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NH₃ selective catalytic reduction of NO: A large surface TiO₂ support and its promotion of V₂O₅ dispersion on the prepared catalyst

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ABSTRACT

A titania support with a large surface area was developed, which has a BET surface area of 380.5 m²/g, four times that of a traditional titania support. The support was ultrasonically impregnated with 5 wt% vanadia. A special heat treatment was used in the calcination to maintain the large surface area and high dispersion of vanadium species. This catalyst was compared to a common V₂O₅-TiO₂ catalyst with the same vanadia loading prepared by a traditional method. The new catalyst has a surface area of 117.7 m²/g, which was 38% higher than the traditional V₂O₅-TiO₂ catalyst. The selective catalytic reduction (SCR) performance demonstrated that the new catalyst had a wider temperature window and better N₂ selectivity compared to the traditional one. The NO conversion was >80% from 200 to 450 °C. The temperature window was 100 °C wider than the traditional catalyst. Raman spectra indicated that the vanadium species formed more V-O-V linkages on the catalyst prepared by the traditional method. The amount of V-O-Ti and V=O was larger for the new catalyst. Temperature programmed desorption of NH₃, temperature programmed reduction by H₂ and X-ray photoelectron spectroscopy results showed that its redox ability and total acidity were enhanced. The results are helpful for developing a more efficient SCR catalyst for the removal of NO_x in flue gases.

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1. Introduction

PM_{2.5} is a major environmental problem in China and all developing countries due to fast industrial growth. The emission of NO_x from stationary sources, natural sources and mobile sources [1] together with SO₂ and VOCs act as pollutant precursors. After complex chemical reactions in the atmosphere, they lead to the formation of PM_{2.5} and cause other pollution like acid rain and photochemical smog [2]. Pollutants like these

are detrimental to human health and cause respiratory complications [3]. Among the sources that form the PM_{2.5}, NO_x from power plants contribute 30% to the total NO_x emission in China [4]. In order to reduce the emission of NO_x, efforts to develop high efficiency denitrification (DeNO_x) systems have been made. Selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR) are the two most widely used DeNO_x technologies in power plants. They both use NH₃ as the reducing agent. However, compared to SNCR, SCR has a much lower

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operating temperature, lower N_2O formation, lower NH_3 escape and higher NO_x conversion. SCR by NH_3 is a mature technology that is widely applied in coal power plants and other industrial furnaces to control NO_x emission in China. In the De NO_x system, the catalyst is the key factor for the high efficiency removal of NO_x . The type of catalyst used determines the reaction temperature range, N_2 selectivity and poison tolerance ability. So far, the three most widely used and favored classes of catalysts are vanadium-based catalysts [5], non-vanadium transitional metal oxide-based catalysts [6] and zeolites [7]. Among these, the vanadium-based catalyst has excellent sulfur and water vapor resistance, long term stability and the lowest cost [8]. $\text{V}_2\text{O}_5\text{-TiO}_2$ is a basic vanadium-based catalyst with a simple manufacturing process. For its industrial production, metavanadate is first dissolved by ethanolamine or oxalic acid. Then it is mixed with commercial anatase TiO_2 and used in an ordinary impregnation method. Finally, after a drying process, the powder is calcined at 500 °C to make the catalyst. Although research has shown that it has excellent SCR performance at temperatures from 250 to 350 °C [9], the actual flue gas temperature may fluctuate with load. The flue gas temperature of a low load power plant is below the catalyst temperature range. This practical problem at the actual working condition reduces the catalytic efficiency of the catalysts. Efforts have been made to solve this problem. One way is to reheat the inlet flue gas into the SCR system [10]. However, reheating the flue gas for the SCR reaction would need the reconstruction of the heat cycle system and cause redundant resource waste, thus increasing cost considerably. So it is necessary to develop a catalyst with a wider temperature window, especially in the lower temperature range.

It is well known that the redox and acidity properties are two key factors for SCR performance [11]. A previous study proved that V=O species facilitate the reaction in the redox cycle [12] and V-OH species in the acid site cycle [13]. Most recent studies focused on adding promoters to the catalyst system to enhance the dispersion of vanadium [14] and provide more acid site capacity [15]. $\text{V}_2\text{O}_5\text{-WO}_3\text{-TiO}_2$ and $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2$ are the most commercialized promoted vanadium-based catalysts. Recently, transitional metal elements including Nb, Cu, Cr, and Fe [16–19] were used as dopants in the catalyst system to enhance the SCR performance. A recent work has shown that the addition of Mn to the $\text{V}_2\text{O}_5\text{-TiO}_2$ system significantly enhanced the activity of the $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst for $\text{NH}_3\text{-SCR}$ below 400 °C [20]. Although promising promotion effects in acidity and redox ability were found in these works, the actual industrial production of the catalyst was not realistic because of the high cost of the raw materials. However, little attention has been paid to the study of the catalyst support. Research on the support mainly focused on pretreatment like sulfation of the support [21] and utilizing different methods like a sol-gel or hydrothermal treatment to prepare a nanoscale support to enhance the SCR performance [22]. Although better results were obtained, they were not promising for practical production. In contrast, this study used a relatively simple method for manufacturing the catalyst. A low cost large surface area titania was used as the support to enhance the dispersion of vanadium species and thus optimize the SCR per-

formance. Together with the support ultrasonic impregnation and a special heat treatment were also used, and a catalyst with a higher surface area was successfully developed. SCR performance and N_2 selectivity were used to characterize its De NO_x ability, and compared it with a catalyst made by the traditional method. A stability test was conducted with a specific concentration of H_2O and SO_2 for 20 h. The promotion effect on the dispersion of vanadate on this catalyst support was studied. N_2 adsorption-desorption was used to characterize the surface area and pore distributions of the support and catalyst. In addition, the microstructure and textural structure were observed by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The particle diameter was calculated by the Scherrer formula to compare with the results from TEM images. The form of the vanadium species existing on the catalyst support was studied using Raman spectroscopy. Temperature programmed desorption of NH_3 ($\text{NH}_3\text{-TPD}$) and temperature reduction of H_2 ($\text{H}_2\text{-TPR}$) were conducted to characterize NH_3 adsorption properties and redox properties of the catalysts, respectively.

2. Experimental

2.1. Catalysts preparation

Two anatase titania samples with different BET surface area were used. The small surface area titania support sample (90.0 m^2/g , denoted as L- TiO_2) was obtained commercially from Millennium Chemical Inc, and the large one was manufactured in a special method using metatitanic as the raw material by Sichuan Huatie Vanadium and Titanium Technology Co., Ltd. In this method, metatitanic was first mashed into a powder. Then deionized water was added to form a slurry. Ammonia was added gradually to adjust the pH of the solution. The final pH was 8. The slurry was then pressure filtered, dehydrated and desulfurized to form the final product. With a BET surface area of over 300 m^2/g (denoted as H- TiO_2).

$\text{V}_2\text{O}_5\text{-TiO}_2$ catalysts were prepared using these two supports by different methods. Equal amounts of ammonium metavanadate (Sinoreagent Chemical Reagent Co., Inc. 99.99%) were dissolved in oxalic acid solution in two beakers and then stirred for 15 min to form a solution. The total weight of the oxalic acid used in each solution was 0.4 g. 4.5 g H- TiO_2 and 4.5 g L- TiO_2 was then added into the beakers, respectively. The total V_2O_5 loading of the two catalysts was 5 wt%. L- TiO_2 was stirred for 3 h at a rate of 300 r/min. On the other hand, the solution of H- TiO_2 was stirred for 1 h, followed by sonication for 15 min and then stirred further for 2 more hours. Then the two solutions in the beakers were magnetic stirred and heated to evaporate the water. After 12 h of magnetic stirring (300 r/min) at 80 °C, the solid was obtained. The solid was scraped off with a spatula and ground into a powder. The powder was dried at 110 °C for 12 h in the oven. After that, the impregnated H- TiO_2 was placed into a muffle furnace and heated to 110 °C at a rate of 10 °C/min, then to 300 °C at a rate of 2 °C/min, and finally to 500 °C at a rate of 10 °C/min and calcined for 1.5 h. The reason for this step-by-step sintering method was to de-

crease the surface area loss in the calcination process. However, the impregnated L-TiO₂ was put into the muffle furnace and heated directly to 500 °C at a rate of 10 °C/min and calcined for 1.5 h. Both catalysts were cooled in the furnace. They were referred to as H-TiO₂-Cat and L-TiO₂-Cat.

2.2. SCR performance

Measurement of SCR performance was performed in a 6-mm diameter fixed bed reactor using 200 mg of the catalyst. The catalyst powder was first compressed at a loading of 20 MPa, and then was crushed to small particles. After they were mesh screened, particles from 40 to 60 mesh were used as the test sample. A mixed feed gas containing 0.05% NO, 0.05% NH₃, 5% O₂ and N₂ as the balance gas was used as flue gas. In the stability test, 0.05% NO, 0.05% NH₃, 0.02% SO₂, 5% O₂, 10% H₂O was used as the feed gas. N₂ was used as the balance gas. The gases used in this study were supplied by Beijing Zhao Ge Gas Technology Co., Ltd. The total flow rate of the feed gas was 200 ml/min. The total gas hourly space velocity (GHSV) was 60000 mL/(gcat·h). The outlet gas concentrations (NO, NH₃ and N₂O) were measured using an FTIR gas analyzer (GASMET FTIR DX-4000).

The NO conversion was expressed as $X(\text{NO})$, which was calculated using Eq. (1). The N₂ selectivity was expressed as $S(\text{N}_2)$, which was calculated using Eq. (2).

$$X(\text{NO}) (\%) = ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}})/[\text{NO}]_{\text{in}} \times 100 \quad (1)$$

$$S(\text{N}_2) (\%) = (1 - 2[\text{N}_2\text{O}]_{\text{out}})/([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}) \times 100 \quad (2)$$

The SCR reaction is first order in NO and zero order in NH₃ [23]. To evaluate the catalytic activity, the reaction rate constant k (cm³/(g·s)) was used to compare the two catalysts. The reaction rate constant was calculated using Eq. (3).

$$k = -V/W \times \ln(1 - X(\text{NO})) \quad (3)$$

In the above equation, V is the total gas flow rate (cm³/s), W is the mass of the catalyst (g), and $X(\text{NO})$ is NO conversion [24].

2.3. Catalyst characterization

The BET surface area and specific pore properties were measured by N₂ adsorption-desorption at −196 °C using an adsorption unit (Quantachrome, Autosorb-1). The samples were outgassed at 300 °C for 3 h before the test. The crystal and textural structure were determined by the XRD method. The patterns were recorded on a Rigaku (D/max 2200) X-ray diffractometer using Cu K α radiation ($\lambda = 0.15405$ nm, 40 mV and 200 mA) with a 2θ range of 10° to 80° and a step rate of

5°/min. Detailed surface images of the support samples were examined by high resolution TEM (HRTEM, JEOL 2011). The compositions of the supports and catalysts were determined using X-ray fluorescence spectrometry (XRF-1800, Shimadzu).

Raman spectroscopy was carried out using a Renishaw Raman microscope (RM2000). The laser wavelength was 514.5 nm. The spectra were recorded from 200 to 1200 cm^{−1} with a resolution of 1 cm^{−1}. The pattern was cut from 800 to 1200 cm^{−1} to show the specific difference.

H₂-TPR experiments were performed on a chemisorption analyzer (Micromeritics, ChemiSorb2720 TPx) under a 10 % H₂/Ar gas flow (50 mL/min) at a rate of 10°C/min up to 1000 °C. The samples were pretreated at 350 °C in He for 1 h before testing. The H₂ consumption of each catalyst was calculated by comparison with that of a CuO standard.

X-ray photoelectron spectroscopy (XPS) spectra of the catalysts were recorded on scanning X-ray microprobe (PHI Quantera, ULVAC-PHI, Inc.) using Al K α radiation. The binding energies of V 2p and O 1s were calibrated using the C 1s peak (BE = 284.8 eV). NH₃-TPD was carried out in a fixed bed quartz reactor with a diameter of 6 mm. 500 mg of the catalyst particles sample was used. The sample was purged under 0.05% NH₃ at room temperature after being pretreated in N₂ at 350 °C for 1 h. After isothermal removal of physically adsorbed NH₃, the temperature was raised to 600 °C at a rate of 10 °C/min. The concentration of NH₃ was monitored by a MultiGas TM 2030 FTIR.

3. Results and discussion

3.1. Structural properties

Table 1 summarizes the physical properties of the supports and catalysts. The BET surface area, total pore volume, total micro pore volume and average pore diameter were calculated from the nitrogen adsorption-desorption isotherm. The results showed that L-TiO₂ had a BET surface area of 93.2 m²/g. On the other hand, H-TiO₂ prepared in this study has a much larger BET surface area of 380.5 m²/g. This will facilitate the dispersion of metavanadate on the support surface in the impregnation process. To compare the difference in the dispersion of vanadium species, the surface area of support per one vanadate molecule was calculated based on monolayer dispersion. This hypothesis is widely used for the dispersion for V₂O₅ loading less than 7 wt% [25]. At a V₂O₅ loading of 5 wt% of the catalyst, the surface area per one vanadate molecular in the impregnation process was calculated and discussed. The results are also shown in Table 1. On H-TiO₂, there was one vanadate molecule

Table 1
Physicochemical properties of the supports and catalysts.

Sample	BET surface area (m ² /g)	Pore volume (ml/g)	Micropore volume (× 10 ^{−3} ml/g)	Average pore diameter (nm)	Surface area per one vanadia after impregnation (/nm ²)	Particle size calculated by Scherrer Formula (nm)
L-TiO ₂	93.2	0.43	40.3	18.3	1.7	15.7
H-TiO ₂	380.5	0.47	163.3	5.0	0.4	6.4
L-TiO ₂ -Cat	85.1	0.30	37.0	14.9	1.9	19.1
H-TiO ₂ -Cat	117.7	0.32	50.9	10.2	1.4	12.3

per 2.38 nm² surface area. For L-TiO₂, the number was 0.57 nm². The difference leads to the conclusion that the larger BET surface area of the support contributed to a better dispersion of vanadium species in the impregnation. The distance between vanadium species was further on the large surface area. The catalyst BET surface area was also characterized. The results indicated that after calcination, there was a surface area loss for both catalysts. This was due to the sintering of the titania grains [26]. However, the new support had better thermal stability. Although a loss of surface area was observed in both catalysts, H-TiO₂-Cat made from H-TiO₂ still had a surface area of 117.7 m²/g. It was 38% higher than the L-TiO₂-Cat. Similarly, the surface area per one vanadate was calculated for the catalysts. They were 1.4 /nm² for H-TiO₂-Cat and 1.9/nm² for L-TiO₂-Cat. This showed that the vanadate was still better dispersed after calcination. During the sintering of titania grains, vanadium species formed chemical bonds to the supports. The larger distance would reduce the possibility of forming crystalline V₂O₅ [27]. Information on the pore structure showed the microstructure was finer for H-TiO₂ and H-TiO₂-Cat. The value for H-TiO₂ was 0.47 ml/g, which was larger than L-TiO₂, 0.43 ml/g. After calcination, due to the collapse of some of the pore structures, the value became smaller. But the pore volume of H-TiO₂-Cat was still a little larger than L-TiO₂-Cat. Even though the total pore volume seemed similar for L-TiO₂-Cat and H-TiO₂-Cat, because the difference was within 5%, the difference in H-TiO₂-Cat and L-TiO₂-Cat micropore volume was quite obvious. The micropore volume was 40.3 × 10⁻³ ml/g for L-TiO₂ and 163.3 × 10⁻³ ml/g for H-TiO₂. The surface area loss was due to the reduction of micropore volume because after calcination the value decreased to 50.9 × 10⁻³ ml/g for H-TiO₂-Cat. For L-TiO₂-Cat, the value did not change much. Finally, the average pore diameter for the supports and the catalysts was calculated. The average pore diameter was 18.3 nm for L-TiO₂, 5.0 nm for H-TiO₂, 14.9 nm for L-TiO₂-Cat and 10.2 nm for H-TiO₂-Cat. The results are easily understood because of the difference in the micropore volume in the two supports. The pore structure results were consistent with the BET surface area result. The better structural properties with a larger surface area and more micropore volume provide a larger amount of physical adsorption sites for the adsorption of NH₃. Apart from this, later results would show that the degree of vanadium species polymerization would be different for these two catalysts.

3.2. Textural properties

The XRD patterns of the supports are shown in Fig. 1. Only the characteristic peaks of anatase phase TiO₂ (JCPDS 21-1272) were observed. The full width at half maximum (FWHM) of the (101) plane of the anatase phase (2θ = 25.3°) was obviously larger for H-TiO₂ than for L-TiO₂. This showed that compared to the commercial titania L-TiO₂, H-TiO₂ had lower crystallinity. This result was consistent with the structural properties. After calcination, the patterns of the catalysts were also recorded. There was a narrowing of the peaks in the patterns for L-TiO₂-Cat and H-TiO₂-Cat, which was due to the sintering of the particles. However, the FWHM of H-TiO₂-Cat was still

Fig. 1. XRD patterns of the catalysts and the supports made by wet impregnation method and calcined at 500 °C. (1) L-TiO₂; (2) H-TiO₂; (3) L-TiO₂-Cat; (4) H-TiO₂-Cat.

clearly wider than that of L-TiO₂-Cat. This revealed that although some of the amorphous titania support was transformed into anatase titania during the calcination process, the degree of crystallinity was much lower [28] for H-TiO₂-Cat than L-TiO₂-Cat. The XRD patterns demonstrated that the particles of H-TiO₂ and H-TiO₂-Cat were smaller than L-TiO₂ and L-TiO₂-Cat. The characteristic peaks corresponding to V₂O₅ did not appear in the patterns, which meant that no crystalline V₂O₅ was formed during the manufacturing of both catalysts. This was because the V₂O₅ loading did not exceed 7 wt%, the upper limit of monolayer dispersion. Later, for accurate characterization, the particle sizes of the supports and catalysts were calculated by Scherrer formula (Eq. (4))

$$D = K\lambda/(\beta\cos\theta) \quad (4)$$

where D is the average particle diameter, K is the Scherrer constant, λ is the wavelength of X-ray radiation (0.1541 nm), β is the FWHM of diffraction peaks of samples, and θ is diffraction angle. After including the constant and some unit adjustment, the equation is Eq. (5)

$$D = 0.89 \times 0.1506/(\beta - 0.09)/(180 \times \pi \times \cos\theta) \quad (5)$$

The average crystallite sizes of the supports and catalysts are listed in Table 1, which showed a big particle size difference between the different supports and catalysts. The average particle diameter calculated for L-TiO₂ and H-TiO₂ were 15.8 and 6.4 nm, respectively. After impregnation and calcination, the particle became bigger because of the merging and growing of the titania particle. The particle diameter was 19.2 nm for L-TiO₂-Cat and 12.4 nm for H-TiO₂-Cat, in accordance with the TEM results.

Fig. 2 shows the microstructures of the supports and catalysts. The morphologies of the two supports were totally different. H-TiO₂ was composed of smaller particles with an average diameter of 4 nm, while L-TiO₂ was composed of clusters of anatase particles with an average diameter of 16 nm. This was because in the manufacturing process of H-TiO₂, the calcination process was implemented conditionally so as to maintain the large surface area. After wet ultrasonic impregnation and calcination, the particles grew to an average diameter of 20 nm for

Fig. 2. TEM images of different samples. (a) L-TiO₂-Cat; (b) L-TiO₂; (c) H-TiO₂-Cat; (d) H-TiO₂ particles.

L-TiO₂-Cat. Each cluster became bigger in size and some of the individual particles were sintered to adhere to the cluster. On the other hand, the average diameter of H-TiO₂-Cat was 13 nm. Sintering was also found on this catalyst, but not as severe. This was due to the special step-by-step heat treatment. From the XRD and TEM results, it was concluded that H-TiO₂ had smaller particles than L-TiO₂. The better thermal stability of H-TiO₂ during the calcination would improve the dispersion of vanadia on the surface and increase the amount of active sites [29].

3.3. XRF results

The element analysis of the sample were performed by XRF. No substance with >0.5 wt% was detected. Table 2 showed the XRF results for the three major constituents; the trace substances were not shown. The TiO₂ content of L-TiO₂, H-TiO₂, L-TiO₂-Cat and H-TiO₂-Cat were 99.19, 99.17, 94.29, and 94.48 wt%. Vanadium loading of the catalysts L-TiO₂-Cat and H-TiO₂-Cat were 4.962 and 4.959 wt%, respectively. SO₄²⁻ was the major trace substance. This was due to the use of sulfur acid in the dissolution method to prepare TiO₂. However, the content of SO₄²⁻ did not exceed 0.700 wt%. It was seen that despite the preparation methods being different, no specific impurities were introduced into the supports or catalysts, and the contents of SO₄²⁻ were similar. Also, the results verified that the final contents of V₂O₅ for both catalysts were the same after

Table 2

Content analysis of supports and catalysts by XRF.

Sample	Content (wt%)		
	TiO ₂	V ₂ O ₅	SO ₄ ²⁻
L-TiO ₂	99.19	0	0.651
H-TiO ₂	99.17	0	0.4
L-TiO ₂ -Cat	94.29	4.962	0.442
H-TiO ₂ -Cat	94.48	4.959	0.383

calcination, which meant that the impregnation method successfully loaded the same amount of vanadium species onto the supports. So, the difference in SCR performance and other properties can only be related to the structure of the supports and catalysts or the different forms of vanadium species on the catalysts.

3.4. Raman spectra

In order to discuss the vanadium surface species on the catalysts in detail, the Raman spectra of L-TiO₂-Cat and H-TiO₂-Cat were analyzed. The results are shown in Fig. 3. In the detection range of 200 to 1200 cm⁻¹, three major peaks at 391, 516 and 638 cm⁻¹ were detected for both catalysts. Those peaks are the representative Raman frequencies for anatase TiO₂ [30]. The peaks for bulk V₂O₅ (993 cm⁻¹) [31] were not observed in the whole range. This was in line with the XRD results that no crystalline V₂O₅ was formed during the calcination. To compare the difference in the Raman spectra and study the existing form of vanadium species on the supports, the pattern was shown from 800 to 1200 cm⁻¹. The peaks in the range of 900 to 950 cm⁻¹ and 1000 to 1050 cm⁻¹ represented the terminal V=O bond of isolated vanadyl and polymeric vanadate species, respectively [32]. Shifts of the peaks were due to the electron density change, which means a change of chemical bond strength [33]. As shown in Fig. 3, the peaks of H-TiO₂-Cat appeared at 920 and 1024 cm⁻¹. There was an upwards shift of the peaks for L-TiO₂-Cat. The peaks of L-TiO₂-Cat appeared at 930 and 1026 cm⁻¹. The shifts in the peak position demonstrated a difference in the forms of the vanadium species. During the impregnation, aqueous solution of NH₄VO₃ were anchored to the Ti-OH species on the support. After drying and calcination, V-OH and Ti-OH formed V-O-Ti by dehydration

Fig. 3. Raman spectra of H-TiO₂-Cat and L-TiO₂-Cat.

condensation [31]. At the same time, linkages of V-O-V can form between the V-OHs by dehydration condensation or the dehydration condensation of V=O and V-OH. The forming of V-O-V would decrease the amount of V-O-Ti and V=O, and thus reduce the activity of the vanadium species on the surface [34]. The shifts in the frequency of the Raman peak at 920 to 930 cm^{-1} demonstrated the forming of V-O-V linkages from isolated vanadyl centers [31]. It can be concluded that because of the larger surface area of the support, the vanadium species was better dispersed on the surface in the impregnation process. Other than that the ultrasonic process promoted the dispersion of isolated vanadyl centers so that in the calcination process, there were less V-O-V formed between V-OHs or V=O and V-OHs. The larger surface area of the support and the smaller surface area loss during the step-by-step calcination method helped to retain the amount of isolated vanadyl centers on the surface, which finally resulted in more V-O-Ti. In conclusion, H-TiO₂-Cat has better dispersion of vanadium species because less V-O-V linkages were formed, and so the degree of polymerization was higher for L-TiO₂-Cat than H-TiO₂-Cat. As a result, with better dispersed vanadium species and more V-O-Ti, V=O would provide more active redox sites on the surface of H-TiO₂-Cat than of L-TiO₂-Cat. According to the catalytic cycle of SCR on V₂O₅/TiO₂ proposed by Topsoe et. al. [12], this would increase the SCR performance at low temperatures.

3.5. H₂-TPR and XPS results

As the redox ability is important in one of the catalytic cycle of the vanadium species, the H₂-TPR profiles of the two catalysts are shown in Fig. 4 in order to elucidate the change in the redox property as a function of temperature. The position of the reduction peak and the total amount of H₂ consumed were used to compare the redox ability of L-TiO₂-Cat and H-TiO₂-Cat. A previous study concluded that the peak near 450 °C was due to the reduction of surface V⁵⁺ species [35]. It was shown that the reduction peak position of H-TiO₂-Cat was 452.81 °C, and that for L-TiO₂-Cat was 465.40 °C. This meant that H-TiO₂-Cat had better redox ability than L-TiO₂-Cat. The total amount of H₂ used was calculated by integrating the peak area of the two patterns. The integrated area of the TCD signal from H-TiO₂-Cat was 5.0, and the peak area of L-TiO₂-Cat was 4.2. H-TiO₂-Cat has a larger reduction peak area than L-TiO₂-Cat. The larger peak area of H-TiO₂-Cat indicated that the amount of active redox sites was larger than that of L-TiO₂-Cat. This can be attributed to the difference in the vanadium species of the catalysts. According to the Raman results, there were more V=O species on H-TiO₂-Cat than L-TiO₂-Cat. Thus the reduction peak position due to the reduction of surface V⁵⁺ species would be lower for H-TiO₂-Cat. In addition, the larger amount of V-O-V

Fig. 4. H₂-TPR profiles of H-TiO₂-Cat and L-TiO₂-Cat.

linkages formed on L-TiO₂-Cat would decrease the amount of H₂ used by the catalysts. The redox ability and the vanadium species were mutually confirmed. Besides, the structure of the supports also contributed to the difference in the amount of H₂ used. From the structural properties discussed in section 3.1, H-TiO₂-Cat has a larger surface area and micropore volume. This would also be beneficial to the reduction by H₂ because the total contact area of the surface and H₂ was larger.

XPS results are shown in Table 3. For H-TiO₂-Cat the ratio of O₂/(O₁+O₂) was higher, and the concentration of V⁴⁺ was lower. These results were in accordance with the H₂-TPR results. The higher O₂/(O₁+O₂) showed that there were more active oxygen atoms, thus the reduction peak for H-TiO₂-Cat appeared at a lower temperature. The lower V⁴⁺ concentration would lead to more H₂ consumption in H₂-TPR, so the reduction peak area was larger for H-TiO₂-Cat. The results of H₂-TPR supported those of XPS, which made the conclusions more evident.

3.6. NH₃-TPD results

The amount of acid sites and their strength were measured using NH₃-TPD. Fig. 5 showed the NH₃-TPD results of H-TiO₂-Cat and L-TiO₂-Cat. There were two peaks in the temperature range from 100 to 600 °C. For both catalysts, the peaks appeared at 310 and 540 °C. The similar peak position illustrated that the strength of the NH₃ adsorption on the catalysts were the same. This was due to that the species of adsorption were identical. However, the amount of NH₃ adsorbed on the catalysts was different for the two catalysts. At both peaks, the peaks for H-TiO₂-Cat were larger than L-TiO₂-Cat. The integration of the total area of the pattern showed that the amount of NH₃ adsorbed was larger for H-TiO₂. As the desorption peak temperature was detected above 200 °C, the adsorption mode was attributed to the chemisorption of NH₃. Former studies attributed the peak at lower temperature around 300 °C to

Table 3
XPS results of the catalysts.

Sample	Position (eV)				Area				Area ratio (%)	
	O ₁	O ₂	V ⁵⁺	V ⁴⁺	O ₁	O ₂	V ⁵⁺	V ⁴⁺	O ₂ /(O ₁ +O ₂)	V ⁴⁺ /(V ⁵⁺ +V ⁴⁺)
H-TiO ₂ -Cat	530.1	531.6	517.1	516.2	77670	11314	9835	1923	12.7	16.4
L-TiO ₂ -Cat	530.2	531.1	517.4	516.5	119398	6781	9488	5156	5.37	35.2

Fig. 5. NH_3 -TPD profiles of H-TiO₂-Cat and L-TiO₂-Cat.

Brønsted acid sites and the peak at higher temperature to Lewis acid sites [36]. From this prospect, this result was partly due to that the vanadium species were better dispersed on the higher surface area. The amount of V-OH was larger for H-TiO₂-Cat than L-TiO₂-Cat, thus providing more Brønsted acid sites [37] on the catalyst. On the other hand, considering the Lewis acid sites, as the V-O-V formed on the surface provided little acidity, the polymerization of vanadium species V-O-V covered the catalyst surface and affected the amount of NH_3 adsorbed on TiO₂. The NH_3 adsorbed would be less for the catalyst with the smaller amount of V=O. As a result, the amount of NH_3 adsorbed on the V-OH species and titania at both temperatures for H-TiO₂-Cat was larger than that for L-TiO₂-Cat. In addition, the amount of Ti-OH also affected the amount of Lewis acid sites the catalysts can provide. From the microstructure results shown in Table 2, there was more micropore volume for H-TiO₂-Cat. The larger surface area and increased micropore volume increased the Ti-OH exposed on the surface and thus enhanced the amount of adsorbed NH_3 on the catalyst. In conclusion, the better dispersed vanadium species on the surface of the catalysts together with the microstructure of the support explained the acidity increase for H-TiO₂-Cat.

3.7. SCR performance and stability

Finally, the SCR performance and catalyst stability with the existence of SO₂ and H₂O were tested. The NO conversion by H-TiO₂-Cat and L-TiO₂-Cat for NH_3 -SCR at temperatures from 150 to 500 °C (the Tammann temperature of titania) are shown in Fig. 6. The result showed that the temperature range of the catalyst was wider for H-TiO₂-Cat compared to L-TiO₂-Cat. There was no NO conversion at 100 °C for both catalysts. As the temperature went higher, the NO performance of H-TiO₂-Cat increased faster. At 200 °C, the NO conversion of H-TiO₂-Cat was 84%, while the conversion of L-TiO₂-Cat was 44%. Both catalysts demonstrated 100% NO conversion in the range of 250 to 400 °C. At 450 °C, NO conversion over H-TiO₂-Cat was 85%, while L-TiO₂-Cat's NO conversion was 74%.

Furthermore, the reaction rate constant k of the catalysts was calculated at 200 and 450 °C. The results are reported in Table 4. The structure-activity relationship was discussed in

Fig. 6. NO conversion of the catalysts. Reaction conditions: 200 mg catalysts, $[\text{NO}] = [\text{NH}_3] = 0.05\%$, $[\text{O}_2] = 5\%$, GHSV = 60000 mL/(gcat·h).

detail. H-TiO₂-Cat displayed a higher reaction rate constant over the entire temperature range. The reaction rate constant was normalized by the surface area of the catalyst to better understand the promotion effect of the surface area. At 200 °C, the k of H-TiO₂-Cat after normalization was more than twice as large as the smaller one. As was shown in the NH_3 -TPD profile, no desorption peak was observed at 200 °C, meaning that NH_3 adsorption was strong in this temperature range. So the controlling factor is the dispersion of the vanadium species. According to the Raman and H₂-TPR results, the larger amount of V=O and V-O-Ti species on the surface of the catalysts promoted the redox ability at lower temperature, and the adsorbed NH_3 was thus easier activated to react with NO. At 450 °C, the k was still larger for H-TiO₂-Cat, but the difference became smaller. This was mainly due to that the acidity was enhanced for H-TiO₂-Cat. At higher temperatures, NH_3 adsorbed on the surface reached activation [38]. The amount of NH_3 adsorbed was the controlling factor in the NO conversion. According to the NH_3 -TPD results, the better dispersion of vanadium species and the microstructure of the catalysts provided more Brønsted acid sites and Lewis acid sites, so these increased the total amount of the NH_3 adsorbed. As a result, the NO conversion at higher temperatures was promoted.

N₂ selectivity from 150 to 500 °C is shown in Fig. 7. H-TiO₂-Cat has better N₂ selectivity when the temperature was above 400 °C. At 450 °C, the N₂ selectivity for H-TiO₂-Cat was 81%, while it was below 60% for L-TiO₂-Cat. When the temperature reached 500 °C, the selectivity of L-TiO₂-Cat was below 10%. However, for H-TiO₂-Cat, it was still above 50%. This was because at high temperature, the polymerization of vanadium species would lead to the oxidation of NH_3 to N₂O [39], thus this affected the N₂ selectivity calculated by Eq.(2).

The effects of the presence of SO₂ and H₂O in the flue gas on the SCR performance of the catalysts were studied. The results

Table 4

Reaction rate constant k and normalized k by the surface area of the catalysts at 200 and 450 °C.

Catalyst	k (cm ³ /(g·s))		$10^2 \times k/S_{\text{BET}}$ (cm ³ ·m ² /s)	
	200 °C	450 °C	200 °C	450 °C
L-TiO ₂ -Cat	10.0	21.8	11.7	25.7
H-TiO ₂ -Cat	29.5	34.0	25.1	28.9

Fig. 7. N₂ selectivity of the catalysts. Reaction conditions: 200 mg catalyst, [NO] = [NH₃] = 0.05%, [O₂] = 5%, GHSV = 60000 mL/(gcat·h).

are shown in Fig. 8. The NO conversion was tested at 250 °C for both catalysts to demonstrate stability. After addition of SO₂ and H₂O to the flue gas, the NO conversion of L-TiO₂-Cat decreased from 91% to 74%. The NO conversion of H-TiO₂-Cat was suppressed from 100% to 89%. The influence of SO₂ and H₂O on L-TiO₂-Cat was larger than on H-TiO₂-Cat. The existence of H₂O and SO₂ affect the NO conversion due to competitive adsorption with NH₃ which formed sulfate on the catalyst surface [40]. After 20 h, the addition of SO₂ and H₂O was switched off. The NO conversion for both catalysts recovered to the original level. From the results, H-TiO₂-Cat showed better H₂O and SO₂ tolerance in the whole period, which meant that H-TiO₂-Cat has better practical application prospect.

4. Conclusions

Two V₂O₅ catalysts supported on TiO₂ with different surface area were prepared and compared. H-TiO₂-Cat was made from a new large surface area support H-TiO₂. A special ultrasonic impregnation method and heat treatment process were used to maintain the surface area advantage, and thus promote the dispersion of vanadium species on the support. For comparison, a commercial anatase L-TiO₂ was used as the support and L-TiO₂-Cat was prepared using a traditional method. H-TiO₂-Cat

was demonstrated to have better SCR performance over the whole temperature range and better stability at low temperature. The NO conversion of H-TiO₂-Cat at 200 °C was 84%, which was 40% higher than L-TiO₂-Cat. At 450 °C, the conversion by H-TiO₂-Cat and L-TiO₂-Cat were 85% and 74%, respectively. XRD, N₂ desorption and TEM results illustrated that the new support had better thermal stability, a larger surface area and smaller particle size. After calcination, the BET surface area of H-TiO₂-Cat was 117.7 m²/g, which was 38% larger than L-TiO₂-Cat. The particle size for H-TiO₂-Cat and L-TiO₂-Cat were 12 and 19 nm, respectively. The dispersion of vanadium species was also better on H-TiO₂-Cat, and the surface area per vanadium center was 12.4 nm for L-TiO₂-Cat and 19.2 nm for H-TiO₂-Cat. The Raman spectra showed that for the low surface area support, vanadium species tended to polymerize during calcination. More V-O-V linkages were formed due to the poorer dispersion which thus reduced the amount of V=O species and V-O-Ti species. H₂-TPR and NH₃-TPD results showed the redox ability and total acidity were better for H-TiO₂-Cat, which confirmed the conclusion from the Raman spectra. All the changes in the properties of the catalysts were correlated to the reaction rate constant *k* at 200 and 450 °C. The V₂O₅-TiO₂ catalyst that used the new support and the special preparation method was better than the traditional V₂O₅-TiO₂ for the control of NO_x emission from stationary sources.

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Fig. 8. Stability test of the catalysts. Reaction conditions: 200 mg catalyst, [NO] = [NH₃] = 0.05%, [SO₂] = 0.02%, [O₂] = 5%, [H₂O] = 10%, GHSV = 60000 mL/(gcat·h).

Graphical Abstract

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NH₃ selective catalytic reduction of NO: A large surface TiO₂ support and its promotion of V₂O₅ dispersion on the prepared catalyst

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A better SCR catalyst was developed by specific method using a new large surface area titania support. The dispersion of vanadium species was promoted. The better dispersed vanadium species and the larger surface area improved the redox ability and acid sites of the catalyst. As a result, the newly developed catalyst showed better SCR performance and stability.

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一种新型高比表面积 TiO₂ 载体在 NH₃ 选择性催化还原反应中对 V₂O₅ 分散性的促进作用

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摘要: 燃煤电厂及工业窑炉的氮氧化物减排是改善空气质量的关键。现阶段选择性催化还原氮氧化物是最有效的技术途径,核心是采用以 TiO_2 为载体的钒基催化剂净化烟气。催化剂的活性是决定烟气净化效率的重要因素。近些年的研究主要集中在活性组分的替换上,但是由于其成本高昂,抗水抗硫性能较差,在实际中使用的效果不佳。本文从载体入手,制备了新型 TiO_2 载体,并采用特殊制备手段研发了新型高比表面积钒钛体系催化剂。通过对载体和催化剂的物化表征,研究了高比表面积 TiO_2 载体对于活性组分钒在表面分散的促进作用,及分散性的提高对氧化性和酸性的影响。所制新型 TiO_2 载体比表面积达到 $380.5 \text{ m}^2/\text{g}$,较商业化 TiO_2 载体提高了 5 倍。以此为载体,采用超声浸渍法和分段烧结的热处理方式,制备了钒负载量为 5 wt% 的新型钒钛催化剂。结果发现,高比表面载体显著提高了钒基催化剂比表面积为 $117.7 \text{ m}^2/\text{g}$,比传统钒钛催化剂提高了 38%。计算结果表明,这种方式还提高了钒物种在载体表面的分散性。XRF 结果表明,超声浸渍法和普通浸渍法均可将 5 wt% 的钒成功地负载到了载体上。通过模拟实际烟气成分对催化剂的脱硝效果进行了测试,结果表明,所制催化剂具备更宽的温度窗口及更好的 N_2 选择性, NO_x 转化率在 200–450 °C 时能保持在 80% 以上,比传统方法制备的催化剂温度窗口宽 100 °C。且 N_2 选择性在 400 °C 以上时也明显更高。对两种催化剂样品的抗水抗硫能力进行了考察,发现在烟气中存在 H_2O 或 SO_2 时,高比表面积催化剂样品相较传统方法制备的催化剂具有更高的活性。Raman 结果发现,在传统商业载体上钒物种由于分散不充分,更易在烧结过程中形成 V-O-V 物种,从而降低了催化剂的氧化还原性。而新型催化剂表面的 V-O-Ti 及 V=O 物种数量更多,这些物种活性更高,从而使得催化剂在低温下具有更高的 NO_x 转化率。采用 NH_3 -TPD, H_2 -TPR 和 XPS 技术研究了活性提高与催化剂结构的关系。结果发现,高比表面积载体通过对钒物种的分散作用,在载体表面由于二氧化钛载体的孔结构和钒物种的高活性,也使得该催化剂具有较高的酸量和氧化还原性。本文为制备新型烟气脱硝催化剂提供了理论依据,该技术方法具有较高的应用价值。

关键词: 钒钛体系催化剂; 脱硝; 二氧化钛; 比表面积; 分散性

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