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Alkali resistance promotion of Ce-doped vanadium-titanic-based NH₃-SCR catalysts

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ARTICLE INFO

Article history:

Received 18 December 2017

Revised 23 January 2018

Accepted 26 January 2018

Available online 7 February 2018

Keywords:

Selective catalytic reduction

Ammonia

Nitrogen oxides

V₂O₅/WO₃-TiO₂

Alkali deactivation

ABSTRACT

The effect of K deactivation on V₂O₅/WO₃-TiO₂ and Ce-doped V₂O₅/WO₃-TiO₂ catalysts in the selective catalytic reduction (SCR) of NO_x by NH₃ was studied. Ce-doped V₂O₅/WO₃-TiO₂ showed significantly higher resistance to K deactivation than V₂O₅/WO₃-TiO₂. Ce-doped V₂O₅/WO₃-TiO₂ with K/V = 4 (molar ratio) showed 90% NO_x conversion at 350°C, whereas in this case V₂O₅/WO₃-TiO₂ showed no activity. The fresh and K-poisoned V₂O₅/WO₃-TiO₂ and Ce-doped V₂O₅/WO₃-TiO₂ catalysts were investigated by means of *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), NH₃-temperature progress decomposition (NH₃-TPD), X-ray photoelectron spectroscopy (XPS) and H₂-temperature program reduction (H₂-TPR). The effect of Ce doping on the improving resistance to K of V₂O₅/WO₃-TiO₂ were discussed.

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Introduction

Selective catalytic reduction (SCR) of nitrogen oxides (NO_x) by NH₃ is one of the most successful technologies for the control of NO_x emission from power plant flue gas and diesel exhaust. The SCR system for coal-fired power plants is commonly in the high-dust (HD) configuration, in which the SCR catalyst is upstream of the electrostatic dust precipitator and processes high dust flue gas with a temperature range of 300–400°C. Vanadium-titanic-based catalysts (*e.g.*, V₂O₅-WO₃/TiO₂), the most widely used SCR catalysts, can provide high performance NO_x reduction in the temperature range 300–400°C (Pârăulescu *et al.*, 1998; Xu *et al.*, 2017; Zhu *et al.*, 2017). However, a major problem in practical application of V₂O₅-WO₃/TiO₂ catalysts has

been their strong deactivation by deposition of alkali and alkaline earth metals in fly ash. For example, 1% K₂O-doped V₂O₅-WO₃/TiO₂ gives almost no SCR activity at temperatures from 250 to 400°C (Kamata *et al.*, 1999). The effect of alkali and alkaline earth metals on both tungsten-free and tungsten-containing vanadium-titanic-based catalysts has been well studied (Chen *et al.*, 2010; Due-Hansen *et al.*, 2009; Kamata *et al.*, 1999; Lietti *et al.*, 1993; Lisi *et al.*, 2004; Nicosia *et al.*, 2007, 2008; Tang *et al.*, 2010; Wu *et al.*, 2013). The Brønsted acidity of catalysts and the amount of NH₃ adsorbed on the surface can be decreased by alkali metals like K, which cause the decrease of SCR activity (Kamata *et al.*, 1999; Lietti *et al.*, 1993). Nicosia *et al.* (2008) explained the deactivation of V₂O₅/WO₃-TiO₂ catalysts by alkali and alkaline earth metals by a mechanism whereby the

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poisoning element (Ca, K) occupies the non-atomic hole sites of the (010) V_2O_5 surface, such that both Brønsted acid and $V^{5+} = O$ sites are blocked.

Besides the effect on surface acidity, the reducibility of V_2O_5/TiO_2 catalysts could be another reason for the poisoning effect of Na^+ and Ca^{2+} (Tang et al., 2010). Yu et al. (2013) found that the isolated vanadia species over the $V_2O_5-WO_3/TiO_2$ catalyst were more reactive with potassium than polymeric vanadia species. Chen et al. (2010) proposed that decreases in NH_3 adsorption, surface chemisorbed oxygen and reducibility of surface vanadium species could be the main factors in the poisoning effect of alkali metal.

In our previous study, cerium–titanium (Ce/TiO_2 , $CeTiO_x$, $CeWTiO_x$) catalysts were developed and showed high activity for NH_3 -SCR (Shan et al., 2011, 2012; Xu et al., 2008). Chen et al. (2009) and Peng et al. (2012) reported that substitution part of W by Ce in V_2O_5/WO_3-TiO_2 (0.1 or 0.4 wt.% of V_2O_5) can promote SCR activity in the temperature range 200–450°C and enhance the catalyst's alkali poisoning resistance. Xu et al. (2015) studied the addition of Ce and Sb to the V_2O_5/TiO_2 (5 wt.% of V) can improve the low temperature activity for NH_3 -SCR of NO_x . Here, the promotional effect of Ce-doping on the alkali metal resistance of the V_2O_5/WO_3-TiO_2 catalyst was investigated. The effect of K-poisoning on V_2O_5/WO_3-TiO_2 and Ce-doped V_2O_5/WO_3-TiO_2 were studied by means of activity measurements, X-ray photoelectron spectroscopy (XPS), NH_3 -temperature progress decomposition (NH_3 -TPD), *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and H_2 -temperature program reduction (H_2 -TPR).

1. Materials and methods

1.1. Catalyst preparation

The catalysts were prepared by a wet impregnation method. TiO_2 powder containing 5 wt.% WO_3 was used in this work. Ammonium metavanadate was dissolved in an oxalic acid solution. The TiO_2 powder was impregnated in the mixed solution by stirring for 1 hr. After rotary evaporation, the sample was dried at 110°C overnight and then calcined at 500°C in air for 3 hr. V_2O_5/WO_3-TiO_2 catalysts with 1 wt.% V_2O_5 were prepared and denoted as VWTi. Ce-doped V_2O_5/WO_3-TiO_2 catalysts with 6 wt.% Ce were prepared by adding a cerium nitrate solution into the solution of ammonium metavanadate and oxalic acid, and followed by a process similar to the preparation of V_2O_5/WO_3-TiO_2 catalysts. Ce-doped V_2O_5/WO_3-TiO_2 catalysts were denoted as Ce-VWTi. The K-containing samples were prepared by impregnating the dry powder with KNO_3 solution for 8 hr, then dried in air at 100°C overnight and calcined at 500°C for 3 hr. The Ca and Mg poisoning samples were prepared by the same procedures according to the molar ratio of $Ca/V = Mg/V = 4$. All catalysts were ground and sieved to 40–60 mesh for activity testing.

1.2. Catalytic activity measurements

The reaction conditions were controlled as follows: 500 ppm NO , 500 ppm NH_3 , 5 vol.% O_2 , N_2 balance; 150 mg catalyst, total flow rate of 500 mL/min and gas hourly space velocity (GHSV) = 100,000 hr^{-1} . The effluent gas was analyzed using an FTIR

spectrometer (Nexus 670, Nicolet, USA) equipped with a heated, low volume multiple-path gas cell (2 m), which can continuously analyze the NO , NO_2 , N_2O and NH_3 in the effluent gas. The spectra were collected when the SCR reaction reached a steady state. NO_x conversion was calculated as follows (Liu et al., 2009):

$$NO_x \text{ conversion} = \left(1 - \frac{[NO]_{out} + [NO_2]_{out}}{[NO]_{in}} \right) \times 100\% \quad (1)$$

where $[NO]_{out}$, $[NO]_{in}$ and $[NO_2]_{out}$ refer to the NO concentrations at the outlet and inlet, and the NO_2 concentration at the outlet, respectively.

1.3. Catalyst characterization

The *in situ* DRIFTS experiments were performed on an Fourier transform infrared spectroscopy (FTIR) spectrometer (Nexus 670, Nicolet, USA) equipped with a mercury cadmium telluride (MCT) detector cooled by liquid nitrogen and an *in situ* DRIFTS reactor cell with ZnSe window connected to a purging/adsorption gas control system, collecting 100 scans at spectral resolution of 4 cm^{-1} . The reaction temperature was controlled precisely by an Omega programmable temperature controller. Each sample was pretreated at 350°C in a flow of 20 vol.% O_2/N_2 for 1 hr, and cooled down to 50°C in N_2 . The sample was saturated at 50°C with 0.5% NH_3 in N_2 for about 30 min, and purging with N_2 at 50°C for 1 hr, then heating up to 150°C. The spectra were recorded at 150°C.

Ammonia temperature-programmed desorption (NH_3 -TPD) experiments were used to determine the NH_3 storage capacity of SCR catalysts. The test sample (100 mg) was pretreated at 400°C for 30 min by 20 vol.% O_2/N_2 , and then cooled down to 150°C. NH_3 was introduced until the adsorption on the sample was saturated. The sample was then sufficiently purged with N_2 to remove excess adsorbate from the surface of the sample. The TPD was conducted by heating the sample in N_2 from 150 to 500°C at a rate of 10°C/min and the NH_3 in the outlet gas was analyzed by an online NEXUS 670-FTIR (Nexus 670, Nicolet, USA) spectrometer.

The catalysts were analyzed using X-ray photoelectron spectroscopy (XPS) to identify the surface nature. The XPS data were taken on using Al K α radiation (AXIS Ultra, Kratos, Japan). The binding energy was corrected using the energy of adventitious carbon (284.7 eV).

H_2 -TPR experiments were performed in a flow of 10% H_2/Ar mixture (50 cm^3/min) over 50 mg of catalyst using a heating rate of 10°C/min. The consumption of H_2 was detected by thermal conductivity detector (TCD) (AutoChem II 2920, Micromeritics, USA).

2. Results and discussion

2.1. SCR activity evaluation

Commonly, the operating temperature window of vanadium based catalysts for reducing NO_x from stationary sources is between 300 and 400°C. To investigate the effect of K doping on the VWTi and Ce-VWTi catalysts, the NH_3 -SCR activity of fresh and K-doped catalysts was tested. Fig. 1a–b shows the NH_3 -SCR activity and of VWTi and Ce-VWTi catalysts with different K loadings at the temperature range from 275 to

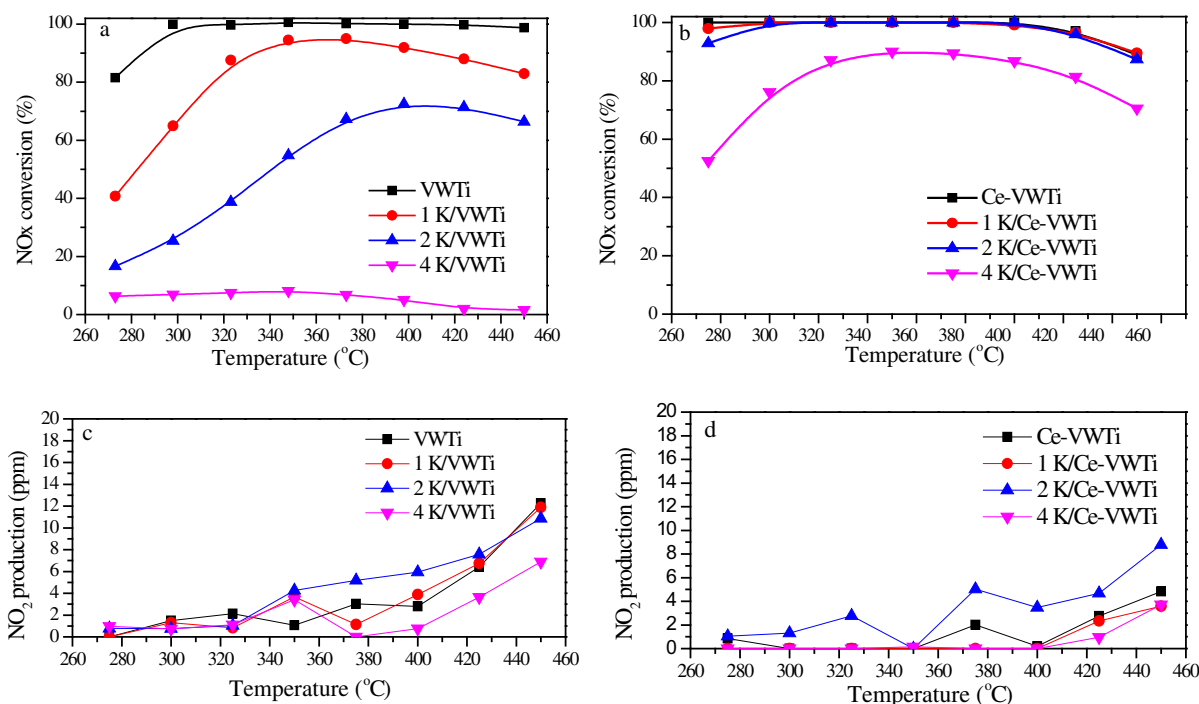


Fig. 1 – NO_x conversion and N₂O production as a function of K loading (molar ratio of K/V) for VWTi and Ce-VWTi. (a) NO_x conversion and (c) N₂O production of fresh and K doping VWTi; (b) NO_x conversion and (d) N₂O production of fresh and K doping Ce-VWTi.

450°C under a fixed GHSV of 100,000 hr⁻¹. As can be seen in Fig. 1a, poisoning of VWTi catalysts with K led to a decrease in NH₃-SCR activity. NO_x conversion of VWTi catalysts decreased with the increase of K loading, and decreased almost to zero with a K/V molar ratio of 4 at all temperatures.

A clearly improved SCR activity was obtained on Ce-VWTi catalysts at 275°C, where the NO_x conversion over VWTi was increased from 81% to almost 100% by addition of Ce (Fig. 1a). Ce-VWTi catalysts showed much better resistance to K poisoning compared with VWTi catalysts. The NO_x conversion of Ce-VWTi catalysts remained at almost 99% even with a K/V molar ratio of 1 at all temperatures. For the Ce-VWTi catalyst, 90% NO_x conversion still could be obtained with a K/V molar ratio of 4 at temperatures above 350°C, whereas in this case VWTi showed no activity.

The concentrations of N₂O in the out gas from the SCR reaction over fresh and K doping VWTi and Ce-VWTi were shown in Fig. 1c and d. It can be seen that, the formation of N₂O was little for all the test samples. The highest concentration of N₂O in out gas was formed at around 12 ppm, which was produced from SCR reaction over fresh VWTi catalysts at 450°C.

The addition of Ce to V₂O₅/WO₃-TiO₂ can also improve the resistance to poisoning of Ca²⁺ and Mg²⁺. The results in Fig. 2 showed that the NO_x conversion of Ce-VWTi were obviously higher than that of VWTi, after the deactivated by the same amount of Ca²⁺ and Mg²⁺ (the molar ratio of Ca/V = Mg/V = 4).

2.2. In situ DRIFTS of adsorbed NH₃ species

The alkali metals can affect the Brønsted acidity and the amount of NH₃ adsorbed on the V₂O₅/TiO₂ catalyst surface

(Kamata et al., 1999; Lietti et al., 1993). The *in situ* DRIFTS results of NH₃ adsorption for fresh and K-containing (K/V molar ratio of 4) VWTi and Ce-VWTi catalysts are shown in Fig. 3. The region of 2250–3500 cm⁻¹ is typical of the stretching vibration of weakly-adsorbed ammonia species, and the bands at 3365, 3248 and 3160 cm⁻¹ can be assigned to N-H stretching vibrations (Chen et al., 2009; Peng et al., 2012). The negative bands around 1621 and 3641 cm⁻¹ can be assigned to surface O-H stretching, which is caused by the hydroxyl consumption through interaction with NH₃ to form NH₄⁺ (Chen et al., 2009; Peng et al., 2012). The bands around 1677 and 1457 cm⁻¹ are due

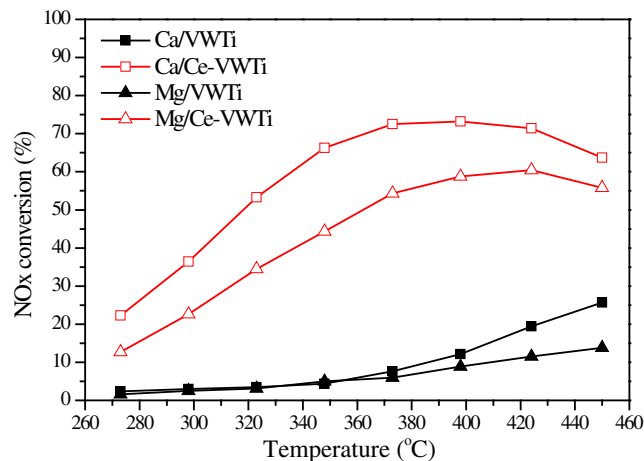


Fig. 2 – NO_x conversion of Ca and Mg posing V_{1.0}WTi and Ce-V_{1.0}WTi: Ca/V (molar ratio) = Mg/V (molar ratio) = 4.

to NH_4^+ chemisorbed on the Brønsted acid sites, whereas the bands at 1602 cm^{-1} can be assigned to the asymmetric bending vibrations of ammonia species coordinated to Lewis acid sites (Chen et al., 2010; Lietti et al., 1993; Nicosia et al., 2008).

From the spectra, the bands corresponding to Brønsted acid sites (1677 and 1457 cm^{-1}) showed higher intensity than the bands corresponding to Lewis acid sites (1602 cm^{-1}). The band of Lewis acid sites was covered by the bands of Brønsted acid sites and was difficult to distinguish on fresh catalysts. Adsorbed NH_3 species observed on VWTi and Ce-VWTi gave signals at almost the same wavelength positions, as shown in Fig. 3.

The effect of K on the adsorbed NH_3 species on VWTi was similar to that on the Ce-VWTi catalyst. A significant decrease in the intensity of signals of NH_3 coordinated to Brønsted acid sites (1457 and 1677 cm^{-1}) was observed for alkali-poisoned catalysts, while the intensity of signals of NH_3 coordinated to Lewis acid sites (1602 cm^{-1}) was almost unchanged. Those results are in accordance with the studies of Nicosia et al. (2008) and Chen et al. (2010).

2.3. NH_3 -TPD

The surface acidity of the SCR catalysts was also studied by NH_3 -TPD experiments. The NH_3 -TPD profiles are shown in Fig. 4. As expected, the NH_3 storage capacity of VWTi and Ce-VWTi significantly decreased after K doping. The NH_3 storage capacity of Ce-VWTi decreased from 322 to $90\text{ }\mu\text{mol/g}$ and that of VWTi decreased from 364 to $128\text{ }\mu\text{mol/g}$, when the K doping amount was $\text{K/V} = 2$. The results showed that the addition of ceria to VWTi did not increase the NH_3 storage capacity of the K poisoned catalysts. It indicates that the better alkali resistance of Ce-VWTi has no relation with the surface acidity of SCR catalysts.

2.4. XPS results

The XPS results of O 1s on fresh and K-containing VWTi and Ce-VWTi are shown in Fig. 5. The O 1s peak was deconvoluted into two sub-bands by searching for the optimum combination of Gaussian bands with correlation coefficients (r^2) above 0.997. The sub-band at lower binding energy (with peak around 530.5 eV) corresponded to lattice oxygen O^{2-} (denoted as O_β), and the sub-band at higher binding energy (with peak around 531.4 eV) corresponded to surface-adsorbed oxygen (denoted as O_α), such as O_2^- or O^- belonging to defect-oxide or hydroxyl-like groups (Chen et al., 2010; Kang et al., 2007; Liu et al., 2009). It can be seen that the O_α ratio calculated by $\text{O}_\alpha / (\text{O}_\alpha + \text{O}_\beta)$ for VWTi and Ce-VWTi catalysts was decreased by K poisoning. A decrease in O_α ratio after doping alkali metals (K, Na) on $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts was also observed by Chen et al. (2010). Usually, O_α is more reactive in oxidation reactions due to its higher mobility than O_β , and a higher O_α ratio could be correlated with higher SCR activity (Gu et al., 2010; Kang et al., 2007; Liu et al., 2009; Shan et al., 2012). The higher O_α ratio on Ce-VWTi means that more surface oxygen vacancies existed, which is beneficial for higher SCR activity at 275°C , compared with VWTi. The O_α ratio on K-containing Ce-VWTi (46%) is higher than that on K containing VWTi (40%), which could be one of the contributors to the promotion of K resistance.

Fig. 6 shows the XPS results of V 2p and Ce 3d for fresh and K-poisoned VWTi and Ce-VWTi catalysts (Chen et al., 2009; Gu et al., 2010; Guo et al., 2009; Shi et al., 2011). The binding energy of V $2p_{2/3}$ was found at 516.2 eV for VWTi and 516.6 eV for Ce-VWTi (Guo et al., 2009; Shi et al., 2011). This suggests that vanadium in VWTi and Ce-VWTi existed as V^{4+} and V^{5+} . Higher V $2p_{2/3}$ binding energy for Ce-VWTi indicated that the ratio of $\text{V}^{4+}/\text{V}^{5+}$ on VWTi was affected by the Ce doping, with increasing

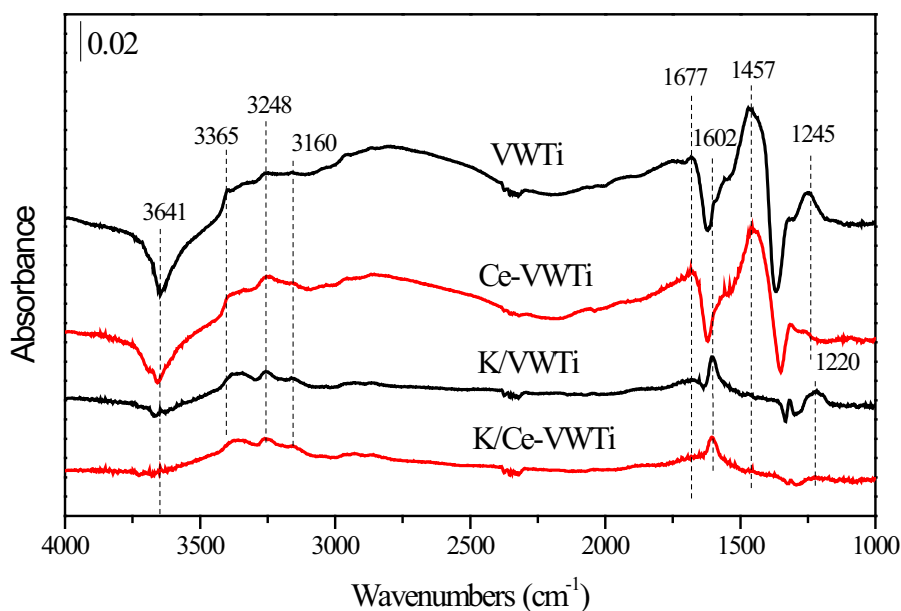


Fig. 3 – In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra of adsorbed ammonia species on fresh and K-containing catalysts ($\text{K/V} = 4$, molar ratio), recorded after exposure in $0.5\% \text{ NH}_3/\text{N}_2$ for 0.5 hr at 50°C and then purging by N_2 for 1 hr , then heating up to 150°C .

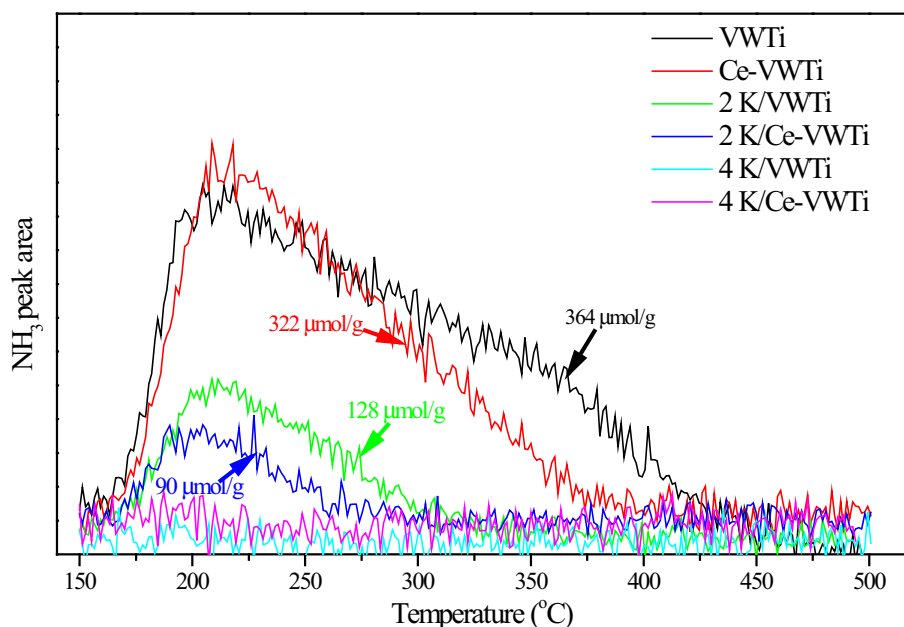


Fig. 4 – NH₃-temperature-programmed desorption (NH₃-TPD) profiles and NH₃ storage capacity of fresh and K poisoning VWTi and Ce-VWTi catalysts.

V⁵⁺ (Guo et al., 2009; Shi et al., 2011). The binding energy of V 2p_{2/3} for VWTi and Ce-VWTi did not shift after K poisoning. This result indicates that K poisoning did not affect the states of vanadium in the catalysts. From the XPS spectra of Ce 3d, a decrease in intensity of the pair of peaks corresponding to Ce³⁺ (u1,v1) and increase in intensity of the peaks corresponding to

Ce⁴⁺ (u, u2, u3, v, v2, v3) was observed on K/Ce-VWTi (Chen et al., 2009; Peng et al., 2012). This suggested that K poisoning caused the decrease of Ce³⁺ species and increase of Ce⁴⁺ species on the catalyst. A higher Ce³⁺/Ce⁴⁺ ratio indicates that more oxygen vacancies can be generated in the catalyst, which is beneficial for the NH₃-SCR reaction (Gu et al., 2010; Shan et al., 2012). A certain amount of Ce³⁺ species was found to be retained in Ce-VWTi with K/V = 4 (molar ratio). This might one of factors for the high SCR activity of this catalyst.

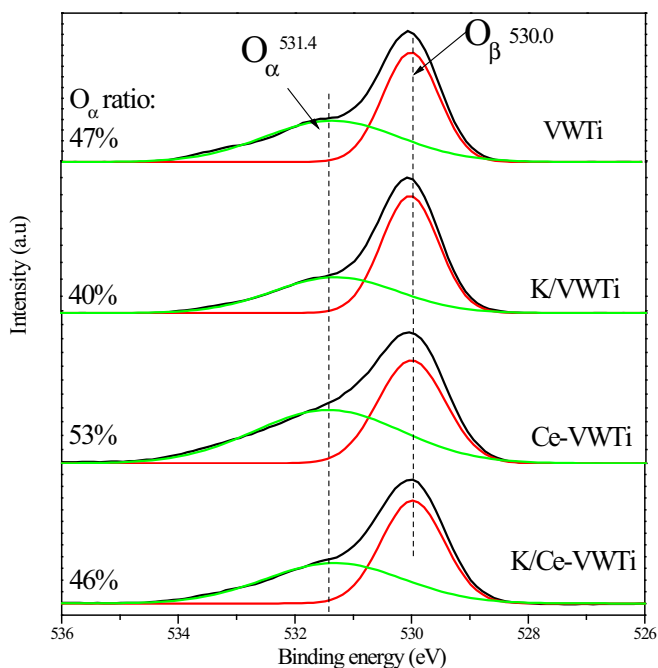


Fig. 5 – O 1s X-ray photoelectron spectroscopy (XPS) results over fresh and K-poisoned catalysts (K/V = 4, molar ratio). O_α: surface-adsorbed oxygen; O_β: lattice oxygen O²⁻.

2.5. H₂-TPR results

The reducibility of vanadium species over V₂O₅(-WO₃)/TiO₂ can be diminished by alkali metal poisoning, which is one of the main factors for the decrease of SCR activity (Chen et al., 2010; Tang et al., 2010). Therefore, H₂-TPR experiments were carried out to examine the influence of the alkali metals on the reduction behavior of the VWTi and Ce-VWTi catalysts. The H₂-TPR profiles of fresh and K-poisoned catalysts are shown in Fig. 7. It can be seen that the TPR profiles for all samples are similar. The first strong peak at 380°C for VWTi can be attributed to the reduction of V⁵⁺ to V³⁺ (Chen et al., 2009, 2010; Shi et al., 2011; Tang et al., 2010). The strong peak at 472°C for Ce-VWTi can be attributed to the reduction of V⁵⁺ and Ce⁴⁺. The results suggested that the reduction behavior of the catalysts is greatly influenced by the K poisoning. The first strong peaks on K/VWTi and K/Ce-VWTi shifted to higher temperatures, at around 530°C. This indicated that the K doping into the catalysts decreased the reducibility of active metal species (V and Ce). Those results are in agreement with the results of Tang et al. (2010) and Chen et al. (2010), who found that the reduction peaks of V species over alkali metal-poisoned V₂O₅/TiO₂ and V₂O₅/WO₃-TiO₂ shifted to higher temperature. The results showed that the difference in the

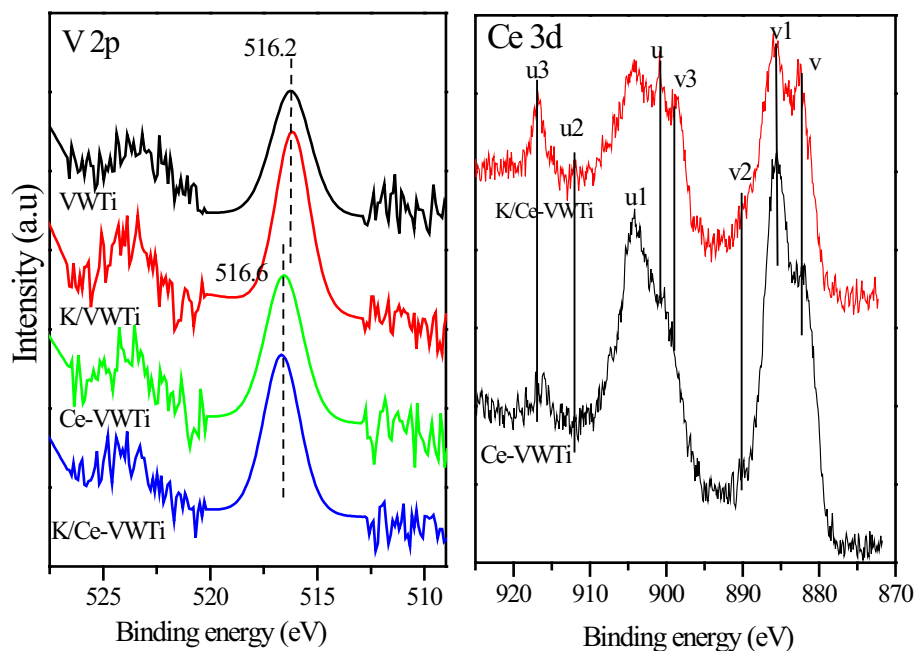


Fig. 6 – V 2p and Ce 3d XPS results for fresh and K-poisoned catalysts (K/V = 4, molar ratio).

temperature of first strong reduction peaks between fresh and K-containing catalyst was much higher with VWTi than for Ce-VWTi. This suggested that the decrease of reducibility of active metal species over Ce-VWTi due to K doping was much lower than that over VWTi.

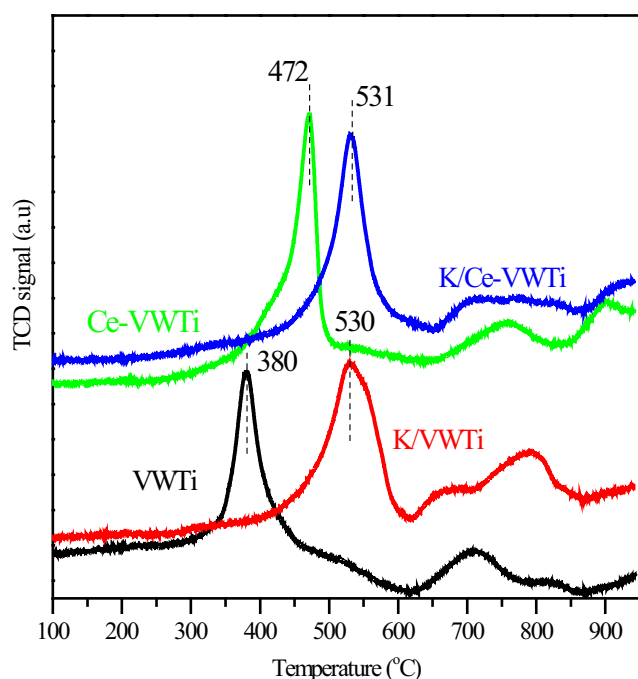


Fig. 7 – H₂-temperature program reduction (H₂-TPR) profiles of fresh and K-poisoned catalysts (K/V = 4, molar ratio). TCD: thermal conductivity detector.

It is generally accepted that the vanadia species over vanadia-tungsta-titania are the active sites for SCR reaction which act as both acid sites and redox sites (Marberger et al., 2016). The blockage or occupation of active sites by alkali metals resulted in the loss of SCR activity (Nicosia et al., 2008). Peng et al. (2012) ascribed the promotion of alkali resistance of V_{0.4}-W₁₀/Ti by substitution 5% W by Ce to the enhancement of the reducibility of the catalyst, Ce acting as an alkali metals' reservoir, and the transformation of alkali metal to ceria phase more possibly than to TiO₂. Chen et al. (2015) considered that tungsten oxide can act as a sacrificial agent for the K poisoning of V₂O₅-WO₃/TiO₂, and the residual vanadia active sites were critical to SCR activity of poisoned V₂O₅-WO₃/TiO₂. Therefore, the V₂O₅-WO₃/TiO₂ with highest V loading showed the best alkali resistance in their study (Chen et al., 2015). On the other hand, the Ce species are generally considered as the redox sites for Ce-based SCR catalysts (Shan et al., 2011, 2012). From the results in Appendix A Fig. S1, the CeWTi showed obviously better K resistance than VWTi and lower K resistance ability than Ce-VWTi. Additionally, the significant decrease of surface acidity can be observed for both VWTi and Ce-VWTi. Taking those things into account, we considered that, the enhancement of alkali resistance of Ce-VWTi might be mainly attributed to the increase of remained active sites for SCR reactions by Ce.

3. Conclusions

The effect of K poisoning on SCR activity was investigated on V₂O₅/WO₃-TiO₂ and Ce-doped V₂O₅/WO₃-TiO₂ catalysts. The addition of Ce improved the K resistance of V₂O₅/WO₃-TiO₂ catalysts. The Ce-V₂O₅/WO₃-TiO₂ catalysts gave much higher NO_x conversion compared with V₂O₅/WO₃-TiO₂, after being deactivated by the same dosage of K. The effect of K deactivation

on the acid sites resulted in a significant decrease of Brønsted acid sites, while Lewis acid sites were almost unchanged, both for V_2O_5/WO_3-TiO_2 and $Ce-V_2O_5/WO_3-TiO_2$ catalysts. The higher K resistance of $Ce-V_2O_5/WO_3-TiO_2$ might be attributable to the increase of remained active sites for SCR reactions by Ce after K doping.

Acknowledgements

This work was financially supported by the National Key research & development (R&D) Program of China (No. 2017YFC0211101), the Key Project of National Natural Science Foundation (No. 21637005) and Science and Technology Program of Tianjin, China (No. 16YFXTSF00290).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jes.2018.01.024>.

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