

Article

Selective Catalytic Removal of High Concentrations of NO_x at Low Temperature

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Abstract: Three vanadium-based catalysts were used to remove high concentrations of nitrogen oxides, and the catalysts' performance of de-NO_x and anti-H₂O under the high concentrations of NO_x were investigated. The V-Mo-W/TiO₂ catalysts were tested under 1500 mL/min gas flow (GHSV = 500 h⁻¹, 2.4% NO₂, 4.78% NH₃, 13% O₂, 4% H₂O, 5% CO₂) and characterized by BET, SEM, EDS, XRD, XPS, H₂-TPR, and NH₃-TPD; then, their physical and chemical properties were analyzed. The results showed that under the influence of H₂O, the NO_x conversion of the V-Mo-W/TiO₂ catalysts remained above 97% at 200–280 °C indicating that the catalysts had high catalytic activity and strong water resistance. The analysis of the characterization results showed that the larger specific surface area of the catalyst, the higher acid content, stronger redox ability, and higher V⁴⁺ and V³⁺ content were the reasons for the high NO_x conversion. The surface area decreased and the microstructure become smoother after the reaction, which may be caused by thermal sintering, but the overall morphology did not change. Comparing the H₂-TPR and NH₃-TPD of V_{1.6}Mo_{1.7}W_{1.8}/TiO₂ before and after NH₃-SCR reaction, it was found that the reduction peak and the intensity of the acid sites of the sample had not changed, which indicated that the catalyst had good anti-sintering performance and a long lifetime. This is significant for followup long-term engineering application experiments.

Keywords: high concentration; NO_x; SCR; V-Mo-W; NH₃



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1. Introduction

Extensive use of fossil fuels produce pollutants such as nitrogen oxides [1–3], causing great damage to the environment. The generated NO_x causes environmental problems such as acid rain, photochemical smog, and ozone layer destruction [4–6] and great harm to human health. Therefore, how to efficiently remove NO_x has become a hot spot in environmental management.

In the treatment of nitrogen oxides, the commonly used technology is selective catalytic reduction (SCR) [7,8], in which the selective reduction of NO_x with NH₃ as a reductant [9] under the action of a catalyst is one of the most effective and widely used NO_x removal technologies. With NH₃ as the reductant, the reaction equations [10] are mainly divided into the following categories:

- (1) The standard SCR reaction: $4\text{NH}_3 + 4\text{NO} + \text{O}_2 = 4\text{N}_2 + 6\text{H}_2\text{O}$;
- (2) The NO₂-SCR reaction: $4\text{NH}_3 + 2\text{NO}_2 + \text{O}_2 = 3\text{N}_2 + 6\text{H}_2\text{O}$;
- (3) The fast SCR reaction: $4\text{NH}_3 + 2\text{NO} + 2\text{NO}_2 = 4\text{N}_2 + 6\text{H}_2\text{O}$.

For NH₃-SCR technology, its crux is the NH₃-SCR catalyst [11–13]. In today's industry, the most widely used catalyst is V-W/TiO₂ [14–16]. The V-W/TiO₂ catalyst has good catalytic activity at a mid-range temperature and outstanding performance in sulfur resistance. The studies in [17,18] found that the VO_x in the V/TiO₂ catalyst mainly existed in the form

of monomeric vanadyl species and polymeric vanadyl species, and the NH_3 -SCR activity is higher in the form of polymeric vanadyl species. Yadolah et al. [19] studied the effect of anatase TiO_2 on the performance of $\text{VO}_x\text{-TiO}_2$ by in situ spectroscopies, arguing that the ability to form V-pairs appeared to be the only requirement for catalytic activity. At present, the surface acidity and thermal stability of the V/TiO_2 catalysts have mainly been improved by introducing W [20–22], Mo [23,24], or Si, thereby enhancing their NH_3 -SCR activity. Lai et al. [25] studied the catalytic active sites, reaction mechanism, and reaction kinetics in the NH_3 -SCR process through the $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst. Chen et al. [26] found that the doping of W promoted electron transfer, thereby generating more highly active V^{4+} and V^{3+} . Pan et al. [27] used the sol–gel method to support Si on $\text{V}_2\text{O}_5/\text{TiO}_2$ for modification and found that the number of acid sites and oxidation performance of Si-doped $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts improved, thereby improving the catalytic activity for denitrification. In addition, Kobayashi et al. [28] used the coprecipitation method to prepare $\text{V}_2\text{O}_5/\text{SiO}_2\text{-TiO}_2$ and found that the catalytic activity of the catalyst was improved, and its durability was greatly increased.

However, the production process of nitric acid, uranyl nitrate, etc., introduces the problem of high concentrations of NO_x in flue gas. In the production of uranium oxide by denitration of uranyl nitrate, the reaction is “ $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{UO}_3 + 1.86\text{NO}_2 + 0.14\text{NO} + 0.57\text{O}_2 + 6\text{H}_2\text{O}$ ” [29]. In the industrial production of UO_3 , it will decompose to produce ultra-high concentrations of NO_x , which far exceed the national standard. The waste gas generated in the production process of uranyl nitrate is mainly N_2 , CO_2 , NO_2 , O_2 , and H_2O , and the temperature is usually 200–500 °C; after some NO_2 is removed by spraying water, the NO_2 concentration drops to 30,000–50,000 mg/ Nm^3 . In the existing studies, the nitrogen oxide concentrations used are small, but the volumetric space velocity is large, which differs from most engineering.

Therefore, in this paper, high concentrations of nitrogen oxides were used for NH_3 -SCR experiments, the NH_3 -SCR efficiency of vanadium-titanium catalysts in an environment with high concentrations of nitrogen oxides was studied through a fixed-bed reactor, and the NH_3 -SCR activity of V-W-Mo/TiO_2 was tested by comparative experiments. The microstructural changes before and after the reaction of the catalyst were analyzed.

2. Experiment

2.1. Catalysts' Preparation

We studied the removal of NO_x from the exhaust gas produced during uranyl nitrate denitrification to produce UO_3 by NH_3 -SCR. After investigation, three common commercial catalysts were selected for the NH_3 -SCR experiments, which have been widely applied in flue gas denitrification projects and provide a reference for subsequent projects. The catalysts were prepared by the mixing process of an SCR honeycomb denitration catalyst [30], and the structures of the three catalysts are shown in Figure 1. The three catalysts used in the experiments were composed of V, Mo, W, Al, Si, Ti elements, etc. In addition to Ti, V, Mo, and W, the Al, Si, and other elements can enhance the mechanical properties of the catalyst. The catalysts were named $\text{V}_{1.6}\text{Mo}_{1.7}\text{W}_{1.8}/\text{TiO}_2$ (V: 1.6 wt%, Mo: 1.7 wt%, W: 1.8 wt%), $\text{V}_{2.7}\text{Mo}_{3.0}\text{W}_{1.0}/\text{TiO}_2$ (V: 2.7 wt%, Mo: 3.0 wt%, W: 1.0 wt%), and $\text{V}_{1.6}\text{Mo}_{2.5}\text{W}_{0.5}/\text{TiO}_2$ (V: 1.6 wt%, Mo: 2.5 wt%, W: 0.5 wt%) respectively.

2.2. Catalysts' Characterization

X-ray Diffraction (XRD) was performed on a D8 ADVANCE X-ray diffractometer with a $\text{Cu K}\alpha$ radiation source, 2θ were measured in the range of 10–90° in steps of 5°. The specific areas and pore sizes were measured in a Micromeritics ASAP 2020 analyzer and subjected to isothermal N_2 adsorption-desorption measurements at 220 °C. The morphology and microstructure were observed by Scanning Electron Microscope (SEM) and Energy-dispersive X-ray Spectroscopy (EDS) on a TESCAN G0AIA3 XMH. The X-ray Photoelectron Spectroscopy (XPS) was performed on the Thermo Scientific ESCALAB 250 Xi instrument, and the data of samples were calibrated using the C1s peak (284.8 eV). The

Temperature Programmed Desorption of ammonia (NH₃-TPD) study was performed on an AutoChem II 2920 instrument; first, 0.1 g of the sample was pretreated in helium at 250 °C for 60 min. Then, after the sample was cooled to 80 °C, 5% NH₃ in helium was purged to the tube at a flow rate of 30 mL/min for 2 h; then, the temperature was raised from 80 to 600 °C at a rate of 10 °C/min in helium. The Temperature Programmed Reduction of hydrogen (H₂-TPR) data were acquired by an AutoChem II 2920 instrument; first, 0.1 g samples were pretreated in O₂ flow at 300 °C for 1 h. After the temperature of the samples was cooled to 30 °C, 10% H₂ in argon was flowed through the tube at a flow rate of 50 mL/min, as the temperature was raised from room temperature to 900 °C at a rate of 10 °C/min.

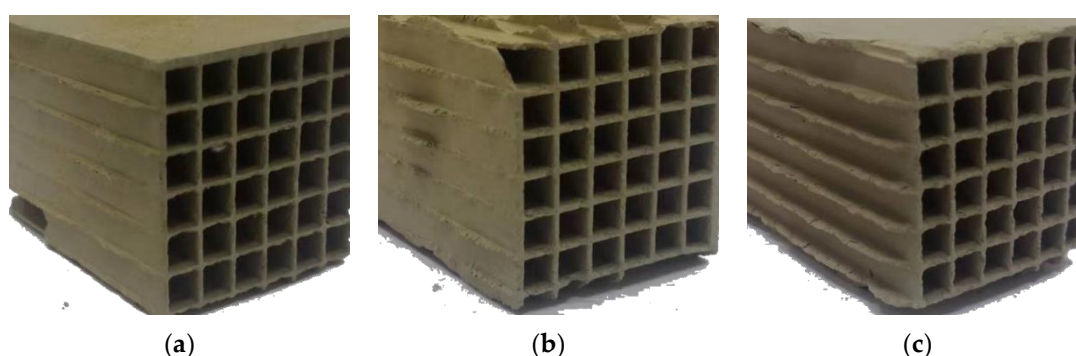


Figure 1. The structures of the three catalysts: (a) V_{1.6}Mo_{1.7}W_{1.8}/TiO₂; (b) V_{2.7}Mo_{3.0}W_{1.0}/TiO₂; (c) V_{1.6}Mo_{2.5}W_{0.5}/TiO₂.

2.3. Activity Test

The activity test of the catalyst was carried out on the fixed-bed catalyst evaluation device, as shown in Figure 2. The catalyst sample volume was 180 cm³ (30 mm × 30 mm × 200 mm with 30 holes). The total gas flow was 1500 mL/min, and the volumetric space velocity (GHSV) = 500 h^{−1}, in which the content of NO₂ was 2.4%, NH₃ varied with the ratio of NH₃:NO₂, O₂ was 13%, H₂O was 4%, CO₂ was 5%, and the balance gas was N₂. The catalyst was first heated to 200 °C in a nitrogen atmosphere. When the temperature remained unchanged, the mixed gas was passed into the reactor for the catalytic reaction, and a flue gas analyzer was used at the outlet of the reactor for exhaust gas detection. Due to the presence of NO₂ and H₂O in the inlet flue gas, some NO was produced in the gas and entered the reactor. The efficiency of the catalyst was calculated according to the following formula:

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

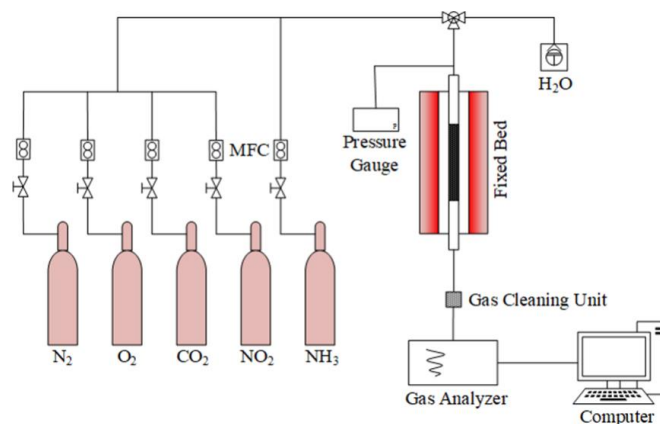


Figure 2. Schematic diagram of the experimental apparatus for catalytic performance.

3. Results and Discussion

3.1. Catalytic Activity Evaluation

Figure 3 shows the change in the catalytic performance of $V_{1.6}Mo_{2.5}W_{0.5}/TiO_2$ with the ratio of $NH_3:NO_2$ at 220 °C. No matter the change in the ratio of $NH_3:NO_2$, the catalytic activity of NH_3 -SCR of $V_{1.6}Mo_{2.5}W_{0.5}/TiO_2$ was excellent, and the NO_x conversion reached more than 96%. As the ratio of $NH_3:NO_2$ increased, the NO_x conversion also increased; however, when the ratio of $NH_3:NO_2$ exceeded 1.5, the increase in the rate of NO_x conversion became smaller.

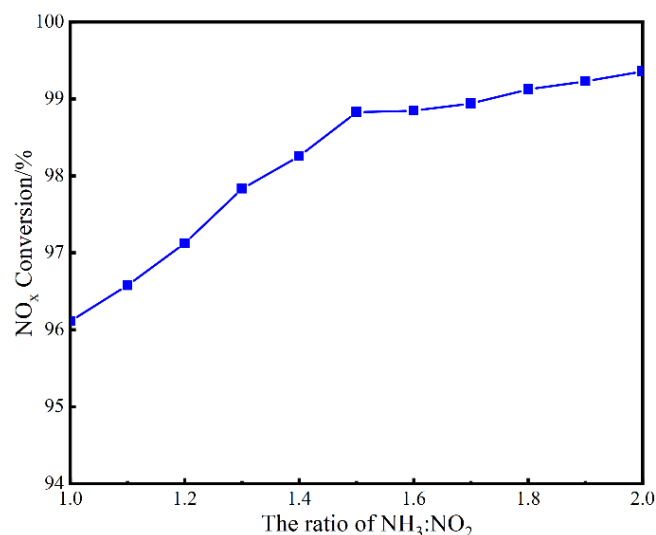


Figure 3. The relationship between the de- NO_x efficiency of $V_{1.6}Mo_{2.5}W_{0.5}/TiO_2$ and the ratio of $NH_3:NO_2$ at 220 °C.

Figure 4 shows the NH_3 -SCR catalytic performance of $V_{1.6}Mo_{1.7}W_{1.8}/TiO_2$, $V_{2.7}Mo_{3.0}W_{1.0}/TiO_2$, and $V_{1.6}Mo_{2.5}W_{0.5}/TiO_2$ at 200–280 °C, when the ratio of $NH_3:NO_2$ was 2. At high concentrations of nitrogen oxides and 4% H_2O , the catalytic activity of the NH_3 -SCR of the three catalysts in the range of 200–280 °C was generally excellent, and the NO_x conversion reached more than 97%. Among them, the catalytic activity of $V_{1.6}Mo_{1.7}W_{1.8}/TiO_2$ was the highest. The three catalysts showed strong anti- H_2O ability.

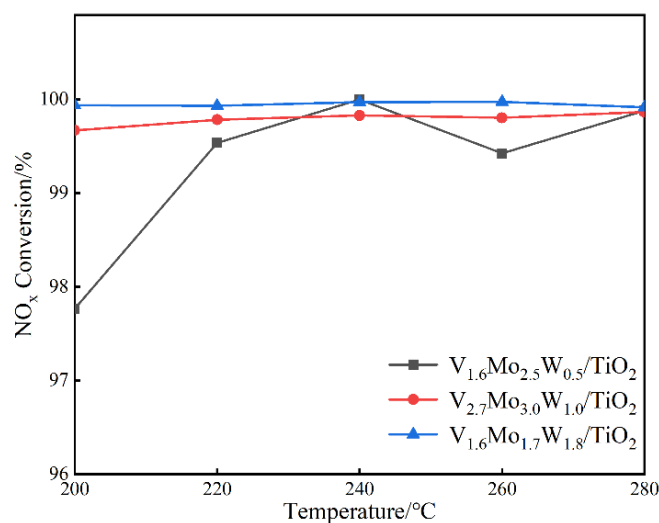


Figure 4. The NO_x conversion of the three catalysts.

3.2. Characterization of the Catalysts

3.2.1. BET

According to the experiment, the samples of the three catalysts were subjected to BET characterization test to understand the changes in the specific surface area, pore volume, and average pore diameter of each catalyst before and after the reaction, so as to better study and analyze the catalysts. The BET test results are shown in Table 1:

Table 1. BET test results of the three catalysts.

Catalyst		Surface Area (m ² /g)	Surface Area Reduction Percentage (%)	Pore Volume (cm ³ /g)	Pore Size (nm)
V _{1.6} Mo _{1.7} W _{1.8} /TiO ₂	before reaction	75.23	5.69	0.267	11.54
	after reaction	70.95		0.250	11.64
V _{2.7} Mo _{3.0} W _{1.0} /TiO ₂	before reaction	70.90	5.98	0.284	13.32
	after reaction	66.66		0.297	12.88
V _{1.6} Mo _{2.5} W _{0.5} /TiO ₂	before reaction	83.14	23.09	0.303	12.59
	after reaction	63.94		0.251	12.39

As shown in Table 1, the surface area of these three catalysts was around 70–80 m²/g, and the V_{1.6}Mo_{2.5}W_{0.5}/TiO₂ had the highest surface area, which was 83.14 m²/g; however, after the reaction, the surface area of the three catalysts decreased, and the surface area of V_{1.6}Mo_{2.5}W_{0.5}/TiO₂ decreased the most, followed by V_{2.7}Mo_{3.0}W_{1.0}/TiO₂, and V_{1.6}Mo_{1.7}W_{1.8}/TiO₂ decreased the least. This may be one of the reasons for the highest catalytic activity of V_{1.6}Mo_{1.7}W_{1.8}/TiO₂. In addition, the pore volume and pore size of the three catalysts were not significantly different, which also indicated that the activity of the three catalysts were comparable. Comparing the surface area, pore volume, and pore size of the three catalysts before and after the NH₃-SCR reaction, the catalysts after the reaction had decreased, but the difference was not large. The reason for the decrease in surface area may be the valence change of the V and Mo atoms and thermal sintering [31].

3.2.2. Morphology Evolution

The SEM/EDS images in Figures 5 and 6, respectively, display the morphology and sizes of the V-rich, Mo-rich, and W-rich particles of V_{1.6}Mo_{1.7}W_{1.8}/TiO₂ before and after the NH₃-SCR reaction. It can be seen from Figure 5a that the combination of the active components and the catalyst was good, the catalyst surface before the NH₃-SCR reaction was smooth, and the structure was relatively tight. As shown in Figure 6a, the microstructure of V_{1.6}Mo_{1.7}W_{1.8}/TiO₂ became smoother after the NH₃-SCR reaction; however, it can be seen that the morphology of the V_{1.6}Mo_{1.7}W_{1.8}/TiO₂ did not change much after the NH₃-SCR reaction, and the original structure was basically maintained. The stability of the catalyst was high, which was also reflected in the activity test. Comparing the EDS images before and after the NH₃-SCR reaction, the V and Mo elements were uniformly distributed in the catalyst, but the W element appeared agglomerated after the NH₃-SCR reaction, which may be caused by thermal sintering [31].

3.2.3. XRD

In order to better determine the material structure of the catalyst, the catalyst crystal was further tested by the XRD characterization method. It can be seen from Figure 6a–c that the XRD peak patterns of the three catalysts were basically the same, and the main structural substances were TiO₂. Comparing the XRD images of the three catalysts before and after the NH₃-SCR reaction, it can be found that the crystal changed little after the reaction. As shown in Figure 7a–c, the presence of anatase TiO₂ peaks can be clearly observed in the XRD images, and the X-ray diffraction peaks appeared at 25.3°, 37.8°, 48°, 54°, 55°, 62.8°, 69°, 70.3°, and 75°. The peak shape was sharp, the intensity was large, and the crystallinity was good. At the same time, no other diffraction peaks were detected. This

showed that the metal oxides of V and Mo were evenly dispersed on the surface of the TiO_2 support, and the crystal form of the support was not affected [32]. This was consistent with the characterization results of the SEM and EDS.

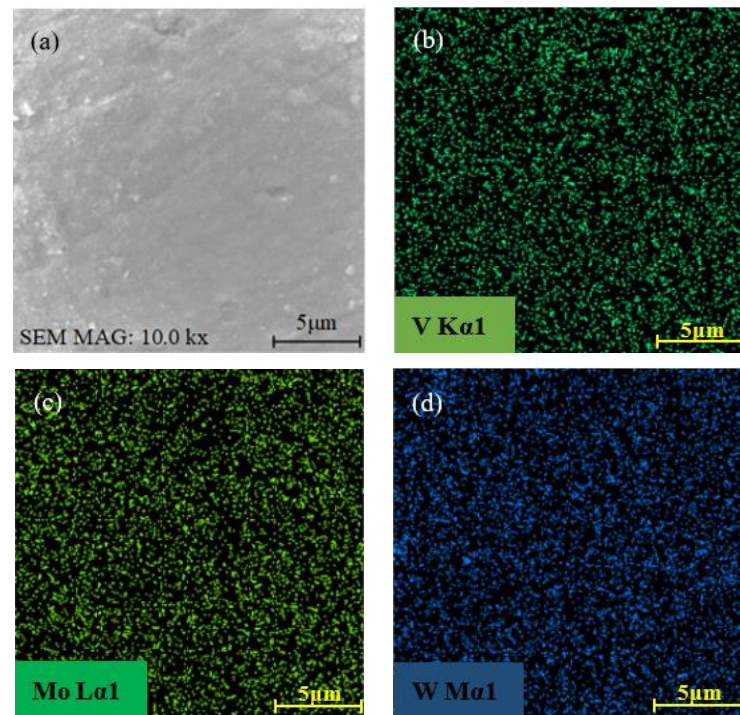


Figure 5. Morphology of the $\text{V}_{1.6}\text{Mo}_{1.7}\text{W}_{1.8}/\text{TiO}_2$ before reaction. (a) SEM image, 10.0 kx; (b) EDS image V element dispersion; (c) EDS image Mo element dispersion; (d) EDS image W element dispersion.

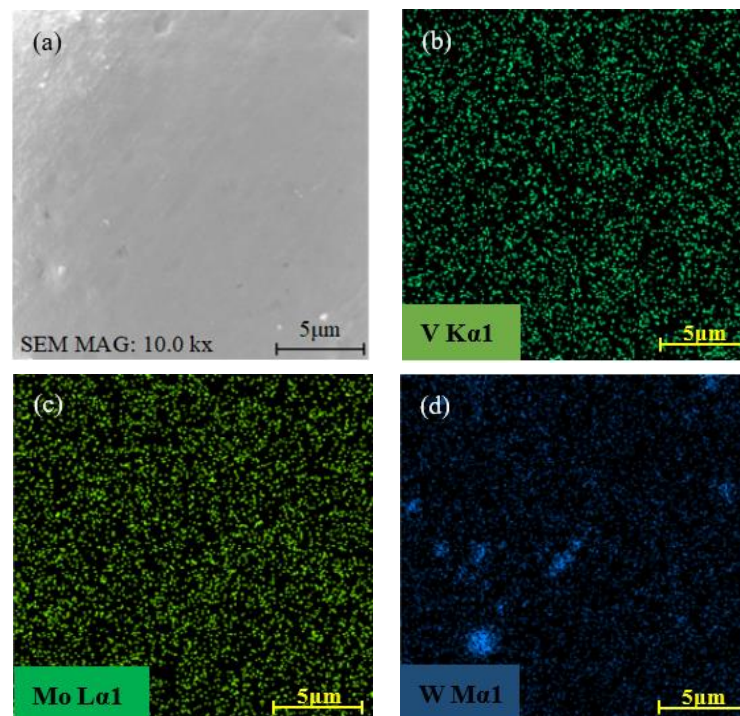


Figure 6. Morphology of the $\text{V}_{1.6}\text{Mo}_{1.7}\text{W}_{1.8}/\text{TiO}_2$ after reaction. (a) SEM image, 10.0 kx; (b) EDS image V element dispersion; (c) EDS image Mo element dispersion; (d) EDS image W element dispersion.

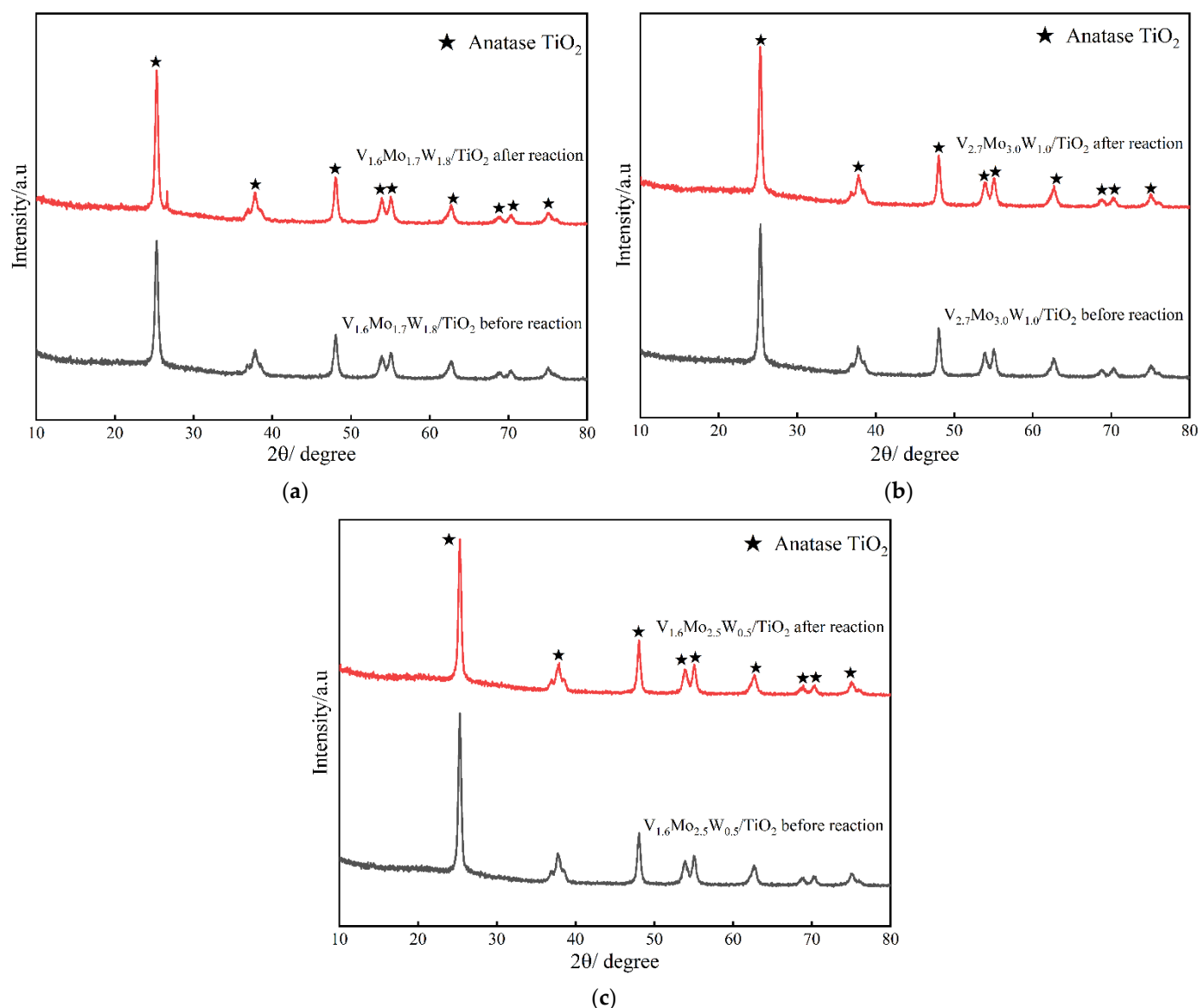


Figure 7. XRD pattern of three catalysts: (a) $\text{V}_{1.6}\text{Mo}_{1.7}\text{W}_{1.8}/\text{TiO}_2$; (b) $\text{V}_{2.7}\text{Mo}_{3.0}\text{W}_{1.0}/\text{TiO}_2$; (c) $\text{V}_{1.6}\text{Mo}_{2.5}\text{W}_{0.5}/\text{TiO}_2$.

3.2.4. XPS

Figure 8a shows the XPS spectra of O1s for the samples. The peak at 530 eV was attributed to lattice oxygen (O_β), while the peak at 532 eV corresponded to chemisorbed oxygen (O_α). The ratios of $\text{O}_\alpha/(\text{O}_\alpha + \text{O}_\beta)$ of the $\text{V}_{1.6}\text{Mo}_{1.7}\text{W}_{1.8}/\text{TiO}_2$, $\text{V}_{2.7}\text{Mo}_{3.0}\text{W}_{1.0}/\text{TiO}_2$, and $\text{V}_{1.6}\text{Mo}_{2.5}\text{W}_{0.5}/\text{TiO}_2$ were 0.127, 0.220, and 0.143, respectively. The chemisorbed oxygen played an important role in the oxidation reactions due to its high mobility, and high O_α content can promote “fast SCR” reactions [33]. Figure 9a shows the XPS spectra of O1s for $\text{V}_{1.6}\text{Mo}_{1.7}\text{W}_{1.8}/\text{TiO}_2$, in which the content of O_α increased after the NH_3 -SCR reaction. As shown in Table 2, the ratio of $\text{O}_\alpha/(\text{O}_\alpha + \text{O}_\beta)$ in the $\text{V}_{1.6}\text{Mo}_{1.7}\text{W}_{1.8}/\text{TiO}_2$ after the NH_3 -SCR reaction increased from 12.74% to 16.36%, which was helpful for the stability of the reactivity of $\text{V}_{1.6}\text{Mo}_{1.7}\text{W}_{1.8}/\text{TiO}_2$.

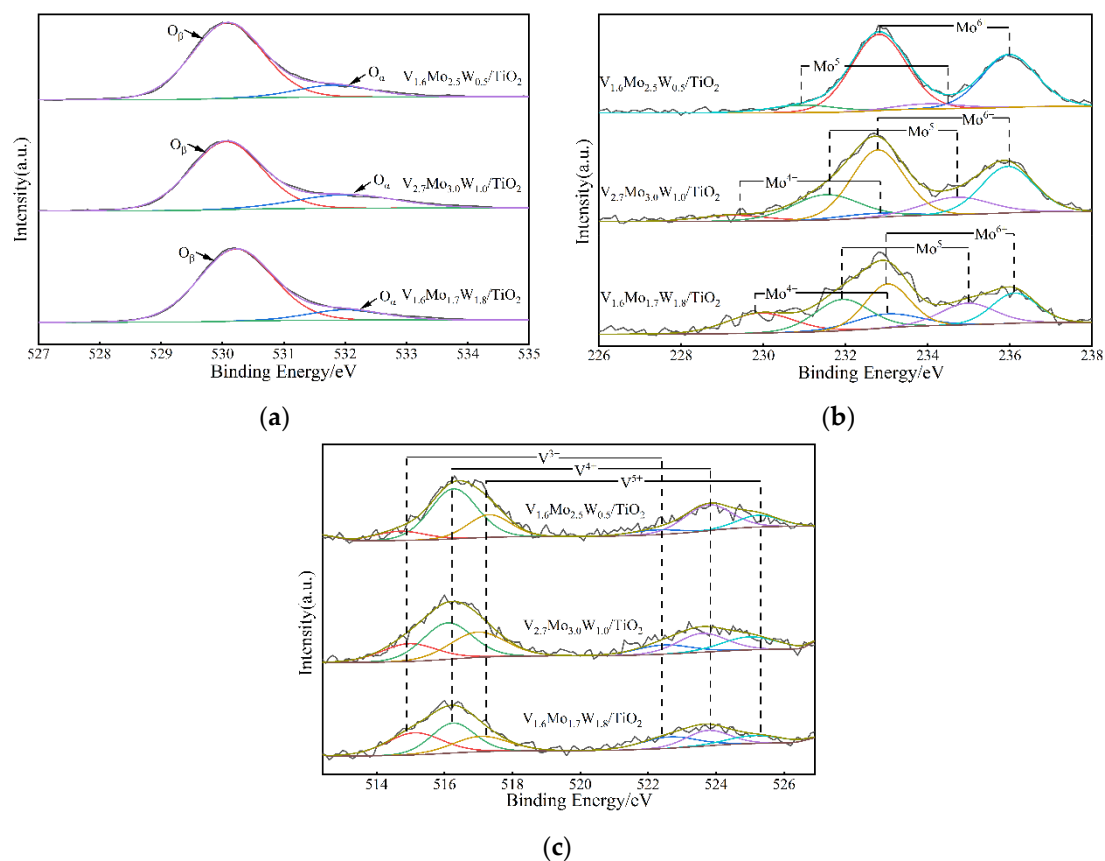


Figure 8. Deconvoluted XPS spectra of the three catalysts: (a) O1s; (b) Mo3d; (c) V2p.

Table 2. The chemical states and the ratios of the relative concentrations of O, V, and Mo for different catalysts.

Catalyst	O _β (%)	O _α (%)	O _α /(O _α + O _β) (%)	(V ³⁺ + V ⁴⁺)/V ⁵⁺ (%)	Mo ⁶⁺ /(Mo ⁶⁺ + Mo ⁵⁺ + Mo ⁴⁺) (%)
V _{1.6} Mo _{1.7} W _{1.8} /TiO ₂ before reaction	87.3%	12.7%	0.127	2.967	0.392
V _{1.6} Mo _{1.7} W _{1.8} /TiO ₂ after reaction	83.6%	16.4%	0.164	6.541	0.600
V _{2.7} Mo _{3.0} W _{1.0} /TiO ₂	78.1%	21.9%	0.220	1.985	0.627
V _{1.6} Mo _{2.5} W _{0.5} /TiO ₂	85.7%	14.3%	0.143	2.901	0.894

Figure 8b shows the XPS spectra of Mo3d for the catalysts. The peaks at 230.5 eV and 232.8 eV were peaks of Mo⁴⁺, the peaks at 231.5 eV and 234.6 eV were attributed to Mo⁵⁺, and the peaks of Mo⁶⁺ corresponded to the binding energies of 232.9 and 235.9 eV. As shown in Table 2, the Mo⁶⁺/(Mo⁶⁺ + Mo⁵⁺ + Mo⁴⁺) ratio of the V_{1.6}Mo_{1.7}W_{1.8}/TiO₂ was the smallest, which was 0.392. As shown in Figure 9b, the ratio of Mo⁶⁺/(Mo⁶⁺ + Mo⁵⁺ + Mo⁴⁺) increased after the SCR reaction, because an increase in the content of V⁴⁺ and Mo⁶⁺ resulted from the transfer of electrons in the Mo-O-V species between V⁵⁺ and Mo⁴⁺ and Mo⁵⁺, the imbalance of which charged oxygen deficiency, which was beneficial to the catalyst activity [34].

Figure 8c shows the XPS spectra of V2p for the samples, and Figure 9c shows the XPS spectra of V2p for the V_{1.6}Mo_{1.7}W_{1.8}/TiO₂ before and after reaction. The peaks around 517.3 eV and 525.4 eV were characteristic peaks of V⁵⁺, the peaks around 516.3 eV and 523.7 eV corresponded to V⁴⁺, and the peaks at 515.1 eV and 522.5 eV were assigned to V³⁺. It can be seen from Table 2 that the ratio of (V³⁺ + V⁴⁺)/V⁵⁺ of V_{1.6}Mo_{1.7}W_{1.8}/TiO₂ was 2.97, which was higher than other catalysts. According to the literature, low-valence vanadium oxides can easily adsorb oxygen to generate reactive oxygen species during the

SCR reaction, which was significant for the low-temperature SCR activity [35,36]. It can be seen from Table 2 that the ratio of $(V^{3+} + V^{4+})/V^{5+}$ in the $V_{1.6}Mo_{1.7}W_{1.8}/TiO_2$ increased after the NH_3 -SCR reaction, which was helpful for the catalytic activity. The V^{4+} and V^{5+} on the surface of the NH_3 -SCR catalyst mainly existed in the form of $V-OH$, and $V=O$. NO was oxidized to NO_2 , and $V^{5+}=O$ was reduced to $V^{4+}-OH$, both of which promoted the fast SCR reaction, thereby improving the low-temperature activity of the catalyst [37].

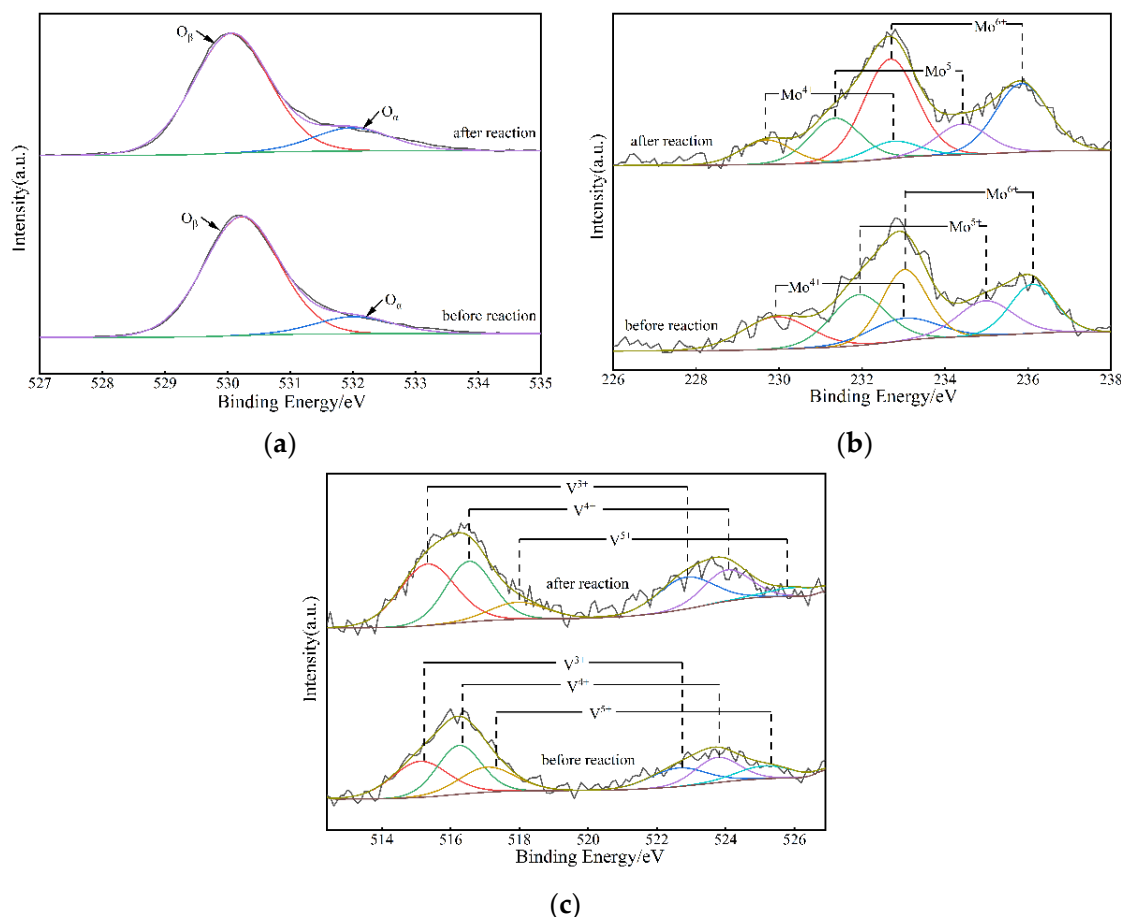


Figure 9. Deconvoluted XPS spectra of the $V_{1.6}Mo_{1.7}W_{1.8}/TiO_2$ before and after reaction: (a) O1s; (b) Mo3d; (c) V2p.

3.2.5. H_2 -TPR

H_2 -TPR was carried out on the three catalyst samples, respectively, and the test results are shown in Figure 10a. The $V_{1.6}Mo_{1.7}W_{1.8}/TiO_2$ had two reduction peaks. The reduction peak at around 500 °C corresponded to the reduction of the VO_x and MoO_x species on the $V_{1.6}Mo_{1.7}W_{1.8}/TiO_2$ [38,39], while the reduction peak at 619 °C was attributed to the reduction of the TiO_2 ($Ti^{4+} \rightarrow Ti^{3+}$) or $V-O-Ti$ species [40,41]. The peak areas of the other two catalysts were comparable to those of $V_{1.6}Mo_{1.7}W_{1.8}/TiO_2$, but the temperature of the reduction peak of $V_{1.6}Mo_{1.7}W_{1.8}/TiO_2$ was lower than that of the other two catalysts, which indicated that the reduction performance of $V_{1.6}Mo_{1.7}W_{1.8}/TiO_2$ was better. As shown in Figure 10b, $V_{1.6}Mo_{1.7}W_{1.8}/TiO_2$ showed two reduction peaks before and after reaction, which were located around 502 °C and 619 °C, respectively. The position of the reduction peak did not occur, which indicated that the catalytic activity of $V_{1.6}Mo_{1.7}W_{1.8}/TiO_2$ was relatively stable.

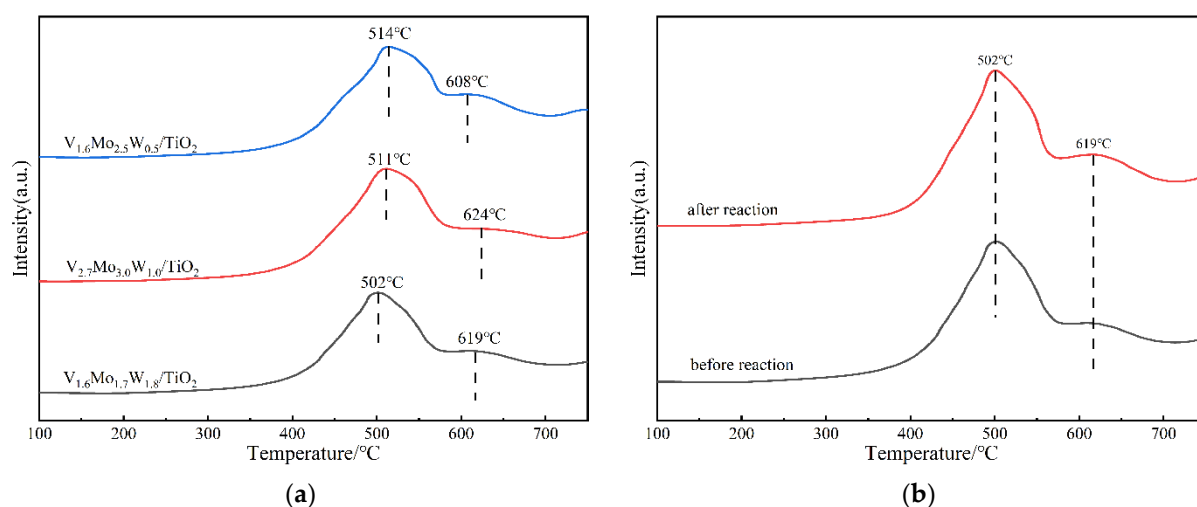


Figure 10. H₂-TPR profiles of the three catalysts: (a) the three fresh catalysts and (b) $V_{1.6}Mo_{1.7}W_{1.8}/TiO_2$ before and after reaction.

3.2.6. NH₃-TPD

As shown in Figure 11a, the catalyst of $V_{1.6}Mo_{1.7}W_{1.8}/TiO_2$ showed NH₃ desorption peaks at 207 °C and 447 °C. Affected by the partial NH₄⁺ bound to the weakly acidic site (Brønsted acid), the NH₃ desorption peak of $V_{1.6}Mo_{1.7}W_{1.8}/TiO_2$ at 207 °C was the same as that of the other two catalysts, which was mainly attributed to the bridge structure of MoO_x or MoO_x and VO_x [42]; the NH₃ desorption peak at 447 °C was attributed to the desorption of the coordinated NH₃ bound to the strongly acidic site (Lewis acid). Compared with the other two catalysts, the strong acid site of $V_{1.6}Mo_{1.7}W_{1.8}/TiO_2$ was more intense, and the desorption temperature was lower. The higher the acidity of the catalyst, the more catalytically active the centers were, which was conducive to the progress of the catalytic reaction. As shown in Figure 11b, the NH₃ desorption peak of $V_{1.6}Mo_{1.7}W_{1.8}/TiO_2$ remained basically unchanged after the NH₃-SCR reaction, which indicated that the catalyst had good stability.

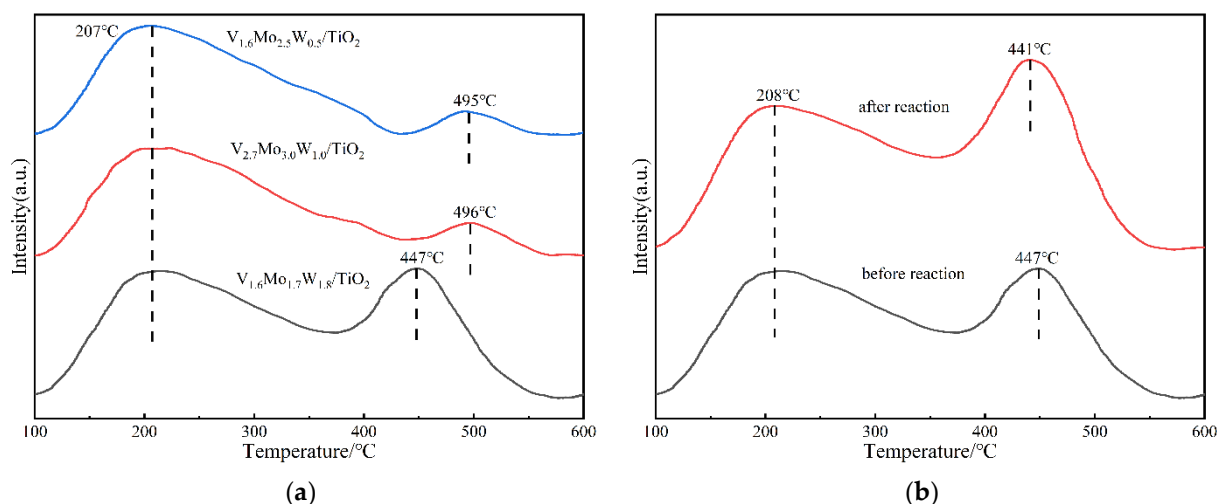


Figure 11. NH₃-TPD of the three catalysts: (a) the three fresh catalysts and (b) $V_{1.6}Mo_{1.7}W_{1.8}/TiO_2$ before and after reaction.

4. Conclusions

In summary, this study focused on examining the activity of the three catalysts used for NH₃-SCR at high concentrations of NO_x and on understanding the physical and chemical

properties of the catalysts that play an important role in catalysis at high concentrations of NO_x . Three catalysts were tested for NH_3 -SCR catalytic activity and the microstructure changes before and after the NH_3 -SCR reaction were analyzed using microscopic characterization methods. The conclusions include:

- (1) Under high concentration NO_x and 4% H_2O , the three vanadium-based catalysts all showed excellent de- NO_x activity, and the NO_x conversion reached more than 97% at 200–280 °C.
- (2) After the NH_3 -SCR reaction, the valence changes in the V and Mo atoms and thermal sintering may lead to changes in the microstructure of the catalyst and thus reduce its lifetime.
- (3) The higher content of V^{4+} and V^{3+} and active oxygen on the surface of the catalysts were beneficial to the fast SCR reaction, which improved the low-temperature activity of the catalyst.
- (4) After the NH_3 -SCR reaction, neither the microstructure of the catalyst intensely changed nor the acid content or the intensity of the reduction peak changed, which indicated that the $\text{V}_{1.6}\text{Mo}_{1.7}\text{W}_{1.8}/\text{TiO}_2$ had strong stability.

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