 5 min of NO and O_2 flow, both Brønsted and Lewis acid sites at the surface were consumed.

These results suggest that although the NH_3 adsorbed on the Brønsted acid sites exhibited low activity at low temperatures, it was reactive at 300 °C. When the order of gas flow was reversed, only weak nitrite species were observed in the IR spectrum after the introduction of NO gas. Once NH_3 and O_2 were introduced, the signals corresponding to these nitrite species disappeared and considerable amounts of NH_3 molecules were detected.

3.6. Temperature-dependent pathway

Based on the results and discussion above, the SCR reaction mechanism for CeZr and S-CeZr should be the same (Fig. 10). The different SCR performance of these two catalysts results from their surface acidity and redox properties. The CeZr samples have excellent reducibility, which leads to higher oxidation ability towards NO or NH_3 , whereas the S-CeZr samples provide large amounts of Brønsted acid sites that are strongly bound to the surface. This means that the amount of NO bound to the S-CeZr surface is lower and the bonding is weaker compared with that in CeZr. Combined with the results on the SCR performance, we can conclude that at low temperatures the redox properties of the catalysts contribute more to the activity than does the surface acidity. At high temperatures, however, the

Fig. 10. Schematic diagram of the temperature-dependent SCR mechanism.

SCR activity is primarily determined by the surface acidity, especially the strong Brønsted acid sites. At low temperatures, the activity may be limited by higher surface acidities, which would result in tightly bonded NH_3 molecules that cannot be easily activated by the lattice oxygen atoms. In contrast, at high temperatures, a higher reducibility may improve the oxidation of NH_3 with O_2 and result in low N_2 selectivity. Therefore, although the S-CeZr samples exhibited low activity below 200 °C, their high-temperature activity was enhanced and formation of N_2O was reduced at temperatures above 200 °C.

4. Conclusions

CeZr catalysts showed higher SCR performance than S-CeZr samples at low temperatures (<200 °C) but lower activity at high temperatures (>200 °C). S-CeZr catalysts contained greater quantities of surface acid (mainly Brønsted acid) sites and had higher surface acidities than CeZr. In addition, the reaction mechanisms of the CeZr and S-CeZr catalysts were studied at 150 and 300 °C, and we concluded that a temperature-dependent pathway is followed. At low temperatures the redox properties of the catalyst contribute more to the activity than does the surface acidity, and at high temperatures the SCR per-

formance is mainly determined by the surface acidity, especially by the strong Brønsted acid sites.

References

- [1] G. Busca, L. Lietti, G. Ramis, F. Berti, *Appl. Catal. B*, **1998**, 18, 1–36.
- [2] G. Ramis, G. Busca, F. Bregani, P. Forzatti, *Appl. Catal.*, **1990**, 64, 259–278.
- [3] N. Y. Topsoe, *Science*, **1994**, 265, 1217–9.
- [4] A. Trovarelli, *Catal. Rev. Sci. Eng.* **1996**, 38, 439–520.
- [5] M. V. Ganduglia-Pirovano, M. Veronica, A. Hofmann, J. Sauer, *Surf. Sci. Rep.*, **2007**, 62, 219–270.
- [6] Y. Peng, C. X. Liu, X. Y. Zhang, J. H. Li, *Appl. Catal. B*, **2013**, 140–141, 276–282.
- [7] Y. Peng, K. Z. Li, J. H. Li, *Appl. Catal. B*, **2013**, 140–141, 483–492.
- [8] W. P. Shan, F. D. Liu, H. He, X. Y. Shi, C. B. Zhang, *Appl. Catal. B*, **2012**, 115–116, 100–106.
- [9] Y. Peng, J. H. Li, L. Chen, J. H. Chen, J. Han, H. Zhang, W. Han, *Environ. Sci. Technol.* **2012**, 46, 2864–2869.
- [10] X. Q. Wang, A. J. Shi, Y. F. Duan, J. Wang, M. Q. Shen, *Catal. Sci. Technol.*, **2012**, 2, 1386–1395.
- [11] Z. M. Liu, S. X. Zhang, J. H. Li, J. Z. Zhu, L. L. Ma, *Appl. Catal. B*, **2014**, 158–159, 11–19.
- [12] Z. M. Liu, S. X. Zhang, J. H. Li, L. L. Ma, *Appl. Catal. B*, **2014**, 144, 90–95.
- [13] J. P. Dunn, H. G. Stenger, I. E. Wachs, *Catal. Today*, **1999**, 51, 301–318.
- [14] J. P. Dunn, H. G. Stenger, I. E. Wachs, *Catal. Today*, **1999**, 53, 543–556.
- [15] J. P. Dunn, H. G. Stenger, I. E. Wachs, *J. Catal.*, **1999**, 181, 233–243.
- [16] S. J. Yang, Y. F. Guo, H. Z. Chang, L. Ma, Y. Peng, Z. Qu, N. Q. Yan, C. Z. Wang, J. H. Li, *Appl. Catal. B*, **2013**, 136–137, 19–28.
- [17] Z. B. Wu, R. B. Jin, Y. Liu, H. Q. Wang, *Catal. Commun.*, **2008**, 9, 2217–2220.
- [18] F. D. Liu, K. Asakura, H. He, W. P. Shan, X. Y. Shi, C. B. Zhang, *Appl. Catal. B*, **2011**, 103, 369–377.
- [19] T. T. Gu, Y. Liu, X. L. Weng, H. Q. Wang, Z. B. Wu, *Catal. Commun.*, **2010**, 12, 310–313.
- [20] S. T. Choo, Y. G. Lee, I. S. Nam, S. W. Ham, J. B. Lee, *Appl. Catal. A*, **2000**, 200, 177–188.
- [21] Li, H. Cheng, D. Y. Li, Y. S. Qin, Y. M. Xie, S. D. Wang, *Chem. Commun.*, **2008**, 1470–1472.

Graphical Abstract

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Influence of sulfation on $\text{CeO}_2\text{-ZrO}_2$ catalysts for NO reduction with NH_3

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At low temperature the redox property of catalysts presents more contributions to activity than surface acidity. At high temperature, however, the surface acidity especially the strong Brønsted acid sites mainly determines SCR activity.

- [22] K. B. Zhou, X. Wang, X. M. Sun, Q. Peng, Y. D. Li, *J. Catal.*, **2005**, 229, 206–212.
- [23] B. Reddy, A. Khan, Y. Yamada, T. Kobayashi, S. Lorient, J. Volta, *J. Phys. Chem. B*, **2002**, 106, 10964–10972.
- [24] C. Z. Wang, S. J. Yang, H. Z. Chang, Y. Peng, J. H. Li, *J. Mol. Catal. A*, **2013**, 376, 13–21.
- [25] K. I. Hadjiivanov, *Catal. Rev. Sci. Eng.*, **2000**, 42, 71–144.
- [26] L. Chen, J. M. Li, M. F. Ge, L. Ma, H. Z. Chang, *Chin. J. Catal.*, **2011**, 32, 836–841.
- [27] G. S. Qi, R. Yang, *J. Catal.*, **2003**, 217, 434–441.

硫酸化对CeO₂-ZrO₂催化剂上NH₃选择催化还原NO反应的影响

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摘要: 由发电厂等固定源和柴油机等移动源排放的一氧化氮(NO)造成的环境污染问题日益严重. 随着严苛的排放法规出台, NO排放控制技术受到越来越多关注. NH₃选择性催化还原(SCR)技术是目前去除NO应用最为广泛的方法之一. 商业催化剂V₂O₅-WO₃/TiO₂在300–400 °C温度窗口内显示出优越的NO去除效率, 但仍存在一些问题, 如钒氧化物的毒性以及在高温时形成N₂O和SO₃. 因此, 开发出低钒或无钒的新型催化剂是解决上述问题的关键.

CeO₂和含铈材料是重要的催化剂载体, 具有良好的还原能力和氧存储功能, 因而广泛应用于催化领域. CeO₂添加到商用催化剂中不仅可以降低钒用量, 而且可以提高催化剂抗碱金属中毒能力. CeO₂-WO₃催化剂在200 °C以上时比商用催化剂具有更宽的温度窗口, 并展现出较高的抗SO₂和碱金属中毒能力. CeO₂-ZrO₂催化剂通过添加过渡金属元素可以提升其SCR活性, 在较宽的温度窗口内具有较高的催化活性.

废气中SO₂可导致催化剂失活, 在实际应用中催化剂硫中毒是较为常见的催化剂失活原因. 通常情况下, 锰基和铁基催化剂最容易硫中毒. 然而CeO₂催化剂在硫酸化处理后却展现出良好的SCR活性. 催化剂硫酸化主要包括气相、液相和前驱体硫化三种方法. 三种方法各有异同, 但在催化剂表面形成的硫物种都是SO₄²⁻. 硫酸化可以增强Ce基催化剂的SCR活性, 但是对于硫化引起的催化剂表面酸性、氧化还原性以及NO吸附脱附性质的详细研究报道较少.

本文通过液相法对CeO₂-ZrO₂ (CeZr)催化剂进行了硫酸化. XRD结果表明, 硫酸化并未对催化剂结晶结构产生影响. TPD和TPR结果表明, 硫酸化后催化剂(S-CeZr)表面酸性增强, 但抑制了其氧化性. 通过原位红外光谱技术系统研究了催化剂在SCR反应过程中表面物种的变化, 结果发现, CeZr和S-CeZr的催化机理相同, 不同的SCR活性主要是由表面酸性和氧化性引起的. CeO₂基催化剂在不同温度窗口遵循不同反应机理. CeZr催化剂具有较强的氧化还原性, 使其对NO和NH₃具有很强的氧化能力, 所以其在低于200 °C时具有较好的SCR活性. 而S-CeZr催化剂具有更多的Brønsted酸性位, 导致NO不易吸附在催化剂表面, 所以其在低温时SCR活性较差, 但在高温时(>200 °C)具有优良的SCR活性. 通过SCR活性和反应机理研究, 发现在高温时(>200 °C), 表面酸性尤其是强酸Brønsted酸性位在SCR反应中起到决定性作用; 而在低温时(<200 °C), 酸性位对NH₃分子较强的键合作用导致NH₃难以被氧化, 所以较强的酸性位对SCR活性具有抑制作用, 而氧化还原性在低温时对SCR反应起到主要作用. 同时, 在高温时, 较高的氧化性可使NH₃被O₂直接氧化, 导致N₂选择性降低.

关键词: 硫酸化; 氮氧化物去除; 选择性催化还原; 氧化铈; 氧化锆

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