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Effect of $V^{4+(3+)}/V^{5+}$ ratio on the denitration activity for $V_2O_5-WO_3/TiO_2$ catalyst

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Abstract: In this study, the $V^{4+(3+)}/V^{5+}$ valence ratio on the surface of $V_2O_5-WO_3/TiO_2$ catalyst was adjusted by changing the oxygen flux in the calcination process and the effect on the denitration activity was evaluated. The physicochemical properties of catalysts were characterized by X-ray diffraction (XRD), H_2 temperature programmed reduction (H_2 -TPR), NH_3 *in situ* infrared spectroscopy (NH_3 -DRIFT) and N_2 adsorption-desorption. The results showed that an appropriate $V^{4+(3+)}/V^{5+}$ ratio is beneficial to improve the denitration activity due to the increased acidic sites, which decreases the apparent activation energy (E_a) and ensures the electron transfer in the process of the mutual transformation of $V^{4+(3+)}$ and V^{5+} . Too high or low $V^{4+(3+)}/V^{5+}$ ratio is unfavorable to the denitration activity.

Keywords: $V_2O_5-WO_3/TiO_2$, $V^{4+(3+)}/V^{5+}$ ratio, electron transfer, catalytic reduction

1. Introduction

NH₃ selective catalytic reduction (NH₃-SCR) technique is an effective way for the controlled emission of NO_x^[1,2]. The typical V₂O₅-WO₃/TiO₂ catalyst has been widely used for thermal power plants and other stationary sources. Nowadays, there are many studies to improve the low-temperature activity of V₂O₅-WO₃/TiO₂ catalyst by increasing the active component content. However, the active components of vanadium species are toxic. Therefore, it is significant to improve the properties of the active component, while the vanadium content is fixed to increase the application scope of the catalyst. Meanwhile, the active temperature of the typical V₂O₅-WO₃/TiO₂ catalyst was 300-450 °C. And many experiment results also have been reported in Ming Kong et al.^[3], Patrick G.W.A et al.^[4], Chizhong Wang et al.^[5] and Anju Shi et al.^[6] studies for the V₂O₅-WO₃/TiO₂ catalysts. In these reports, catalysts show good denitration activity above 300 °C. But the low temperature activity was not good. NO conversion was below 60% at 250 °C, and the conversion was about 20% at 200 °C. Additionally, due to the high toxicity and the low resistance to SO₂, the content of the active component V₂O₅ was as low as 2wt.%^[7-9]. On the other hand, as accelerator and stabilizer^[10], the content of WO₃ was usually 8-10 wt.%^[11]. Moreover, WO₃ plays some other roles including preventing the sintering of TiO₂^[12], increasing the amount of Brönsted acidic sites^[5], improving the catalytic activity, widening the active temperature window, stabilizing the specific surface area of the catalysts^[8,10] and improving the electron transfer between V⁴⁺⁽³⁺⁾ and V⁵⁺ to increase the reduction of V₂O₅^[13].

Over the last decades, researchers have great interest in the development of low temperature SCR catalysts and there are several factors such as active component content, specific surface area, and surface acidity to affect the denitration activity of $V_2O_5-WO_3/TiO_2$ catalysts. The $V^{4+(3+)}/V^{5+}$ valence ratio of $V_2O_5-WO_3/TiO_2$ is an important factor which has been found by many researchers^[14-17] and our previous work. Furthermore, the E-R mechanism which involves the transformation process of V^{4+} and V^{5+} in the NH_3 -SCR process has been widely accepted^[18]. The species of $V^{5+}-O \cdots ^+H_3-N \cdots H-O-V^{4+}$ and $V^{5+}-O \cdots ^+H_3-N-N-O \cdots H-O-V^{4+}$ play a critical role in the SCR process. There are two processes in the electron transform route: the reduction process of $V^{5+}=O$ by NH_3 to form $^+H_3-N \cdots H-O-V^{4+}$ species and the oxidation process of $H-O-V^{4+}$ to $V^{5+}=O$. It is clear that V^{4+} plays an important role in the whole oxidation-reduction reaction through the E-R mechanism. Lazaro and co-authors found that NO conversion reached a high value with surface vanadia coverage at approximately half a monolayer for carbon-coated catalysts doped with tungsten and vanadia, and the good NO conversion was related to the well dispersed and dissociated vanadia species^[19]. The maximum NO conversion was ascribed to the high Brønsted proton acid (V^{4+}) concentration, and the amount of V^{4+} decreases with the increase of vanadia. The catalysts loaded with 3wt% V had the highest V^{4+}/V^{5+} ratio, whereas higher or lower vanadia loading amount corresponded to lower V^{4+}/V^{5+} ratio.

In fact, V^{4+} existed on the surface of $V_2O_5-WO_3/TiO_2$ catalyst, and the existence of VO_x species can be changed by the interaction between W and V atoms. Meanwhile,

the content of V^{4+} is influenced by the loading amount of tungsten^[20]. Tungsten ions with an excessive positive charge as Lewis acid sites are responsible for the water dissociation and will lead to the formation of Brønsted acid sites. This phenomenon will result in the change of V^{4+}/V^{5+} and W^{6+}/W^{5+} ratios. Therefore, for $V_2O_5-WO_3/TiO_2$ catalysts with different loading amount of W, two kinds of surface species are dominant depending on the tungsten content: $V^{4+}-O-W^{6+}$ at higher tungsten content and $V^{5+}-O-W^{5+}$ at lower tungsten content^[14].

There are two reasons for the transformation process of V^{5+} and V^{4+} . Firstly, the oxidation of the VO_x species on catalyst surface will change the valence state of vanadia species due to different content. Secondly, the reduction of the species on catalyst surface will lead to the diffusion of inner vanadium atom. $WO_3-V_2O_5$ solid solution was formed by the substitution of some W atoms for V atoms in the vanadia structure, and the reduction of the nearest vanadium atoms from V^{5+} to V^{4+} was finished simultaneously. A possible formation mechanism based on the *in situ* UV-vis results was proposed by Shimizu^[21]: the adsorbed NH_3 causes the reduction of V^{5+} to V^{4+} and the increase of the conductivity. However, V^{4+} existed really on the surface of the catalyst before the SCR reaction. The physicochemical characteristics of the sub-monolayer $V_2O_5-WO_3/TiO_2$ de NO_x catalyst were investigated through electron paramagnetic resonance (EPR) by Lietti^[22]. EPR results indicated that V^{4+} ions are in magnetically isolated, clustered and magnetically interacting form on the surface of TiO_2 . The presence of tungsten oxide stabilizes the V^{4+} ions on the surface and modifies the redox properties of V_2O_5/TiO_2 samples. In addition, some researchers

found that there is a correlation between the ratio of $(V^{4+}+V^{3+})/V^{5+}$ or V^{4+}/V^{5+} and the NO conversion^[23]. Boningari also confirmed that the SCR performance of catalysts prepared by flame-assisted spray pyrolysis was indeed correlated with the concentrations of $(V^{3+}+V^{4+})/V$ and V^{4+}/V^{5+} on the surface^[15].

It can be inferred that there is a significant relation between the V^{4+}/V^{5+} ratio and the deNO_x activity. And it is important to make clear the relation. In this study, the valence state of vanadium was adjusted by changing calcined atmosphere to study the effect of $(V^{4+}+V^{3+})/V^{5+}$ or V^{4+}/V^{5+} ratio on the NH₃-SCR denitration activity.

2. Experiment section

2.1 Preparation of catalyst

All catalysts in this work were prepared by the substep-wet impregnation method. Typically, a certain amount of ammonium metavanadate (AR grade, 99%) and ammonium paratungstate (AR grade, 99%) with appropriate ratio were dissolved successively in oxalic acid solution assisted with ultrasonic action and then adding the commercial TiO₂(Nanjing Emperor Nano Material Co.,ltd.) into the solution. The mixture was stirred and heated at 80 °C for 2 h, dried at 120 °C for 4h and then grinded to powder. Then the catalysts were calcined at 500°C for 3 h in tube furnace under different oxygen concentration atmosphere flow of 100 h⁻¹. The loading amount of V₂O₅ and WO₃ was fixed by 3wt.% and 8wt.% to TiO₂, respectively. The atmosphere with different oxygen concentration is pure N₂, 15% O₂ in N₂, air and pure O₂. The catalysts were named as V3W8Ti (a-d).

2.2 Characterization

BET surface areas of the catalysts were measured by N₂ adsorption-desorption using a Builder SSA-4200 (China, Builder Company). X-ray photoelectron spectroscopy (XPS) measurements were performed on a K-Alpha spectrometer (Thermo Fisher SCIENTIFIC, America). Al K α radiation (1486.6eV) was used as the source, vacuum degree is 5×10^{-7} kPa, working voltage is 12.5 kV, and current is 20 mA. The X-ray powder diffraction (XRD) was examined on a Rigaku D/max-TTR-III diffractometer at a scan rate of 10°/min in the 2 θ range from 10° to 80° using Cu K α radiation ($\lambda = 0.15405$ nm). Raman spectra were measured by Microscopic Confocal Raman Spectrometer (Perkin Elmer, station 400F) under ambient conditions using a laser with wavelength of 785 nm. The spectra were recorded with a resolution of 1 cm and a scan number of 20 from 200 to 1200 cm⁻¹.

H₂ temperature-programmed reduction (TPR) and NH₃ temperature-programmed desorption (TPD) were conducted using a self-made setup with a TCD detector (GC-14C, SHIMADZU). Briefly, about 100 mg sample was used for every experiment. The sample was pretreated in argon flow at 300 °C for 1 h and cooled to room temperature. For NH₃-TPD experiment, the adsorption of NH₃ on the catalyst was performed with feeding anhydrous NH₃ gas for about 10 min at room temperature, and then the catalyst was sufficiently purged by argon stream to remove the excessive adsorbate. The TPD was conducted by heating the sample in argon (80 mL/min) from 50 °C to 600 °C with a heating rate of 10 °C/min. The TPR method was carried out with the linear heating rate (10 °C/min) from 50 °C to 800 °C in a mixture of 5% H₂-Ar at a flow rate of 30 mL/min.

The *in situ* DRIFTS experiments were performed on an FTIR spectrometer (Nicolet 6700) equipped with a Harrick DRIFT cell containing KBr windows and MCT detector. Prior to each experiment, the sample was pretreated at 300 °C for 1 h in argon flow. The background spectrum was collected in flowing argon and automatically subtracted from the sample spectrum. The reaction conditions were controlled as follows: 120 mL min⁻¹ total flow rate, 0.1% (v/v) NH₃, and argon balance. All spectra were recorded by accumulating 100 scans with a resolution of 4 cm⁻¹.

2.3 Catalytic activity

The catalytic test was carried out with a fixed-bed tubular reactor at a flow rate of 15000 h⁻¹ at atmospheric pressure from 100 to 450 °C. The inlet concentrations were: NO=1000ppm, NH₃=1000ppm and O₂=3% using Ar as balance gas. The measurement was performed at fixed temperatures per 50 °C from 100 to 450 °C and kept for 20 min at each point. The reaction temperature was measured by a type K thermocouple inserted into the catalyst bed. The inlet and outlet concentrations of NO, N₂O and NO₂ were measured by a gas analysis system PFEIFFER GSD320 (ThermoStar TM, Germany). NO_x conversion (%) was obtained by the following equations.

$$\text{NO}_x \text{ conversion (\%)} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} - [\text{NO}_2]_{\text{out}} - 2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100\% \quad (1)$$

$$\text{NO conversion (\%)} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100\% \quad (2)$$

3. Results and Discussion

3.1 XRD and BET



Fig. 1 Color of V_2O_5 - WO_3 / TiO_2 catalysts calcined in different atmosphere

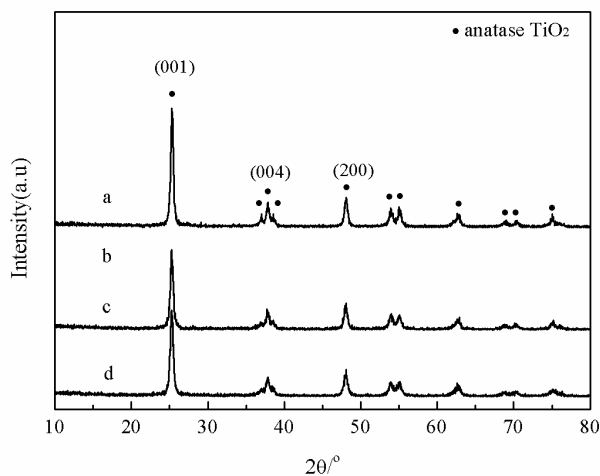


Fig. 2 XRD patterns of V_2O_5 - WO_3 / TiO_2 catalysts calcined at different atmosphere

(a: V3W8Ti (a); b: V3W8Ti (b); c: V3W8Ti (c); d: V3W8Ti (d))

In Fig. 1, the colors of the catalysts calcined at different atmospheres show that the degree of oxidation is different. In the corresponding XRD patterns (Fig. 2), the diffractions peaks can be directly indexed to anatase TiO_2 , and V_2O_5 or WO_3 cannot

be detected, indicating that V_2O_5 or WO_3 species are well dispersed on carrier surface or existed in amorphous form or microcrystal. The specific surface area of catalysts shows a decreased tendency in the order of V3W8Ti (a) > V3W8Ti (b) > V3W8Ti (c) > V3W8Ti (d), demonstrating that the oxidation of catalysts has an effect in the calcination process. It can be considered that V or W atom will snatch O atom from TiO_2 lattice to form oxide species when the amount of oxygen decreased, resulting in the strong interaction between V or W atom. With the increase of oxygen, V or W atom will be oxidized sufficiently to weaken the interaction between TiO_2 carrier and vanadia or tungsten oxide to decrease the specific surface area.

The number of atoms on unit area can be calculated as follows.

$$N_{\text{number}} = \frac{WN_A}{MA_{\text{BET}}}$$

Where N_{number} denotes as atom number of element on unit area, W represents the percentage of element, N_A is avogadro constant, M is relative atomic mass of element, and A_{BET} is BET specific surface area.

Monolayer surface coverage of the vanadia overlayer on different oxide supports is found to be approximately 7-8 atoms per nm^2 by Wachs^[24]. In Table 1, the atomic number on unit area catalyst surface shows a slightly increase from 5.17 to 5.58 with the increase of oxygen in the calcination process and the degree of aggregation of vanadia species is slightly enhanced. But the numbers of V or W atom and the sum are all less than $7/\text{nm}^2$ indicating that vanadia and tungsten oxide species are highly dispersed on catalyst surface, corresponding well to the XRD results.

Table 1 Properties of V_2O_5 - WO_3 / TiO_2 catalysts calcined at different atmosphere

sample	calcination atmosphere	catalyst color	BET (m ² /g)	wt%		atomic number (1/nm ²)		
				V	W	V	W	sum
TiO ₂	-	white	120	-	-	-	-	-
V3W8Ti(a)	N ₂	gray	69.58	1.46	5.72	2.48	2.69	5.17
V3W8Ti(b)	15% O ₂ /N ₂	gray green	67.89	1.48	5.69	2.58	2.74	5.32
V3W8Ti(c)	air	faint yellow	66.25	1.49	5.68	2.66	2.80	5.46
V3W8Ti(d)	O ₂	yellow	65.17	1.51	5.65	2.74	2.84	5.58

3.2 Raman analysis

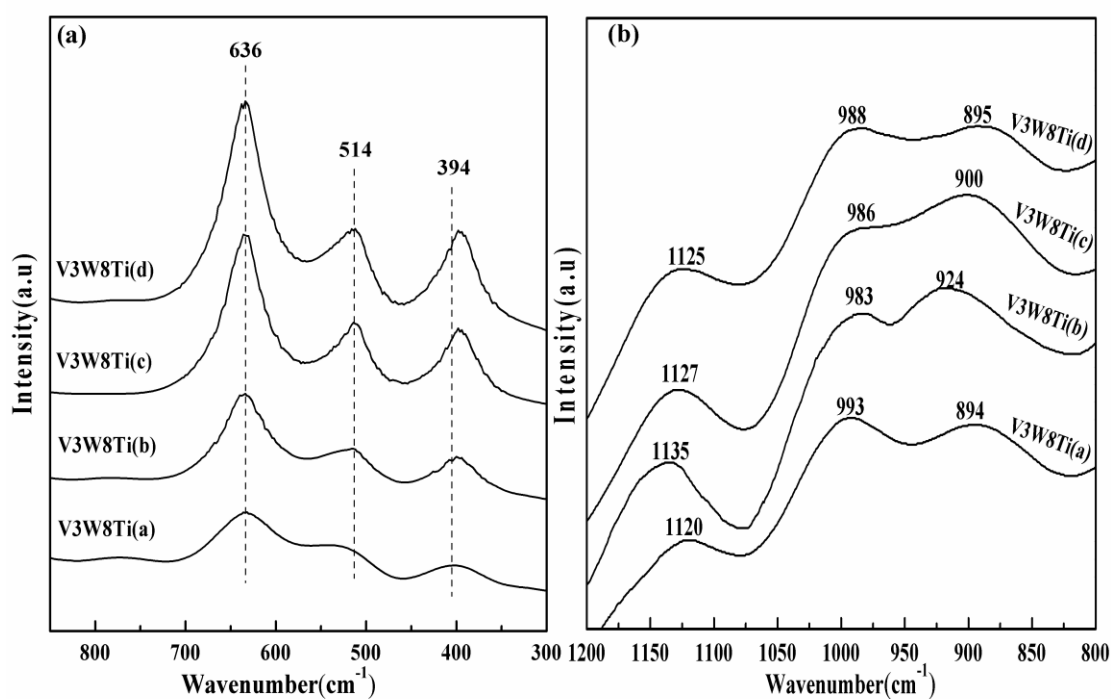


Fig. 3 Raman spectra of TiO₂(a) and vanadia species(b) of V3W8Ti catalysts

The atomic interreaction on sample surface could not be found in XRD results because of the highly dispersed active component. So Raman spectra were used to study V=O vibration in vanadia on the catalyst surface for its sensitivity. In Fig. 3(a), the peaks at 394 cm⁻¹, 514 cm⁻¹ and 636 cm⁻¹ are attributed to anatase TiO₂. In

Fig.3(b), the peak at 1120 -1135 cm^{-1} was assigned to the monolayer dispersed vibration of V=O from isolated vanadia species^[25]. With the increase of the oxygen content in the calcination process, the wave number of the vibration peaks increased first and then decreased, indicating that the content of isolated vanadium species or the content of polymerized VO_x species has the same tendency. The shift to higher wavenumber means that more isolated vanadia species or polymerized VO_x species are formed. The peak at 988 - 993 cm^{-1} in the tendency of decrease first then increase is the coefficient result of the V=O in monolayer dispersed VO_x and W=O in WO_x species,^[4] indicating that the content of VO_x species exist in this state is in the same tendency. For V3W8Ti(a) catalyst, a certain amount of oxygen in V-O bond was mainly come from lattice oxygen of TiO_2 forming $\text{V}\cdots\text{O}\cdots\text{W}$ and $\text{V}\cdots\text{O}\cdots\text{Ti}$ bond. And the Raman peak move to maximum 993 cm^{-1} corresponding to $\text{O}=\text{V}\cdots\text{O}\cdots\text{W}=\text{O}$ and $\text{O}=\text{V}\cdots\text{O}\cdots\text{Ti}=\text{O}$ action meaning that the exist of strong interaction. For other catalysts calcined in containing oxygen atmosphere, the oxygen in V-O bond were mainly come from O_2 , the interreaction of $\text{V}\cdots\text{O}\cdots\text{W}$ and $\text{V}\cdots\text{O}\cdots\text{Ti}$ were weak and the V^{5+} were easy to reduce. The peak at 983-988 cm^{-1} shifted to lower wavenumber compared to 993 cm^{-1} is due to the weak interaction between V-O and W(Ti). The peak at 894-924 cm^{-1} was assigned to the vibration of V-O-V from polymerized VO_x species^[25]. For V3W8Ti(b) catalyst, the largest peak wavenumber at 924 cm^{-1} and 1135 cm^{-1} and the smallest peak wavenumber at 983 cm^{-1} indicate that the vanadia mainly exists in the form of dispersed and polymerized species on catalyst surface and weakest interaction.

3.3 Valence state and its ratio

XPS spectra of the catalysts calcined at different atmosphere are shown in Fig. 4, and the results are summarized in Table 2. V2p was de-convoluted to three peaks of different valence states: $V^{5+}2p_{2/3}$ (515.5eV), $V^{4+}2p_{2/3}$ (516.3eV), $V^{3+}2p_{2/3}$ (517.3eV). W^{5+} and W^{6+} were corresponded to two peaks respectively: $W^{6+}4f_{7/2}$ (35.75eV), $W^{6+}4f_{5/2}$ (37.7eV) and $W^{5+}4f_{7/2}$ (34.9eV), $W^{5+}4f_{5/2}$ (36.7eV). Ti2p was also separated into two peaks: $Ti^{4+}2p_{3/2}$ (458.13eV), $Ti^{4+}2p_{1/2}$ (464.49eV) and $Ti^{3+}2p_{3/2}$ (456.80eV), $Ti^{3+}2p_{1/2}$ (463.5eV).

Table 2 Valence state of elements and atomic percentage on catalysts surface

sample	V2p			Ti2p	W2p	O1s	surface atomic percentage(%)			
	V^{4+}/V^{5+}	$V^{4+(3+)}/V^{5+}$	$V^{4+(3+)}/V$	Ti^{4+}/Ti	W^{6+}/W	$O_{\alpha}/(O_{\alpha}+O_{\beta})$	V	W	O	Ti
V3W8Ti(a)	3.54	6.48	0.866	0.686	0.706	0.15	17.8	2.4	58.0	21.7
V3W8Ti(b)	1.03	1.35	0.574	0.921	0.688	0.30	20.3	2.2	57.7	19.8
V3W8Ti(c)	0.80	1.05	0.512	0.846	0.617	0.25	20.9	2.0	59.6	17.5
V3W8Ti(d)	0.76	0.94	0.484	0.812	0.595	0.24	20.7	2.0	59.5	17.8

For V3W8Ti(a), V is mainly in V^{4+} and V^{3+} valence state and the content of V^{3+} is approximately equal to the content of V^{4+} due to the insufficient oxidation in oxygen lacking atmosphere. The amount of Ti^{3+} states was more than the other catalysts due to the enhanced interaction between V-O and W(Ti). This was coincident with Raman results. Meanwhile, the reason why the surface atomic percentage of V(17.8%) was small than other catalysts was that strong interaction between V-O and W(Ti) result in the more exposure of W and Ti atom.

While for other catalysts, Ti was mainly in Ti^{4+} states. V was mainly in form of V^{4+} and V^{5+} valence states, indicating the enhancement of the oxidation of vanadium. With the increase of oxygen content, the oxidation is sufficient and the content of high valence V is increased, resulting in the decrease of the $\text{V}^{4+}/\text{V}^{5+}$ or $(\text{V}^{4+}+\text{V}^{3+})/\text{V}^{5+}$ ratio. Meanwhile, the decreased $\text{V}^{4+}/\text{V}^{5+}$ or $(\text{V}^{4+}+\text{V}^{3+})/\text{V}^{5+}$ ratio means that the oxidation ability of the atmosphere decreased in the sequence of purity oxygen, air and 15% O_2/N_2 . Thus the catalysts showed different colors (Fig. 1).

W existed as W^{6+} and W^{5+} valence states, but mainly in the form of W^{6+} . Contrasted to V, the effect of calcination atmosphere on W valence states was not obviously. But the amount of W^{6+} states increased with the increase of the amount of lower valence state V. And the amount of V^{5+} and W^{5+} increased with the increase of oxygen content in calcination atmosphere. The conclusion was coincident with M. Najbar et al. results^[14]. That is the ratio of $\text{V}^{4+}/\text{V}^{5+}$ has some conclusive effect on W^{6+}/W ratio.

In Table 2, O1s peaks could be fitted into two peaks: the peak of lattice oxygen at 529.7 eV (denoted as O_β) and the chemisorbed oxygen at 531.0 eV (denoted as O_α) assigned to the defect-oxide or hydroxyl-like group^[26,27]. The chemisorbed oxygen ions existed in the state of O^- and O_2^{2-} have a significant action to the deep oxidation of reducing substance^[28]. Surface chemisorbed oxygen has been reported to be the most active oxygen and plays an important role in oxidation reactions^[29]. The high relative concentration ratio of $\text{O}_\alpha/(\text{O}_\alpha+\text{O}_\beta)$ on catalyst surface could be correlated with the high SCR activity^[30]. In Table 2, the $\text{O}_\alpha/(\text{O}_\alpha+\text{O}_\beta)$ ratio for $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2(\text{a})$

catalyst is the lowest because there was no participation of oxygen in the calcination process. It means that surface oxygen was mainly from lattice. While for other catalysts, chemisorbed oxygen share larger percentage. The oxygen concentration of 15% O₂/N₂ is sufficient to oxidize V atom on V₂O₅-WO₃/TiO₂(b) surface. With the increase of oxygen in the calcination process, the O_α/(O_α+O_β) ratio decreased, which shows an identical changing regularity with V⁴⁺/V⁵⁺ and (V⁴⁺+V³⁺)/V⁵⁺ ratio. The results show that oxygen is indispensable in the calcination process. The content of chemisorbed oxygen on catalyst surface has no inevitable relationship with the content of oxygen in the calcination atmosphere. The V⁴⁺/V⁵⁺ ratio and the O_α/(O_α+O_β) ratio both reach their own maximum values simultaneously. The increase of V⁴⁺ content and lattice defects oxygen are due to the increase of surface chemisorbed oxygen^[31].

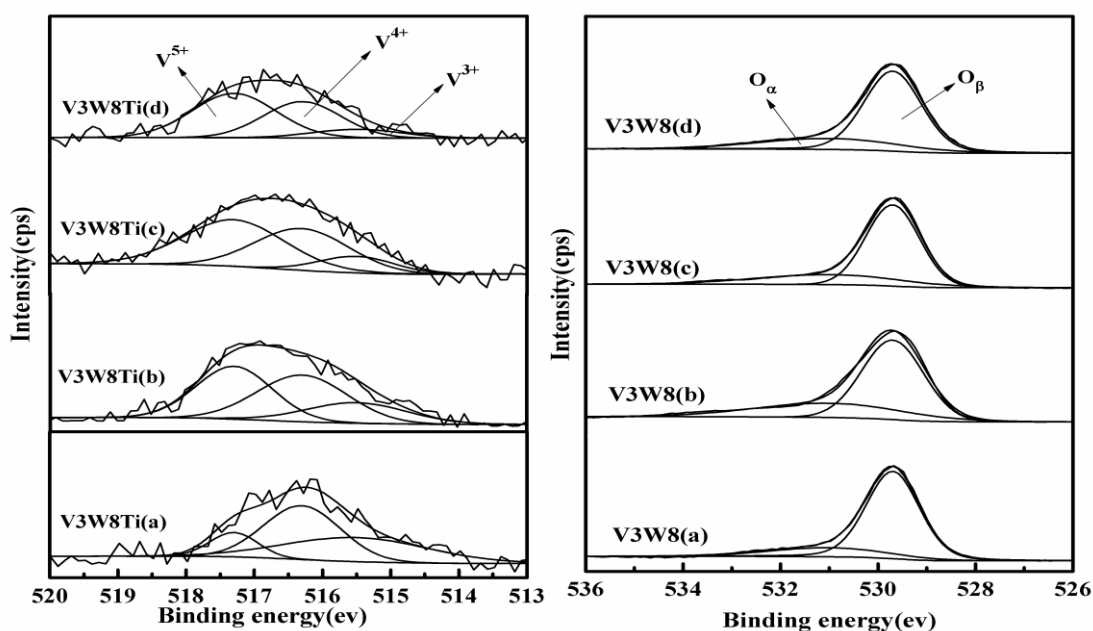


Fig. 4 XPS analysis of V2p and O1s on V₂O₅-WO₃/TiO₂ catalysts

3.4 H₂-TPR analysis

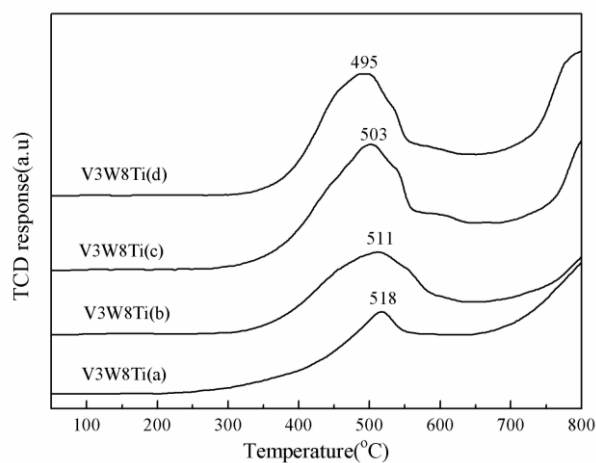


Fig. 5 H₂-TPR profiles of V₂O₅-WO₃/TiO₂ catalysts

Table 3 H₂ consumption of V₂O₅-WO₃/TiO₂ catalysts

sample	T _{max} (°C)	H ₂ consumption (μmol/g)
V3W8Ti(a)	518	93.8
V3W8Ti(b)	511	345
V3W8Ti(c)	503	351
V3W8Ti(d)	495	353

H₂-TPR test was performed to study the influence of oxygen content on redox property in the calcination process. In Fig. 5, the reducing peak at 500°C~550°C can be attributed to the reduction of dispersed vanadia species on catalyst surface, corresponding to the reducing processes of V⁵⁺ to V³⁺ and V⁴⁺ to V³⁺. The peak shifts to lower temperature with the increase of the oxygen content, indicating that V species are easy to reduce (Table 3). For V3W8Ti(a) catalyst, V exists mainly in low valence state. One reason of lowest H₂ consumption is the lowest V⁵⁺ content on catalyst surface lacking of the participation of oxygen in the calcination process which leading to the dependence of oxidation on lattice oxygen in oxidation process of V

species. The other is the strong interaction between V species and carrier resulting in the difficult reduction. While for other catalysts, the content of high valence V is increasing and the H₂ consumption is increasing too, which is consistent with Raman results.

3.5 Surface acidity

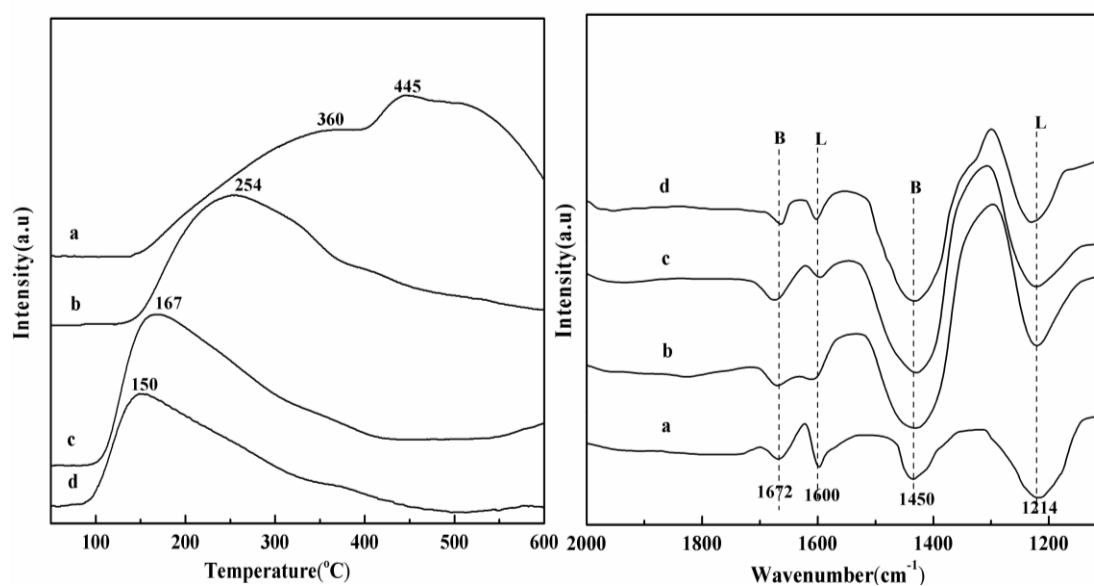


Fig. 6 NH₃-TPD(a) and NH₃-FTIR(b) of V₂O₅-WO₃/TiO₂ catalyst calcined in different conditions

Table 4 NH₃-TPD and Integral of NH₃ peak area adsorbed on the Brønsted acid (1450 cm⁻¹) or Lewis acids (1214 cm⁻¹) at 50°C

sample	peak area of Brønsted acid	peak area of Lewis acid	B/L	adsorption amount of NH ₃ (×10 ⁻⁷ mol)
V3W8Ti(a)	21.48	41.02	0.50	4.57
V3W8Ti(b)	176.87	127.13	1.51	17.85
V3W8Ti(c)	151.18	110.92	1.24	11.25
V3W8Ti(d)	121.56	98.66	1.23	9.02

3.5.1 NH₃-TPD

NH₃-TPD results of V₂O₅-WO₃/TiO₂ catalysts were tested in order to investigate the influence of the oxygen amount on surface acidity in the calcination process^[32]. In Fig.6(a) and Table 4, the desorption peaks in the range of 100-300 °C can be ascribed to the weak acidic sites which correspond to physisorbed ammonia and partially ionic NH₄⁺ bounded to Brønsted acid sites^[33]. Desorption peaks corresponded in the range of 400 -500 °C are ascribed to the desorption of coordinated NH₃ bounded to Lewis acid sites^[34]. For V3W8Ti(a) catalyst, these two kinds of desorption peaks were mainly due to the presence of low valence vanadium (V⁴⁺, V³⁺) on the catalyst surface. Medium and strong acid sites provided by the low valence vanadium on surface are attributed to Brønsted acid sites and Lewis acid sites^[15,34]. The ammonia desorption peak at high temperature was assigned to Lewis acid sites from surface Ti-OH^[35]. For the catalysts calcined in oxygen atmosphere, the desorption peaks of ammonia in the range of 100-400 °C and will shift to lower temperature with the increase of oxygen for the sake of the amount of the high valence vanadium. At the same time, tungsten on catalyst surface is also increased. In addition, V⁵⁺-OH and W⁶⁺-OH on catalyst surface were provided by Brønsted acid sites^[35]. There are more low valence vanadium (V⁴⁺, V³⁺) than the high valence vanadium (V⁵⁺) for the calcined catalyst at 15% O₂/ N₂ atmosphere, which produce medium and low temperature desorption peaks. The main valence of vanadium on the catalysts surface calcined in air and oxygen is the high valence vanadium (V⁵⁺), producing low temperature desorption peaks. As shown in Table 4, the adsorbed amount of NH₃ is the lowest for catalyst calcined without oxygen. The amount of the adsorbed ammonia reduces with the

increase of oxygen content because the catalysts calcined in containing oxygen atmosphere are consistent with the trend of ratios of V^{4+}/V^{5+} and $(V^{4+}+V^{3+})/V^{5+}$. This further illustrates that the ratio of V^{4+}/V^{5+} and $(V^{4+}+V^{3+})/V^{5+}$ on the catalyst surface will affect the acidity strength on catalyst surface, thus affecting the adsorption capacity of ammonia on catalysts surface.

3.5.2 NH₃-DRIFT

Although the NH₃ desorption-temperature on the Brønsted acid was usually lower than that on the Lewis acid, NH₃-TPD still can not distinguish Brønsted and Lewis acid sites, *i.e.*, the weak acid sites may contain some Lewis acid sites and the strong acid sites may contain a few Brønsted acid sites. To further investigate the influence of calcination conditions on the strength of Brønsted acid sites and Lewis acid sites, it needs to combine with the NH₃-DRIFT test analysis, as shown in Fig. 6(b) and Table 4. The bands at 1214 and 1600 cm⁻¹ with low intensities can be assigned to symmetric (δ_s) and asymmetric (δ_{as}) vibrations of the N–H bonds in NH₃ coordinated to Lewis acid sites^[36]. The bands at 1450 and 1672 cm⁻¹ were corresponded to asymmetric (δ_{as}) and symmetric (δ_s) vibrations of NH₄⁺ ions chemisorbed on Brønsted acid sites^[16,37].

High valence state V⁵⁺, W⁶⁺ and Ti⁴⁺ may mainly provide Brønsted acid sites, While low valence state can mainly provide Brønsted and Lewis acid sites^[35]. According to NH₃-DRIFT test results (Fig.6 (b)), Brønsted acid sites and Lewis acid sites were both existed on V₂O₅-WO₃/TiO₂ catalyst calcined in different conditions. For V3W8Ti(a) catalyat with the lowest B/L, the peak area of Lewis acid sites δ_s is larger than that of Brønsted acid sites δ_{as} on the catalyst calcined without oxygen

(Table 4), which indicates that the strength of Lewis acid sites is stronger than that of Brønsted acid sites, and Lewis acid sites mainly exist on catalyst surface. High V^{4+}/V^{5+} ratio and high content of Ti^{3+} result in the remarkable decrease of B acid sites and increase of Lewis acid sites. For other catalysts, the peak area of Brønsted acid sites δ_{as} is larger than that of Lewis acid sites δ_s on the catalyst calcined with oxygen, illustrating the strength of Brønsted acid sites is stronger than that of Lewis acid sites and Brønsted acid sites mainly exist on the catalyst surface. These results are consistent with the NH_3 -TPD analysis results. It is difficult to confirm the exact amounts of Brønsted and Lewis acid sites via the NH_3 -TPD because there is a difference in molar extinction coefficients between Brønsted acid and Lewis acid. With the increase of oxygen, both areas of Brønsted acid sites δ_{as} and Lewis acid sites δ_s become smaller for catalysts calcined in containing oxygen atmosphere, illustrating the strength of Lewis acid sites and the strength of Brønsted acid sites become weaker. The decreased strength of Brønsted and Lewis acid sites because of the decreased W^{6+} content and the decreased V^{4+}/V^{5+} or $(V^{4+}+V^{3+})/V^{5+}$ ratio showed a coincident regularity. The ratio (B/L) of Brønsted acid sites δ_{as} and Lewis acid sites δ_s also become smaller, which is consistent with the trend of the ratios of V^{4+}/V^{5+} , $(V^{4+}+V^{3+})/V^{5+}$ and W^{6+}/W , because there are more low valence vanadium (V^{4+} , V^{3+}) and high valence tungsten W^{6+} than the high valence vanadium V^{5+} and low valence tungsten W^{5+} for the catalyst calcined in 15% O_2/N_2 atmosphere. So, combined with XPS results, we can make a conclusion that ratios of V^{4+}/V^{5+} and $(V^{4+}+V^{3+})/V^{5+}$ on catalyst surface are consistent with the change tendency of Brønsted acid sites, the

strength of Lewis acid sites and the adsorbed amount of NH_3 .

3.6 DeNO_x activity

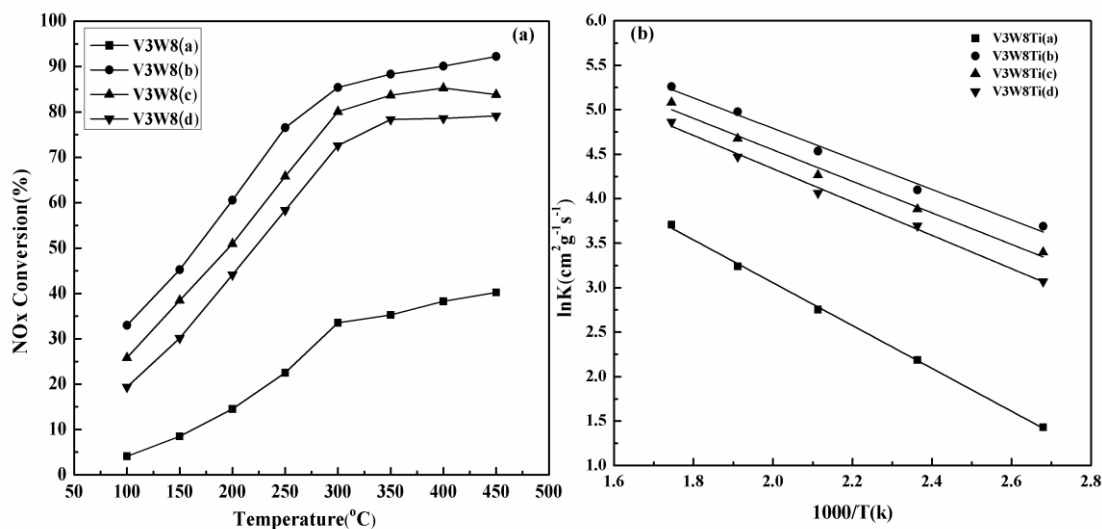


Fig. 7 The denitration activity of $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst (a) and the corresponding Arrhenius reaction rate constant(b)

Fig. 7 (a) shows the catalytic activity of the catalysts calcined at different conditions. The low valence vanadium (V^{4+} , V^{3+}) mainly exists on the surface of catalyst calcined without oxygen, the amount of the high vanadium (V^{5+}) is lowest, the catalytic activity is lowest. There are more low valence vanadium (V^{4+} , V^{3+}) than the high valence vanadium (V^{5+}) on the catalyst calcined in 15% O_2/N_2 , its de- NO_x activity is highest. The amount of V^{5+} ions on the catalyst surface is increased with the increased amount of oxygen in the calcination process, the catalyst de- NO_x activity is decreased, and the catalyst de- NO_x activity shows a little difference for calcined catalysts in air and pure oxygen, the changed tendency of catalyst de- NO_x activity is consistent with the changed tendency of the ratio of $\text{V}^{4+}/\text{V}^{5+}$ (Table 2) for the catalyst calcined with oxygen. It reveals that ratios of $\text{V}^{4+}/\text{V}^{5+}$ and $(\text{V}^{4+} + \text{V}^{3+})/\text{V}^{5+}$ on catalysts

surface will affect the de-NO_x activity. In a certain range, the higher of the V⁴⁺/V⁵⁺ and (V⁴⁺+V³⁺)/V⁵⁺ ratio, the higher of the de-NO_x activity. However, when the ratio of V⁴⁺/V⁵⁺ is further increased to a certain extent, the de-NO_x activity is decreased. Although the ratio of V⁴⁺/V⁵⁺ is the highest, the de-NO_x activity is the lowest. Because the electron transfer occurs between the low valence vanadium (V⁴⁺, V³⁺) and the high valence vanadium (V⁵⁺) in the de-NO_x process^[38], the rate of the SCR reaction and the de-NO_x activity could be improved only when the electron transfer of total V⁴⁺⁽³⁺⁾ is equal to the V⁵⁺ in the conversion process. When the ratios of V⁴⁺/V⁵⁺ and (V⁴⁺+ V³⁺)/V⁵⁺ are too high or too low, the rate of redox reaction and the de-NO_x activity of catalyst will decrease.

3.7 Kinetics for catalyst

The macroscopic dynamics were explored to further investigate the influence of the ratio of V⁴⁺⁽³⁺⁾/V⁵⁺ on intrinsic activity of V₂O₅-WO₃/TiO₂ catalyst at low temperature. To avoid the external diffusion effect, the steady-state condition experiments were carried out at a high space velocity of 300,000 h⁻¹ in the temperature range of 100 to 300 °C. NH₃-SCR reaction on V₂O₅-WO₃/TiO₂ catalyst was generally considered to be a first order reaction with respect to NO^[33-35]. The rate equation is $r=kC_{NO}$ and the rate constant can be described as following equations.

$$k = -\frac{F_0}{[NO]_0 W_{cat}} \ln(1-x) \quad (3)$$

$$k = A \exp\left(\frac{E_a}{RT}\right) \quad (4)$$

Where k is the reaction rate coefficient (mol g⁻¹ s⁻¹), F_0 is the NO feed rate

(mol min⁻¹), $[NO]_0$ is the inlet NO molar concentration (mol mL⁻¹), W_{cat} is the catalyst weight (g), X is the NO conversion (%), A is the pre-exponential factor, E_a is the apparent activation energy (kJ mol⁻¹), R is the gas constant and T is the temperature (K).

Table 5 Kinetic parameters (E_a , A) of the catalysts calcined in different conditions

Sample	V3W8Ti(a)	V3W8Ti(b)	V3W8Ti(c)	V3W8Ti(d)
E_a (kJ mol ⁻¹)	20.1	14.2	14.7	15.5
A	2.63×10^3	3.71×10^3	3.27×10^3	3.23×10^3

Based on the reaction rate in Fig. 7(b), E_a values worked out through Arrhenius fitting curve which are list in Table 5. E_a for the catalyst calcined in different oxygen content shows a changing tendency of V3W8Ti (b) < V3W8Ti (c) < V3W8Ti (d) < V3W8Ti (a). Combining with the activity results in Fig. 6(a) and Table 2, the ratios of V^{4+}/V^{5+} and $(V^{4+}+V^{3+})/V^{5+}$ are the highest and the E_a is the lowest for the V3W8Ti(b) catalyst with the highest activity. Both the ratios of V^{4+}/V^{5+} and the E_a are highest for V3W8Ti(a), while the de-NO_x activity is lowest. For V3W8Ti(c) and V3W8Ti(d) catalysts with the decreased de-NO_x activity, the ratios and E_a are both lower, illustrating that certain ratios of V^{4+}/V^{5+} and $(V^{4+}+V^{3+})/V^{5+}$ can reduce the E_a value and improve the de-NO_x activity. The trend of the pre-exponential factor A which represents the number of active sites in catalytic process^[39] and the de-NO_x activities are similar. A is highest for V3W8Ti(b) catalyst indicating that certain ratios of V^{4+}/V^{5+} and $(V^{4+}+V^{3+})/V^{5+}$ can increase the number of active sites in catalytic process, thus reducing the activation energy and improving the deNO_x activity.

4. Conclusion

V^{4+}/V^{5+} and $(V^{4+}+V^{3+})/V^{5+}$ ratios of vanadium on the surface of V_2O_5 - WO_3/TiO_2 catalyst are affected by the oxygen content during the calcination process. The increase of V^{4+}/V^{5+} ratios in an appropriate range is beneficial to increase the amount of Lewis acid on the catalyst surface. At the same time, the oxygen content for the dispersion state of the vanadium was a significant factor. An appropriate increased V^{4+}/V^{5+} and $(V^{4+}+V^{3+})/V^{5+}$ ratio is in favor of increasing the amount of polymeric vanadia species, chemisorbed oxygen, active reaction sites and acidic sites on catalyst surface. Moreover, high V^{4+}/V^{5+} and $(V^{4+}+V^{3+})/V^{5+}$ ratios are conducive to decrease apparent activation energy.

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