

New Insight into the Effect of Potassium on Commercial SCR Catalyst: Promotion of Thermal Stability

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Abstract Thermal stability is one of the most important indexes determining the practical applications of selective catalytic reduction (SCR) catalysts. The influence of typical alkali element on the thermal stability of industrial V_2O_5 - WO_3 / TiO_2 catalyst is first reported in this work. The activity of the sample is measured, and physicochemical properties are characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman spectrum, field emission scanning electron microscope (FE-SEM), N_2 adsorption-desorption, temperature programmed desorption of NH_3 (NH_3 -TPD), and in situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS). The sintering and anatase-to-rutile phase transformation at high temperature will cause deactivation of SCR catalyst, and low concentration of K can increase the thermal stability. Under the same thermal treatment, the activity (380 °C) of sample deposited by K is more than three

times higher than that of the fresh sample without K. Aggregation of vanadia in conventional SCR catalyst favors the sintering and anatase-to-rutile phase transformation of catalysts. Incorporation of K can modify the structure of partial V-OH and form V-OK, which hinders the aggregation of vanadia species and further increases the thermal stability of catalysts.

Keywords SCR catalyst · Thermal stability · Potassium · Sintering · Crystal transformation

1 Introduction

Nitrogen oxides (NO_x), which can cause photochemical smog, acid rain, ozone depletion, and so on, are one of the main air pollutants emitted from combustion of fossil fuels (Lietti et al. 1998). Selective catalytic reduction of NH_3 (NH_3 -SCR) is the most popular technique to abate NO_x from stationary source (Cheng et al. 2014; Fu et al. 2014). The commonly commercial catalyst for NH_3 -SCR is V_2O_5 - WO_3 / TiO_2 , in which V_2O_5 is the main activity phase, WO_3 is the promoter which can decrease the SO_2 oxidation, and TiO_2 (anatase) is the support supplying a large capacity of specific surface areas (Lietti et al. 1998; Zhang and Zhong 2013). However, rutile is more stable than anatase phase in thermodynamics and high temperature favors rutilization (anatase to rutile transformation) (Miao et al. 2004; Vargas et al. 2007; Casanova et al. 2012). The operation temperature of V_2O_5 - WO_3 / TiO_2 catalyst is generally in the range from 300 to 450 °C, but

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temperature in deNO_x section is unstable, and the catalyst would suffer from high temperature (>450 °C) occasionally due to complex combustion conditions, so the thermal stability is highly important for the catalyst.

The sintering of carrier or rutilization due to operation under high temperature for a long time will result in the decrease of specific surface area and catalytic activity (Vargas et al. 2007; Nova et al. 2001). In order to simulate the effect of long-term operation under high temperature, it is a common method at laboratory that SCR catalysts are treated under very high temperature (higher than 700 °C) (Casanova et al. 2012; Nova et al. 2001). Nova et al. studied the thermal deactivation of commercial SCR catalyst by calcining samples at temperature from 500 to 900 °C and concluded that catalysts operated for long term in gas firing at high temperature were no longer appropriate for commercial use (Nova et al. 2001). Odenbrand found that higher vanadia content would accelerate the sintering of SCR catalysts (Odenbrand 2008), while other researchers found that rare earth elements, such as zirconia and barium, could increase the thermal stability of vanadate SCR catalysts due to the change of vanadia morphologies (Casanova et al. 2006, 2012; Shi et al. 2011; Choung et al. 2006). For SCR catalysts used in coal or biomass power plants, it is unavoidable that alkali elements in the flue gas will deposit on the catalyst (Zheng et al. 2004). In previous research, most of researchers were focused on the effect of alkali elements on activity of the catalyst and found that a mass of alkali elements caused the deactivation of the catalyst (Yu et al. 2014; Zheng et al. 2004; Peng et al. 2012). But, there was little research about the influence of alkali elements on thermal stability of SCR catalysts. Alkali elements could modify the structure of vanadia, thus might affect the thermal stability. The research about the influence of alkali elements on thermal stability of SCR catalysts might help us find more details about the process of sintering and rutilization, which might benefit the improvement of SCR catalysts.

In this research, the influence of potassium on thermal stability of SCR catalysts was investigated. The activity of each sample was tested, and the textual and physical properties of all samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman spectrum, field emission scanning electron microscope (FE-SEM), N₂ adsorption-desorption, temperature programmed desorption of NH₃ (NH₃-TPD), and in situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS).

2 Experiment

2.1 Catalyst Preparation

The catalyst sample used in experiment was a commercial honeycomb SCR catalyst. According to results of X-ray fluorescence (XRF), the catalyst mainly consisted of V₂O₅ (1.29 wt%), WO₃ (3.66 wt%), and TiO₂ (85.42 wt%). Samples were cut into small cubic structure with 16 channels (about 3.2×3.2×4 cm in length, width, and height). The fresh sample (Fresh) was impregnated in 0.5 (D0.5), 1 (D1), and 2 wt% (D2) KNO₃ solution for 1 h, respectively. Then, samples were first calcined in air at 500 °C for 3 h. The concentrations of K in fresh, D0.5, D1, and D2 samples were determined by ICP-OES, and contents were 392, 1373, 2023, and 3202 ppm, respectively. In order to simulate the influence of high reaction temperature on SCR catalysts, the samples were calcined in air at 800 °C for 4 or 5 h (Casanova et al. 2012; Nova et al. 2001). More details could be found in Table 1.

2.2 Activity Tests

Catalytic activity was evaluated at a fixed-bed quartz reactor (Φ 10×600 mm). Catalyst sample (20–40 mesh, 2.5 mL) was placed in the middle of the reactor. The total gas flow rate was 1250 mL/min and consisted of NO (700 ppm), NH₃ (700 ppm), and O₂ (4 %) in N₂. Concentrations of O₂ and NO were measured by a flue gas analyzer (T-350, Testo Company, Germany), and N₂O was detected by gas chromatography (7890A, Agilent Technologies, USA). The NO conversion was defined by

$$x = \frac{C_{\text{NO,in}} - C_{\text{NO,out}}}{C_{\text{NO,in}}} \times 100\% \quad (1)$$

where the $C_{\text{NO,in}}$ and $C_{\text{NO,out}}$ were the NO concentrations of the gas stream in the inlet and outlet of the reactor.

2.3 Catalyst Characterizations

Samples were preheated at 300 °C in vacuum for 3 h, and then, nitrogen adsorption-desorption was measured at −196 °C on a NOVA 2000e surface area and pore size analyzer (Quantachrome, USA). The particle morphology of catalyst surface was observed by FE-SEM

Table 1 Textural properties of catalyst samples

Sample	Time ^a (h)	S _{BET} (m ² /g)	V _p ^b (cm ³ /g)	r _A (nm)	d _{cryst} (nm)
Fresh	–	52.9	0.3063	11.6	23.7
Fresh-4 h	4	10.4	0.0796	15.3	52.2
Fresh-5 h	5	4.4	0.0140	6.4	86.6
D0.5	–	55.5	0.2973	10.7	23.7
D0.5-4 h	4	19.4	0.2060	21.2	37.4
D0.5-5 h	5	4.8	0.0239	10.0	65.1
D1	–	52.7	0.3095	11.9	23.7
D1-4 h	4	44.1	0.2930	15.1	25.7
D1-5 h	5	31.9	0.2756	17.3	28.1
D2	–	55.6	0.3134	11.3	23.8
D2-4 h	4	46.1	0.3011	14.3	25.2
D2-5 h	5	34.0	0.2847	16.7	26.1

^a Calcined at 800 °C

^b Obtained at relative pressure of $P/P_0=0.99$

(S-4800, Hitachi, Japan). FTIR was recorded by Bruker Vertex 70 (Bruker, Germany), and the air was used as background spectrum, 32 scans, 4 cm⁻¹. XRD of powder sample was detected by X'Pert Pro XRD diffractometer (PANalytical B.V., Holland) with Cu palladium and K α ray. The crystallite size of anatase TiO₂ was calculated by Scherrer equation based on full width at half maximum (FWHM) of the (101) plane. NH₃-TPD was carried out on a Quantachrome ChemBET-3000TPR-TPD chemisorption analyzer, and the signal of NH₃ was detected by mass spectrum (DYCOR LC-D100, Ametek Company, USA).

In situ DRIFTS was collected using a Bruker Vertex 70 infrared spectrometer with a mercury-cadmium-telluride (MCT) detector cooled by liquid nitrogen. The catalyst sample powder was preheated in the reaction cell at 500 °C for 1 h under a stream of nitrogen (50 mL/min) and then cooled to 50 °C. The background spectrum was collected. After that, the powder was exposed to 3000 ppm NH₃/N₂ for 15 min and purged by N₂ for another 15 min. The spectrum was obtained by subtracting the background from the collected spectrum.

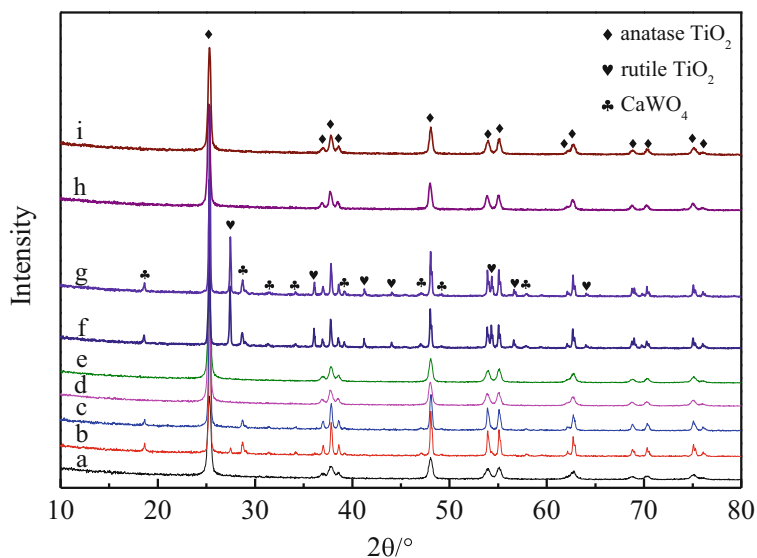
3 Results and Discussion

3.1 XRD and FE-SEM

The results of XRD for all samples are shown in Fig. 1. Fresh sample only showed typical diffraction peaks of

anatase TiO₂, indicating that V₂O₅ and WO₃ had a good dispersion over the support. D0.5, D1, and D2 samples also showed same peaks (shown in Fig. S1) and had no significant difference from fresh sample, suggesting that deposit of K had a negligible effect on crystal form of the carrier. After fresh catalyst was calcined at high temperature for 4 h, rutilization occurred and new peaks assigned rutile TiO₂ appeared (Nova et al. 2001; Cristallo et al. 2001). The peaks assigned to CaWO₄ were also found. According to other research, CaWO₄ should come from the reaction between WO₃ and CaO in high temperature and the solid state reaction is favored by sintering of the support (Nova et al. 2001). In order to increase the mechanical property of commercial catalysts, some additives which contained CaO were added to catalysts (Nova et al. 2001). When calcined time of fresh sample extended to 5 h, intensities of peaks assigned to rutile TiO₂ increased remarkably, implying that thermal influence on Fresh-5 h was more serious. However, when D0.5 sample was treated at high temperature for 4 h, only new peaks assigned to CaWO₄ appeared; the peaks assigned to rutile TiO₂ could not be found. While peaks assigned to rutile TiO₂ were clear in D0.5-5 h sample. For D1-4 h, D1-5 h, D2-4 h, and D2-5 h samples, only the peaks assigned to anatase TiO₂ were detected, indicating that thermal treatment did not cause an obvious rutilization of D1 or D2 sample. Mean crystallite sizes (d_{cryst}) of anatase TiO₂ for all samples calculated by Scherrer equation are shown in Table 1. The d_{cryst} of fresh sample was 23.7 nm, similar to other

Fig. 1 The results of XRD for catalyst samples. **a** Fresh, **b** Fresh-4 h, **c** D0.5-4 h, **d** D1-4 h, **e** D2-4 h, **f** Fresh-5 h, **g** D0.5-5 h, **h** D1-5 h, and **i** D2-5 h)



research (Nova et al. 2001; Madia et al. 2002). It seemed that deposition of K did not affect the crystallite sizes of anatase. After fresh sample was treated under high temperature, d_{crys} increased largely and varied with time, suggesting that serious sintering occurred. The d_{crys} of D0.5 sample also increased significantly and showed the same trend, while it was lower than that of fresh sample treated under the same conditions. When samples were treated at high temperature for 5 h, d_{crys} of D1-5 h and D2-5 h samples were obviously lower than Fresh-5 h and D0.5-5 h, suggesting that sintering degree of anatase in D1 and D2 were lower than fresh and D-0.5 samples. Thereby, it can be concluded that thermal stability of SCR catalyst was affected largely by deposition of K. The deposition of K should have a suppressive effect on sintering or rutilization of catalyst carrier.

FE-SEM photos of Fresh, D0.5, Fresh-4 h, and D0.5-4 h are shown in Fig. 2. The surface of fresh sample was loose, and particles were small. After treated by KNO_3 solution, the surface changed slightly compared with fresh catalyst (D1 and D2 samples also showed the similar surface and can be found in Fig. S2). However, when the fresh catalyst was treated under high temperature for 4 h, the surface of the catalyst changed remarkably and the particles were larger than fresh sample. The sintering and rutilization should be main reasons for the variation (Cristallo et al. 2001). The surface of D0.5-4 h was also significantly different from D0.5 sample, and the size of particles increased. But, the particles size of

D0.5-4 h was much smaller than that of Fresh-4 h. The influence of thermal treatment on fresh catalyst should be larger than the catalyst deposited with K.

3.2 FTIR and Raman Spectra

The results of FTIR for catalyst samples are shown in Fig. 3. Fresh sample showed a broad peak in the range from 900 to 400 cm^{-1} , which could be associated with anatase TiO_2 (Cristallo et al. 2001). D0.5, D1, and D2 samples also only showed a broad peak in the range from 900 to 400 cm^{-1} (shown in Fig. S3), indicating that the deposition of K did not lead to the crystal change of anatase TiO_2 , which was consistent with results of XRD. When fresh catalyst was calcined at high temperature for 4 h, the broad peak splits into three peaks and the new peaks became clearer when calcined time extended to 5 h, demonstrating that sintering occurred (Cristallo et al. 2001). For D0.5 sample, the same trend as Fresh sample was found. But when D1 and D2 samples were calcined at high temperature for 4 or 5 h, the broad peak showed only a slight change, not as significant as Fresh or D0.5 sample, indicating that the influence of high temperature on D1 and D2 samples was not as obvious as Fresh and D0.5 samples. The results of FTIR were in accordance with the data of XRD, indicating that the deposition of K increased the thermal stability of SCR catalyst.

The results of Raman spectra after normalizing for Fresh, D0.5, D1, and D2 samples are shown in Fig. 4. All samples presented a peak around 795 cm^{-1} , which was assigned to titanium-oxygen vibration of TiO_2

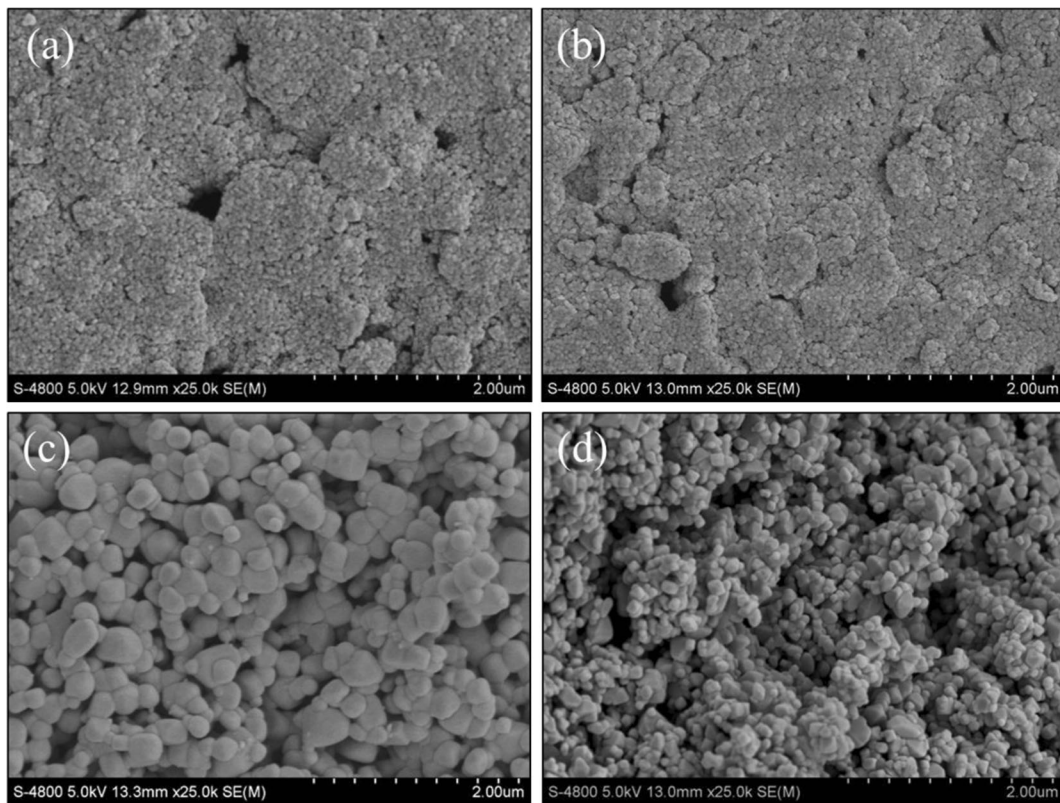


Fig. 2 FE-SEM photos of catalyst samples. **a** Fresh, **b** D0.5, **c** Fresh-4 h, and **d** D0.5-4 h

(Kamata et al. 1999). Fresh sample also showed a slight peak around 1028 cm^{-1} and a shoulder peak around 1008 cm^{-1} , which could be associated with monomeric vanadyl species and $\text{W}=\text{O}$ (Choo et al. 2003).

Compared with fresh sample, D0.5 sample showed no significant difference for the peak around 1028 or 1008 cm^{-1} . While for D1 sample, a new peak at 980 cm^{-1} appeared. The new peak moved to lower wave

Fig. 3 The results of FTIR for catalyst samples. **a** Fresh, **b** Fresh-4 h, **c** D0.5-4 h, **d** D1-4 h, **e** D2-4 h, **f** Fresh-5 h, **g** D0.5-5 h, **h** D1-5 h, and **i** D2-5 h

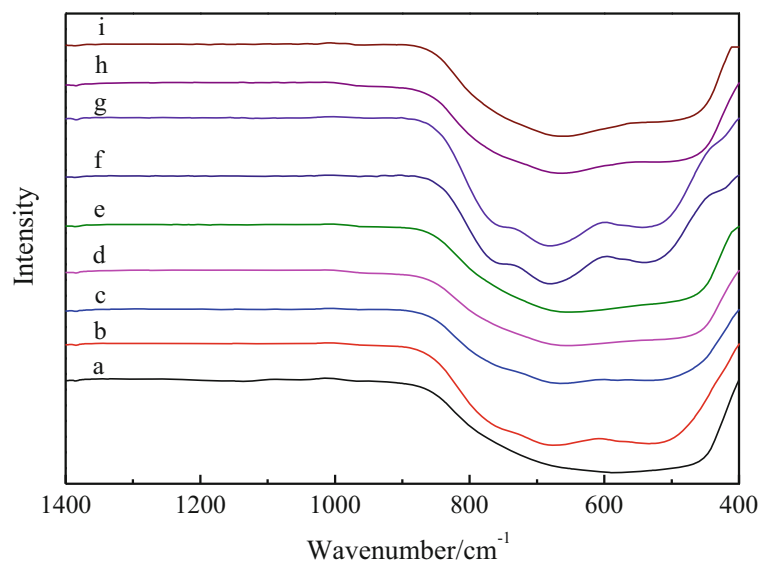
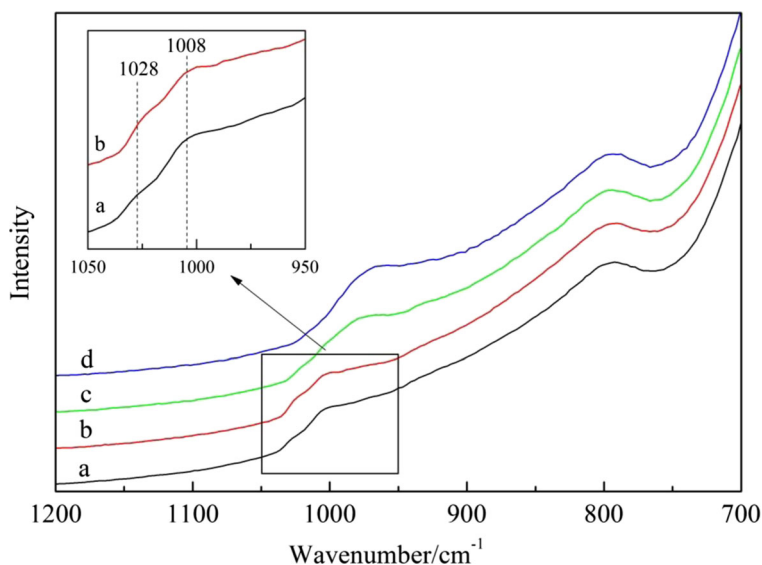


Fig. 4 The results of Raman spectra for catalyst samples. **a** Fresh, **b** D0.5, **c** D1, and **d** D2



number (about 970 cm^{-1}) for D2 sample, in agreement with the results of other research. Raman location of V species moved to lower wave number with the increase of K content (Kamata et al. 1999; Bulushev et al. 2001). K could react with V species and formed KVO_3 or other substance, inducing the movement of location (Bulushev et al. 2001).

3.3 N_2 Adsorption-Desorption

The specific surface areas (S_{BET}), total pore volume (V_{p}), and average pore radius (r_{A}) of samples are shown in Table 1. As Table 1 had shown, the thermal treatment affected the specific surface area significantly. The specific surface area of Fresh sample was $52.9\text{ m}^2/\text{g}$, but only remaining 20 % after the catalyst was calcined at high temperature for 4 h. When the calcined time extended to 5 h, the specific surface area was only 8 % of fresh catalyst, suggesting that sintering and rutilization largely decreased specific surface area. The deposit of K did not have a significant impact on the specific surface area and pore structure of the catalyst. After thermal treatment, the specific surface area of D0.5-4 h decreased significantly, but remained about two times of fresh-4 h, while the specific surface area of D0.5-5 h was similar to fresh-5 h. Compared with fresh and D0.5 samples, the specific surface areas of D1 and D2 were obviously higher after thermal treatment. The thermal treatment could cause the decrease of specific

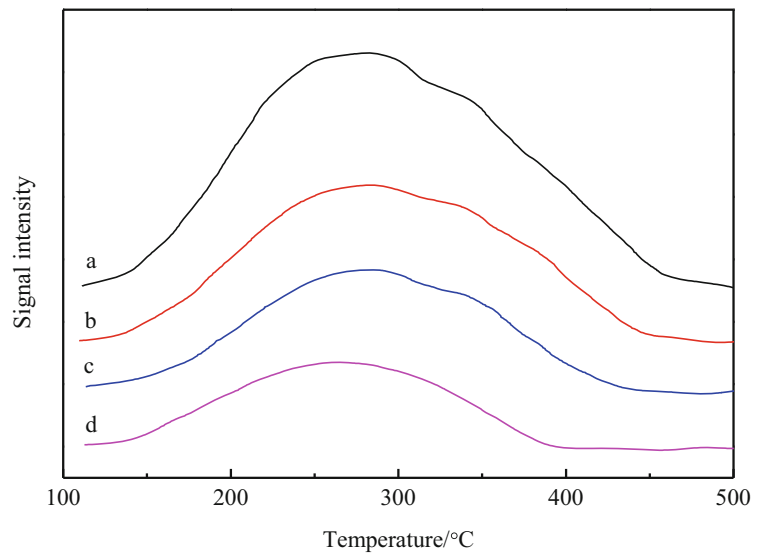
surface area, while the specific surface area of catalyst after thermal treatment increased with the addition of K content.

3.4 NH_3 -TPD and In Situ DRIFTS

V main was presented as two morphologies on the surface of catalyst, $\text{V}=\text{O}$ and $\text{V}-\text{OH}$, which were displayed as Lewis and Brønsted acid sites (Chen et al. 2011; Du et al. 2015). The influence of K on acid sites was measured by NH_3 -TPD and in situ DRIFTS. The results of NH_3 -TPD are shown in Fig. 5. Fresh sample showed a broad signal from about 120 to $450\text{ }^\circ\text{C}$. However, with increase of K concentration, the intensity of signal decreased and the temperature range narrowed. According to integration areas of the peak, the amount of acid sites of D0.5, D1, and D2 were about 63.1, 43.3, and 30.7 % to Fresh sample, respectively. The deposition of K decreased the amount of acid sites on catalysts, according to other research (Yu et al. 2014; Kamata et al. 1999; Chen et al. 2011).

The in situ DRIFTS spectra of Fresh, D0.5, D1, and D2 samples are shown in Fig. 6. After treated by 3000 ppm NH_3/N_2 for 15 min and purged by N_2 for another 15 min, the bands at 1220, 1460, 1603, and 1670 cm^{-1} appeared in fresh sample. The bands at 1460 cm^{-1} could be associated with NH_4^+ absorbed on Brønsted acid sites (main was $\text{V}-\text{OH}$) (Yu et al. 2014; Pan et al. 2013), and the bands at 1603 cm^{-1}

Fig. 5 NH_3 -TPD profiles of catalyst samples. **a** Fresh, **b** D0.5, **c** D1, and **d** D2



could be assigned to NH_3 absorbed on Lewis acid sites (main was $\text{V}=\text{O}$) (Yu et al. 2014; Pan et al. 2013). When the fresh catalyst was impregnated by KNO_3 solution, it could be found that the bands associated with NH_4^+ absorbed on Brønsted acid sites decreased largely, suggesting that the deposit of K had a large influence on the Brønsted acid sites, while the bands associated with NH_3 absorbed on Lewis acid sites changed little. K could modify the structure of V-OH and form V-OK on the surface of SCR catalyst (Zheng et al. 2004; Chen et al. 2011).

3.5 SCR Reaction Activity

The NO conversion of each sample is shown in Fig. 7. Fresh sample presented the highest activity from 300 to 450 °C. While with increase of K concentration, the activity decreased to some extent. The thermal treatment caused obvious decrease of activity. The NO conversion at 380 °C was only 32.7 and 15.4 % when the fresh catalyst was calcined at high temperature for 4 and 5 h. The activities of D0.5, D1, and D2 samples also decreased to

Fig. 6 The in situ DRIFTS spectra of catalyst samples. **a** Fresh, **b** D0.5, **c** D1, and **d** D2

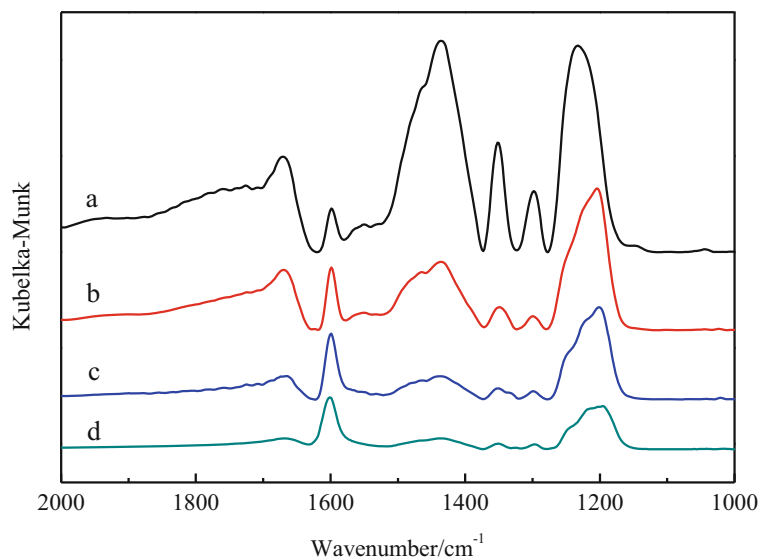


Fig. 7 The NO conversion of catalyst samples

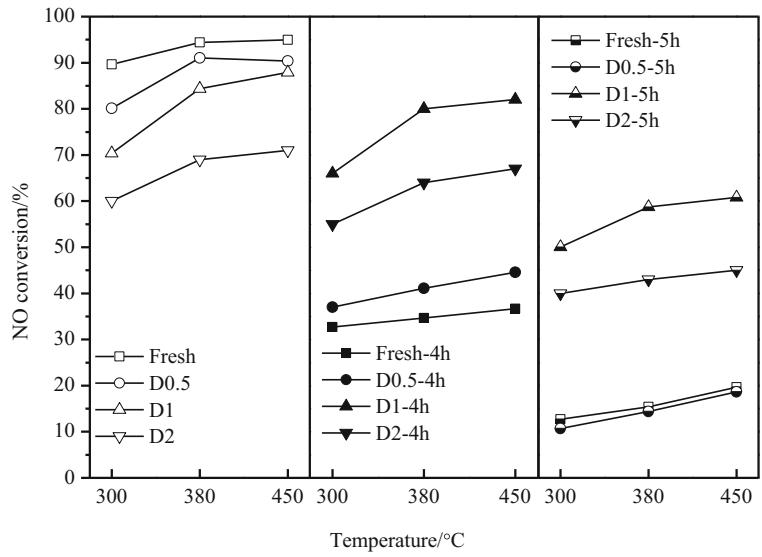


Fig. 8 The production of N₂O for catalyst samples

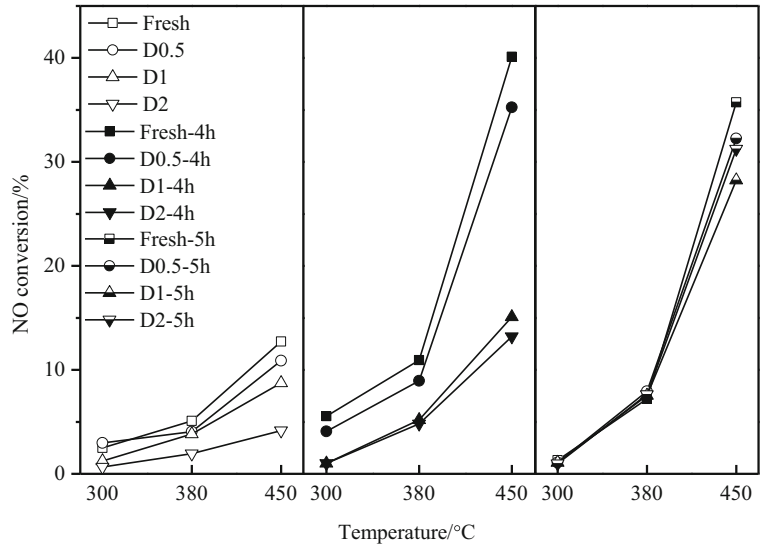
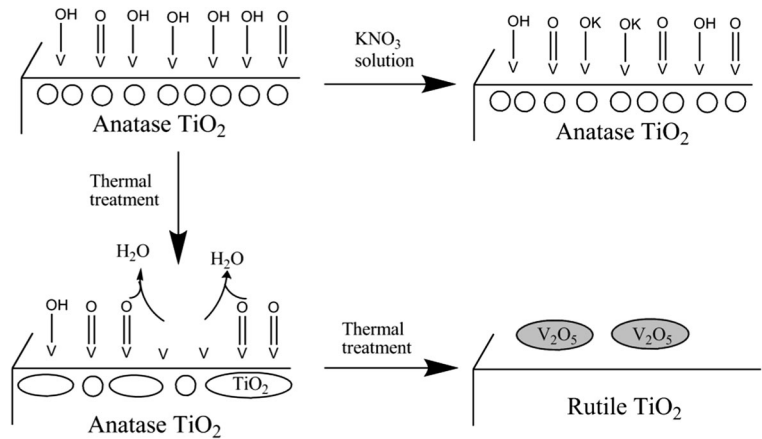


Fig. 9 The process of sintering and rutilization for SCR catalyst



some extent after thermal treatment. However, the activity of D0.5-4 h was still higher than that of fresh-4 h. Among the samples calcined for 5 h, it could be found that the activity of D1-5 h was the highest (55.7 %, 380 °C), significantly higher than that of fresh-5 h (15.4 %, 380 °C), indicating that a small quantity of K can counteract the thermal deactivation of SCR catalysts to some extent.

N₂O is the major by-product of SCR reaction (Zhang et al. 2012; Xu et al. 2015), and production of N₂O for all samples are shown in Fig. 8. The production of N₂O increased with reaction temperature for all samples. After Fresh sample was processed by thermal treatment, the N₂O concentration increased significantly at 450 °C, suggesting that operation for a long time under high temperature could cause the increase of by-products for SCR reaction. The samples deposited with K under high temperature also presented the same trend, and D1-5 h showed the lowest production of N₂O among samples treated under high temperature.

3.6 The Role of K in Prohibiting Sintering and Rutilization of Catalyst Carrier

According to the previous discussion, it could be found that the sintering and anatase-to-rutile phase transformation at high temperature caused deactivation of SCR catalyst and the deposit of K had a large influence on thermal stability of commercial V₂O₅-WO₃/TiO₂ catalyst. It seemed that K can hinder the sintering and rutilization of the catalyst carrier. As the results have shown, K main modified partial V-OH and formed V-OK on the surface of catalyst, so V-OH on the surface should be a key factor for thermal stability of SCR catalyst. The role of V-OH played on thermal transformation might be described as the following (Fig. 9). Under high temperature, the -OH of V-OH on the surface of catalyst would escape from the surface as H₂O, and then, vanadia should have a trend of aggregation. The aggregation of vanadia favored sintering and rutilization of TiO₂ (Odenbrand 2008; Peng et al. 2012). After K deposit on the surface of catalyst, the V-OK was formed (Fig. 9) and V-OK would hinder the aggregation of vanadia under high temperature. The unfavorable aggregation of vanadia would increase the thermal stability of SCR catalyst.

4 Conclusions

Due to sintering and anatase-to-rutile phase transformation, high temperature would result in the decrease of activity, increase of by-products for SCR catalysts, and significantly decrease of specific surface areas. However, the thermal stability of catalyst increased with the addition of K content and activity of sample deposited by K was higher than fresh sample without K under the same thermal treatment. The aggregation of vanadia should be an important step in the process of sintering and rutilization of commercial SCR catalysts. V-OH on the surface made an important contribution to aggregation of vanadia. The deposition of a small quantity of K could increase the thermal stability of V₂O₅-WO₃/TiO₂ catalyst, due to the formation of V-OK, which hindered the aggregation of vanadia under high temperature. The prevention of vanadia aggregation should be an effective method to increase the thermal stability of SCR catalyst.

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