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The way to enhance the thermal stability of V₂O₅-based catalysts for NH₃-SCR

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ABSTRACT

A series of V2O5/WO3-TiO2 and V2O5/SiO2-WO3-TiO2 catalysts containing 2 wt%, 3.5 wt% and 5 wt% V2O5, respectively, were prepared by impregnation method. The NH₃-SCR activity and thermal stability of the catalysts were investigated. It is noted that both V₂O₅ loading and SiO₂ modification could affect the thermal stability of the V_2O_5/WO_3 -TiO₂ catalysts. Increasing V_2O_5 loading improved the low temperature SCR activity of the catalvsts in fresh state, but high V₂O₅ loading aggravated the deactivation of the catalysts upon aging. With relatively high V2O5 loading (3.5 wt% and 5 wt% V2O5), V2O5/SiO2-WO3-TiO2 showed remarkably improved thermal stability than V2O5/WO3-TiO2 NH3-SCR catalysts. The catalysts were characterized by BET, XRD, SEM, Raman, XPS, H₂-TPR and NH₃-TPD. The results indicated that high V₂O₅ loading on V₂O₅/WO₃-TiO₂ catalyst can accelerate the phase transition of anatase TiO_2 to rutile TiO_2 upon thermal aging, which resulted in the loss of surface area and consequently led to the deactivation, while introduction of silica prevented the phase transition of TiO₂, therefore enhancing the thermal stability of the catalysts.

1. Introduction

Nitrogen oxides (NO_x) emitted from diesel engines is considered to be a key factor causing air pollution and environmental issues, which are harmful to human health [1]. Selective catalytic reduction of NO_r with NH₃ (NH₃-SCR) is one of the most efficient methods for the removal of NO_x in exhaust gas from diesel engines [2,3]. Vanadium-based catalysts, which are widely used as NH₃-SCR catalysts for stationary sources, have also been applied for the abatement of NO_x from heavyduty diesel vehicles, due to their high catalytic efficiency, economy and sulfur resistance [1,4].

The commercial vanadium-based SCR catalyst typically consists of V₂O₅ as the active redox species, anatase TiO₂ as support material, and WO₃ or MoO₃ as both structural and chemical promoters [2,4]. Surface vanadium remains in the amorphous phase of monolayer over the high surface area TiO₂. At low vanadia loading, vanadium is dispersed mainly as monomeric vanadyl species over the catalyst surface, while polymeric vanadate species and crystalline V2O5 can be formed with higher vanadia loading [5-10]. Extensive research has been undertaken to improve different aspects of vanadium-based SCR catalysts, such as improving low temperature activity [11-15], promoting alkali resistance [16-19] and inhibiting the SO₂ oxidation by V₂O₅ [14,15,20].

However, one of the major issues of V2O5/WO3-TiO2 catalysts for diesel vehicle applications is their poor thermal stability in high-temperature exhaust gas [21]. The vanadium content was found to have a major influence on the thermal stability of V₂O₅/WO₃-TiO₂ catalysts [9,21-24]. Moreover, SiO₂ has been studied as a structural and chemical promoter to vanadium-based SCR catalyst. Pârvulescu et al. [25] prepared mesoporous V2O5-TiO2-SiO2 catalysts by one-pot sol-gel and hydrothermal methods and found higher intrinsic SCR activity than conventional V2O5-TiO2 catalyst. Kobayashi et al. [20,26] reported that vanadium-titanium catalysts using TiO2-SiO2 as support showed higher SCR activity than those using TiO2 alone. Pan et al. [27] observed that Si-doped V₂O₅/TiO₂ catalysts showed improved acid sites and oxidation properties, which enhanced SCR activity. However, little information on comprehensive effects of V2O5 loading and metal oxide-doping on the thermal stability of vanadium-based SCR catalysts has been reported to date.

In this study, a series of V_2O_5/WO_3 -TiO₂ and V_2O_5/SiO_2 -WO₃-TiO₂ catalysts with different V2O5 loading were prepared and thermally

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treated at 650 $^{\circ}$ C for 36 h. The effects of different V₂O₅ loading and silica modification on the NH₃-SCR performance and thermal stability of the catalysts were investigated.

2. Experimental

2.1. Catalyst preparation

A series of V₂O₅/WO₃-TiO₂ and V₂O₅/SiO₂-WO₃-TiO₂ catalysts with V₂O₅ loading amounts of 2 wt%, 3.5 wt% and 5 wt% were prepared by impregnation method, using commercial WO₃-TiO₂ and SiO₂-WO₃-TiO₂ as supports. Desired amount of NH₄VO₃ was dissolved in deionized H₂O with oxalic acid as solubilizing assistant, and then mixed with WO₃-TiO₂ (WT, "Tiona DT-52", 10 wt% WO₃ and 90 wt% TiO₂, Cristal Global, Thann, France) or SiO₂-WO₃-TiO₂ (SiWT, "Tiona DT-58", 10 wt% SiO₂, 9 wt% WO₃ and 81 wt% TiO₂, Cristal Global, Thann, France) powders. After stirring for 1 h, the water of the slurry was evaporated using a rotary evaporator, and the sample was dried at 120 °C for 12 h. Finally, the sample was grinded thoroughly and calcined at 500 °C in a muffle oven for 3 h (fresh catalyst). The obtained catalysts were denoted as *xV*/WTi and *xV*/SiWTi, where *x* represents V₂O₅ content (wt %). Thermal aging was carried out at 650 °C in air for 36 h to obtain the aged supports and catalysts, which were denoted with an "A" suffix.

2.2. Activity measurements

The NH₃-SCR activities were tested in a fixed-bed quartz tube flow reactor at atmospheric pressure. The reaction conditions were as follows: 500 ppm NO, 500 ppm NH₃, 5 vol% O₂, balance N₂, and 500 mL/ min total flow rate. During the test, 300 mg of powder catalyst (sieved to 40–60 mesh) was used, which gave a GHSV of 50,000 h⁻¹. The effluent gas, including NO, NH₃, NO₂ and N₂O was continuously analyzed by an online NEXUS 670-FTIR spectrometer equipped with a gas cell with 0.2 dm³ volume.

2.3. Characterizations

The surface areas of the samples were obtained by N₂ adsorption/ desorption analysis at -196 °C, using a Quantachrome Quadrasorb SI-MP. Prior to the N₂ physisorption, the catalysts were degassed at 300 °C for 4 h. Surface areas were determined by BET equation in 0.05-0.35 partial pressure range.

The surface morphologies and elemental compositions of the samples were investigated using a scanning electron microscope (SEM, Hitachi, S-3000 N) combined with an energy dispersive X-ray (EDX) attachment. The accelerating voltage was 5.0 kV.

Powder X-ray diffraction (XRD) measurements were carried out on a computerized PANalytical X'Pert Pro diffractometer with Cu K α (λ = 0.15406 nm) radiation. The data of 2 θ from 5° to 90° were collected with a step size of 0.07°.

Raman spectra were measured on a UVR-DICP-DL03 Raman spectrometer using a 532 nm laser as the exciting source. The samples were heated from room temperature to 400 °C under an oxygen flow in an *in situ* reaction cell, and then the Raman spectra were acquired.

X-ray photoelectron spectroscopy (XPS) analysis of the samples was carried out by a VG Systems-MICROLAB 300A instrument using Mg K α radiation to excite photoelectrons. The energy scale was calibrated versus the Au 4f7/2 signal at 84.0 eV. The binding energy was normalized with respect to the position of the C 1s peak resulting from adsorbed hydrocarbon fragments.

 $\rm H_2$ temperature-programmed reduction (H₂-TPR) was conducted on a Micromeritics AutoChem II 2920. The samples (60 mg) were pretreated at 300 °C in a flow of 20% O₂/Ar (50 mL min⁻¹) for 30 min and cooled down to room temperature followed by Ar purging for 0.5 h. Then reduction profiles were obtained by passing a flow of 10% H₂/Ar (50 mL/min) through the sample from 50 to 1000 °C at a ramp heating



Fig. 1. NO_x conversion of the fresh and thermally aged catalysts: (a) V/WTi, (b) V/SiWTi.

rate of 10 $^{\circ}$ C min⁻¹. The consumption of H₂ was continuously monitored using a thermal conductivity detector (TCD).

 $\rm NH_3$ temperature-programmed desorption (NH_3-TPD) was performed with the same apparatus used for catalytic activity. The samples (100 mg) were pretreated at 400 °C in a flow of 20% O_2/N_2 (125 mL min^{-1}) for 30 min and cooled down to room temperature. Prior to NH_3-TPD, the samples were saturated by 50 ppm NH_3 at 50 °C. The TPD experiment was performed from 50 to 500 °C by ramp heating rate of 10 °C min^{-1}. The effluent gas was continuously analyzed by an online NEXUS 670- FTIR spectrometer.

3. Results

3.1. Catalytic activity

To investigate the effects of V₂O₅ loading on the thermal stability, the NH₃-SCR activity of fresh and thermal-aged V/WTi and V/SiWTi catalysts were tested. The NO_x conversions of the catalysts with different V₂O₅ loading at temperatures from 150 °C to 450 °C under a fixed GHSV of 50,000 h⁻¹ are shown in Fig. 1. The results showed that, in the fresh state, the NH₃-SCR activities of both V/WTi and V/SiWTi catalysts increased with increasing V₂O₅ loading in the low temperature region.

Upon thermal aging, all of the catalysts exhibited decreased NO_x reduction activity over the whole temperature range, and the increase of V_2O_5 loading aggravated the deactivation of the catalysts. For both of the V/WTi and V/SiWTi catalysts with 2 wt% of V_2O_5 loading, only slight decrease of NH_3 -SCR activities was observed upon aging. Aged 2 V/WTi and 2 V/SiWTi catalyst still demonstrated 100% NO_x conversion in the range of 275–400 °C. However, when the V_2O_5 loading was increased to 3.5 wt% and 5 wt%, there is a significant difference of thermal stability between V/WTi and V/SiWTi catalysts. 3.5 V/WTi and 5 V/WTi catalysts were deactivated severely upon aging, while 3.5 V/

Table 1

Specific surface area, pore volume and pore diameter of the fresh and thermally aged supports and catalysts.

Catalysts	Specific surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	
WTi	89	0.31	14.4	
SiWTi	98	0.31	13.3	
WTiA	50	0.27	23.1	
SiWTiA	81	0.30	14.7	
2 V/WTi	80	0.30	15.2	
2 V/SiWTi	84	0.29	14.0	
2 V/WTiA	19	0.13	28.3	
2 V/SiWTiA	58	0.63	18.0	
3.5 V/WTi	62	0.28	18.1	
3.5 V/SiWTi	83	0.31	14.8	
3.5 V/WTiA	0.90	0.015	65.1	
3.5 V//SiWTiA	28	0.12	16.8	
5 V/WTi	70	0.30	16.9	
5 V/SiWTi	75	0.27	14.4	
5 V/WTiA	0.096	0.0013	56.1	
5 V/SiWTiA	6.3	0.039	24.5	

SiWTi and 5 V/SiWTi catalysts showed remarkably improved thermal stability.

3.2. Characterization of supports and catalysts

3.2.1. BET surface area

The BET specific surface areas (SSA), pore volumes and pore diameters of the supports (WTi and SiWTi) and the catalysts (V/WTi and V/SiWTi) are summarized in Table 1. For the unloaded supports, fresh SiWTi possesses larger SSA than WTi (by ca. $9 \text{ m}^2/\text{g}$). Upon aging, the SSA of SiWTi ($17 \text{ m}^2/\text{g}$, 17%) decreased obviously less than that of WTi ($39 \text{ m}^2/\text{g}$, 44%). This result indicates that doping of Si could inhibit the loss of SSA, which would be beneficial for the thermal stability.

For the V₂O₅-loaded catalysts, the SSAs of fresh catalysts were lower than those of the unloaded supports, while V/SiWTi catalysts still possesses lager SSAs than those of V/WTi catalysts. The SSAs of all the supports and catalysts decreased upon thermal aging. Fig. 2 shows the percentages of the SSA loss of supports and catalysts upon aging. It is evident that increasing V₂O₅ loading enhanced the SSA loss of the catalysts upon aging.

Similar with the unloaded supports, V/SiWTi catalysts showed less SSA decrease upon aging than V/WTi catalysts with same V_2O_5 loading. With 3.5 wt% and 5 wt% V_2O_5 , evident differences of SSAs were observed between V/WTi and V/SiWTi catalysts, as V/WTi lost almost all of the SSA upon aging, while aged V/SiWTi remained 28 and 6 m²/g



Fig. 2. SSA loss upon aging of the supports and catalysts.

SSAs, respectively. Considering the SCR performance, surface area is a significant factor for the thermal stability of the catalysts with high V_2O_5 loading. Therefore, it is important to inhibit the loss of surface area induced by thermal conditions.

3.2.2. SEM

Scanning electron microscope (SEM) was carried out to investigate the surface topography and compositions of the supports (WTi and SiWTi) and the catalysts (V/WTi and V/SiWTi). The SEM patterns of the thermal aged samples are shown in Fig. 3. The particle sizes of the unloaded supports and V₂O₅-loaded catalysts were similar in fresh condition (Fig. S2). However, upon aging, there was a big difference among the surface topography of the catalysts with different V₂O₅ loadings. With 2 wt% of V₂O₅ loading, the particle size of both aged V/ WTi and V/SiWTi catalysts were similar with the fresh samples. However, with 3.5 wt% and 5 wt% of V₂O₅ loading, the particle sizes of the aged catalysts apparently increased. This result indicated that thermal aging could induce serious sintering and surface area loss on V/WTi and V/SiWTi catalysts with high V₂O₅ loading. Therefore, the development of low V₂O₅ content catalyst with high activity would be a way to obtain high thermal stability.

3.2.3. XRD

The Powder X-ray diffraction (XRD) patterns of the fresh and thermally aged supports and catalysts are shown in Fig. 4. For all of the fresh supports and catalysts, only XRD peaks of anatase TiO₂ were observed. After thermal aging, the XRD patterns of WTi support, SiWTi support, 2 V/WTi catalyst and 2 V/SiWTi catalyst were similar with those of the fresh samples. However, diffraction peaks for rutile TiO₂ were observed in the patterns of the V/WTiA and V/SiWTiA catalysts with 3.5 wt% and 5 wt% V₂O₅ loadings. For XRD pattern of 5 V/WTiA, rutile TiO₂ diffraction peaks predominated, which indicated that high V₂O₅ loading on the catalyst can accelerate the phase transition from anatase to the rutile TiO₂. As a result, the surface area (as shown by BET results) reduced and the activity decreased.

On the other hand, with 3.5 wt% and 5 wt% of V_2O_5 loadings, notably more anatase TiO_2 phase and less rutile TiO_2 phase was observed for V/SiWTi than V/WTi, indicating that introduction of silica could prevent the phase transition, and thus enhance the thermal stability of the catalyst. Therefore, the introduction of structure promoter to inhibit phase transition would be a way to enhance thermal stability.

3.2.4. Raman spectra

Further discussion is focused on catalysts with 2% and 3.5% of V_2O_5 loading, due to the significant difference between their thermal stabilities. As the active sites of VWTi catalysts in SCR reaction, the state of vanadia species on the catalyst surface plays a key role on catalytic behavior. Therefore, Raman spectra were collected on fresh and thermal aged V/WTi and V/SiWTi catalysts. Due to the strong peaks below 700 cm⁻¹ arising from the TiO₂ support, spectra for the catalysts are presented in the range from 700 to 1100 cm⁻¹ (Fig. 5).

The well-defined band at 1010-1030 cm⁻¹ were observed for the catalysts in fresh condition, corresponding to the V=O stretching of dispersed vanadia species. For all the catalysts, these bands became weaker after thermal aging, even disappeared for aged 3.5WTi catalyst. The bands around 800 cm⁻¹ consists of the W–O–W stretching of octahedrally co-ordinated W units [21]. These bands were detected on the aged catalysts 2 V/WTiA, 3.5 V/WTiA and 3.5 V/SiWTiA, which indicated that thermal aging also caused WO₃ crystallites separating out on the catalysts.

3.2.5. XPS

X-ray photoelectron spectroscopy (XPS) was carried out to characterize the surface concentrations and oxidation states of V, W and Si. The XPS results of fresh and thermally aged V/WTi and V/SiWTi catalysts with 2 wt% and 3.5 wt% of V_2O_5 loading are summarized in



Fig. 3. SEM micrographs of the thermally aged supports and catalysts.



Fig. 4. XRD patterns of the supports and catalysts: (a) fresh supports and catalysts, (b) thermally aged supports and catalysts. The results were normalized by the strongest diffraction peak.

Table 2.

The V/Ti and W/Ti atomic ratios of all the catalysts and the Si/Ti atomic ratios of all V/SiWTi catalysts increased after thermal aging, indicating the increase of V, W and Si concentrations on the surface of correspondent aged catalysts, which may be caused by the decrease of SSA of the catalysts.

The V 2p BE measured for all the fresh catalysts was from 516.15 to 516.6 eV, which was lower than the value for bulk V-containing phases (516.8–517.7 eV) [21]. Low V 2p BE is associated with the presence of well dispersed vanadia on the support. After aging, a significant increase of V 2p BE was observed for all the catalysts, indicating that the dispersion of vanadia declined, potentially with the transition from monolayer to multilayer vanadia, corresponding to V/Ti atomic ratios increasing after aging [21]. The W 4f7 BE remained at a similar value of 2 V/WTi, 2 V/SiWTi and 3.5 V/SiWTi after aging, while a lower W 4f7 BE (34.95 eV) was measured for 3.5 V/WTi and increased to 35.6 eV after aging. The Si 2p BE measured for 2 V/SiWTi and 3.5 V/SiWTi in fresh and aged condition remained in a small range of value (102.8–103.1 eV), indicating a stable oxidation states of Si after thermal aging.

3.2.6. H2-TPR

 H_2 temperature-programmed reduction (H₂-TPR) was carried out to investigate the effects of thermal aging on the redox properties of the catalysts. The H₂-TPR profiles of the fresh and thermally aged 3.5 V/WTi and 3.5 V/SiWTi catalysts are shown in Fig. 6. For the fresh



Fig. 5. Raman spectra of the fresh and thermally aged 2 V/WTi, 3.5 V/WTi, 2 V/SiWTi, and 3.5 V/SiWTi catalysts.

Table 2

XPS results for the fresh and thermally aged catalysts.

Sample	V/Ti atomic ratio	W/Ti atomic ratio	Si/Ti atomic ratio	V 2p BE (eV)	W 4f7 BE (eV)	Si 2p BE (eV)
2 V/WTi 2 V/WTiA 3.5 V/WTi 3.5 V/WTiA 2 V/SiWTi 2 V/SiWTiA	0.054 0.112 0.083 0.205 0.055 0.056	0.083 0.146 0.084 0.205 0.108 0.154	- - - 0.562 0.694	516.2 517 516.15 517.6 516.3 517.25	35.25 35.15 34.95 35.6 35.6 35.7	- - - 103.1 103
3.5 V/SiWTi 3.5 V/SiWTiA	0.068 0.168	0.121 0.164	0.592 0.884	516.6 517.1	35.4 35.45	102.85 102.8



Fig. 6. $\rm H_2\text{-}TPR$ profiles of the fresh and thermally aged 3.5 V/WTi and 3.5 V/ SiWTi catalysts.

catalysts, three reduction peaks are observed at about 460 °C, 570 °C and 760–830 °C. The first peak is ascribed to the co-reduction of V⁵⁺ to V³⁺ corresponding to surface vanadia species [17,28]. The peak around



Fig. 7. NH₃.TPD curves of the fresh and thermally aged 3.5 V/WTi and 3.5 V/ SiWTi catalysts.

570 °C is ascribed to the reduction of W^{6+} to W^{4+} of tungsten oxide [17,28]. The third peak, at 760–830 °C, is ascribed to the reduction of W^{4+} to W^0 [28].

For the thermally aged catalysts, two catalysts showed the peak centered at about 480 °C, which is ascribed to the reduction of V^{5+} to V^{3+} of surface vanadia species [17,28]. The peak at 560 °C was only observed in 3.5 V/WTiA, which was caused by the superimposed reduction of $V^{5\, +}$ to $V^{3\, +}$ of crystalline vanadia and $W^{6\, +}$ to $W^{4\, +}$ of tungsten oxide. Comparing with the fresh catalyst, the redox capability of V/WTiA dramatically decreased. Moreover, the reduction peaks corresponding to surface vanadia species was severely weakened, which correlates with the Raman results, indicating the formation of Ti-V-O solid solution. The peak at around 650 °C, is ascribed to the reduction of W^{6+} to W^{4+} on the surface of crystalline WO₃ [29,30]. The third peak, centered at 760-830 °C, is ascribed to the reduction of W⁴⁺ to W⁰. The H₂-TPR results indicated that the redox functions of both catalysts decreased after thermal aging, and the decrease for 3.5 V/WTi was more severe. The decrease of redox functions is associated with the loss of low-temperature activity due to thermal aging.

3.2.7. NH3-TPD

NH₃ temperature-programmed desorption (NH₃-TPD) was carried out to investigate the change of surface acidity of the catalysts after thermal aging. The NH₃-TPD curves of the fresh and thermally aged samples are shown in Fig. 7. The amount of NH₃ adsorptions at 50 °C for 3.5 V/WTi, V/SiWTi, V/WTiA and V/SiWTiA catalysts were 542, 478, 379 and 230 µmol/g, respectively. As shown in Fig. 7, all the curves indicate two NH₃ desorption peaks, which correspond to the desorption of NH₃ bond to weak Brønsted acid site and Brønsted and Lewis acid sites, respectively [31]. 3.5 V/SiWTi showed an increase in the number and strength of acid sites than 3.5 V/WTi, which is associated with the higher surface area of 3.5 V/SiWTi. After thermal aging, more significant decrease in surface acidity is observed on V/WTiA than V/ SiWTiA, which is associated with the loss of high-temperatures SCR activity.

4. Discussions

The results reported above indicate that vanadium content has a remarkable influence on the thermal stability of both V_2O_5/WO_3 -TiO₂ and V_2O_5/SiO_2 -WO₃-TiO₂ catalysts. With low V_2O_5 loading (2 wt%), slight decrease of NH₃-SCR activities was observed upon aging, while increasing V_2O_5 loading aggravated the deactivation of aged catalysts. As a result, dramatic decrease of NH₃-SCR activities was observed with high V_2O_5 -loaded (5 wt%) catalysts upon aging.

BET, SEM and XRD were carried out to study the structural properties of the supports and catalysts. It is evident from the results that increasing V_2O_5 loading enhanced the loss of SSA of the catalysts upon aging, due to the sintering of anatase TiO₂ and the phase transition from anatase to rutile TiO₂, which is considered to be a major factor contributing to the deactivation of aged catalysts.

Considering the change of vanadium state upon thermal aging, XPS results indicate that V concentrations on the surface of the catalysts increased after aging, while the V 2p BE increased to a significant higher value that is close to the BE value of bulk V phases, indicating declined vanadia dispersion. However, from the results of Raman spectra, the band assigned to V=O stretching was dramatically weakened upon aging. This result suggests that the vanadia phase was reduced and became incorporated into the titania support as $V_xTi_{1-x}O_2$ solid solution upon thermal aging, which accelerated the phase transition of TiO₂ [9].

In the meanwhile, Si modified catalysts showed higher thermal stability with relatively high V_2O_5 loading (3.5 wt% and 5 wt%). Remarkably higher NH₃-SCR activities was observed for aged 3.5 V/SiWTi and 5 V/SiWTi catalysts, comparing to aged V/WTi catalysts with same V_2O_5 loading. Upon aging treatment, V/SiWTi catalysts reserved higher BET SSA, due to the less phase transition from anatase to rutile TiO₂. H₂-TPR and NH₃-TPD indicated that thermal aged 3.5 V/SiWTiA also showed higher redox capability and greater amount of surface acidity than 3.5 V/WTiA. This is consistent with the results of Raman spectra, which showed the difference between vanadium state of 3.5 V/SiWTi and 3.5 V/WTi upon aging. The Raman band corresponding to V species disappeared in aged 3.5 V/SiWTi catalysts, while weakened broader band can be observed in 3.5 V/SiWTi catalysts, indicating that the formation of V_x Ti_{1-x}O₂ solid solution during titania phase transition was prevented by Si introduction.

Adjusting V₂O₅ loading of V₂O₅-based NH₃-SCR catalysts is a tradeoff between low temperature SCR activity and thermal stability. The introduction of SiO₂ significantly enhanced the thermal stability of V₂O₅/WO₃-TiO₂ catalysts with relatively high V₂O₅ loading, as the added SiO₂ could prevent the phase transition of TiO₂ and loss of surface area. V₂O₅/SiO₂-WO₃-TiO₂ with optimum V₂O₅ loading showed good SCR activity and high thermal stability. This study revealed the effects of SiO₂ introduction on the thermal stability of V₂O₅/WO₃-TiO₂ catalyst, and paves a way toward the development and design of highefficient V₂O₅-based NH₃-SCR catalysts with high thermal stability.

5. Conclusions

A series of V2O5/WO3-TiO2 and V2O5/SiO2-WO3-TiO2 catalysts with different V₂O₅ loading amount (2 wt%, 3.5 wt% and 5 wt%) were prepared by impregnation method for NH₃-SCR. Both V₂O₅ loading and SiO₂ doping can affect the thermal stability of V₂O₅/WO₃-TiO₂ catalysts. Increasing V2O5 loading aggravated the deactivation of the catalysts upon aging. From the results of BET, SEM and XRD, it is noted that high V₂O₅ loading can accelerate the phase transition from anatase to rutile TiO₂ upon thermal aging, which resulted in the loss of surface area and consequently led to the deactivation of the catalysts. Raman and XPS results indicated that the vanadia phase was reduced and became incorporated into the titania support as V_xTi_{1,x}O₂ solid solution upon thermal aging, which accelerated the phase transition of TiO₂₀ Furthermore, thermal aged catalysts showed weakened redox capability and less amount of surface acidity, by the results from H₂-TPR and NH₃-TPD. The development of low V₂O₅ content catalyst with high activity would be a way to obtain high thermal stability.

The introduction of SiO₂ remarkably promoted the thermal stability of V₂O₅/WO₃-TiO₂ catalysts with relatively high V₂O₅ loading (3.5 wt% and 5 wt% V₂O₅). The added SiO₂ could prevent the phase transition of TiO₂, and thereby enhancing the thermal stability of the catalysts. V₂O₅/SiO₂-WO₃-TiO₂ with optimum V₂O₅ loading showed good SCR activity and high thermal stability. The introduction of structure promoter to inhibit phase transition would also be a way to enhance thermal stability.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cattod.2019.07.037.

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