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Thermal stability of Si-doped $V_2O_5/WO_3–TiO_2$ for selective catalytic reduction of NO_x by NH_3

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Abstract The selective catalytic reduction of NO_x with NH_3 (NH_3-SCR) is a very effective technology to control the emission of NO_x, and the thermal stability of NH_3-SCR catalyst is very important for removal of NO_x from diesel engines. In this work, $V_2O_5/WO_3–TiO_2$ (VWT) and SiO_2-doped $V_2O_5/WO_3–TiO_2$ ($VWTSi_{10}$) catalysts were prepared by impregnation method and characterized by Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD), Raman, temperature programmed reduction by hydrogen (H_2-TPR), X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption by ammonia (NH_3-TPD). The doping of SiO_2 promotes the thermal stability of $V_2O_5/WO_3–TiO_2$ for NH_3-SCR significantly. After calcination at 650 °C for 50 h, the operation window of 10% SiO_2-doped $V_2O_5/WO_3–TiO_2$ is 220–480 °C, while the maximum NO_x conversion on $V_2O_5/WO_3–TiO_2$ is about 77%. The presence of SiO_2 obviously blocks the transformation of TiO_2 from anatase to rutile and stabilizes the dispersion of VO_x and WO_3 on the surface. It is available for the existence of V^{4+} and the amount of surface acid sites increases, which inhabits the NH_3 oxidation at the high temperature range and promotes NH_3-SCR activity.

Keywords $V_2O_5/WO_3–TiO_2$; SiO_2; NH_3-SCR; Thermal stability

1 Introduction

Diesel engines have been widely used due to their high fuel efficiency and power output. However, the removal of NO_x from diesel engine exhaust is a major challenge in environmental catalysis and air pollution control [1]. The selective catalytic reduction of NO_x with NH_3 (NH_3-SCR) is one of the best available technologies to control the emission of NO_x [2].

Among the current commercial SCR catalysts, $V_2O_5/WO_3–TiO_2$ has also been used successfully since 2005 in European on-road mobile applications [3]. There are still some problems for the $V_2O_5/WO_3–TiO_2$ catalyst [4–6], such as the thermal deactivation in high temperature exhaust gas [7]. When the diesel exhaust temperature exceeds 600 °C, it will lead to TiO_2 sintering with crystal phase transforming from anatase to rutile and accompanying loss of surface area, which causes aggregation or even volatilization of vanadium species [8, 9].

Casanova et al. [4, 5, 7] found that the presence of rare earths elements (Tb, Er) could lead to the formation of rare earth vanadates which hinder phase structure transformation of TiO_2 and surface area loss. The composite supports were also used to improve high temperature activity and stability, such as $TiO_2–Al_2O_3$, $TiO_2–ZrO_2$ and $TiO_2–SiO_2$ [10–12]. Among them, SiO_2 is widely used due to its large specific surface area and excellent thermal stability. Kobayashi et al. [13] reported that $V_2O_5/TiO_2–SiO_2$ behaved better SCR activity and higher N_2 selectivity than V_2O_5/TiO_2 due to the remarkably stronger acidity, higher BET surface area and a lower crystallite sizes of TiO_2, resulting in a good thermal stability and a higher vanadia dispersion. Pan et al. [14] reported that SiO_2 doping could keep Lewis acid unchanged and significantly increased

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Brönsted acid, which had been proven to be beneficial for the low temperature activity. In addition, it could easily generate V^{4+}. Zhao et al. [15] found that co-introduction of SiO_2 and Al_2O_3 into TiO_2 greatly increased Brunauer–Emmett–Teller (BET) surface area and the amount of surface acid sites, which promoted SCR activity. Therefore, the Si-doped V_2O_5/WO_3–TiO_2 catalyst may not only improve the high temperature activity but also improve the thermal stability under harsh conditions.

In this work, the SiO_2-doped V_2O_5/WO_3–TiO_2 were prepared and the effects of silica on structure, surface properties and catalytic performance of V_2O_5/WO_3–TiO_2 catalysts were investigated.

2 Experimental

2.1 Catalysts preparation

SiO_2-doped WO_3–TiO_2 was prepared by impregnation TiO_2–WO_3 powder (90 wt%TiO_2–10 wt%WO_3, Kailong Lanfeng New Material Technology Co., Ltd) with tetraethyl orthosilicate [16], which was denoted as $WTSi_x$ (where x is the content of SiO_2 respect to WO_3–TiO_2). The catalysts were prepared by conventional incipient impregnation method and the oxalic acid solution of NH_4VO_3 was used as precursor. After impregnation, the samples were dried overnight at 100 °C and calcination at 550 or 650 °C for 6 h to obtain the fresh catalysts, which were assigned to VWT-550 °C and $VWTSi_x$-650 °C. After further calcination at 550 or 650 °C for 50 h, the VWT-550 °C-50 h and $VWTSi_x$-650 °C-50 h were obtained. The V_2O_5 loadings in all catalysts were 3 wt%.

2.2 Activity test

The steady-state NH_3-SCR activities of catalysts were tested in a fixed-bed reactor at atmospheric pressure with 0.3 ml catalysts (250–380 μm). The feed gas containing 500×10^{-6} NO, 500×10^{-6} NH_3, 5 vol% O_2, 2 vol% H_2O (when used), 100×10^{-6} SO_2 (when used) and balanced argon passed through the catalytic bed at a flow rate of 300 $ml \cdot min^{-1}$. The NO_x concentration of outlet gas was detected from 100 to 550 °C by an online Chemiluminescence NO–NO_2–NO_x analyzer (Thermal-Scientific Model 42i-HL). The steady NO_x conversion was obtained after keeping at each set temperature for 30 min. The temperature range corresponding to more than 80% NO_x conversion was defined as the operation window.

The NH_3 oxidation activities were measured by a Nicolet 6700 (Thermo Scientific) with gas analysis cell (2 m optical path) with 500 min^{-1} NH_3 and 5 vol% O_2 in argon as a feed from 100 to 550 °C. The catalysts were kept at each set temperature for 30 min to obtain a stable conversion.

2.3 Catalyst characterization

The powder X-ray diffraction (XRD) patterns were recorded on a BrukerD8 Focus X-ray diffractometer with Cu Kα radiation, the mean crystallite sizes of TiO_2 were calculated based on Scherer equation. The surface areas of samples were measured on a Micromeritics ASAP 2400 instrument by N_2 adsorption–desorption at − 196 °C. The Raman spectra of the catalysts were obtained on a confocal micro-Raman apparatus (IDSpec Aurora, China) using Ar^+ laser with a charged coupled device (CCD) detector, the wavelength of laser was 632.8 nm and the exposure time was 20 s.

Temperature programmed reduction by hydrogen (H_2-TPR) was performed on a commercial temperature-programming system. 100 mg catalyst was heated in 5 vol% H_2/N_2 (40 $ml \cdot min^{-1}$) from 100 to 800 °C at the rate of 10 $°C \cdot min^{-1}$ after pretreated at 500 °C for 1 h in a flow of 40 $ml \cdot min^{-1}$ N_2. Temperature programmed desorption by ammonia (NH_3-TPD) experiment was performed using the same apparatus. 100 mg catalyst was pretreated at 500 °C for 1 h in N_2 (50 $ml \cdot min^{-1}$) and cooled down to 120 °C, then 10 vol% NH_3/N_2 (50 $ml \cdot min^{-1}$) passed through catalyst bed for 1 h to obtain saturation. After purging with N_2 for 1 h, the temperature was raised up to 700 °C at the rate of 10 $°C \cdot min^{-1}$.

X-ray photoelectron spectroscopy (XPS) spectra were obtained on a Thermo ESCALAB 250 spectrometer with a monochromatized Al Kα X-ray source. All binding energies were calibrated by the deposit C 1s at 284.6 eV.

3 Results and discussion

3.1 NH_3-SCR activity

The activities of SiO_2-doped V_2O_5/WO_3–TiO_2 catalysts for NH_3-SCR reaction are shown in Fig. 1a. The operation window was 185–470 °C on VWT-550 °C catalyst. The doping of SiO_2 slightly decreases the light-off activity, but the activity in the high temperature range is enhanced significantly, which broadens the operation window. Among them, $VWTSi_{10}$-550 °C behaves the optimum performance with the operation window of 205–520 °C. When the content of SiO_2 exceeds 10%, the high temperature activity decreases gradually with the increase of SiO_2 content.

After calcination at 650 °C, the light-off curve of VWT-650 °C obviously shifts to higher temperature, and NO_x conversion at the high temperature range also decreases

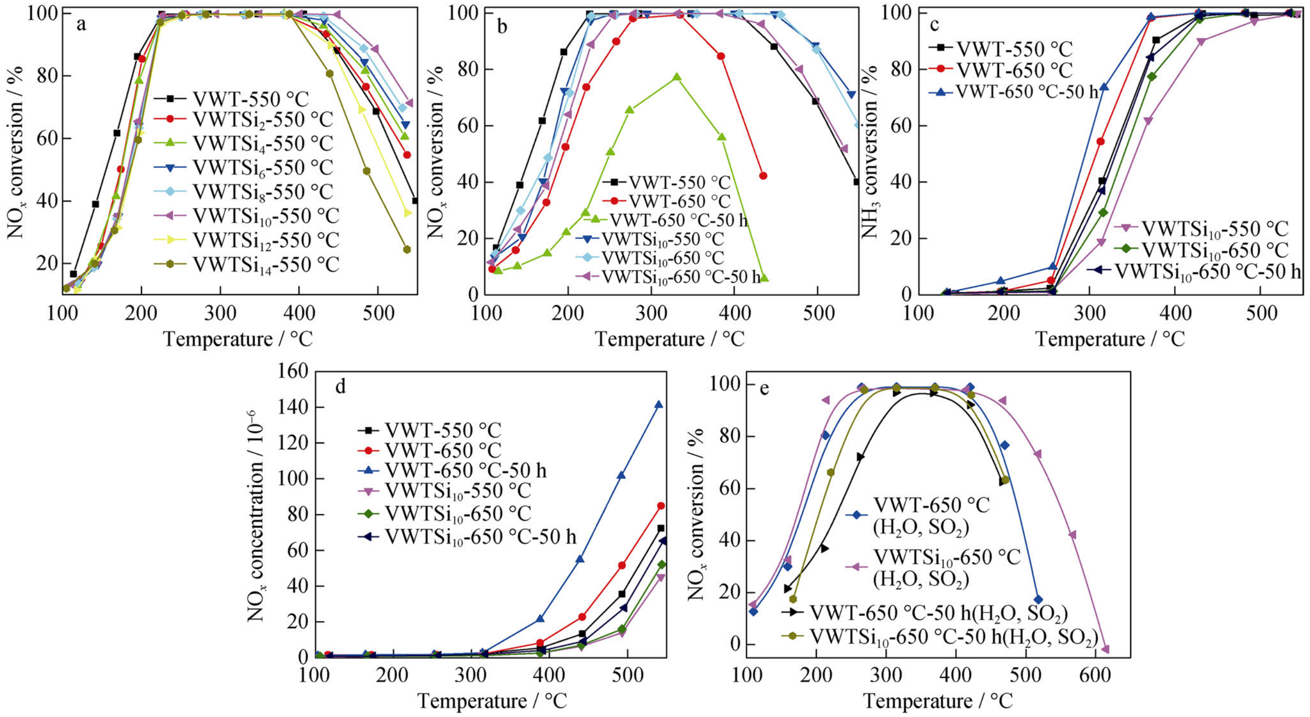

Fig. 1 Catalytic performances of **a**, **b**, **e** NH_3-SCR and **c**, **d** NH_3 oxidation on different catalysts

significantly, resulting in a narrow operation window of 235–390 °C (Fig. 1b). For VWT-650 °C-50 h, the maximum NO_x conversion is about 77%. However, VWTSi$_{10}$-650 °C shows nearly same SCR activity as VWTSi$_{10}$-550 °C. Furthermore, the light-off property and high temperature activity slightly decrease with the calcination time extending to 50 h, and operation window still is 220–480 °C, indicating that the deposition of SiO_2 dramatically improves the thermal stability of VWT catalyst.

As shown in Fig. 1c, d, VWTSi$_{10}$-550 °C behaves lower activity for NH_3 oxidation than VWT-550 °C. After calcination at 650 °C for 6 and 50 h, the NH_3 oxidation activities of all catalysts increase. However, the increasing extent of VWTSi$_{10}$ is obviously smaller than that of VWT, which indicates that the doping of SiO_2 suppresses NH_3 oxidation and results in higher SCR activity in higher temperature range.

The activities of SiO_2-doped $V_2O_5/WO_3–TiO_2$ catalysts for NH_3-SCR reaction on the condition of existing H_2O and SO_2 are shown in Fig. 1e. The operation window is 220–450 °C on VWT-650 °C catalyst. The doping of SiO_2 slightly increases the light-off activity, and the activity in the high temperature range is also enhanced significantly, which broadens the operation window. After extending the calcination time to 50 h, the catalytic activities decrease significantly. However, the catalytic activity of VWTSi$_{10}$-650 °C-50 h is higher than that of VWT-650 °C-50 h, and it shows the temperature operation window in the range of 240–440 °C. Hence, the doping of SiO_2 could improve the high catalytic activity and enhance the stability of resisting H_2O and SO_2.

3.2 BET surface and XRD

XRD patterns are shown in Fig. 2, and the average crystallite sizes of TiO_2 are calculated and listed in Table 1. For VWT-550 °C, only anatase-TiO_2 phases are detected, and the peaks corresponding to V_2O_5 and WO_3 are not observed, suggesting that V_2O_5 and WO_3 are highly dispersed on TiO_2. After calcination at 650 °C, the diffraction

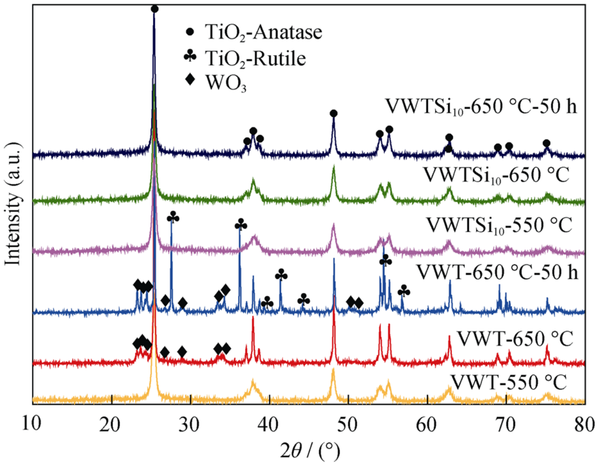

Fig. 2 XRD patterns of different catalysts

Table 1 Textural and structural properties of catalysts

Catalyst	Surface area/($m^2·g^{-1}$)[a]	Particle size/nm[b]	V surface concentration[c]	$V^{5+}/(V^{4+} + V^{5+})$[c]
VWT-550 °C	65.8	19.1	0.21	0.50
VWT-650 °C	24.3	45.2	0.27	0.70
VWT-650 °C-50 h	7.1	61.0	0.26	0.75
$VWTSi_{10}$-550 °C	111.0	17.0	0.19	0.38
$VWTSi_{10}$-650 °C	65.1	19.8	0.20	0.60
$VWTSi_{10}$-650 °C-50 h	32.6	24.8	0.21	0.68

[a] Measured by N_2 adsorption–desorption experiment

[b] Obtained by XRD data

[c] Obtained by XPS analysis

peaks corresponding to WO_3 are detected on VWT-650 °C. When the calcination time increases to 50 h, the peak intensities of WO_3 greatly enhance, and significant rutile-TiO_2 could also be detected. Meanwhile, the surface area of VWT-650 °C catalyst decreases to 7.1 $m^2·g^{-1}$, accompanying the significant increase of crystallite sizes of TiO_2 from 45.2 to 61.0 nm.

There is no observable difference between the structure of VWT-550 °C and $VWTSi_{10}$-550 °C, but the deposition of SiO_2 decreases the crystallite sizes of TiO_2 and increases the surface area significantly. After the calcination at 650 °C for 6 h, the surface area of $VWTSi_{10}$-650 °C decreases by about 41% but is much higher than that of VWT-650 °C, while the crystallite size of TiO_2 also slightly increases from 17 to 19.8 nm. Further extending the calcination time to 50 h, only anatase-TiO_2 is detected on $VWTSi_{10}$-650 °C-50 h, and the surface area of $VWTSi_{10}$-650 °C-50 h and crystallite sizes of TiO_2 are about 4.6 and 0.41 times that of VWT-650 °C-50 h, respectively. Combing BET and XRD results, it could be concluded that the doping of SiO_2 improves the surface area and thermal stability of VWT significantly.

3.3 Raman

The Raman spectra of VWT and $VWTSi_{10}$ catalysts calcined at different temperature are shown in Fig. 3. All catalysts show the characteristic bands of anatase TiO_2 at 145, 197, 396, 515 and 635 cm^{-1} [17], and the band intensities increase with the increase of calcination temperature and time.

For VWT-550 °C, a weak band assigned to the stretching vibration of W=O could be at 803 cm^{-1} [18], which is enhanced significantly after calcination at 650 °C for 6 h. The new bands of crystalline WO_3 are observed at 270, 324 and 713 cm^{-1} on VWT-650 °C, corresponding to the W–O–W deformation and the bending vibrations of W=O, respectively. Meanwhile, the bands assigned to the bending vibration of the bridging V–O–V, V=O and the stretching vibration of V=O are detected at 285, 303 and 994 cm^{-1}, respectively [19–21]. For VWT-650 °C-50 h, the Raman spectrum is similar with that of VWT-650 °C, except that the bands of TiO_2, WO_3 and V_2O_5 are strengthened. These results show the agglomeration of W and V species on the VWT.

For $VWTSi_{10}$-550 °C, only the characteristic bands of TiO_2 are detected, and the peak intensities are much weaker than those of VWT-550 °C, which coincides with the results of XRD, the doping of SiO_2 induces the structural distortion and decreases the crystallite size of TiO_2. A weak band of V_2O_5 is detected at 994 cm^{-1} on $VWTSi_{10}$-650 °C. After further calcination at 650 °C for 50 h, the bands corresponding to WO_3 and V_2O_5 are observed at 803 and 994 cm^{-1}, respectively, but their intensities are significantly weaker than those of VWT-650 °C and VWT-650 °C-50 h, indicating that the modification of SiO_2 could improve the dispersion and thermal stability of V and W species significantly.

3.4 H_2-TPR

H_2-TPR profiles of VWT and $VWTSi_{10}$ catalysts calcined at different temperatures are shown in Fig. 4. For VWT-550 °C, the overlapping reduction peak at 300–650 °C could be assigned to the co-reduction of monomeric/polymeric surface vanadia species (V^{5+}/V^{4+}) to V^{3+} and $W^{6+} \rightarrow W^{4+}$ [22–24]. The reduction peak centered at around 800 °C could be ascribed to the reduction of W^{4+} to W^0 [24, 25]. The doping of SiO_2 slightly decreases the reduction ability of VWT, and all reduction peaks shift to higher temperature, which agrees with the little lower SCR catalytic activity in the low temperature range, as shown in Fig. 1b.

Compared with those on VWT-550 °C and $VWTSi_{10}$-550 °C, the co-reduction peaks of V and W species on VWT-650 °C and $VWTSi_{10}$-650 °C distinctly shift to high

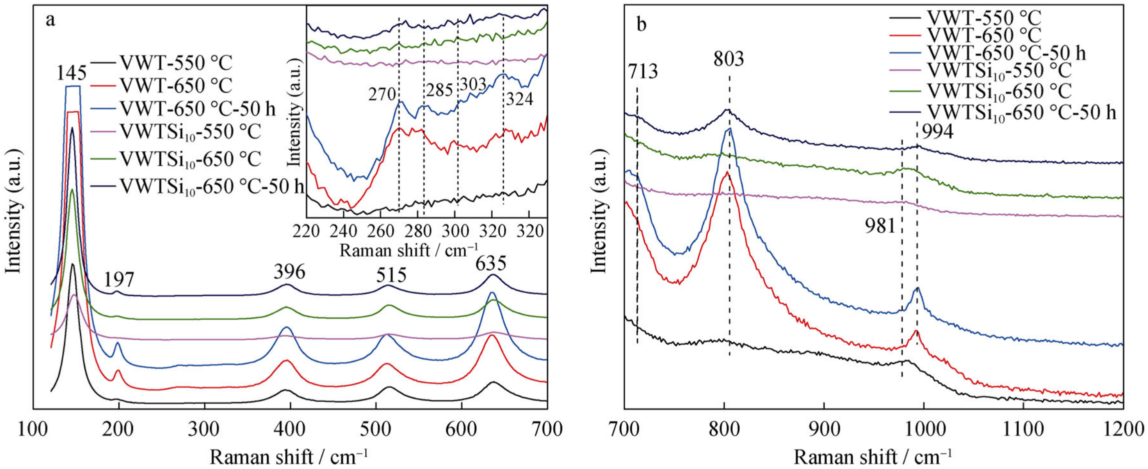

Fig. 3 Raman spectra of different catalysts in the Raman shift range of **a** 100–700 cm^{-1} and **b** 700–1200 cm^{-1}

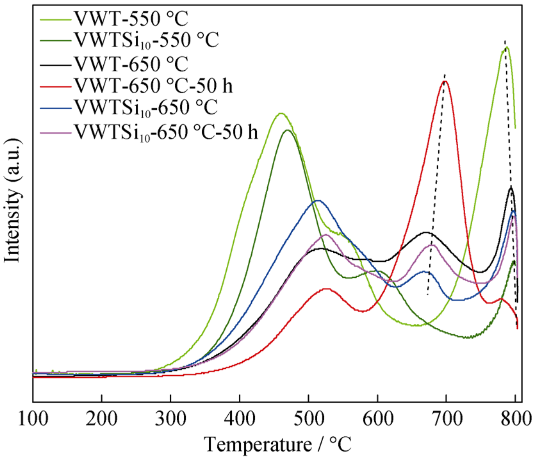

Fig. 4 H_2-TPR profiles of different catalysts

temperature and the peak intensity decreases, indicating the reducibility decrease of surface V and W species. Meanwhile, a new reduction peak generated at around 600–750 °C could be assigned to the reduction of W^{6+} to W^{4+} of bulk phase WO_3 [22, 26]. Combined with XRD and Raman results, the decreased reduction ability of VWT-650 °C and $VWTSi_{10}$-650 °C in the low temperature range may be induced by the agglomeration and separation of V and W species.

By increasing calcination time to 50 h, the reduction peak intensity in the temperature range of 300–600 °C further decreases. The presence of SiO_2 suppresses the decrease of reduction peak, and the reduction peak area of $VWTSi_{10}$-650 °C-50 h is still larger than that of VWT-650 °C, implying that the V and W species could keep stable on $VWTSi_{10}$-650 °C-50 h and the reduction ability is maintained. Combined with the results of Fig. 1b, the doping of SiO_2 could enhance the thermal stability of VWT catalyst, and $VWTSi_{10}$-650 °C-50 h shows much higher activity than VWT-650 °C and VWT-650 °C-50 h through the stabilization of V and W species on the surface.

3.5 XPS analysis

The V 2p XPS spectra are shown in Fig. 5. Compared with the catalysts calcined at 550 °C, the peaks of V 2p shift to higher binding energy after calcination at 650 °C for 6 and 50 h, which indicates the increase of oxidation state of V species. The ratio of V^{5+} listed in Table 1 which is obtained by the fitting of V 2p spectra according to the Ref. [27] also confirms that the ratio of V^{5+} increases with the increase of calcination temperature and time. It is suggested to be induced by the increase of crystalline V species on the surface of catalyst [28], which coincides with results of Raman and XRD.

The results in Table 1 also show that the doping of SiO_2 obviously decreases the surface concentration of V, which may be induced by the larger surface area of catalysts containing SiO_2. Meanwhile, the surface ratio of V^{5+} on

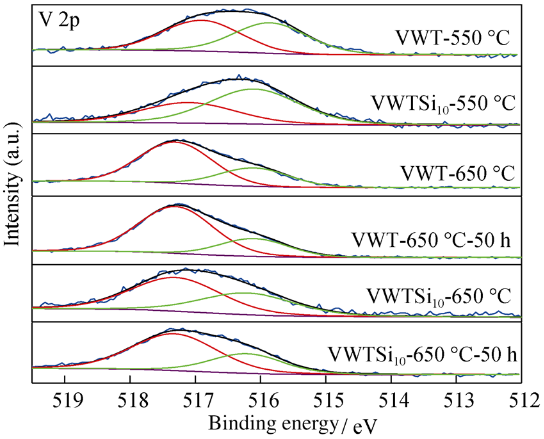

Fig. 5 XPS spectra of V 2p in different catalysts

$VWTSi_{10}$ is obviously less than that of VWT calcined at the same condition, indicating that the presence of SiO_2 improves the dispersion of V species on the surface and the stability of V^{4+}. Kobayashi et al. [13] reported that the modification of SiO_2 was available for the existence of V^{4+} on V_2O_5/TiO_2. Lee et al. [29] reported that VO_x ($x < 2.5$) could improve the reduction and/or re-oxidation properties of catalysts. H_2-TPR result (Fig. 4) confirms that the reduction peak of V species shifts to higher temperature after calcination at 650 °C.

3.6 NH_3-TPD

NH_3-TPD profiles of different catalysts are shown in Fig. 6. A wide NH_3 desorption peak and a relative weak shoulder peak are observed on VWT-550 °C at the temperature range of 100–300 °C (α peak) and 300–500 °C, corresponding to the Brönsted and Lewis acid sites, respectively [15, 20, 30]. The desorption peak area of $VWTSi_{10}$-550 °C is much larger than that of VWT-550 °C, which indicates that the presence of SiO_2 improves the amount surface acid sites significantly. After calcination at 650 °C, α peak decreases significantly on VWT-650 °C, which could be ignored on VWT-650 °C-50 h. However, α peak is maintained on $VWTSi_{10}$-650 °C, and has a slight decrease even on $VWTSi_{10}$-650 °C, indicating that the doping of SiO_2 enhances the stability of surface acid sites significantly.

In addition, two strong desorption peaks are observed on the catalysts calcined at 650 °C at the range of 250–500 °C. Busca et al. reported that VO_x and WO_x could generate both strong Brönsted and Lewis acid sites [1]. He et al. [31] reported that oligomeric surface V species could produce more acid sites than isolated V species. Combined with Raman results, it could be drawn that isolated or highly dispersed VO_x behaves relatively weak Brönsted acid, and the aggregation of VO_x and/or WO_x would produce new strong acid sites after calcination at 650 °C.

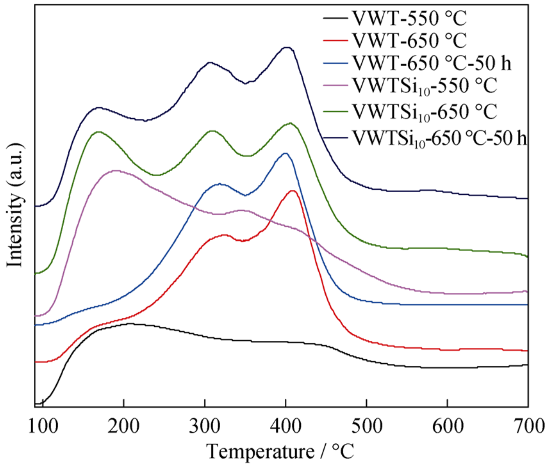

Fig. 6 NH_3-TPD profiles of different catalysts

As mentioned above, the doping of SiO_2 not only improves surface area of catalyst, but also stabilizes the structure of TiO_2, which could stabilize and improve the dispersion of VO_x and WO_3 species on the surface. The isolated or highly dispersed VO_x species is available for the existence of V^{4+} and increases the amount of surface acid sites, which could inhabit NH_3 oxidation at the high temperature range and promote NH_3-SCR activity [32] even after calcination at 650 °C.

4 Conclusion

The SiO_2-doped 3 wt% $V_2O_5/WO_3–TiO_2$ catalysts were prepared and the catalytic performances for NH_3-SCR were investigated. Among them, $VWTSi_{10}$-550 °C behaves the maximum operation window of 205–520 °C, which still maintains at the temperature range of 220–480 °C even after calcination at 650 °C for 50 h, while the maximum NO_x conversion is about 77% on VWT-650 °C. The characterization results show that the doping of SiO_2 obviously increases the surface area of catalysts and blocks the transformation of TiO_2 from anatase to rutile after calcination at 650 °C, which could stabilize and improve the dispersion of VO_x and WO_3 species on the surface. The existence of V^{4+} and stabilized surface acid sites would inhabit the NH_3 oxidation at the high temperature range and promote NH_3-SCR activity.

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