available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

Promotional effects of Zr on K⁺-poisoning resistance of CeTiO_x catalyst for selective catalytic reduction of NO_x with NH₃

Baoqiang Xu^a, Haidi Xu^{b,c,*}, Tao Lin^a, Yi Cao^a, Li Lan^a, Yuanshan Li^d, Xi Feng^d, Maochu Gong^a, Yaoqiang Chen^{a,c,#}

^a Key Laboratory of Green Chemistry & Technology of the Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, Sichuan, China

^b Institute of New Energy and Low-Carbon Technology, Sichuan University, Chengdu 610064, Sichuan, China

^c Sichuan Provincial Environmental Protection Environmental Catalytic Materials Engineering Technology Center, Chengdu 610064, Sichuan, China

^d College of Chemical Engineering, Sichuan University, Chengdu 610064, Sichuan, China

ARTICLE INFO

Article history:

Received 27 February 2016

Accepted 2 April 2016

Published 5 August 2016

Keywords:

Cerium-titanium mixed oxide

Zirconium

Potassium-poisoning resistance

Selective catalytic reduction

Nitrogen oxides

ABSTRACT

CeTiO_x and CeZrTiO_x catalysts were prepared by a coprecipitation method and used for selective catalytic reduction of NO_x by NH₃ (NH₃-SCR). Various amounts of KNO₃ were impregnated on the catalyst surface to investigate the effects of Zr addition on the K⁺-poisoning resistance of the CeTiO_x catalyst. The NH₃-SCR performance of the catalysts showed that the NO_x removal activity of the Zr-modified catalyst after poisoning was better than that of the CeTiO_x catalyst. Brunauer-Emmett-Teller data indicated that the Zr-containing catalyst had a larger specific surface area and pore volume both before and after K⁺ poisoning. X-ray diffraction, Raman spectroscopy, and transmission electron microscopy showed that Zr doping inhibited anatase TiO₂ crystal grain growth, i.e., the molten salt flux effect caused by the loaded KNO₃ was inhibited. The Ce 3d X-ray photoelectron spectra showed that the Ce³⁺/Ce⁴⁺ ratio of CeZrTiO_x decreased more slowly than that of CeTiO_x with increasing K⁺ loading, indicating that Zr addition preserved more crystal defects and oxygen vacancies; this improved the catalytic performance. The acidity was a key factor in the NH₃-SCR performance; the temperature-programmed desorption of NH₃ results showed that Zr doping inhibited the decrease in the surface acidity. The results suggest that Zr improved the K⁺-poisoning resistance of the CeTiO_x catalyst.

© 2016, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

NO_x is a major air pollutant and is responsible for environmental problems such as photochemical smog, acid rain, and ozone layer depletion. Exposure to high concentrations of NO_x can cause health problems for humans [1,2]. Selective catalytic

reduction (SCR) of NO_x, a proven technique, gives higher NO_x control efficiency than do many other NO_x treatment methods [3–5]. V₂O₅–WO₃(MoO₃)/TiO₂ is a common commercial SCR catalyst for NO_x removal [2,3]. However, there are problems with this catalytic system, e.g., the toxicity of vanadium species, low N₂ selectivity at high temperatures [6,7], and deactivation

* Corresponding author. Tel/Fax: +86-28-85418451; E-mail: xuhaidi@scu.edu.cn

Corresponding author. Tel/Fax: +86-28-85418451; E-mail: nic7501@scu.edu.cn

This work was supported by the Major Research Program of Sichuan Province Science and Technology Department (2012FZ0008), the National Natural Science Foundation of China (21173153), the National High Technology Research and Development Program of China (863 Program, 2013AA065304), and the Sichuan University Research Foundation for Young Teachers (2015SCU11056).

DOI: 10.1016/S1872-2067(15)61102-0 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 8, August 2016

caused by loading of alkali and alkaline earth metal salts in the ashes [8,9]. It is therefore necessary to develop novel environmentally friendly catalysts with high SCR performance. CeTiO_x is a promising catalyst for NH_3 -SCR and has high activity and excellent selectivity for N_2 [10–13]. Shan et al. [12] reported that the NH_3 -SCR performance of a CeO_2 - TiO_2 catalyst was better than those of V_2O_5 - WO_3 / TiO_2 and Fe-ZSM-5 catalysts under the same conditions.

Alkali metals poison NH_3 -SCR catalysts such as V_2O_5 / TiO_2 [14,15], V_2O_5 - CeO_2 / TiO_2 [15], and CeTiO_x , especially in biomass combustion plants. Energy generation from biomass contributes to the carbon eco-cycle and helps to maintain the carbon balance on Earth, but there is a high concentration of K species in biomass such as straw and municipal waste [16], and this limits the use of CeTiO_x catalysts.

Decreased surface acidity [17] and redox reactivity [8,18] are two important factors in NH_3 -SCR catalyst deactivation. Wang et al. [19] proposed that the mechanism of alkali metal poisoning of CeTiO_x catalysts involved enlargement of the CeO_2 nanoparticles, a decreased $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox cycle rate, and changes in the surface acidity, which could be major factors in the decline of the SCR activity of the Ce/TiO_2 catalyst after loading with Na^+ or Ca^{2+} ions. Du et al. [16] conducted a theoretical study of the effects of K^+ or Na^+ doping on the NH_3 -SCR based on density functional theory calculations. The results showed that the alkali atoms interacted strongly with the oxygens on Ce and Ti, decreasing the reducibility and surface acidity, respectively.

ZrO_2 is an acid–base amphoteric oxide with good redox properties, and it is widely used in catalysis as an inhibitor of crystal transformations and as a cocatalyst [20]. The addition of Zr can improve the stability and redox properties of Ce-based oxygen-storage materials, i.e., three-way catalysis. The addition of Zr to CeTiO_x can improve resistance to alkali metal poisoning, and therefore increase the surface acidity and improve the redox properties.

In this work, CeTiO_x and CeZrTiO_x catalysts were prepared by a coprecipitation method, and alkali metal poisoning over both catalysts was investigated by catalyst impregnation with various contents of K^+ to determine the effects of Zr addition to CeTiO_x on the K^+ -poisoning resistance. The Brunauer-Emmett-Teller (BET) method, X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption of NH_3 (NH_3 -TPD) were used to characterize the fresh and poisoned catalysts.

2. Experimental

2.1. Catalyst preparation

CeTiO_x and CeZrTiO_x catalysts were prepared using a conventional coprecipitation method. $\text{Ce}(\text{NO}_3)_3$ (AR grade, Jinshan, Chengdu, China), zirconyl nitrate hydrate (AR grade, 99%, Yutai, Shangdong, China), and titanylsulfate (AR grade, Dandong, Liaoning, China) were used as precursors. The precursors were mixed at appropriate molar ratios in an aqueous solution and

then precipitated with an alkaline buffer solution until the pH reached approximately 9. The obtained precipitates were dried at 90 °C for 24 h, and then calcined in air at 550 °C for 3 h. The obtained CeTiO_x and CeZrTiO_x powders are denoted by CT and ZCT. For both catalysts, the Ce/Ti molar ratio was kept at 0.2:1, and the Zr/Ti molar ratio in CeZrTiO_x was also 0.2:1.

CT and ZCT catalysts were impregnated with KNO_3 at K/Ce molar ratios of 0.1:1 and 0.2:1, and calcined in air at 550 °C for 3 h. The K^+ -poisoned samples are denoted by K0.1-CT, K0.2-CT, K0.1-ZCT, and K0.2-ZCT.

2.2. Catalyst characterization

The surface areas, pore sizes, and pore volumes of the catalysts were determined using the BET method based on N_2 adsorption at –196 °C (Quantachrome automated surface area and pore size analyzer, Autosorb SI). The samples were treated at 300 °C for 3 h prior to measurements.

Powder XRD was performed using a Rigaku D/max-RA diffractometer with $\text{Cu } K\alpha$ ($\lambda = 0.15406 \text{ nm}$) radiation. The tube voltage and current were 40 kV and 100 mA, respectively. The powder XRD patterns were recorded at 0.03°/s intervals in the range 20°–80°. The crystalline phases were identified by reference to the database of the International Center for Diffraction Data (ICDD).

Raman spectroscopy was performed using a Lab-RAM HR laser Raman instrument with a Nd:Yag laser at a 532 nm excitation wavelength. All specimens were illuminated through a 50 × objective and in powder form to prevent diffusion problems. Raman spectra were recorded over the range 100–1000 cm^{-1} . The grating specification was 600 g/mm.

TEM was performed using a JEM-100CX instrument at an accelerating voltage of 80 kV.

XPS was performed with a British Kratos XSAM-800 instrument at 13 kV and 20 mA electron current, using $\text{Mg } K\alpha$ radiation. Binding energies were calibrated using the C 1s peak (284.8 eV). The pressure in the analytical chamber was about $1 \times 10^{-9} \text{ Pa}$.

NH_3 -TPD was performed in a fixed-bed quartz reactor. A sample mass of 100 mg and a gas flow rate of 30 mL/min were used. The experiment included four stages: (1) degasification of the sample in Ar at 450 °C for 1 h, (2) adsorption of 2% NH_3 at 80 °C for 1 h, (3) isothermal desorption in Ar at 80 °C until no NH_3 was detected, and (4) TPD in Ar at 8 °C/min to 600 °C. A thermal conductivity detector was used.

2.3. Catalytic activity tests

Catalytic activity measurements were performed in a fixed-bed quartz flow reactor. The reactor consisted of a quartz tube of diameter 8 mm filled with 0.25 g of catalyst. Temperatures were measured using a thermocouple placed at the center of the bed. The concentrations of the simulated gases were 0.05% NO , 0.05% NH_3 , 5% O_2 , and balance N_2 . The gas hourly space velocity (GHSV) was about 60000 h^{-1} . The original and effluent NO concentrations at different temperatures were continuously monitored using an IR detector (ANTARIS IGS ana-

lyzer, Thermo Scientific). The data were collected after the reaction had stabilized for 30 min at each temperature. The NO_x conversions were calculated as follows: $\text{NO}_x \text{ conversion} = ([\text{NO}_x]_{\text{inlet}} - [\text{NO}_x]_{\text{outlet}})/[\text{NO}_x]_{\text{inlet}} \times 100\%$.

3. Results and discussion

3.1. SCR performance

The activities of CT and ZCT with different K^+ loadings were tested to compare their anti-alkali metal abilities; the results are shown in Fig. 1(a). The catalysts without K^+ gave 90% NO_x conversions over a wide temperature range from 250 to 450 °C; CT performed slightly better than ZCT. Impregnation with K^+ decreased the NO_x removal activities of CT and ZCT. NO_x conversion declined further when the K/Ce molar ratio was increased to 0.2. The poisoning effect was so distinct that K0.2-CT had nearly no activity or even gave negative NO_x conversions at high temperatures because of non-selective NH_3 oxidation.

The mechanism of the decrease in activity with increasing K^+ loading was clarified by investigating NO_x conversion at 350 °C as a function of the K/Ce molar ratio; the results are shown in Fig. 1(b). CT and ZCT achieved nearly 100% NO_x conversions, and there was little difference between the performance of the two catalysts. ZCT gave better NO_x conversion than the catalyst without Zr addition after impregnation with K^+ . The NO_x conversions by K0.1-CT and K0.1-ZCT were 90% and 62%, respectively; for K0.2-CT and K0.2-ZCT, the conversions were 48% and 13%, respectively. The catalytic activity of ZCT therefore decreased more slowly than that of CT with increasing K^+ loading.

The NO_x removal activity of ZCT remained higher than that of CT after K^+ poisoning, indicating that Zr addition improved the resistance of CT to K^+ poisoning.

3.2. Characterization

3.2.1. BET analysis

The textural properties of the two catalysts before and after

Table 1
Textural properties of catalysts.

Sample	Specific surface area (m^2/g)	Pore volume (mL/g)	Average pore radius (nm)
CT	101.7	0.34	6.6
K0.1-CT	67.9	0.33	9.7
K0.2-CT	64.6	0.30	9.3
ZCT	142.6	0.42	5.9
K0.1-ZCT	88.8	0.36	8.0
K0.2-ZCT	80.4	0.34	8.3

poisoning are shown in Table 1. Previous studies have shown that a high surface area and large pore volume promote effective mass transfer by providing more active sites for adsorption of reactant molecules and intermediates, consequently improving the catalytic performance [21]. The specific surface area of CT was $101.7 \text{ m}^2/\text{g}$ and the pore volume was $0.34 \text{ mL}/\text{g}$. After poisoning by K^+ , the specific surface areas dropped to 67.9 and $64.6 \text{ m}^2/\text{g}$ and the pore volume also decreased slightly. Similar changes were observed for ZCT. The specific surface areas of ZCT, K0.1-ZCT, and K0.2-ZCT were 142.6, 88.8, and $80.4 \text{ m}^2/\text{g}$, respectively. The specific surface areas and pore volumes of the K^+ -poisoned catalysts decreased significantly compared with those of the fresh catalyst, showing that K^+ damaged the textural properties of CT and ZCT. The sharp decrease in the specific surface area was in line with the significant decline in NH_3 -SCR activities.

The specific surface area and pore volume of ZCT were higher than those of the CT catalyst without K^+ loading. After poisoning by K^+ , ZCT still showed better textural properties. It is therefore concluded that Zr addition improved the textural properties of the CT catalyst even after poisoning by K^+ ; this might be why the catalytic activity of ZCT was better than that of CT.

3.2.2. XRD

The effects of Zr addition on the structural properties of the fresh and poisoned catalysts were clarified by examining their crystal structures using powder XRD. The crystalline phases were identified by comparison with ICDD files. The XRD pat-

Fig. 1. (a) NO conversion as a function of temperature; (b) NO conversion at 350 °C as a function of K/Ce molar ratio. Reaction conditions: $[\text{NO}] = [\text{NH}_3] = 0.05\%$, $[\text{O}_2] = 5\%$, balance N_2 , GHSV = 60000 h^{-1} .

Fig. 2. XRD patterns for CT (a) and ZCT (b) catalysts.

terns of the CT catalysts are shown in Fig. 2(a). Only anatase TiO_2 was detected and no diffraction peaks from CeO_2 were observed for any of the catalysts. This indicates that Ce was highly dispersed or amorphous. The diffraction peaks of anatase TiO_2 grew sharper with increasing K^+ loading, showing that amorphous TiO_2 was gradually transformed into the crystalline phase. Crystallite growth decreases the surface area, as shown by the data in Table 1.

Fig. 2(b) shows that K^+ poisoning did not significantly change the ZCT phase; this indicates that Zr prevented the formation of crystalline TiO_2 and inhibited crystal nucleus growth after doping with K^+ . These results show that Zr improved the structural stability of CT, even when it was poisoned by K^+ , and this enabled ZCT to retain a higher NO_x conversion ability compare with that of CT.

3.2.3. Raman spectroscopy

Raman spectroscopy was used to obtain information on the surfaces of the CT and ZCT catalysts with different K^+ contents. Fig. 3(a) shows the Raman spectra from 100 to 1000 cm^{-1} for the CT catalyst. The peaks at 147 and 642 cm^{-1} are attributed to anatase TiO_2 [22]; these peaks gradually became more intense and sharper with increasing K^+ loading; this is in accordance with the XRD results. No Raman bands were observed for the fresh and poisoned ZCT catalysts (Fig. 3(b)), showing that the catalysts were amorphous. The Raman results confirmed that Zr addition stabilized the structure of the CT catalyst.

3.2.4. TEM

The morphologies, structures, and particle sizes of the cata-

Fig. 3. Raman spectra of CT (a) and ZCT (b) catalysts.

lysts were further examined using TEM. The images in Fig. 4 were obtained at $\times 140000$ magnification. The CT particle size increased with increasing K^+ content; this is in accordance with the XRD results. The average grain sizes of CT, K0.1-CT, and K0.2-CT were about 7, 13, and 15 nm, respectively. In contrast, the ZCT crystal size did not change. The average particle sizes of ZCT, K0.1-ZCT, and K0.2-ZCT were about 5, 8, and 10 nm, respectively. This clearly shows that Zr addition inhibited particle aggregation and therefore enhanced the structural stability of CT.

The XRD, Raman, and TEM results indicate that the size of the crystalline anatase TiO_2 particles increased after K^+ loading. The changes are mainly ascribed to the molten salt flux effect [19]. Under real flue gas conditions or in a simulated loading–calcination process, the loaded KNO_3 forms a molten salt flux on the surface of the CT catalyst and covers the TiO_2 nanoparticles. Under these conditions, the crystal size of the TiO_2 nanoparticles increases and their crystallinity improves [19].

3.2.5. XPS

The Ce 3d XPS spectra of the fresh and K^+ -poisoned catalysts are shown in Fig. 5. The XPS peaks labeled u_1 and v_1 represent Ce^{3+} , and those labeled u , u_2 , u_3 , v , v_2 , and v_3 are assigned to Ce^{4+} .

There is an oxidation–reduction cycle between Ce^{3+} and Ce^{4+} . Most of the Ce in the catalyst was in the Ce^{4+} state [16]. A larger amount of Ce^{3+} gives a catalyst with higher oxygen-storage capacity and better redox properties [16]. Ce^{3+} on the catalyst surface is crucial in the SCR reaction because Ce^{3+} can create a charge imbalance, resulting in the formation of

Fig. 4. TEM images of the catalysts.

more vacancies and unsaturated chemical bonds on the catalyst surface, leading to an increased amount of chemisorbed oxygen on the catalyst surface [23,24]. The Ce^{3+}/Ce ratio therefore reflects the catalyst redox properties or catalytic activity to some extent. The Ce^{3+}/Ce ratio was calculated from the total area of u_1 and v_1 , which are attributed to Ce^{3+} , divided by the total area of the ten peaks assigned to Ce. The Ce^{3+}/Ce ratios of various catalysts are listed in Table 2. The Ce^{3+}/Ce ratio was always less than 0.5, indicating that Ce^{4+} was the main Ce valence state in the two catalysts.

The Ce^{3+}/Ce ratios for CT, K0.1-CT, and K0.2-CT were 31%, 26%, and 17%, respectively, i.e., they decreased with increasing

K^+ content. These changes show that K^+ significantly affected Ce oxidation. This is attributed to the interactions between K^+ and Ce species inhibiting Ce^{4+} reduction to Ce^{3+} , resulting in a sharp decrease in the Ce^{3+} concentration [19]. Because Ce^{3+} is formed from CeO_2 defects, the amount of Ce^{3+} decreased with increasing particle size [25,26]. This is in accordance with the XRD and Raman results.

For the ZCT, K0.1-ZCT and K0.2-ZCT catalysts, the Ce^{3+}/Ce values were 30%, 29%, and 27%, separately. There was no obvious decrease in the amount of Ce^{3+} with increasing K^+ impregnation of the ZCT catalyst, showing that Zr prevented the transformation of Ce^{3+} to Ce^{4+} . For the fresh catalyst, the Ce^{3+}/Ce values for CT and ZCT were nearly the same. The proportions of Ce^{3+} for the two catalysts both gradually decreased with increasing K^+ content, and Ce^{3+}/Ce ratios for the ZCT catalysts were always clearly higher than those for the CT catalysts. This is why the K^+ -poisoned ZCT performed better than the K^+ -poisoned CT catalysts.

The XRD and XPS results show that K^+ impregnated on the CT surface can lead to the crystallization of CeO_2 nanoparticles and a reduction in the amounts of CeO_2 defects and Ce^{3+} . These combined results suggest that the Ce^{3+}/Ce values for the ZCT catalysts were higher than those for the CT catalysts after poisoning, therefore, the ZCT catalysts had better oxygen-storage capacities and redox properties, and more surface defects; these factors cocontributed to their higher NH_3 -SCR activities.

3.2.6. NH_3 -TPD

According to the mechanism proposed by Topsøe et al. [27], NH_3 adsorption on the catalyst surface is crucial for the SCR reaction. The acid sites, on which NH_3 is adsorbed, are therefore a key factor in the catalytic performance. Previous reports

Fig. 5. Ce 3d XPS spectra of CT (a) and ZCT (b) catalysts.

Table 2
 Ce^{3+}/Ce ratios of the catalysts.

Sample	Ratio of Ce^{3+}/Ce (%)		
	K/Ce = 0	K/Ce = 0.1	K/Ce = 0.2
CT	31	26	17
ZCT	30	29	27

 Fig. 6. NH_3 -TPD profiles of catalysts.

Table 3

 Peak areas in NH_3 -TPD profiles of the catalysts.

Sample	Peak area		
	K/Ce = 0	K/Ce = 0.1	K/Ce = 0.2
CT	1071	104	54
ZCT	854	320	168

focusing on alkali metal poisoning of catalysts for NO_x removal attributed deactivation to a decrease in the number of acid sites [28,29], which would result in low NH_3 adsorption.

Fig. 6 shows the NH_3 -TPD curves of the fresh and K^+ -containing catalysts in the range 120–600 °C. The peak areas for the catalysts are listed in Table 3. On K^+ addition, these peak areas decreased significantly. The calculated peak areas for CT, K0.1-CT, and K0.2-CT were 1071, 104, and 54, respectively, i.e., poisoning strongly affected NH_3 adsorption. The sharp decrease in surface acidity was in keeping with the decreased NH_3 -SCR activity. This is also in accordance with the conclusion that decreased surface acidity was one of the main reasons for the decreased activity after doping with K^+ [9,30].

The peak areas for ZCT, K0.1-ZCT, and K0.2-ZCT were 854, 320, and 168, respectively. After Zr addition, the catalyst acidity was better retained after poisoning by K^+ , showing that the decrease in the surface acidity was inhibited by Zr doping. The ZCT catalyst therefore gave higher NO_x conversion than did the CT catalyst after K^+ poisoning.

4. Conclusions

Catalytic activity results showed that a CeTiO_x catalyst was

seriously poisoned by KNO_3 ; but it performed distinctly better by Zr doping. The BET data showed that Zr improved the textural properties of the CT catalyst. The XRD, Raman, and TEM results showed that crystal grain growth caused by the molten salt flux effect was inhibited by Zr addition, suggesting that the structural properties of the CT catalysts were stabilized by the addition of Zr. XPS results showed that K^+ loading led to the transformation of Ce^{3+} to Ce^{4+} , resulting in decreased concentrations of oxygen vacancies and Ce^{3+} in CeO_2 particles. The larger amounts of Ce^{3+} and surface defects on the ZCT catalysts than on the CT catalysts suggest that the redox properties of the CT catalysts were stabilized by Zr addition. The acidity of the catalyst with added Zr was better retained after K^+ poisoning, showing that destruction of the surface acidity was inhibited by Zr doping.

References

- [1] K. Skalska, J. S. Miller, S. Ledakowicz, *Sci. Total Environ.*, **2010**, 408, 3976–3989.
- [2] G. Busca, L. Lietti, G. Ramis, F. Berti, *Appl. Catal. B*, **1998**, 18, 1–36.
- [3] X. X. Cheng, X. T. Bi, *Particuology*, **2014**, 16, 1–18.
- [4] Z. M. Liu, S. I. Woo, *Catal. Rev.-Sci. Eng.*, **2006**, 48, 43–89.
- [5] B. Guan, R. Zhan, H. Lin, Z. Huang, *Appl. Therm. Eng.*, **2014**, 66, 395–414.
- [6] S. Roy, M. S. Hegde, G. Madras, *Appl. Energy*, **2009**, 86, 2283–2297.
- [7] L. Chen, Z. C. Si, X. D. Wu, D. Weng, R. Ran, J. Yu, *J. Rare Earths*, **2014**, 32, 907–917.
- [8] D. Nicosia, I. Czekaj, O. Kröcher, *Appl. Catal. B*, **2008**, 77, 228–236.
- [9] F. S. Tang, B. L. Xu, H. H. Shi, J. H. Qiu, Y. N. Fan, *Appl. Catal. B*, **2010**, 94, 71–76.
- [10] W. Q. Xu, Y. B. Yu, C. B. Zhang, H. He, *Catal. Commun.*, **2008**, 9, 1453–1457.
- [11] X. Gao, Y. Jiang, Y. Zhong, Z. Y. Luo, K. F. Cen, *J. Hazard. Mater.*, **2010**, 174, 734–739.
- [12] W. P. Shan, F. D. Liu, H. He, X. Y. Shi, C. B. Zhang, *Catal. Today*, **2012**, 184, 160–165.
- [13] W. P. Shan, F. D. Liu, Y. B. Yu, H. He, *Chin. J. Catal.*, **2014**, 35, 1251–1259.
- [14] Q. C. Li, S. F. Chen, Z. Y. Liu, Q. Y. Liu, *Appl. Catal. B*, **2015**, 164, 475–482.
- [15] Z. M. Liu, S. X. Zhang, J. H. Li, J. Z. Zhu, L. L. Ma, *Appl. Catal. B*, **2014**, 158–159, 11–19.
- [16] X. S. Du, X. Gao, R. Y. Qu, P. D. Ji, Z. Y. Luo, K. F. Cen, *ChemCatChem*, **2012**, 4, 2075–2081.
- [17] L. Chen, J. H. Li, M. F. Ge, *Chem. Eng. J.*, **2011**, 170, 531–537.
- [18] J. Due-Hansen, S. Boghosian, A. Kustov, P. Frisrup, G. Tsilomelekis, K. Stahl, C. H. Christensen, R. Fehrmann, *J. Catal.*, **2007**, 251, 459–473.
- [19] H. Q. Wang, X. B. Chen, S. Gao, Z. B. Wu, Y. Liu, X. L. Weng, *Catal. Sci. Technol.*, **2013**, 3, 715–722.
- [20] S. Verdier, E. Rohart, H. Bradshaw, D. Harris, Ph. Blchon, G. Delahay, *SAE Technical Paper*, 2008-01-1022, **2008**.
- [21] M. Machida, D. Kurogi, T. Kijima, *Chem. Mater.*, **2000**, 12, 3165–3170.
- [22] Z. M. Liu, Y. Yi, J. H. Li, S. I. Woo, B. Y. Wang, X. Z. Cao, Z. X. Li, *Chem. Commun.*, **2013**, 49, 7726–7728.
- [23] Y. Jiang, Z. M. Xing, X. C. Wang, S. B. Huang, X. W. Wang, Q. Y. Liu, *Fuel*, **2015**, 151, 124–129.
- [24] S. X. Yang, W. P. Zhu, Z. P. Jiang, Z. X. Chen, J. B. Wang, *Appl. Surf.*

Graphical Abstract

Chin. J. Catal., 2016, 37: 1354–1361 doi: 10.1016/S1872-2067(15)61102-0

Promotional effects of Zr on K⁺-poisoning resistance of CeTiO_x catalyst for selective catalytic reduction of NO_x with NH₃

Baoqiang Xu, Haidi Xu*, Tao Lin, Yi Cao, Li Lan, Yuanshan Li,
Xi Feng, Maochu Gong, Yaoqiang Chen*
Sichuan University; Sichuan Provincial Environmental Protection
Environmental Catalytic Materials Engineering Technology Center

CeTiO_x catalyst for NH₃-SCR reaction was seriously poisoned by K⁺. The addition of Zr inhibited the grain growth of anatase TiO₂, meaning that the “molten salt flux effect” caused by K⁺ loading was inhibited.

The addition of Zr promoted the K⁺ poisoning resistance of CeTiO_x catalyst

Sci., **2006**, 252, 8499–8505.

[25] P. Dutta, S. Pal, M. S. Seehra, Y. Shi, E. M. Eyring, R. D. Ernst, *Chem. Mater.*, **2006**, 18, 5144–5146.

[26] X. W. Liu, K. B. Zhou, L. Wang, B. Y. Wang, Y. D. Li, *J. Am. Chem. Soc.*, **2009**, 131, 3140–3141.

[27] N. Y. Topsoe, *Science*, **1994**, 265, 1217–1219.

[28] H. Kamata, K. Takahashi, C. U. I. Odenbrand, *J. Mol. Catal. A*, **1999**, 139, 189–198.

[29] M. Klimczak, P. Kern, T. Heinzelmann, M. Lucas, P. Claus, *Appl. Catal. B*, **2010**, 95, 39–47.

[30] R. T. Guo, Q. S. Wang, W. G. Pan, W. L. Zhen, Q. L. Chen, H. L. Ding, N. Z. Yang, C. Z. Lu, *Appl. Surf. Sci.*, **2014**, 317, 111–116.

Zr 的添加对 CeTiO_x NH₃-SCR 催化剂抗碱金属中毒能力的提升

徐宝强^a, 徐海迪^{b,c,*}, 林涛^a, 曹毅^a, 兰丽^a, 李元山^d, 冯锡^d, 龚茂初^a, 陈耀强^{a,c,#}

^a四川大学化学学院绿色化学与技术教育部重点实验室, 四川成都 610064

^b四川大学新能源与低碳技术研究院, 四川成都 610064

^c四川省环境保护环境催化材料工程技术中心, 四川成都 610064

^d四川大学化学工程学院, 四川成都 610064

摘要: CeTiO_x 具有高的 NH₃ 选择性催化还原 (NH₃-SCR) 活性和 N₂ 选择性, 被认为是具有应用前景的催化剂。但是, CeTiO_x 不抗碱金属中毒, 在含有大量 K 离子的生物质柴油的燃烧装置中中毒尤为严重, 因而限制了 CeTiO_x 催化剂在生物质燃料装置上的进一步应用。

本文通过在 CeTiO_x 催化剂中掺杂 Zr 元素来提升其抗 K⁺中毒的能力。采用共沉淀法制备了 CeTiO_x (CT) 和 CeZrTiO_x (ZCT) 两种 NH₃-SCR 催化剂。将不同含量的硝酸钾 (K⁺/Ce = 0.1, 0.2) 负载在催化剂表面, 焙烧处理后得到 K⁺中毒的催化剂 (K0.1-CT, K0.2-CT, K0.1-ZCT 和 K0.2-ZCT)。通过测定各催化剂的催化活性来研究 Zr 的添加对 CT 催化剂抗 K⁺中毒能力的影响。

NH₃-SCR 活性数据表明, CT 和 ZCT 催化剂都达到了接近 100% 的 NO_x 转化率, 且两种新鲜催化剂的催化性能基本无差别。浸渍不同含量的 K⁺之后, ZCT 催化剂明显优于 CT 催化剂: K0.1-CT 和 K0.1-ZCT 上的 NO_x 转化率分别为 90% 和 62%; 而 K0.2-CT 和 K0.2-ZCT 上分别为 48% 和 13%。可见, 随 K⁺添加, ZCT 催化剂活性降低更缓慢, 表明 Zr 的添加提高了 CT 催化剂抗 K⁺中毒能力。

BET 数据显示, 在新鲜催化剂中, Zr 的添加增加了催化剂比表面积和孔体积; K⁺中毒之后, ZCT 仍然表现出比 CT 更好的结构性能。X 射线衍射和拉曼光谱结果显示, 随着 K⁺负载量的增加, 锐钛矿 TiO₂ 的衍射峰逐渐变得尖锐, 说明无定形 TiO₂ 逐渐结晶并不断长大, 从而导致催化剂比表面积下降。与 CT 相比, 随着 K⁺负载量增加, 催化剂晶型并没有明显变化。这说明 Zr 的添加可以抑制锐钛矿 TiO₂ 的结晶及长大。由此可见 Zr 的添加可抑制因 K⁺中毒而引起的催化剂结构变化, 所以仍能保持较高的 NO_x 转化率。透射电镜 (TEM) 结果表明, 随着 K⁺负载量逐渐增加, 催化剂的晶粒尺寸逐渐变大: CT, K0.1-CT 和 K0.2-CT 的平均晶粒尺寸分别为 7, 13 和 15 nm, 而 ZCT 催化剂晶粒尺寸增大并不明显, 分别为 5, 8 和 10 nm。很明显, Zr 的添加抑制了催化剂晶粒长大, 从而提高了其结构稳定性能。综上所述, 由负载 KNO₃ 而引起的“熔盐效应”得到了有效抑制。

X 射线光电子能谱结果表明, 随着 K⁺负载量增加, CeZrTiO_x 催化剂的 Ce³⁺/Ce⁴⁺ 值下降得比 CeTiO_x 更缓慢, 说明加入 Zr 之后, 催化剂具有更多的晶格缺陷和氧空缺, 因而有利于 NH₃-SCR 活性的提高。

另外, 催化剂酸性也是影响 $\text{NH}_3\text{-SCR}$ 活性的关键因素. NH_3 程序升温脱附结果显示, Zr 的添加可以使 CeTiO_x 催化剂在 K^+ 中毒之后仍保持较高的酸性, 即 Zr 的添加抑制了 K^+ 对催化剂表面酸性的巨大破坏作用. 综上可知, Zr 的添加提升了 CeTiO_x 催化剂抗 K^+ 中毒能力.

关键词: 铈钛复合氧化物; 氧化锆; 抗钾中毒; 选择性催化还原; 氮氧化物

收稿日期: 2016-02-27. 接受日期: 2016-04-02. 出版日期: 2016-08-05.

*通讯联系人. 电话/传真: (028)85418451; 电子信箱: xuhaidi@scu.edu.cn

#通讯联系人. 电话/传真: (028)85418451; 电子信箱: nic7501@scu.edu.cn

基金来源: 四川省科技支撑计划 (2012FZ0008); 国家自然科学基金 (21173153); 国家高技术研究发展计划 (863 计划, 2013AA065304); 四川大学青年教师科研启动基金 (2015SCU11056).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).