available at www.sciencedirect.com

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

Article

Effects of silica additive on the NH_3 -SCR activity and thermal stability of a $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$ catalyst

Xuesong Liu^{a,b}, Xiaodong Wu^{a,b,*}, Tengfei Xu^a, Duan Weng^{a,b,#}, Zhichun Si^b, Rui Ran^a^a Key Laboratory of Advanced Materials of Ministry of Education, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China^b Advanced Materials Institute, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, Guangdong, China

ARTICLE INFO

Article history:

Received 4 February 2016

Accepted 14 April 2016

Published 5 August 2016

Keywords:

 $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$

Silica

 NH_3 -SCR

Hydrothermal stability

Polymeric vanadia

De- NO_x

ABSTRACT

$\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$ and $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2\text{-SiO}_2$ catalysts were prepared by a wetness impregnation method, and both the catalysts were hydrothermally aged at 750 °C in 10 vol% $\text{H}_2\text{O}/\text{air}$ for 24 h. The catalysts were evaluated for NO_x conversion using NH_3 as the reductant. Hydrothermal ageing decreased the NO_x conversion of $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$ catalyst severely over the entire measured temperature range. Interestingly, the NH_3 -SCR activity of the silica-modified catalyst at 220–480 °C is enhanced after ageing. The catalysts were characterized by X-ray diffraction, nitrogen adsorption, X-ray fluorescence, Raman spectroscopy, H_2 temperature-programmed reduction, and NH_3 temperature-programmed desorption. The addition of silica inhibited the phase transition from anatase to rutile titania, growth of TiO_2 crystallite size and shrinkage of catalyst surface area. Consequently, the vanadia species remained highly dispersed and the hydrothermal stability of the $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$ catalyst was significantly improved.

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

Published by Elsevier B.V. All rights reserved.

1. Introduction

Nitrogen oxides (NO_x) emitted from diesel engines are major air pollutants as they cause severe environmental issues, such as acid rain, photochemical smog, ozone depletion and haze events [1]. NO_x reduction has received much attention because of increasing environmental attention and stringent worldwide emission regulations [2,3]. Selective catalytic reduction (SCR) of NO_x by NH_3 in the presence of oxygen is the most widely used method for the control of NO_x emissions in exhaust gas from diesel engines because of its efficiency, selectivity and economy [4,5]. V_2O_5 is the most commonly used main active phase metal oxide catalyst because of its high catalytic efficiency and economy at a given mass percent. Anatase TiO_2 is em-

ployed as a support because of its large surface areas and porous structure. WO_3 is used as an active additive and structural promoter to stabilize the anatase phase of TiO_2 support, increase the catalyst surface acidity and to prohibit catalyst poisoning by SO_2 .

Although sulfur tolerant, one major problem confronted by $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts is their thermal deactivation in high-temperature exhaust gas, which can reach 750 °C under certain conditions [6]. The deactivation is primarily due to the poor thermal stability of the catalysts. High-temperature exposure of the catalysts can lead to TiO_2 sintering, phase transition from anatase TiO_2 into the inactive rutile phase and segregation or even volatilization of vanadia and tungsta species [7–10]. One way to improve the thermal stability of catalysts is to dope

* Corresponding author. Tel/Fax: +86-10-62792375; E-mail: wuxiaodong@tsinghua.edu.cn

Corresponding author. Tel/Fax: +86-10-62785986; E-mail: duanweng@tsinghua.edu.cn

This work was supported by the National Natural Science Foundation of China (51372137) and the National High Technology Research and Development Program of China (863 Program, 2015AA034603).

DOI: 10.1016/S1872-2067(15)61109-3 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 8, August 2016

the TiO₂ support with other components such as alumina, zirconia and silica [11]. Among these oxides, silica has been found to be a good candidate to improve TiO₂ support properties [12–14]. Wang et al. [12] found that the introduction of Si into TiO₂ not only hindered phase transformation and particle sintering, but also led to the generation of Ti³⁺ near the catalyst surface during the thermal diffusion process of Si and Ti atoms, which facilitated the photocatalytic degradation of methyl orange [12]. Kobayashi et al. [13] observed that the Brunauer-Emmett-Teller (BET) surface area and surface acid sites of Si-doped TiO₂ increased, but the oxidative property was weakened and the sulfur tolerance was thereby improved. Zhong et al. [14] concluded that TiO₂ supports doped with Si enhanced both the number of acid sites (especially Brönsted acids) and oxidation properties, which improved the deNO_x catalytic activity. However, little information on the mechanisms of thermal stability improvement by metal oxide-doping for vanadia-based SCR catalysts has been reported to date.

In the present study, V₂O₅/WO₃-TiO₂ and V₂O₅/WO₃-TiO₂-SiO₂ catalysts were hydrothermally treated at 750 °C in 10 vol% H₂O/air for 24 h. The NH₃-SCR activities of the fresh and hydrothermally aged catalysts were evaluated. The effects of silica modification on the structural properties and NH₃-SCR activities of catalysts were also investigated.

2. Experimental

2.1. Catalyst preparation

A V₂O₅/WO₃-TiO₂ catalyst with 1.5 wt% V₂O₅ and 8 wt% WO₃ was prepared via wetness impregnation [15]. NH₄VO₃ (Dalian Galaxy, Dalian, China) was dissolved in deionized water and mixed with commercial WO₃-TiO₂ (Millennium Inorganic Chemicals Inc., Thann, France) powders. The liquid was dried at 80 °C using a rotary evaporator employing a vacuum pump. The powders were dried at 100 °C for 12 h and calcined at 620 °C for 4 h, and the obtained catalyst was denoted as VWT. A V₂O₅/WO₃-TiO₂-SiO₂ catalyst with 1.5 wt% V₂O₅, 8 wt% WO₃ and 5 wt% SiO₂ was prepared by a similar method using NH₄VO₃ and WO₃-TiO₂-SiO₂ (Millennium Inorganic Chemicals Inc., Thann, France) powders as the precursors, and the obtained catalyst was denoted as VWTS. WO₃-TiO₂ and WO₃-TiO₂-SiO₂ powders were denoted as WT and WTS, respectively. The supports and catalysts were hydrothermally treated at 750 °C in 10 vol% H₂O/air for 24 h, and the aged samples were denoted with an “A” suffix.

2.2. Activity measurement

The NH₃-SCR activity was evaluated in a fixed-bed quartz reactor, and the effluent gases were monitored by an infrared spectrometer (Thermo Nicolet 380). The reaction gas consisted of 500 ppm NO, 500 ppm NH₃, 5% O₂, 10% H₂O and N₂ in balance. The flow rate of the reaction gas was 1000 mL/min, the amount of catalyst (sieved to 50–80 mesh) used was 300 mg, and the gas hourly space velocity (GHSV) was maintained at 100000 h⁻¹. The concentrations of NO_x (NO, N₂O, and NO₂)

were detected at the ppm level. The NO_x conversion and N₂ selectivity of the catalysts were calculated using Eqs. (1) and (2).

$$\text{NO}_x \text{ conversion (\%)} = (\text{NO}_{\text{in}} - \text{NO}_{\text{out}} - \text{NO}_{2\text{out}} - 2\text{N}_2\text{O}_{\text{out}}) / \text{NO}_{\text{in}} \times 100 \quad (1)$$

$$\text{N}_2 \text{ selectivity (\%)} = 2\text{N}_{2\text{out}} / (2\text{N}_{2\text{out}} + 2\text{N}_2\text{O}_{\text{out}} + \text{NO}_{2\text{out}}) \times 100 \quad (2)$$

2.3. Characterization

X-ray powder diffraction (XRD) patterns were recorded on a diffractometer (D8 ADVANCE, Bruker, Germany) employing Cu K_α radiation (λ = 0.15418 nm). Data were collected from 10° ≤ 2θ ≤ 80° with a scanning velocity of 6°/min. The crystallite sizes and phase percentages of the samples were determined by the Rietveld method, using JADE 6.0 software.

Textural properties were determined by nitrogen physisorption at −196 °C using a JW-BK122F (Beijing JWGB, China) instrument. Prior to the measurements, the samples were degassed at 0.01 Pa at 220 °C. The specific surface area and desorption pore volume were assessed using the BET and Barrett-Joyner-Halenda methods, respectively.

Elemental analysis of samples was performed by means of X-ray fluorescence analysis (XRF) on an XRF-1800 instrument (Shimadzu, Japan).

Raman measurements were performed on a Renishaw RM1000 (Renishaw, British) with a confocal microprobe Raman system using a 633 nm (Ar⁺ laser) laser as the excitation source with two scans at a dwell time of 20 s, resolution of 1 cm⁻¹, and power of 50%.

Hydrogen temperature-programmed reduction (H₂-TPR) was performed on a Micromeritics Auto Chem II. Prior (Micromeritics, USA) to the H₂-TPR experiment, the tested sample (50 mg) was treated with He at a total flow rate of 50 mL·min⁻¹ at 300 °C for 30 min and subsequently cooled to room temperature and flushed with He for 10 min. The atmosphere was then changed to 10% H₂/Ar (50 mL·min⁻¹), and the reactor temperature was raised to 600 °C at a heating rate of 10 °C·min⁻¹. H₂ consumption during the experiment was monitored with a thermal conductivity detector.

Ammonia temperature-programmed desorption (NH₃-TPD) analysis was performed using a TP 5000-II multiple adsorption apparatus (Xianquan, China). The samples (50 mg) were pre-treated in He at 500 °C for 30 min. When the temperature decreased to 50 °C, NH₃ was introduced until adsorption on the samples was saturated. The samples were then purged with He to remove residual NH₃ from the surface of the samples. The samples were then heated in He from 100 to 500 °C at a rate of 10 °C·min⁻¹ for subsequent NH₃ desorption. The NH₃ concentration in the outlet gas was monitored by a thermal conductivity detector.

3. Results and discussion

3.1. Structural properties

The XRD patterns of the supports and catalysts are shown in

Fig. 1. For the support, all the XRD peaks are from TiO_2 anatase phase. After hydrothermal treatment, the diffraction peaks assigned to anatase- TiO_2 become sharper and more intense. The addition of silica in the support appears to partially prevent the sintering of TiO_2 ; however, the BET surface areas of the aged supports are similar to each other. It is noted that vanadia loading accelerates the phase transition of TiO_2 . Typical rutile diffraction peaks are observed in the pattern of the aged $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$ catalyst (VWTA). Low melting point active metal oxides accelerate the support sintering and crystal transformation upon thermal ageing. This is consistent with the promoting effects of vanadia on TiO_2 sintering and anatase to rutile transformation [16]. In addition, the hydrothermal treatment leads to the segregation of WO_3 as evidenced by its characteristic peaks. Consequently, the average crystallite size increases drastically from 19.5 to 56.0 nm, and the specific surface area of VWTA decreases to only $3 \text{ m}^2\cdot\text{g}^{-1}$. By introducing SiO_2 , no rutile- TiO_2 and WO_3 are detected on the aged $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2\text{-SiO}_2$ catalyst (VWTSA). This is attributed to the formation of $\text{Si}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions that are distributed at the interface of TiO_2 crystallites. These solid solutions increase the crystal boundary energy and inhibit the transition and sintering of anatase- TiO_2 [12,13]. In addition, the (101) diffraction peaks of anatase TiO_2 of the aged catalysts and supports are shown in Fig. 2. They shift towards slightly higher angles for VWTSA and WTSA, perhaps due to the interaction between silica and titania. Shi et al. [17] observed a slight shift of the (101) peak to lower 2θ values and attributed this to the formation of $\text{Zr}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions. The ionic radius of the met-

Fig. 1. XRD patterns of the supports (a) and catalysts (b).

Fig. 2. XRD patterns of the (101) diffraction peaks of anatase TiO_2 of the aged catalysts and supports.

als follows the order of $\text{Si} > \text{Ti} > \text{Zr}$, and thus the formation of $\text{Si}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions would result in the shift of the (101) peak towards higher angles. Combining this with the BET and XRD results, it can be concluded that the thermal stability of anatase- TiO_2 in the supported catalyst is significantly improved by silica addition.

As indicated by the XRF results in Table 1, the measured V_2O_5 contents in the catalysts are very close to the nominal value, and no loss of V_2O_5 and WO_3 occurred after the hydrothermal treatment. The sulfur content in the catalysts decreases in both the supports and catalysts after hydrothermal treatment.

3.2. Catalytic activity

The temperature dependency of NO_x conversion during the $\text{NH}_3\text{-SCR}$ reaction over the catalysts is shown in Fig. 3(a). On the fresh catalysts, above 80% NO_x conversions are obtained at $350\text{--}550^\circ\text{C}$, and the introduction of SiO_2 decreases the NO_x conversion slightly over the whole temperature range. After the hydrothermal treatment, VWTA deactivates severely, with negative NO_x conversion observed at 550°C due to the over-oxidation of NH_3 to NO_x . It is noted that the hydrothermal treatment improves the activity of the SiO_2 modified catalyst from 220 to 530°C . Fig. 3(b) shows the N_2 selectivity of the catalysts for the $\text{NH}_3\text{-SCR}$ reaction. The N_2 selectivity decreases at high temperatures ($> 350^\circ\text{C}$) over all the catalysts due to the formation of N_2O and NO_2 . It is more significant for the VWTA catalyst and is consistent with the negative NO_x conversion at 550°C . Possible explanations will be given in the following sections.

3.3. Raman spectra

The state of vanadia in the catalyst is the main factor affecting the catalytic behaviour. Fig. 4 shows the Raman spectra of the catalysts under ambient conditions from $1100\text{--}750 \text{ cm}^{-1}$,

Table 1

Structural properties of the samples.

Sample	Phase composition ^a (wt%)			Anatase TiO ₂ crystalline size ^a (nm)	Concentration ^b (wt%)					T ^c	S _{BET} (m ² /g)
	Anatase	Rutile	WO ₃		V ₂ O ₅	WO ₃	TiO ₂	SiO ₂	SO ₃		
WT	100	—	—	18.7	—	8.1	91	—	0.5	0.40	72
WTS	100	—	—	16.6	—	7.8	86	5.5	0.4	0.30	81
WTA	100	—	—	26.3	—	7.9	92	—	0.04	0.06	49
WTSa	100	—	—	18.3	—	7.9	86	5.7	0.04	0.36	53
VWT	100	—	—	19.5	1.47	7.9	90	—	0.3	0.33	52
VWTS	100	—	—	14.6	1.48	7.7	85	5.4	0.2	0.22	71
VWTA	86.3	7.9	5.8	56.0	1.49	8.0	90	—	0.04	0.47	3
VWTSa	100	—	—	23.4	1.50	8.1	85	5.3	0.02	0.08	35

^a Obtained by XRD. ^b Obtained by XRF. ^c Trace metal oxides.

which provides evidence for different states of surface vanadia. All the catalysts exhibit an intense band at 800 cm⁻¹ corresponding to the Ti–O vibration of TiO₂ [18]. For the fresh catalysts, the broad band at 980–990 cm⁻¹ is assigned to the symmetric V=O stretching mode from a combination of monomeric and polymeric surface vanadia [18–20]. After the hydrothermal treatment, a new band at 1011 cm⁻¹ is observed for the SiO₂ modified catalyst, which is assigned to crystalline V₂O₅ [20]. Broadly speaking, the band attributed to vanadia species disappears for VWTA. This suggests that Ti–V–O solid solutions form during hydrothermal treatment, due to the shrinkage of TiO₂ [21]. The shift of the surface vanadia species-related band from 980 to 990 cm⁻¹ reflects the transformation from mono-

meric vanadia to polymeric species on VWTSa. Polymeric surface vanadia is considered the main active species and plays a crucial role in the SCR reaction [18]. Hence, this transition of vanadia species is responsible for the enhancement of catalytic activity of VWTSa compared with the fresh catalyst.

3.4. H₂-TPR studies

H₂-TPR is commonly used for determining types of vanadia species and the redox properties of catalysts. Fig. 5 shows the TPR curves of the fresh and hydrothermally aged catalysts. Three reduction peaks are observed from 300–900 °C. For the fresh catalysts, the peak observed at 400–500 °C is attributed to the reduction of V⁵⁺ → V³⁺ of monomeric surface vanadia species [18,19]. The peak at 500–570 °C is attributed to the co-reduction of V⁵⁺ → V³⁺ of polymeric surface vanadia species and W⁶⁺ → W⁴⁺ of tungsten oxide [18,19]. The third peak, at around 800 °C, is caused by the hydrogen consumption of W⁴⁺ → W⁰ [20]. The two reduction peaks shift towards lower temperatures with SiO₂ addition, which is attributed to a better dispersion of vanadia on the high surface area WO₃-TiO₂-SiO₂ support [22] and correlates well with the Raman results. This indicated that SiO₂ addition decreases the amount of the most active polymeric species, which is consistent with the catalytic activities of the fresh catalysts.

Fig. 3. NO_x conversion (a) and N₂ selectivity (b) of the fresh and hydrothermally aged catalysts for the NH₃-SCR reaction. Reaction conditions: NO 500 ppm, NH₃ 500 ppm, O₂ 5%, H₂O 10% and N₂ in balance. GHSV = 100000 h⁻¹.

Fig. 4. Raman spectra of the fresh and hydrothermally aged catalysts.

Fig. 5. H₂-TPR curves of the fresh and hydrothermally aged catalysts.

For the hydrothermally aged catalysts, the peak observed at 370–500 °C is attributed to the co-reduction of $V^{5+} \rightarrow V^{3+}$ of polymeric surface vanadia species and $W^{6+} \rightarrow W^{4+}$ [17,19]. The second peak, at approximately 600 °C, is attributed to the co-reduction of $V^{5+} \rightarrow V^{3+}$ of crystalline vanadia or vanadia in Ti-V-O solid solutions and $W^{6+} \rightarrow W^{4+}$. The third peak, centred at approximately 800 °C, is caused by the hydrogen consumption of $W^{4+} \rightarrow W^0$. Compared with the fresh catalyst, the reduction peaks of VWTSA corresponding to polymeric surface vanadia species shift towards lower temperatures by interacting with the surface WO_3 generated from hydrothermal treatment [23]. The reducibility of VWTA is severely weakened, and the reduction peaks corresponding to monomeric/polymeric surface vanadia species almost disappear. Instead, a sharp peak assigned to the reduction of inactive Ti-V-O solid solutions is observed [21].

3.5. NH₃-TPD studies

The surface acidity of V_2O_5/TiO_2 catalysts plays an important role in the SCR of NO by NH₃ [24–26]. Ammonia is widely used as a molecular probe to identify types of surface acidic sites. Therefore, NH₃-TPD was performed to investigate the loss in surface acidity of samples caused by the hydrothermal treatment. Fig. 6 shows the NH₃-TPD curves of the fresh and hydrothermally aged supports and catalysts from 100 to 500 °C. As shown in Fig. 6(a), all the curves exhibit three NH₃ desorption peaks centred at approximately 180, 250 and 390 °C, which correspond to weakly bound and strongly bound ammonia respectively related to two different acid sites in intensity [27,28]. The addition of SiO₂ leads to an increase in the number and strength of acid sites on VWTSA, which may be related to the enhancement of a positive charge at Ti–O or Si–O bonds by mixing with SiO₂ or TiO₂ [29]. After the hydrothermal treatment, a significant decrease in surface acidity is observed on VWTA, which should be an important factor responsible for the negative NO_x conversion at high temperatures. Contrarily,

Fig. 6. NH₃-TPD profiles of the fresh and hydrothermally aged catalysts (a) and supports (b).

the loss in surface acidity of VWTSA is much smaller. The effects of silica addition on the surface acidity and hydrothermal stability of the support are similar to the trends of the supported catalysts. Vanadia loading enlarges the difference between the surface acidity of the aged catalysts, which is consistent with the variations in the structural/textural properties listed in Table 1.

4. Conclusions

The roles of silica in the structural properties and NH₃-SCR activity of a V_2O_5/WO_3-TiO_2 catalyst before and after hydrothermal treatment were investigated. The SiO₂-containing catalyst is slightly less active because of the formation of more monomeric surface vanadia species. However, the V_2O_5/WO_3-TiO_2 is severely deactivated after ageing, while the NH₃-SCR activity of the modified catalyst is improved. The superior hydrothermal stability of the $V_2O_5/WO_3-TiO_2-SiO_2$ catalyst is mainly attributed to the stabilizing effect of silica on anatase-TiO₂ via the formation of Ti–O–Si solid solutions at the interface of TiO₂ crystallites. The stable textural property of the modified support results in a relatively high dispersion of vanadia in the form of polymeric species other than V₂O₅ crystallites after hydrothermal treatment. Furthermore, the addition of silica enhances the quantity and strength of surface acid sites, which is also important for SCR reactions, especially at high temperatures.

Graphical Abstract

Chin. J. Catal., 2016, 37: 1340–1346 doi: 10.1016/S1872-2067(15)61109-3

Effects of silica additive on the NH₃-SCR activity and thermal stability of a V₂O₅/WO₃-TiO₂ catalyst

Xuesong Liu, Xiaodong Wu*, Tengfei Xu, Duan Weng*, Zhichun Si, Rui Ran
Tsinghua University

The stable textural property of the TiO₂-WO₃-SiO₂ support results in a relatively high dispersion of vanadia in the form of the most active polymeric species besides V₂O₅ crystallites after hydrothermal treatment.

References

- [1] R. J. Huang, Y. L. Zhang, C. Bozzetti, K. F. Ho, J. J. Cao, Y. Han, K. R. Daellenbach, J. G. Slowik, S. M. Platt, F. Canonaco, P. Zotter, R. Wolf, S. M. Pieber, E. A. Bruns, M. Crippa, G. Ciarelli, A. Piazzalunga, M. Schwikowski, G. Abbaszade, J. Schnelle-Kreis, R. Zimmermann, Z. An, S. Szidat, U. Baltensperger, I. E. Haddad, A. S. H. Prevot, *Nature*, **2014**, 514, 218–222.
- [2] G. Busca, L. Lietti, G. Ramis, F. Berti, *Appl. Catal. B*, **1998**, 18, 1–36.
- [3] V. I. Parvulescu, P. Grange, B. Delmon, *Catal. Today*, **1998**, 46, 233–316.
- [4] L. Lietti, P. Forzatti, F. Bregani, *Ind. Eng. Chem. Res.*, **1996**, 35, 3884–3892.
- [5] S. L. Lin, W. J. Lee, L. Chia-Fon, S. J. Chen, *Energy Fuels*, **2010**, 24, 4522–4533.
- [6] M. A. L. Vargas, M. Casanova, A. Trovarelli, G. Busca, *Appl. Catal. B*, **2007**, 75, 303–311.
- [7] B. M. Reddy, I. Ganesh, B. Chowdhury, *Catal. Today*, **1999**, 49, 115–121.
- [8] I. Nova, L. Dall'Acqua, L. Lietti, E. Giamello, P. Forzatti, *Appl. Catal. B*, **2001**, 35, 31–42.
- [9] S. Djerad, L. Tifouti, M. Crocoll, W. Weisweiler, *J. Mol. Catal. A*, **2004**, 208, 257–265.
- [10] J. W. Choung, I. S. Nam, S. W. Ham, *Catal. Today*, **2006**, 111, 242–247.
- [11] D. M. Chapman, *Appl. Catal. A*, **2011**, 392, 143–150.
- [12] Y. F. Wang, Y. P. Sun, *J. Chin. Ceram. Soc.*, **2011**, 39, 204–209.
- [13] M. Kobayashi, R. Kuma, S. Masaki, N. Sugishima, *Appl. Catal. B*, **2005**, 60, 173–179.
- [14] Y. X. Pan, W. Zhao, Q. Zhong, W. Cai, H. Y. Li, *J. Environ. Sci.*, **2013**, 25, 1703–1711.
- [15] X. S. Liu, X. D. Wu, D. Weng, Z. C. Si, *Catal. Commun.*, **2015**, 59, 35–39.
- [16] S. Djerad, L. Tifouti, M. Crocoll, W. Weisweiler, *J. Mol. Catal. A*, **2004**, 208, 257–265.
- [17] A. J. Shi, X. Q. Wang, T. Yu, M. Q. Shen, *Appl. Catal. B*, **2011**, 106, 359–369.
- [18] W. C. Yu, X. D. Wu, Z. C. Si, D. Weng, *Appl. Surf. Sci.*, **2013**, 283, 209–214.
- [19] C. Z. Wang, S. J. Yang, H. Z. Chang, Y. Peng, J. H. Li, *Chem. Eng. J.*, **2013**, 225, 520–527.
- [20] S. S. R. Putluru, L. Schill, A. Godiksen, R. Poreddy, S. Mossin, A. D. Jensen, R. Fehrmann, *Appl. Catal. B*, **2016**, 183, 282–290.
- [21] M. Casanova, E. Rocchini, A. Trovarelli, K. Scherzmann, I. Begsteiger, *J. Alloys. Compd.*, **2006**, 408–412, 1108–1112.
- [22] H. Y. Zhao, S. Bennici, J. Y. Shen, A. Auroux, *J. Catal.*, **2010**, 272, 176–189.
- [23] C. Z. Sun, L. H. Dong, W. J. Yu, L. C. Liu, H. Li, F. Gao, L. Dong, Y. Chen, *J. Mol. Catal. A*, **2011**, 346, 29–38.
- [24] P. Forzatti, *Appl. Catal. A*, **2001**, 222, 221–236.
- [25] L. Chena, J. H. Li, M. F. Ge, *Chem. Eng. J.*, **2011**, 170, 531–537.
- [26] M. A. L. Vargas, M. Casanova, A. Trovarelli, G. Busca, *Appl. Catal. B*, **2007**, 75, 303–311.
- [27] D. Nicosia, M. Elsener, O. Kröcher, P. Jansohn, *Top. Catal.*, **2007**, 42–43, 333–336.
- [28] L. Lietti, I. Nova, G. Ramis, L. Dall'Acqua, G. Busca, E. Giamello, P. Forzatti, F. Bregani, *J. Catal.*, **1999**, 187, 419–435.
- [29] K. Tanabe, T. Sumiyoshi, K. Shibata, T. Kiyoura, J. Kitagawa, *J. Bull. Chem. Soc. Jpn.*, **1974**, 47, 1064–1066.

Si改性对V₂O₅/WO₃-TiO₂催化剂NH₃-SCR活性和热稳定性的影响

刘雪松^{a,b}, 吴晓东^{a,b,*}, 许腾飞^a, 翁端^{a,b,#}, 司知鑫^b, 冉锐^a

^a清华大学材料学院, 先进材料教育部重点实验室, 北京100084

^b清华大学深圳研究生院, 新材料研究所, 广东深圳518055

摘要: V₂O₅/WO₃-TiO₂是NH₃-SCR领域应用最为广泛的商用脱硝催化剂, 该催化剂具有良好的抗硫中毒性能; 但其水热稳定性却相对较差, 高温条件下运行会严重失活。这主要是由于锐钛型TiO₂在高温下发生团聚或相变, 生成比表面积较小的晶红石型TiO₂, 进而导致活性组分V₂O₅和WO₃团聚或挥发。结局问题的关键是提高载体TiO₂的水热稳定性, 而添加Al, Zr和Si等元素对TiO₂进行改性则被认为是最有效的方法之一。Si改性的V₂O₅/WO₃-TiO₂催化剂水热老化后仍然具有较

高的比表面积、较多的酸性位和稳定晶体结构,但其作用机理仍不明确. 本文分别考察了 750 °C 水热老化处理 24 h 对 V_2O_5/WO_3-TiO_2 和 $V_2O_5/WO_3-TiO_2-SiO_2$ 催化剂结构和催化活性的影响,并采用 X 射线衍射 (XRD)、氢气程序升温还原 (H_2 -TPR)、拉曼光谱 (Raman) 和氨气程序升温脱附 (NH_3 -TPD) 等手段研究了 Si 改善 V_2O_5/WO_3-TiO_2 催化剂水热稳定性的原因.

结果表明,水热老化后, Si 改善的催化剂和载体的比表面积降幅较小. XRD 结果表明, Si 添加到 TiO_2 中可形成 Ti-O-Si 固溶体,固溶体的形成使 TiO_2 晶界能提高,可防止水热老化过程中 TiO_2 的团聚和相变,进而提高其水热稳定性. 负载 V 后, Si 对载体的稳定作用则更加明显. 这主要是因为低熔点的 V_2O_5 会加剧载体的团聚和相变. 结合 H_2 -TPR 和 Raman 结果可知, V_2O_5/WO_3-TiO_2 催化剂水热老化后发生 TiO_2 团聚或相变,进而导致活性组分多聚态 V_2O_5 团聚生成 V_2O_5 晶粒或 Ti-V-O 固溶体,而后者对 SCR 反应活性的贡献非常低;同时,水热老化还使得助剂 WO_3 从 WO_3-TiO_2 中脱离出来,因而导致催化剂活性和选择性下降. 然而由于 $V_2O_5/WO_3-TiO_2-SiO_2$ 催化剂载体具有良好水热稳定性,经水热处理后仍保持着锐钛晶型和较小的晶粒,抑制了活性组分 V_2O_5 的严重团聚或形成固溶体;同时还使得高分散态 V_2O_5 轻微团聚形成主要活性组分多聚态 V_2O_5 ,因此催化活性反而提高.

另外,由于 $V_2O_5/WO_3-TiO_2-SiO_2$ 催化剂中形成了 Ti-O-Si 固溶体,进而产生更多的酸性位,水热处理后,其酸性位降低幅度较小;而 V_2O_5/WO_3-TiO_2 催化剂酸性位数量明显减少,这与其载体和活性组分的烧结和相变相关,这也是导致其失活的主要原因之一.

关键词: V_2O_5/WO_3-TiO_2 ; 硅; NH_3 -SCR; 水热稳定性; 多聚态钒; 脱硝

收稿日期: 2016-02-04. 接受日期: 2016-04-14. 出版日期: 2016-08-05.

*通讯联系人. 电话/传真: (010)62792375; 电子信箱: wuxiaodong@tsinghua.edu.cn

#通讯联系人. 电话/传真: (010)62785986; 电子信箱: duanweng@tsinghua.edu.cn

基金来源: 国家自然科学基金(51372137); 国家高技术研究发展计划(863计划, 2015AA034603).

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>).