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Article

Potassium poisoning of titania supported deNO_x catalysts: Preservation of vanadia and sacrifice of tungsten oxide

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ARTICLE INFO

Article history:

Received 27 March 2015

Accepted 28 April 2015

Published 20 August 2015

Keywords:

Vanadia

Tungsten oxide

Selective catalytic reduction

Alkali deactivation

Active site

Sacrificial agent

ABSTRACT

V₂O₅-WO₃/TiO₂ catalysts were prepared by a wet impregnation method, and the deactivation by KCl of their catalytic activity for selective catalytic reduction of NO_x by NH₃ (NH₃-SCR) was investigated. The fresh and poisoned catalysts were characterized by inductively coupled plasma (ICP), N₂ adsorption, Raman spectroscopy, H₂ temperature-programmed reduction, IR spectroscopy of adsorbed NH₃, and NH₃ oxidation. Vanadia species, which are the active sites for the SCR reaction, were turned into inert potassium vanadate, but they were partially maintained on the catalyst at a high vanadia loading. Tungsten oxide acts as a sacrificial agent that reacts with potassium to form potassium tungstate in addition to its roles in increasing the surface acidity of the catalyst and facilitating the dispersion of vanadia. The V₂O₅-WO₃/TiO₂ catalyst at a high vanadia loading exhibited the best resistance to alkali poisoning.

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1. Introduction

V₂O₅-WO₃/TiO₂ catalysts usually contain 0.5%–3% V₂O₅, 8%–10% WO₃ and TiO₂ as the support, and have been widely adopted for the selective catalytic reduction of NO_x by NH₃ (NH₃-SCR) [1–6]. Exhaust gas from stationary sources such as power plants always contains alkali oxides and salts which can deactivate the catalyst. Potassium exhibits the most serious poisoning effect on vanadium-based catalysts of the alkali and alkali earth metals [7–10]. Among different potassium salts, potassium chloride gives severe deactivation [11–13].

It is generally accepted that the alkali interacts strongly with dispersed vanadia species, neutralizes Brønsted acid sites, decreases the ammonia adsorption capacity and reduces the redox property, leading to a decrease in the SCR activity of cata-

lyst. However, the potassium poisoning mechanism of V₂O₅-WO₃/TiO₂ catalysts has not been well established. The roles of vanadia and especially tungsten oxide in this process have not been clearly clarified. For example, Wan et al. [7] suggested that the formation of inactive metavanadate species such as KVO₃ is responsible for the deactivation caused by alkali (earth) metals on V₂O₅-WO₃/TiO₂ catalysts. Nevertheless, they did not give proof of the existence of these inactive species. Bulushev et al. [13] identified the vanadia species in K-doped V₂O₅/TiO₂ catalysts by H₂ temperature-programmed reduction and FT-Raman spectroscopy as a function of the K/V ratio. They found that K-doped monomeric species were formed with the addition of a small amount of K, and more amorphous KVO₃ existed on the surface at K/V = 1. In our previous study [14], the alkali resistance of V₂O₅-WO₃/TiO₂ cata-

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This work was supported by the National High Technology Research and Development Program of China (863 Program, 2013AA065302) and the Key Laboratory of Solid Waste Reuse for Building Materials (SWR-2013-003).

DOI: 10.1016/S1872-2067(15)60881-6 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 36, No. 8, August 2015

lysts prepared by different impregnation methods was investigated. The wet-impregnated sample with more polymeric vanadia species was found to be less sensitive to potassium than the isolated vanadia species. Kamata et al. [15] also confirmed the formation of KVO_3 on K-impregnated $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst by Raman spectroscopy. They suggested that potassium probably coordinates to the hydroxyl groups on WO_3 but without any experimental evidence support. Thus, it is important to identify the interaction between potassium and the different components from the impregnation of KCl on $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts, and clarify the roles of tungsten oxide and vanadia in the alkali resistance of the catalyst.

In the present work, $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts of various compositions were treated with KCl to investigate their alkali resistance. The surface acidity, structural, textural and redox properties of the catalysts were characterized by a series of methods. The specific roles of vanadia and especially tungsten oxide in the chemical deactivation of the catalysts were discussed.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by excess water solution impregnation. Nano TiO_2 powders (Millennium Chemicals DT51, USA, $S_{\text{BET}} = 81 \text{ m}^2/\text{g}$) were mixed with the ammonium paratungstate solution (Beijing Chemical Reagent, China) by magnetic stirring for 1 h. The mixture was dried at 110°C overnight and calcined at 450°C for 4 h in air to obtain the WO_3/TiO_2 (WT) powders. The nominal mass loading amount of WO_3 was 10%. $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts were prepared by a similar impregnation method using ammonium metavanadate (Beijing Chemical Reagent, China, 99.9%) as the precursor. The catalysts obtained with a nominal V_2O_5 mass loading amount of 1% and 3% were denoted as V1T and V3T, respectively. The $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts were also prepared by impregnating ammonium metavanadate on the WT powder. The catalysts obtained were denoted as V1WT and V3WT, respectively.

The potassium poisoned catalysts were prepared by impregnating an aqueous solution of KCl on the fresh samples with a nominal mass ratio 0.83% of K. The impregnated powders were then dried overnight and calcined at 450°C for 2 h. The samples were denoted as WT-K, V1T-K, V3T-K, V1WT-K and V3WT-K, respectively. According to the TGA study by Salinas et al. [16], the phase transformation from anatase to potassium titanate in 20% $\text{KNO}_3/\text{TiO}_2$ occurred at 670°C , which was much higher than the calcination temperature (450°C). In addition, the K/Ti ratio was also much higher than the K/Ti ratios in the poisoned catalysts. Thus, the formation of potassium titanate was not considered in the present work.

2.2. Activity measurement

The $\text{NH}_3\text{-SCR}$ activity measurement was carried out in a fixed-bed reactor with 200 mg of catalysts (diluted to give 1 mL with silica pellets). The reaction gas mixture consisted of

$5 \times 10^{-4} \text{ NO}$, $500 \times 10^{-4} \text{ NH}_3$, 5% O_2 and N_2 balance. Prior to the measurement, the catalysts were treated in a 20% $\text{O}_2\text{-80\% N}_2$ flow at 450°C for 30 min. The measurement was performed at fixed temperatures from 150 to 450°C with 50°C intervals and kept for 20 min at each point. The gas hourly space velocity (GHSV) was 30000 h^{-1} . The feed and product concentrations were measured by a Nicolet 380 apparatus (ThermoFisher, USA) at 120°C . The NO_x (NO , NO_2 and N_2O) conversions were calculated as $\text{NO}_x \text{ conversion (\%)} = (\text{NO}_{\text{in}} - \text{NO}_{\text{out}} - \text{NO}_{2\text{out}} - 2\text{N}_2\text{O}_{\text{out}})/\text{NO}_{\text{in}} \times 100$.

2.3. Catalyst characterization

The inductively coupled plasma (ICP) analysis was carried out using an ICP emission spectrometer (Vista-MPX, Varian, USA). The specific surface areas of the samples were measured using N_2 adsorption at -196°C by the four-point Brunauer-Emmett-Teller (BET) method using an automatic surface analyzer (F-Sorb 3400, Gold APP, China). The samples were degassed in vacuum at 200°C for 2 h before the measurement. The Raman spectra of the samples were obtained at ambient condition on a confocal micro-Raman apparatus (IDSpec Aurora, China) using Ar^+ laser with a CCD detector. Pure powder supported on a sheet glass was used without any pretreatment and the wavelength of laser was 632.8 nm and the exposure time was 20 s while the spectra were recorded.

H_2 temperature-programmed reduction ($\text{H}_2\text{-TPR}$) was conducted on a chemical adsorption instrument AutoChem II 2920 (Micromeritics, USA). Prior to the test, 100 mg catalyst was purged in O_2 (50 mL/min) at 500°C for 30 min and then cooled down to room temperature. The reactor temperature was raised to 900°C at a heating rate of $10^\circ\text{C}/\text{min}$ in 10% $\text{H}_2\text{-90\% Ar}$ (50 mL/min).

The *in situ* infrared (IR) spectra of ammonia adsorption were recorded on a Nicolet 6700 FT-IR spectrometer (ThermoFisher, USA) equipped with an MCT detector. The catalyst was pretreated in 20% $\text{O}_2\text{-80\% N}_2$ flow (100 mL/min) at 500°C for 30 min, and then saturated with ammonia ($500 \times 10^{-4} \text{ NH}_3$ in N_2 , 100 mL/min) for 30 min. After purging in N_2 for 30 min at different temperatures (from 50 to 450°C at intervals of 50°C), the spectra were collected by accumulating 32 scans at a resolution of 4 cm^{-1} .

3. Results and discussion

3.1. Catalytic activity

Figure 1 shows the $\text{NH}_3\text{-SCR}$ activity of the fresh and poisoned catalysts. As shown in Fig. 1(a), the two fresh $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts showed much higher deNO_x activity than WO_3/TiO_2 , indicating that vanadia species are the active sites for the SCR reaction. Increasing the vanadia loading enhances the catalytic activity of the catalyst [17,18]. Meanwhile, the addition of tungsten oxide improved the deNO_x efficiency of the $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts significantly, as has been reported [1]. The V3WT catalyst achieved above 90% NO_x conversion in a wide temperature window $200\text{--}450^\circ\text{C}$. Almost no NO_2 or N_2O was detected in the

Fig. 1. NH_3 -SCR activity of (a) fresh and (b) poisoned catalysts. Reaction conditions: $\text{NO} = \text{NH}_3 = 5 \times 10^{-4}$, $\text{O}_2 = 5\%$, N_2 in balance, $\text{GHSV} = 30000 \text{ h}^{-1}$.

downstream gas in the whole temperature region, indicating that a high selectivity to N_2 was achieved for all the fresh catalysts.

After impregnation with KCl, the catalysts were deactivated to different degrees as shown in Fig. 1(b). The NO_x conversion of $\text{WO}_3/\text{TiO}_2\text{-K}$ was always close to zero within the whole temperature range measured, and that of V1T-K was generally below 10%. The maximum NO_x conversion of V1WT-K and V3T-K catalysts were 41% and 50% at 350 °C, respectively. V3WT-K exhibited relatively high activity at low temperatures, with the maximum NO_x conversion of 60% was achieved at 250 °C. Notably, the NO_x conversion turned negative (−45%) at 450 °C due to the over-oxidation of ammonia to NO_x at high temperatures. Again, almost no NO_2 or N_2O was detected for these poisoned catalysts, implying that the main product of ammonia oxidation was NO .

3.2. Solid properties

In order to determine the contents of vanadium, tungsten and potassium, ICP measurements were applied. The results are listed in Table 1. It is clear that the poisoned catalysts have similar contents of V_2O_5 and WO_3 to the corresponding fresh catalysts. No significant loss of vanadia occurred because of the alkali poisoning treatment adopted. It has been reported in our previous study that due to its high volatility, the residual content of chloride on $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ was much lower than that of potassium [11]. A similar phenomenon is observed in this work. We also found that the catalyst was hardly deactivated by

such low contents of Cl [11], and therefore the influence of chloride is not discussed here. V3WT-K and V3T-K with a high vanadia loading maintained a similar K content to the nominal mass value (0.83%), while a little bit of potassium were leached out of the V1WT-K, V1T-K and WT-K catalysts. The fresh catalysts have similar BET surface areas of 80–83 m^2/g , which were close to that of the titania support (81 m^2/g). The poisoned catalysts experienced a small loss in the surface area due to pore blocking by the potassium salt. Based on the above results, the physical properties including the potassium content and surface area were not responsible for the different deactivation degree of the catalysts.

3.3. Raman spectra

The states of the tungsten oxide and especially vanadia species on the catalysts are important in determining the catalytic behavior of catalyst. Fig. 2 shows the Raman spectra under ambient conditions. All the catalysts exhibited a broad band at 796 cm^{-1} corresponding to the Ti–O vibration of anatase TiO_2 . V3T and V3WT contained both isolated monomeric vanadyl species (1005 or 1012 cm^{-1}) and polymeric (meta-vanadate-like) species (917 cm^{-1}) [19–21]. These bands became much weaker in the Raman spectra of V1T and V1WT due to the low vanadia loading. The isolated vanadyl band was shifted slightly towards higher frequency (1012 cm^{-1}) and increased in intensity for V3WT compared with V3T. These indicated that the addition of tungsten oxide facilitated the distribution of V^{x+} species in the form of isolated vanadyl. For the WO_3/TiO_2 catalyst, a band at 978 cm^{-1} was assigned to the symmetric $\text{W}=\text{O}$ groups. It was shifted slightly to higher frequency (982 cm^{-1}) in the Raman spectrum of V1WT, which may be caused by the overlapping of the isolated vanadyl band [22].

Two additional Raman bands at 934 and 904 cm^{-1} appeared in the spectra of the poisoned catalysts V1T-K, V3T-K and V1WT-K, which were due to the symmetric O–V–O stretching mode of “amorphous” KVO_3 in the form of small crystalline particles or a thin amorphous layer. This was confirmed by the characteristic bands of standard KVO_3 . Furthermore, the red shift of the high frequency band indicated a lengthening of the

Table 1

Compositions and BET surface area of the catalysts^a.

Catalyst	Element mass contents ^b (%)				$S_{\text{BET}}/(\text{m}^2/\text{g})$
	V_2O_5	WO_3	K	Cl	
V1WT(-K)	0.93 (0.88)	9.91 (9.72)	— (0.75)	— (0.0154)	83 (80)
V3WT(-K)	2.55 (2.46)	9.99 (9.50)	— (0.82)	— (0.0152)	80 (76)
V1T(-K)	0.86 (0.90)	—	— (0.76)	— (0.0159)	82 (78)
V3T(-K)	2.54 (2.63)	—	— (0.82)	— (0.0157)	85 (78)
WT(-K)	—	9.76 (9.35)	— (0.74)	— (0.0116)	83 (80)

^a The data of the fresh and poisoned catalysts are listed outside of and in brackets, respectively.

^b Measured by ICP.

Fig. 2. Raman spectra of (a) fresh and (b) poisoned catalysts.

V=O bond due to the presence of potassium and an electrostatic interaction [23]. Thus, the bands at 982–970 cm^{-1} can be assigned to K-doped monomeric species such as K–O–V=O sites. The main Raman frequency of K_2WO_4 was located at 922 cm^{-1} . The Raman spectra of TiO_2 supported K_2WO_4 could not be analyzed because of the very weak signals detected, as reported by Erdöhelyi et al. [24]. The red shift of the band from 978 to 965 cm^{-1} in the spectrum of WT-K may also be caused by K-doped species such as K–O–W=O sites. Compared with V3T-K, V3WT-K exhibited the band at a slightly higher frequency (982 cm^{-1}). This was related to the overlapping of a shoulder assigned to some residual isolated monomeric species, which was confirmed by the maintaining of the band (917 cm^{-1}) assigned to polymeric metavanadate species [15].

3.4. IR spectra of NH_3 adsorption

It has been established that the surface acidity of $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst plays an important role in the selective reduction of NO_x with NH_3 . To investigate the influences of the catalyst composition and alkali poisoning on the acid sites of the catalyst, the IR spectra obtained after NH_3 adsorption at 50 $^\circ\text{C}$ are shown in Fig. 3. As shown in Fig. 3(a), the bands at 1672

and 1447 cm^{-1} were assigned to the symmetric and asymmetric bending vibrations of NH_4^+ coordinated to Brönsted acid sites, respectively. The bands at 1594 and 1280–1100 cm^{-1} were assigned to the asymmetric and symmetric bending vibrations of NH_3 coordinated to Lewis acid sites [25,26]. The corresponding stretching modes were found at 3391 and 3224 cm^{-1} for coordinated NH_3 , and at 3022 and 2812 cm^{-1} for ammonium ions. It was obvious that the NH_3 adsorbed on Brönsted acid sites was more dominant than that on Lewis acid sites, which is common for vanadium-based catalysts [22,27,28].

The IR spectra of the NH_3 adsorbed at 50 $^\circ\text{C}$ over the potassium poisoned catalysts are shown in Fig. 3(b). Both the ammonium ions (NH_4^+) coordinated to Brönsted acid sites (3022, 2784, 1672 and 1443 cm^{-1}) and NH_3 coordinated to Lewis acid sites (3398, 3260, 1601, 1213 and 1116 cm^{-1}) were observed for all the poisoned catalysts. Nevertheless, NH_3 adsorption was severely suppressed on the poisoned catalysts with bands of much lower intensity. The V3WT-K and V3T-K catalysts exhibited a stronger band at 1447–1443 cm^{-1} than V1WT and V1T. This indicated that there were more Brönsted acid sites on the poisoned catalysts at a high vanadia loading.

The addition of potassium not only suppressed NH_3 chemisorption significantly at 50 $^\circ\text{C}$, but also reduced the stability of

Fig. 3. FT-IR spectra of (a) fresh and (b) poisoned catalysts after NH_3 adsorption at 50 $^\circ\text{C}$ for 30 min. (1) V1WT(-K); (2) V3WT(-K); (3) V1T(-K); (4) V3T(-K); (5) WT(-K).

Fig. 4. Amount of Brönsted acid sites on (a) fresh and (b) poisoned catalysts calculated from the DRIFTS bands centered at $1447\text{--}1443\text{ cm}^{-1}$ as a function of temperature.

adsorbed NH_3 at high temperatures. The amount of Brönsted acid sites was calculated by integrating the area of the band at $1447\text{--}1443\text{ cm}^{-1}$ as a function of temperature. The results are shown in Fig. 4. It is clear that less vanadia in the catalysts led to weaker stability of the ammonium ions adsorbed on Brönsted acid sites. Among the fresh catalysts, the ammonium ions adsorbed on WT showed the highest thermal stability in Fig. 4(a). It is interesting that V1WT presented less thermally stable Brönsted acid sites than WT and V1T. It has been reported that as the temperature goes above $150\text{ }^\circ\text{C}$, the formation of V–O–W bonds, which causes the Brönsted acid site to be unstable, explains a sharp decrease of the surface acidity of the ternary catalyst [29]. Similarly, V3WT exhibited a larger amount of Brönsted acid sites at temperatures lower than $200\text{ }^\circ\text{C}$ and then a similar amount to WT. As shown in Fig. 4(b), the amount of ammonium ions decreased more quickly with temperature on the poisoned catalysts. The surface acidity was quite low when the temperature increased to $250\text{ }^\circ\text{C}$. The advantage of WT for the thermal stability of the acid sites disappeared with the formation of potassium tungstate. With the addition of tungsten oxide as the promoter, V1WT-K and V3WT-K retained more Brönsted acid sites in the whole temperature range than V1T-K and V3T-K, respectively.

3.5. Redox property

The redox property is one of important characteristics of SCR catalysts. Thus the H_2 -TPR tests were performed. The results are shown in Fig. 5. As shown in Fig. 5(a), the fresh WT catalyst showed two peaks at 430 and $755\text{ }^\circ\text{C}$, corresponding to the reduction of highly dispersed WO_x species and WO_3 crystallites, $\text{W}^{6+} \rightarrow \text{W}^{4+}$, respectively [27]. The V1T catalyst showed a distinct peak at $416\text{ }^\circ\text{C}$, which was ascribed to the reduction of $\text{V}^{5+} \rightarrow \text{V}^{3+}$ [3,30]. The reduction peak shifted to $256\text{ }^\circ\text{C}$ with a shoulder at $303\text{ }^\circ\text{C}$ for the V3T catalyst at a high vanadia loading, which can be associated with the reduction of surface isolated and polymeric VO_x species and bulk V_2O_5 , respectively [26]. These reduction peaks were shifted towards lower temperatures (220 and $264\text{ }^\circ\text{C}$) for V3WT. Similarly, the broad peaks at 350 and $426\text{ }^\circ\text{C}$ were ascribed to the reduction of vanadia and tungsten oxide over V1WT, respectively. These results confirmed that the increased vanadia loading and the promoted dispersion of vanadia by the addition of tungsten oxide facilitated the redox property of the catalyst [17,31,32].

After the potassium poisoning, the reduction peaks were shifted to 500 and $842\text{ }^\circ\text{C}$ for WT-K due to the formation of

Fig. 5. H_2 -TPR curves of (a) fresh and (b) K-poisoned catalysts. (1) V1WT(-K); (2) V3WT(-K); (3) V1T(-K); (4) V3T(-K); (5) WT(-K).

finely dispersed and bulk K_2WO_4 , which correlated with the reduction behavior of K_2WO_4 on the titania support [24]. As indicated by the ICP results in Table 1, the molar content of tungsten was two times that of potassium for WT-K. This implied that at least half the tungsten oxide can be maintained as evidenced by the preservation of the peak at 733 °C associated with the reduction of $W^{6+} \rightarrow W^{4+}$ in WO_3 crystallites. For V1T-K, the distinct reduction peak shift from 416 to 494 °C was due to the formation of KVO_3 [13]. The position of the reduction peak of KVO_3 depended not only on the crystallinity of the salt but also on its interaction with the support. The peaks at 380 and 442 °C over V3T-K can be ascribed to the reduction of bulk V_2O_5 and vanadate KVO_3 , respectively. Compared with the fresh sample, the shift of the reduction peak of bulk V_2O_5 on the poisoned catalyst to higher temperatures may be caused by oxide sintering and the weakened interaction with the support. Again, this implied the preservation of some vanadia on the poisoned catalyst at a high vanadia loading. The measured K/V ratio (0.73) was less than 1 for V3T-K. The peaks at 510–525, 740 and 820–830 °C for V1WT-K and V3WT-K can be ascribed to the reduction of highly dispersed K_2WO_4 , bulk WO_3 and bulk K_2WO_4 , respectively. This indicated that tungsten oxide was also combined with potassium besides the formation of KVO_3 over the ternary catalysts. The peaks at 420 and 472 °C for V1WT-K and V3WT-K were likely caused by the overlapping of the reduction of bulk vanadia and potassium vanadate. The reduction peak at a lower temperature (420 °C) demonstrated that there were more bulk vanadia species on V3WT-K than on V1WT-K.

3.6. Interaction of active sites with potassium

Although the calcination temperature of the poisoning treatment was 450 °C, the volatilization of potassium cannot be completely avoided. This depended on the ease of the generation of the potassium salts and their stability. It is seen in Table 1 that almost no loss of potassium occurred on the catalysts at a high vanadia loading, implying a strong interaction between potassium and vanadia to form potassium vanadate during the poisoning treatment. On the other hand, the loss of potassium was small on the catalysts with a low vanadia loading or without vanadia, indicating that potassium also reacted with tungsten oxide strongly to form potassium tungstate, which was evidenced by the Raman and H_2 -TPR results.

During the potassium poisoning treatment, tungsten oxide plays an important role in the preservation of vanadia by the formation of potassium tungstate instead of vanadate on the V1WT-K and V3WT-K catalysts. Again, both the Raman and H_2 -TPR results confirmed the co-existence of KVO_3 and K_2VO_4 on the ternary catalysts. In this way, more vanadia species remained as active sites and acid sites on V3WT-K, resulting in a relatively high SCR activity of the poisoned catalyst as shown in Scheme 1.

3.7. Effects of surface acidity and redox property

The NH_3 -SCR activity of the catalyst has been reported to

Scheme 1. Structure of the K-poisoned V_2O_5 - WO_3 /TiO₂ SCR catalyst.

depend on both the redox property and surface acidity. In this work, the NO_x conversion at 250 °C represented the SCR activity of catalyst. The redox property of catalyst was expressed in the form of the first reduction temperature in the H_2 -TPR curve. The surface acidity of catalyst was shown by the integrated area of the Brönsted acid site band at 1447–1443 cm^{-1} at 250 °C. In this way, the effects of the surface acidity and redox property on the NH_3 -SCR activity of catalysts are shown in Fig. 6. It is seen in Fig. 6(a) that for the fresh catalysts with plenty of surface acidity, the SCR activity was determined by the redox property of catalyst although the NO_2 -assisted fast SCR reaction at low temperature was not important for the V_2O_5 - WO_3 /TiO₂ catalysts due to their low activity for NO oxidation. It has been

Fig. 6. Effects of surface acidity and redox property on NH_3 -SCR activity at 250 °C. (a) Fresh catalysts; (b) Poisoned catalysts. The columns represent the relative surface acidity calculated from the IR band of NH_3 adsorption centered at 1447–1443 cm^{-1} .

reported that the existence of Brönsted acidity is not a requisite for the SCR activity at low temperatures [3,33]. This explains the low SCR activity of the WO_3/TiO_2 catalyst with high Brönsted acidity but poor redox property. The SCR reaction is a redox process that occurs with a redox Mars-van Krevelen mechanism over vanadia-based catalysts [3,25]. The slow step of the SCR reaction can be associated with the catalyst oxidation step by oxygen. The increase in catalyst activity observed in Fig. 6(a) by either increasing the V or W loading is ascribable to the increased redox property of the catalyst.

It was shown in Fig. 6(a) that when NH_3 existed at high coverage, there was a weak dependence of the SCR activity on the NH_3 surface concentration. However, when NH_3 coverage was below a threshold value, which was influenced by the redox property of the catalyst, the rate of the deNO_x reaction depended on the NH_3 surface coverage [34]. This was exactly the case with the poisoned catalysts as shown in Fig. 6(b). It can be seen that the SCR activity depended not only on the activity of the active sites but also on the surface acidity for these poisoned catalysts. The relatively lower surface acidity of V3T-K was an important factor responsible for its lower SCR activity than V3WT-K, although it has a relatively better redox property. It is worth noting that the broad peak centered at 420 °C for V3WT-K in Fig. 5(b) was caused by the overlapping of the reduction of both vanadia and vanadate, while that at 380 °C for V3T-K was assigned to the reduction of bulk vanadia. Furthermore, there were more active vanadia species that survived on V3WT-K than on V3T-K according to the Raman spectra in Fig. 2. Thus, the first H_2 -TPR peak temperature may not be a good indicator of the redox property of the catalyst. On the other hand, the WT-K catalyst was almost totally deactivated with no vanadia as active sites although it maintained some amount of surface acid sites.

4. Conclusions

Based on the similar catalyst surface area and potassium loading, after potassium poisoning, the survival of vanadia active sites instead of forming inert vanadate and tungstate is

critical to the NH_3 -SCR activity of $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts. Increasing the vanadia loading and adding tungsten oxide contributed to the redox property and surface acidity of the catalyst. With sufficient surface acidity, the reactivity of the vanadia species decides the catalytic activity. After potassium impregnation, tungsten oxide acted not only to disperse vanadia but also as a sacrificial agent so that the $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts maintained their active vanadia species. Among the catalysts investigated, the V3WT catalyst showed higher alkali resistance with 60% NO_x conversion at 250 °C after impregnation of a nominal mass amount of 1% K_2O .

References

- [1] Alemany L J, Lietti L, Ferlazzo N, Forzatti P, Busca G, Giamello E, Bregani F. *J Catal*, 1995, 155: 117
- [2] Alemany L J, Berti F, Busca G, Ramis G, Robba D, Toledo G P, Trombetta M. *Appl Catal B*, 1996, 10: 299
- [3] Busca G, Lietti L, Ramis G, Berti F. *Appl Catal B*, 1998, 18: 1
- [4] Kamata H, Takahashi K, Odenbrand C U I. *J Catal*, 1999, 185: 106
- [5] Forzatti P, Nova I, Tronconi E, Kustov A, Thøgersen J R. *Catal Today*, 2012, 184: 153
- [6] Shang X S, Li J R, Yu X W, Chen J S, He C. *Front Chem Sci Eng*, 2012, 6: 38
- [7] Wan Q, Duan L, Li J H, Chen L, He K B, Hao J M. *Catal Today*, 2011, 175: 189
- [8] Klimczak M, Kern P, Heinzelmann T, Lucas M, Claus P. *Appl Catal B*, 2010, 95: 39
- [9] Chen L, Li J H, Ge M F. *Chem Eng J*, 2011, 170: 531
- [10] Nicosia D, Elsener M, Kröcher O, Jansohn P. *Top Catal*, 2007, 42-43: 333
- [11] Wu X D, Yu W C, Si Z C, Weng D. *Front Environ Sci Eng*, 2013, 7: 420
- [12] Lisi L, Lasorella G, Malloggi S, Russo G. *Appl Catal B*, 2004, 50: 251
- [13] Bulushev D A, Rainone F, Kiwi-Minsker L, Renken A. *Langmuir*, 2001, 17: 5276
- [14] Yu W C, Wu X D, Si Z C, Weng D. *Appl Surf Sci*, 2013, 283: 209
- [15] Kamata H, Takahashi K, Odenbrand C U I. *J Mol Catal A*, 1999, 139: 189
- [16] Salinas D, Araya P, Guerrero S. *Appl Catal B*, 2012, 117-118: 260
- [17] Went G T, Leu L J, Rosin R R, Bell A T. *J Catal*, 1992, 134: 492

Graphical Abstract

Chin. J. Catal., 2015, 36: 1287–1294 doi: 10.1016/S1872-2067(15)60881-6

Potassium poisoning of titania supported deNO_x catalysts: Preservation of vanadia and sacrifice of tungsten oxide

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During the deactivation of $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts by KCl, the preservation of vanadia as active sites is critical to the catalytic activity for selective catalytic reduction of NO_x by NH_3 at the cost of increasing the vanadia loading and the sacrifice of tungsten oxide.

- [18] Amiridis M D, Wachs I E, Deo G, Jehng J M, Kim D S. *J Catal*, 1996, 161: 247
- [19] Cai Y P, Ozkan U S. *Appl Catal*, 1991, 78: 241
- [20] Choo S T, Lee Y G, Nam I S, Ham S W, Lee J B. *Appl Catal A*, 2000, 200: 177
- [21] Tian H J, Ross E I, Wachs I E. *J Phys Chem B*, 2006, 110: 9593
- [22] Kobayashi M, Hagi M. *Appl Catal B*, 2006, 63: 104
- [23] Banaś J, Tomašić V, Weselucha-Birczyńska A, Najbar M. *Catal Today*, 2007, 119: 199
- [24] Erdöhelyi A, Németh R, Hancz A, Oszkó A. *Appl Catal A*, 2001, 211: 109
- [25] Ramis G, Yi L, Busca G. *Catal Today*, 1996, 28: 373
- [26] Tang F S, Zhong K, Yang F, Yang L L, Xu B L, Qiu J H, Fan Y N. *Chin J Catal* (唐富顺, 庄柯, 杨芳, 杨利利, 许波连, 邱金恒, 范以宁. 催化学报), 2012, 33: 933
- [27] Zhao H, Bennici S, Cai J, Shen J, Auroux A. *Catal Today*, 2010, 152: 70
- [28] Peng Y, Li J H, Shi W B, Xu J Y, Hao J M. *Environ Sci Technol*, 2012, 46: 12623
- [29] Ramis G, Busca G, Bregani F, Forzatti P. *Appl Catal*, 1990, 64: 259
- [30] Kompio P G W A, Brückner A, Hipler F, Auer G, Löffler E, Grünert W. *J Catal*, 2012, 286: 237
- [31] Chen J P, Yang R T. *Appl Catal A*, 1992, 80: 135
- [32] Lietti L, Forzatti P. *J Catal*, 1994, 147: 241
- [33] Tronconi E, Nova I, Ciardelli C, Chatterjee D, Bandl-Konrad B, Burkhardt T. *Catal Today*, 2005, 105: 529
- [34] Tronconi E, Lietti L, Forzatti P, Malloggi S. *Chem Eng Sci*, 1996, 51: 2965

氧化钒负载脱硝催化剂的碱中毒过程：氧化钒的保留和氧化钨的牺牲

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摘要: V_2O_5 - WO_3 / TiO_2 催化剂目前已广泛用于电厂和工业锅炉燃烧废气脱硝, 但燃烧原料煤及石油中含有的杂质元素碱金属与碱土金属元素可吸附在催化剂上, 不仅会减少催化剂酸性位的数量, 还会与催化活性元素结合生成惰性物种, 导致催化剂失活。因此, 已有许多有关钒钨钼催化剂碱中毒的研究, 从催化剂的氧化还原能力、酸性位损失及表面孔结构等方面进行了讨论。但这些研究大多集中在碱中毒对活性组分 V_2O_5 的影响及中毒催化剂的活性变化, 很少涉及催化剂中 WO_3 的作用, 也缺乏有关不同活性元素与钾盐反应的实验证据。本文采用过量浸渍法制备了不同钒和钨含量的钒钨钼催化剂, 研究了氯化钾对其氨法选择性催化还原(NH_3 -SCR)活性的失活效应。利用感应耦合等离子体、 N_2 吸附、拉曼光谱、 H_2 程序升温还原、 NH_3 吸附红外光谱和 NH_3 氧化活性等手段对新鲜和中毒催化剂的性质进行了表征, 特别探讨了 V_2O_5 和 WO_3 对催化剂抗碱中毒能力的贡献。

催化剂活性测试结果表明, V_2O_5 含量越高, 活性温度窗口越宽, 而且含有 WO_3 的三元催化剂活性高于 V_2O_5 / TiO_2 二元催化剂。催化剂的BET比表面积和孔结构取决于 TiO_2 载体, 随活性组分配比变化不大, 说明催化剂物理结构性质并非影响活性的主要因素。原位红外光谱及 H_2 程序升温还原测试结果表明, 随 V_2O_5 含量提高, 催化剂表面Brönsted酸性位数量及氧化还原能力提高。作为反应的主要活性物种, V_2O_5 在碱中毒处理后变成惰性的偏钒酸钾 KVO_3 , 使催化剂中Brönsted酸性位减少, 热稳定性下降, 并削弱了催化剂的氧化还原能力, 因此低钒含量的催化剂容易严重中毒失活。在高钒负载量(3%)时, 部分 V_2O_5 在碱中毒后得以保留, 从而使催化剂保持了一定的脱硝催化活性。

另外, WO_3 能给催化剂表面提供热稳定的酸性位, 虽然 WO_3 自身的氧化还原能力差, 但其能改善 V_2O_5 的分散性, 从而提高 V_2O_5 - WO_3 / TiO_2 催化剂的活性。除此之外, WO_3 在催化剂碱中毒过程中还能扮演牺牲剂, 与钾反应生成钨酸钾(K_2WO_4), 即在 V_2O_5 与钾离子结合形成 KVO_3 的同时, 部分 WO_3 也会与钾反应形成 K_2WO_4 , 可以使三元催化剂保留更多的活性V物种。因此, 在所研究的催化剂中, 高钒负载量的 V_2O_5 - WO_3 / TiO_2 催化剂表现出最好的抗碱中毒能力。

活性影响因素分析表明, 对于新鲜催化剂, 其表面吸附的 NH_3 量足够多, 催化剂活性与表面酸性相关度不大, 脱硝效率主要取决于催化剂的氧化还原能力。但是, 对于碱中毒处理后的催化剂, 其表面吸附 NH_3 的能力大大削弱, 这时脱硝效率除了受催化剂氧化还原能力影响, 在很大程度上也依赖于催化剂的表面酸性。

关键词: 氧化钒; 氧化钨; 选择性催化还原; 碱失活; 活性位; 牺牲剂

收稿日期: 2015-03-27. 接受日期: 2015-04-28. 出版日期: 2015-08-20.

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基金来源: 国家高技术研究发展计划(863计划, 2013AA065302); 固废资源化利用与节能建材国家重点实验室开放课题(SWR-2013-003).

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>).