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Article

Performance of Cr-doped vanadia/titania catalysts for low-temperature selective catalytic reduction of NO_x with NH₃

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ABSTRACT

Cr–V/TiO₂ catalysts with different Cr/V molar ratios for low-temperature selective catalytic reduction (SCR) of NO with NH₃ were prepared by impregnation. The samples were characterized using X-ray diffraction, NH₃ temperature-programmed desorption, H₂ temperature-programmed reduction, and X-ray photoelectron spectroscopy. The results show that doping with Cr ions increased the amounts of weak and medium acid sites on the catalyst surface, as well as the low-temperature reductive capacity for high-valence V ions, and promoted the chemical adsorption of oxygen on the catalyst surface, which enhanced the rate of the SCR reaction. The catalyst with a Cr/V molar ratio of 0.2:0.8 and 10 wt% loading gave the largest amount of weak acid sites and the best NO_x-removing performance, with a NO_x conversion greater than 90% at 160–300 °C. This catalyst had high stability in the presence of 0.01% SO₂.

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1. Introduction

Nitrogen oxides (NO_x) emitted from thermal power plants and automobile exhaust gases are major air pollutants. The selective catalytic reduction (SCR) of NO_x with NH₃ is the most effective technology for NO_x abatement [1–3]. Currently, V₂O₅–WO₃/TiO₂ and V₂O₅–MoO₃/TiO₂ are the most widely used catalysts, in a narrow temperature window of 300–400 °C [4]. Most SCR systems are installed behind an economizer that allows the flue gas temperature to exceed 300 °C to maintain high catalytic activity. However, the catalyst life is short because it is easily affected by high concentrations of flue dust, SO₂, alkali metals, and other factors. In addition, blockage by (NH₄)₂SO₄ byproducts during high-temperature processes is a

problem that needs to be addressed. The preferred technique is to locate the SCR NO_x-removing (DeNO_x) unit after the desulfurization equipment in coal-fired power plants [5]. In this process, the flue gas temperature can drop to 250 °C below, at which V-based catalysts do not maintain high NO_x conversions [6].

Recent studies suggest that V catalysts have excellent sulfur resistance [7]. Various methods such as use of additives or different supports, e.g., Sb–V₂O₅/TiO₂ [8], V₂O₅–CeO₂/TiO₂ [9], V₂O₅–WO₃/Ti–Si [10], V₂O₅/CeO₂–ZrO₂ [11], and V₂O₅/AC [12] catalysts, have been used to further enhance the low-temperature activities of V catalysts at low temperatures and maintain their high sulfur resistance. The low-temperature activities of these catalysts were improved, but the sulfur resistance of V₂O₅

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decreased.

Improvements in V catalyst activities at low temperatures and maintenance of the sulfur resistance of efficient additive-containing catalysts are particularly important. It has been reported that the low-temperature activity of a $\text{Cr}_2\text{O}_3/\text{TiO}_2$ catalyst was high because more acid sites were present on the surface [13]. Thirupathi et al. [14] obtained 90% NO_x conversion at 180 °C using CrO_x -doped $\text{MnO}_x/\text{TiO}_2$; catalyst characterizations showed that surface acidity (Brønsted and Lewis acid sites) had significantly increased. Tong et al. [15] reported that the conversion of NO reached 80.7% at 330 °C for a Cr–Ce/ TiO_2 catalyst, but dropped from 80.7% to 62.4% after 10 h of sulfur resistance test. Chen et al. [16] prepared Cr–Mn catalysts using the citric acid method; the catalytic activity reached 98.5% at 120 °C but decreased to about 20% after 5 h of sulfur resistance test. Chromium oxide has good low-temperature activity, but its sulfur resistance needs to be improved.

In this study, Cr–V–O/ TiO_2 catalysts were prepared using Cr and V as the active components and TiO_2 as the carrier. The influence of the Cr/V molar ratio and loading was investigated, the catalysts were characterized, and the catalytic mechanism was investigated.

2. Experimental

2.1. Catalyst preparation

Certain amounts of ammonium metavanadate (AR) and chromium nitrate (AR) were dissolved in deionized water. The solution was adequately stirred in a water bath at 60 °C and mixed with TiO_2 powders by magnetic stirring for 20 min. Moisture was removed at 60 °C using a rotary vacuum evaporator. The resulting materials were dried at 110 °C overnight and calcined at 450 °C for 3 h. The samples were compressed into tablets and crushed to 20–30 mesh. $\text{CrO}_x/\text{TiO}_2$ and VO_x/TiO_2 catalysts were prepared using the same method. The Cr–V/ TiO_2 catalysts with different Cr/V molar ratios were denoted by $\text{Cr}_x\text{V}_{1-x}/\text{TiO}_2$ ($x = 0.7, 0.5, 0.3, 0.2, 0.1$) and $\text{Cr}_{0.2}\text{V}_{0.8}/\text{TiO}_2$ catalysts with different weight percentage loadings were denoted by a wt% $\text{Cr}_{0.2}\text{V}_{0.8}/\text{TiO}_2$ ($a = 5, 10, 20, 50$).

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were obtained using a SCINTAG XTRA diffractometer (Ni-filtered $\text{Cu K}\alpha$ radiation) operated at 40 kV and 50 mA. Intensity data were recorded in the 2θ range from 10° to 80°, with a step size of 0.04°.

X-ray photoelectron spectroscopy (XPS) was performed using an ESCALab 220i-XL electron spectrometer (VG Scientific Company) with 300 W Al $K\alpha$ radiation. The pressure was maintained at 3×10^{-9} mbar. The C 1s line at 284.6 eV from carbon was used as a reference, and the binding energies were calculated with respect to this line.

H_2 temperature-programmed reduction (H_2 -TPR) and NH_3 temperature-programmed desorption (NH_3 -TPD) were performed using a Micromeritics Auto Chem FINE SORB-3010E

chemisorption analyzer. Prior to H_2 -TPR analysis, the samples (200 mg) were treated with Ar (30 mL/min at 150 °C for 30 min, cooled to 80 °C, and flushed for 10 min). The atmosphere was changed to 5% H_2/Ar (30 mL/min), and the reactor temperature was increased to 750 °C. For NH_3 -TPD, the samples (150 mg) were heated in a pure He flow at 400 °C for 1 h, and cooled to 100 °C in a He atmosphere. The samples were treated with anhydrous NH_3 for 1 h and then purged with He for 1 h. The temperature was increased linearly at a rate of 10 °C/min, and TPD was performed in pure He over the temperature range 100–900 °C.

2.3. Catalytic activity tests

The SCR activity was measured in a fixed-bed quartz reactor containing 0.5 g of catalyst mixed with 0.5 g of quartz sand, with a gas hourly space velocity (GHSV) of 60000 mL/(h·g). The simulated flue gas composition was as follows: $\phi(\text{NO}) = \phi(\text{NH}_3) = 0.05\%$, $\phi(\text{O}_2) = 5\%$, $\phi(\text{SO}_2) = 0.01\%$ (as needed), $\phi(\text{water}) = 10 \text{ vol}\%$ (as needed), and balance N_2 . The total flow rate was 500 mL/min. The concentrations of NO, NO_2 , O_2 , and SO_2 were monitored continuously using a TESTO350-XL gas analyzer. To ensure stability and accuracy of the data, the data were recorded after 20 min when each test condition was changed.

3. Results and discussion

3.1. XRD analysis

The effects of Cr doping on the bulk structures of the catalysts were investigated using XRD. Fig. 1 shows the XRD patterns of the catalysts. It shows that all the peaks in the patterns were attributable to the anatase phase of TiO_2 . No diffraction peaks attributed to Cr and V species were observed, suggesting that the low-loaded active phase was highly dispersed on the TiO_2 support and had an amorphous or microcrystalline structure.

Fig. 1. XRD patterns of catalysts. (1) TiO_2 ; (2) VO_x/TiO_2 ; (3) $\text{Cr}_{0.2}\text{V}_{0.8}/\text{TiO}_2$; (4) Cr_x/TiO_2 .

Fig. 2. XRD patterns of $\text{Cr}_{0.2}\text{-V}_{0.8}/\text{TiO}_2$ catalysts with different loadings. (1) 50 wt%; (2) 20 wt%; (3) 10 wt%; (4) 5 wt%.

The effect of loading on the catalyst bulk was determined by examining $\text{Cr}_{0.2}\text{-V}_{0.8}/\text{TiO}_2$ catalysts with different loadings. Fig. 2 shows that the composite was highly dispersed on the surface of the TiO_2 support for active component loadings less than 20 wt%. The composite state phase ($\text{Cr}_2\text{V}_4\text{O}_{13}$) was observed on the $\text{Cr}_{0.2}\text{-V}_{0.8}/\text{TiO}_2$ catalyst surface when the loading was 20 wt%. When the loading was increased to 50 wt%, the diffraction peaks of the active component became more apparent.

3.2. NH_3 -TPD analysis

The surface areas and types of acid sites, determined using NH_3 -TPD, for catalysts with various Cr/V molar ratios are summarized in Table 1.

NH_3 -TPD experiments were performed to determine the acid site distributions on the prepared catalysts. The NH_3 -TPD curves are shown in Fig. 3. The peak centered at about 200 °C is caused by NH_3 desorption from weak acid sites, and that centered at about 400 °C is attributed to desorption from medium and strong acid sites. The peak above 400 °C is attributed to NH_3 desorption from strong acid sites. Fig. 3 shows that the desorption peak of the VO_x/TiO_2 catalyst in the range 150–350 °C arises from NH_3 desorption from weak and medium acid sites distributed on the catalyst surface. Addition of Cr

Fig. 3. NH_3 -TPD curves for catalysts with various Cr/V molar ratios. (1) VO_x/TiO_2 ; (2) $\text{Cr}_{0.1}\text{-V}_{0.9}/\text{TiO}_2$; (3) $\text{Cr}_{0.2}\text{-V}_{0.8}/\text{TiO}_2$; (4) $\text{Cr}_{0.3}\text{-V}_{0.7}/\text{TiO}_2$; (5) $\text{Cr}_{0.5}\text{-V}_{0.5}/\text{TiO}_2$; (6) $\text{Cr}_{0.7}\text{-V}_{0.3}/\text{TiO}_2$; (7) $\text{CrO}_x/\text{TiO}_2$.

caused broadening of the desorption peak and the amount of chemisorbed NH_3 increased. These results suggest that the addition of Cr significantly enhanced the concentration and acidity of acid sites [17]. The desorption peak of the $\text{Cr}_{0.2}\text{-V}_{0.8}/\text{TiO}_2$ catalyst appeared in the range 160–300 °C; this catalyst had the largest amounts of weak and medium acid sites on its surface. When the Cr/V molar ratio was greater than 0.2:0.8, the NH_3 desorption peak in the range 450–550 °C was strong. This finding indicates the presence of a large number of strong acid sites on the surfaces of these catalysts; this is not conducive to desorption of NH_3 and is unfavorable for SCR activity. The optimum amount of Cr on the V-based catalyst surface would give the highest amount of weak acid sites and the lowest amount of strong acid sites.

3.3. H_2 -TPR analysis

H_2 -TPR was used to investigate the catalyst reducibility; the results are shown in Fig. 4. The peak at 470 °C for the VO_x/TiO_2 catalyst can be assigned to the reduction of V^{5+} to V^{3+} [18]. The peak observed above 625 °C is ascribed to unsupported V_2O_5 , and could arise from uneven distribution of V on the TiO_2 support. The reduction peak of the catalyst shifted to lower temperatures as the amount of chromium oxide increased. When the Cr/V molar ratio was 0.2:0.8, the reduction temperature of V^{5+} dropped to 460 °C, and no Cr reduction peak was observed. These results indicate good dispersion of Cr species on the cat-

Table 1

Types of acid sites and surface areas for catalysts with various Cr/V molar ratios determined using NH_3 -TPD.

Catalyst	Acid site distribution ^a				A_{BET} (m^2/g)
	Weak	Medium	Strong	Total	
VO_x/TiO_2	0.10	0.26	—	0.36	56.8
$\text{Cr}_{0.1}\text{-V}_{0.9}/\text{TiO}_2$	0.13	0.34	—	0.47	53.7
$\text{Cr}_{0.2}\text{-V}_{0.8}/\text{TiO}_2$	0.12	0.39	—	0.51	56.2
$\text{Cr}_{0.3}\text{-V}_{0.7}/\text{TiO}_2$	0.13	0.11	0.44	0.68	54.7
$\text{Cr}_{0.5}\text{-V}_{0.5}/\text{TiO}_2$	0.14	0.26	0.52	0.92	52.4
$\text{Cr}_{0.7}\text{-V}_{0.3}/\text{TiO}_2$	0.11	0.30	0.58	1.00	56.2
$\text{CrO}_x/\text{TiO}_2$	0.05	0.30	0.59	0.94	83.0

^a The amount of acidity of $\text{Cr}_{0.7}\text{-V}_{0.3}/\text{TiO}_2$ was assigned as 1.0 and compared with the other samples.

Fig. 4. H_2 -TPR curves of catalyst with various Cr/V molar ratios. (1) VO_x/TiO_2 ; (2) $\text{Cr}_{0.1}\text{-V}_{0.9}/\text{TiO}_2$; (3) $\text{Cr}_{0.2}\text{-V}_{0.8}/\text{TiO}_2$; (4) $\text{Cr}_{0.3}\text{-V}_{0.7}/\text{TiO}_2$; (5) $\text{Cr}_{0.5}\text{-V}_{0.5}/\text{TiO}_2$; (6) $\text{Cr}_{0.7}\text{-V}_{0.3}/\text{TiO}_2$; (7) $\text{CrO}_x/\text{TiO}_2$.

alyst surface. A combination of these results with those of the catalyst textural analysis suggests that interactions occurred between the phases (amorphous chromium oxides and vanadium oxides). These interactions could promote the reduction of V^{5+} , which promoted the reaction. When the Cr/V molar ratio was higher than 0.2:0.8, the reduction peak of Cr species was

observed. The CrO_x TPR profile reported in the literature [14] showed two reduction peaks, at 280 and 420 °C; these could be attributed to reduction of Cr^{6+} to Cr^{5+} and of Cr^{5+} to Cr^{3+} , respectively. The results show that the reduction peak of V weakened. Excess Cr therefore occupied the sites of V species, possibly preventing the SCR reaction.

3.4. XPS analysis

XPS was performed to investigate the surface binding energies and valence states of various catalyst species. The results are shown in Table 2 and Fig. 5. As shown in Fig. 5(a), the O 1s photoelectron spectra of the catalysts indicated the presence of two main types of oxygen, namely lattice oxygen (O_α), with a binding energy of 529.0–530.0 eV, and surface oxygen (O_β), with a binding energy of 530.0–531.0 eV [19]. The proportions of surface oxygen in the Cr-doped catalysts were higher than that in the undoped catalyst (Table 2). This finding indicates that the Cr-doped catalyst had a higher proportion of oxygen vacancies than the undoped catalyst. The presence of surface oxygen improves the catalytic activity in the SCR reaction. This effect is an important reason for the increased catalytic activities of the Cr-doped catalysts [20].

The V 2p XPS spectra of the catalyst samples are shown in Fig. 5(b). The peaks at 517.5 and 516.5 eV can be ascribed to the $2p_{3/2}$ binding energies of V^{5+} and V^{4+} [21]. The surface atomic ratios of V^{4+} to V^{5+} are listed in Table 2; these were obtained by deconvolution. The 10 wt% $\text{Cr}_{0.2}\text{-V}_{0.8}/\text{TiO}_2$ catalyst had the highest $\text{V}^{4+}/\text{V}^{5+}$ ratio, and the ratio decreased in the

Table 2

Binding energies and surface atomic concentrations of O, Cr, and V for the prepared catalysts determined from deconvoluted XPS spectra.

Catalyst	Binding energy (eV)			Atomic concentration (%)			$\text{V}^{4+}/\text{V}^{5+}$	$\text{Cr}^{3+}/\text{Cr}^{6+}$	$\text{O}_\beta/\text{O}_\alpha$
	O 1s	V 2p	Cr 2p	O	Ti (Cr)*	V			
10 wt% VO_x/TiO_2	530.02, 531.30	516.88, 517.57	—	68.33	25.70	5.97	0.59	—	0.61
5 wt% $\text{Cr}_{0.2}\text{-V}_{0.8}/\text{TiO}_2$	529.98, 531.17	516.61, 517.26	577.42, 580.05	70.75	26.86	2.39	0.21	0.80	0.92
10 wt% $\text{Cr}_{0.2}\text{-V}_{0.8}/\text{TiO}_2$	529.80, 530.63	516.88, 517.59	577.31, 579.78	68.06	26.91	5.03	0.73	0.97	1.00
20 wt% $\text{Cr}_{0.2}\text{-V}_{0.8}/\text{TiO}_2$	529.82, 530.35	516.75, 517.42	576.93, 579.10	70.86	21.97	7.17	0.48	0.88	0.95

Fig. 5. XPS spectra of O 1s (a), V 2p (b), and Cr 2p (c) of various catalysts. (1) 20 wt% $\text{Cr}_{0.2}\text{-V}_{0.8}/\text{TiO}_2$; (2) 5 wt% $\text{Cr}_{0.2}\text{-V}_{0.8}/\text{TiO}_2$; (3) 10 wt% $\text{Cr}_{0.2}\text{-V}_{0.8}/\text{TiO}_2$; (4) VO_x/TiO_2 .

order 10 wt% $\text{Cr}_{0.2}\text{-V}_{0.8}/\text{TiO}_2 > 10 \text{ wt\% } \text{VO}_x/\text{TiO}_2 > 20 \text{ wt\% } \text{Cr}_{0.2}\text{-V}_{0.8}/\text{TiO}_2 > 5 \text{ wt\% } \text{Cr}_{0.2}\text{-V}_{0.8}/\text{TiO}_2$. A large $\text{V}^{4+}/\text{V}^{5+}$ ratio would generate more free electrons, which are formed from non-stoichiometric V ions in various valence-state-conversion processes.

Fig. 5(c) shows the XPS spectra of Cr 2p on the catalyst surfaces. The Cr atoms on the catalyst surfaces had two valences (Cr^{6+} and Cr^{4+}). The data in Table 2 clearly show that the Cr–V loading on the catalyst had little effect on the $\text{Cr}^{3+}/\text{Cr}^{6+}$ molar ratio.

3.5. Catalyst performance

The NO_x conversions over catalysts with various Cr/V molar ratios as a function of reaction temperature are shown in Fig. 6. VO_x/TiO_2 and $\text{CrO}_x/\text{TiO}_2$ had poor activities at low temperatures, and $\text{CrO}_x/\text{TiO}_2$ had a narrow temperature window. The results show that small variations in the amount of Cr in the Cr–V/TiO₂ catalysts influenced NO_x conversion. The curves for $\text{Cr}_{0.1}\text{-V}_{0.9}/\text{TiO}_2$ and $\text{Cr}_{0.2}\text{-V}_{0.8}/\text{TiO}_2$ show that the catalytic activities were significantly improved at low temperatures with increasing Cr content because this enhanced the weak acidity of the SCR catalyst. However, excess Cr was unfavorable for the reaction because the active sites on the V-based catalyst were occupied by Cr, as shown by the curves for $\text{Cr}_{0.3}\text{-V}_{0.7}/\text{TiO}_2$, $\text{Cr}_{0.5}\text{-V}_{0.5}/\text{TiO}_2$, and $\text{Cr}_{0.7}\text{-V}_{0.3}/\text{TiO}_2$. The NO_x conversion rate exceeded 90% at 160 °C when the Cr/V molar ratio was 0.2:0.8; this catalytic activity at low temperatures is clearly better than those of the other catalysts, and the temperature window of 160–300 °C was broadened. These findings are in agreement with the NH_3 -TPD and H_2 -TPR results.

The effects of the catalyst loading on the activities of the De NO_x catalysts were investigated; the results are shown in Fig. 7. The Cr–V content greatly influenced the NH_3 -SCR activity. NO_x conversions over the catalysts decreased in the order 10 wt% > 20 wt% > 50 wt% > 5 wt%. As shown in Table 2, a 5 wt% loading of the $\text{Cr}_{0.2}\text{-V}_{0.8}/\text{TiO}_2$ catalyst contained only

Fig. 6. NO_x conversions over catalysts with various Cr/V molar ratios. Reaction conditions: GHSV = 60000 mL/(h·g), $\varphi(\text{NO}) = \varphi(\text{NH}_3) = 0.05\%$, $\varphi(\text{O}_2) = 5\%$.

Fig. 7. Effect of active phase loading on NO_x conversion. $\varphi(\text{NO}) = \varphi(\text{NH}_3) = 0.05\%$, $\varphi(\text{O}_2) = 5\%$.

2.39% V on the catalyst surface. The number of active sites affects the adsorption rate, therefore the catalyst with a 5 wt% loading decreased the SCR reaction rate. In contrast, the catalyst containing 10 wt% Cr–V had the highest V content on the catalyst surface. Vanadium has a stable oxidation state of +5; V^{4+} is reduced compared with V^{5+} and has one extra electron, which can act as a free electron because there is no constraint on the atom, which shows high mobility and activity. It is therefore reasonable to conclude that an increased $\text{V}^{4+}/\text{V}^{5+}$ ratio could lead to an increase in the SCR reaction rate, as a result of the free electrons formed in non-stoichiometric V [22]. The catalyst containing 10 wt% Cr–V therefore showed the highest activity and gave nearly 100% NO_x conversion above 200 °C. However, excess loading could lead to aggregation of V_2O_5 and $\text{Cr}_2\text{V}_4\text{O}_{13}$, cover the V active sites, and reduce the De NO_x catalytic activity.

3.6. Sulfur and water vapor resistance of catalyst

Fig. 8 shows the resistance of the $\text{Cr}_{0.2}\text{-V}_{0.8}/\text{TiO}_2$ catalyst to SO_2 poisoning during SCR of NO_x with NH_3 . The $\text{Cr}_{0.2}\text{-V}_{0.8}/\text{TiO}_2$ catalytic activity was high and NO_x conversion was higher than 75% in the absence of SO_2 . In 12 h of test with flue gas contain-

Fig. 8. Resistance to SO_2 of $\text{Cr}_{0.2}\text{-V}_{0.8}/\text{TiO}_2$ catalyst. Reaction conditions: 220 °C or 180 °C, GHSV = 60000 mL/(h·g), $[\text{SO}_2] = 100 \text{ ppm}$.

Fig. 9. Resistance to water and copresence of water + SO₂ of Cr_{0.2}-V_{0.8}/TiO₂ catalyst. Reaction conditions: 220 °C, GHSV = 60000 mL/(h·g), [SO₂] = 100 ppm, [water] = 10 vol%.

ing 100 ppm SO₂, the NO_x conversion below 220 °C remained at about 99%. Moreover, no signs of sulfur poisoning were observed. However, the introduction of SO₂ slightly reduced NO_x conversion at 180 °C, because SO₂ on the catalyst surface was easily adsorbed by the V-based catalyst at low temperatures, covering the active sites and ultimately inhibiting the activity.

The influence of water was tested by injecting 10 vol% water into the reaction. As shown in Fig. 9, the presence of water decreased the NO_x conversion by the Cr_{0.2}-V_{0.8}/TiO₂ catalyst at 220 °C. Several authors have attributed the hindering effect of water vapor to competitive adsorption between water and NH₃ [23]. The Cr_{0.2}-V_{0.8}/TiO₂ catalyst still had sufficiently high catalytic activity to ensure that NO_x conversion was higher than 85% in the copresence of water and SO₂.

4. Conclusions

Doping of Cr ions increased the amounts of weak and medium acid sites on the VO_x/TiO₂ catalyst surface, promoted the

low-temperature reductive capacity of high-valence V ions, and increased the amount of surface oxygen on the catalyst. These factors enhanced the SCR rate. The catalyst with a Cr/V molar ratio of 0.2:0.8 and 10% loading had the largest amount of weak acid sites and gave the best DeNO_x performance, with NO_x conversion greater than 90% at 160–300 °C. This catalyst also showed high stability in the presence of 0.01% SO₂.

References

- [1] Martin J A, Yates M, Avila P, Suarez S, Blanco J. *Appl Catal B*, 2007, 70: 330
- [2] Yang S J, Wang C Z, Li J H, Yan N Q, Ma L, Chang H Z. *Appl Catal B*, 2011, 110: 71
- [3] Yan Z Y, Gao X, Wu J, Jiang Y, Luo Z Y, Ni M J, Cen K F. *J Power Eng* (闫志勇, 高翔, 吴杰, 姜烨, 骆仲决, 倪明江, 岑可法. 动力工程), 2007, 27: 282
- [4] Liu C X, Chen L, Li J H, Ma L, Arandiyana H, Du Y, Xu J M, Hao J M. *Environ Sci Technol*, 2012, 46: 6182
- [5] Tang X L, Hao J M, Xu W G, Li J H. *Chin J Catal* (唐晓龙, 郝吉明, 徐文国, 李俊华. 催化学报), 2006, 27: 843
- [6] Wu Z B, Jin R B, Liu Y, Wang H Q. *Catal Commun*, 2008, 9: 2217
- [7] Yang C, Cheng H, Huang B C. *Chem Ind Eng Prog* (杨超, 程华, 黄碧纯. 化工进展), 2014, 33: 907
- [8] Maqbool M S, Pullur A K, Ha H P. *Appl Catal B*, 2014, 152-153: 28
- [9] Huang Y, Tong Z Q, Wu B, Zhang J F. *J Fuel Chem Technol* (黄妍, 童志权, 伍斌, 张俊丰. 燃料化学学报), 2008, 36: 616
- [10] Huang H F, Zeng L, Lu H F, Zhou C H, Chen Y F. *J Chem Eng Chin Univ* (黄海凤, 曾立, 卢晗锋, 周春何, 陈银飞. 高校化学工程学报), 2009, 23: 871
- [11] Putluru S S R, Riisager A, Fehrmann R. *Catal Lett*, 2009, 133: 370
- [12] Zhu Z P, Liu Z Y, Liu S J, Niu H X. *Appl Catal B*, 2001, 30: 267
- [13] Pena D A, Uphade B S, Smirniotis P G. *J Catal*, 2004, 221: 421
- [14] Thirupathi B, Smirniotis P G. *Appl Catal B*, 2011, 110: 195
- [15] Tong H, Luo J, Tong Z Q, Xia B, Luo H. *Environ Eng Sci*, 2011, 28: 711
- [16] Chen Z H, Yang Q, Li H, Li X H, Wang L F, Tsang S C. *J Catal*, 2010, 276: 56
- [17] Shan W P, Liu F D, He H, Shi X Y, Zhang C B. *Appl Catal B*, 2012, 115-116: 100

Graphical Abstract

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Performance of Cr-doped vanadia/titania catalysts for low-temperature selective catalytic reduction of NO_x with NH₃

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A large V⁴⁺/V⁵⁺ ratio could generate more free electrons, which were formed from the non-stoichiometric vanadium ions at different valence state conversion processes, and they were beneficial in improving the catalytic activity of the SCR reaction.

- [18] Li Q, Yang H S, Nie A M, Fan X Y, Zhang X B. *Catal Lett*, 2011, 141: 1237
- [19] Nagaveni K, Hegde M S, Ravishankar N, Subbanna G N, Madras G. *Langmuir*, 2004, 20: 2900
- [20] Zhao W, Zhong Q, Pan Y X, Zhang R. *Chem Eng J*, 2013, 228: 815
- [21] Chang H Z, Li J H, Chen X Y, Ma L, Yang S J, Schwank J W, Hao J M. *Catal Commun*, 2012, 27: 54
- [22] Choi S H, Cho S P, Lee J Y, Hong S H, Hong S C, Hong S I. *J Mol Catal A*, 2009, 304: 166
- [23] Busca G, Lietti L, Ramis G, Berti F. *Appl Catal B*, 1998, 18: 1

Cr改性钒基催化剂对NH₃低温选择性催化还原NO_x的影响

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摘要: 火电厂和机动车辆等的NO_x排放量与日俱增, NO_x的治理已成为环境保护的重要组成部分。以NH₃作为还原剂的选择性催化还原(SCR)技术是目前消除NO_x最为高效的方法之一。该反应最为典型的催化剂是V₂O₅-WO₃(MoO₃)/TiO₂, 催化活性窗口为250–400 °C。国外通常将SCR系统置于省煤器之后, 此时烟气温度在300 °C以上, 催化剂能保持较高的活性, 但易受到烟气中高浓度烟尘、SO₂和碱金属等的影响, 寿命相对较短。此外, 高温工艺中副产物硫酸铵的堵塞也是一个不可忽视的问题。因此, 将SCR脱硝装置设在脱硫除尘之后成为一种优选技术之一, 但烟气温度会降至250 °C以下, 而常规的钒基催化剂不能满足低温活性要求。通过添加助剂或改变载体可改善钒基催化剂的低温活性, 同时保持其高效的抗硫能力。

本文以Cr和V为活性组分, TiO₂为载体, 采用浸渍法制备了铬钒钛(Cr-VO_x/TiO₂)系列催化剂, 考察了它们的低温脱硝活性和抗水抗硫性, 并通过N₂吸附-脱附、X射线衍射、NH₃程序升温脱附(NH₃-TPD)、H₂程序升温还原(H₂-TPR)和X射线光电子能谱等手段对催化剂进行了表征, 分析了Cr-V催化剂的作用机制。

结果显示, 当 $n(\text{Cr}):n(\text{V})$ 为0.2:0.8, 活性组分负载量为10 wt%时, Cr-VO_x/TiO₂催化剂表现出最佳的低温催化活性; 当反应温度为160 °C时, NO_x转化率达到90%以上, 明显优于其他催化剂, 同时活性窗口(160–300 °C)得到拓宽。NH₃-TPD结果表明, VO_x/TiO₂催化剂表面呈中弱酸性, 随着Cr的添加, 钒基催化剂的NH₃脱附峰向高温拓宽, 说明其表面强酸量有所增加, Cr_{0.2}-V_{0.8}/TiO₂在160–300 °C范围内均出现了NH₃的脱附峰, 此时催化剂表面弱酸量最大。当 $n(\text{Cr}):n(\text{V})$ 大于0.2:0.8时, 催化剂表面出现强酸位, 这种强酸位不利于NH₃脱附, 从而不利于SCR反应的进行。因此适量Cr的添加有助于提高钒基催化剂表面弱酸及中性酸量。H₂-TPR结果发现, 助剂Cr的添加使得催化剂表面氧量增加, 这可能是由于Cr的添加形成了较多的氧空穴和未饱和的化学键。催化剂表面化学吸附氧是氧化还原反应最活跃的氧物种, 在SCR反应中, 表面氧可作为NO的吸附介质参与对催化剂表面反应中, 可有效提高SCR反应速率。通过考察活性组分负载量对催化剂活性的影响, 发现不同负载量催化剂的催化活性依次为10 wt% > 20 wt% > 50 wt% > 5 wt%。XPS分析发现, 当负载量为10 wt%时, 催化剂表面非计量的钒离子和化学性质活跃的自由电子最多, 因此表现出最佳的SCR活性; 当负载量过高时, 大量氧化物堆积烧结形成V₂O₅和Cr₂V₄O₁₃, 覆盖了钒离子活性位点, 降低了催化剂脱硝效率。

催化剂在220 °C表现出良好的抗硫性, 在通入100 ppm SO₂ 12 h后NO_x的转化率仍可达99%以上, 并未出现硫中毒现象。同时该催化剂也表现出较好的抗水性, 在通入10 vol%水蒸气12 h后, NO_x转化率仍能达85%以上。

关键词: 低温; 选择性催化还原; 氨; 铬钒钛催化剂; 烟气脱硝; 抗硫性; 铬掺杂

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