In situ supported VO\textsubscript{x} on carbon nanotubes for the low-temperature selective catalytic reduction of NO with NH\textsubscript{3}

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Abstract. The vanadium oxide/carbon nanotube (VO\textsubscript{x}/CNTs) composite catalyst was prepared by in-situ growth of VO\textsubscript{x} nanoparticles on CNTs with a cetylpyridinium chloride (CPC) assisted reflux route. The in-situ prepared catalysts exhibit better NH\textsubscript{3}-SCR activity in a broader temperature window at low temperature than those prepared by impregnation or a mechanically mixed method. The structural characterizations show that vanadium oxide nanoparticles have a good dispersion on the CNTs surface, with much lower valence vanadium species and chemisorbed oxygen species. The physics-chemistry properties indicate that there is a strong interaction between the VO\textsubscript{x} and CNTs, and the catalysts present a larger amount of stronger acid. The abovementioned reasons have eventually led to the enhancement of NH\textsubscript{3}-SCR activity.

1. Introduction

NO\textsubscript{x} emitted from stationary source plants can cause problems, such as photochemical smog, acid rain, and ozone hole, which harm the environment and human health [1]. Due to high denitration efficiency, and good selectivity, selective catalytic reduction (SCR) has become the mainstream technology for removing NO\textsubscript{x} nowadays [2]. As a typical commercial NH\textsubscript{3}-SCR catalyst, V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}(MoO\textsubscript{3})/TiO\textsubscript{2} catalysts are widely used due to their high NO\textsubscript{x} conversion and SO\textsubscript{2} tolerance. However, there are still some inevitable disadvantages, such as the narrow operation temperature window (300-400°C) and especially the poor low-temperature catalytic activity [3]. Therefore, much focus has been placed on low temperature SCR Catalyst.

Carbonous materials have rich physical and chemical properties, which lend to their high porosity and good surface chemistry. In line with this, carbon-based materials are suitable for use in most catalytic process applications [4]. Studies show that the introduction of carbon materials with large specific surface area (such as activated carbon, graphene and carbon nanotubes) can improve the NO conversion of the catalyst at low temperature [5-10]. Nowadays, carbon nanotubes (CNTs) are recognized as an attractive catalyst support for SCR catalysts due to their electronic properties and unique nanostructure [11,12]. CNT-supported metal oxide catalysts are well-known in the adsorption field and present interesting properties for the denitrification of NO\textsubscript{x} species. Wang et al. [13] reported high NO conversion (≈90%) at a relatively low reaction temperature of 200 to 300°C on the Mn-Ce/CNT catalyst prepared using the incipient-wetness method. Bai et al. [14] investigated the activity of V\textsubscript{2}O\textsubscript{5}/CNT catalysts at a low SCR reaction temperature. They found that V\textsubscript{2}O\textsubscript{5}/CNT catalysts had a higher catalytic activity compared to that of V\textsubscript{2}O\textsubscript{5} particles supported on AC (V\textsubscript{2}O\textsubscript{5}/AC) at 200°C.
reaction temperature. In addition, they also found that the conversion of NO\textsubscript{2} momentously increased and became almost linear at a high level of SCR reaction by V\textsubscript{2}O\textsubscript{5}/CNT (0.1-1 wt %) catalysts in the presence of SO\textsubscript{2}. Therefore, due to the unique promoting effect of SO\textsubscript{2}, the V\textsubscript{2}O\textsubscript{5}/CNT catalyst is justified as one of the most promising catalytic materials for SCR at low temperature.

As the core of the NH\textsubscript{3}-SCR technology, the catalyst needs to work under high temperature, high air flow rate, and high dust environment. Abovementioned catalysts, prepared by the traditional impregnation method or mechanical mixing method, are prone to inactivation by aggregations or fall away from the carrier during using, due to the weaker bonding strength between active component and the carrier during using, which hinders its practical application [15].

Herein, in order to enhance the bonding strength between the active component and the supports, we use a facile method for the fabrication of VO\textsubscript{2} nanoparticles in-suit grown on the surface of CNTs with cetylpyridinium chloride (CPC) assisted reflux method. In the fabrication process, CPC is a kind of cationic surfactant, bonded with CNTs by π-π conjugate. As a result, the surface charges of CNTs were shifted from negative to positive after mixing with CPC, which served as centres for the anchoring and dispersion of metavanadate anions. Subsequently, the in-situ growth of uniform VO\textsubscript{2} nanoparticles on CNTs was achieved via a heat treatment process. The vanadium oxide/carbon nanotube (VO\textsubscript{2}/CNTs) composite catalyst was investigated for its catalytic activities in low temperature SCR reactions. The effect of the weight ratio of CNTs and CPC was also studied.

2. Experimental

2.1. Catalyst preparation

The employed multiwall CNTs were purchased from Qinhuangdao Tai Chi Ring nano products Co. Ltd (China). Cetylpyridinium chloride was purchased from Aladdin. All other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All the reagents had an analytical grade and were used without further purification.

The employed multiwall CNTs were refluxed and oxidized with concentrated HNO\textsubscript{3} (65-68 wt%) under stirring for 6 h to remove carbon nanoparticles and metal species and introduce oxygenated surface groups. The treated CNTs were then washed fully with deionized water and ethanol, and dried at 80°C for 12 h. The purified CNTs was denoted as P-CNTs.

In-situ deposition of VO\textsubscript{2} nanoparticles on the surface of CNTs was prepared by CPC reflux route with different weight rations 1:1, 2:1, and 3:1 of CPC: CNTs, which were labelled as V\textsubscript{2}O\textsubscript{5}/CNTs-1, V\textsubscript{2}O\textsubscript{5}/CNTs-2, and V\textsubscript{2}O\textsubscript{5}/CNTs-3, respectively. Typically, 0.36 g purified CNTs were dispersed with CPC in 80 mL deionized water upon ultrasonic vibration for 1 h to get a stable suspension. Subsequently, 0.27 g ammonium metavanadate (NH\textsubscript{4}VO\textsubscript{3}) was added to 50 mL deionized water and stirred with heating at 80°C for 30 min to form a clear transparent solution. Then the two solutions were mixed and stirred for 30 min to get a uniform solution. The final mixture was refluxed under continuous stirring at 80°C for 12 h. After that, the suspension was filtered and washed fully with distilled water and ethanol, followed by desiccation at 80°C for 12 h. Finally, the sample was calcined at 400°C for 5 h in N\textsubscript{2} atmosphere, and then calcined at 300°C for 30 min in air to make vanadium oxide crystallize.

For comparison, the catalysts were also prepared by impregnation (denoted as V\textsubscript{2}O\textsubscript{5}/CNTs-1) and mechanically mixed method (denoted as V\textsubscript{2}O\textsubscript{5}/CNTs-M). V\textsubscript{2}O\textsubscript{5}/CNTs-1 catalyst was prepared by dissolving ammonium metavanadate into deionized water and then stirring for 12 h at 80°C. Subsequently, the sample was dried at 80°C for 12 h and calcined at 400°C for 5 h in N\textsubscript{2} atmosphere followed by calcination at 300°C for 30 min in air. The V\textsubscript{2}O\textsubscript{5}/CNTs-M catalyst was also prepared by fully grinding the mixture of the purified CNTs and ammonium metavanadate, and then calcined at 400°C for 5 h in N\textsubscript{2} atmosphere followed by calcination at 300°C for 30 min in air.

2.2. Characterization methods

X-ray diffraction (XRD) patterns of the samples were obtained using an X-ray diffractometer (Pert-Pro, PANalytical, Netherlands) with Cu K\textsubscript{α} radiation. The microstructure and morphology of the catalysts
were observed using a field emission transmission microscope (JEM-2100F, Japan Electronics Co. Ltd). Specific surface areas and pore volumes were measured on a fully automated Quantachrome Nova 2200e surface area analyser using nitrogen adsorption at 77 K. The Brunauer-Emmett-Teller (BET) equation was used for the determination of the specific pore volume. The samples were characterized by XRD using a Rigaku D/MAX2500V system with Cu Kα radiation. The operating voltage was 40 kV, the operating current was 40 mA, and the scanning speed was 5° min⁻¹. X-ray Photoelectron Spectroscopy measurements (XPS, ESCALAB 250Xi, Thermo Fisher, USA) were performed using Al Kα radiation as the excitation source. The emission angle between the photoelectron beam and the sample surface was 45°, and the calibration of the binding energy for the electron spectrometer was made using the maximum adventitious C 1s signal at 284.6 eV with the solution of the full width at half maximum (FWHM) being 0.8 eV.

NH₃ temperature programmed desorption (NH₃-TPD) experiments were carried out on a PX200 apparatus (Tianjin Pengxiang Technology Co. Ltd.) with a thermal conductivity detector (TCD). Before NH₃ adsorption, the samples (0.15 g) were pre-treated under He flow (50 mL min⁻¹) at 400°C (ramp 10°C min⁻¹) for 60 min. NH₃ adsorption was done at 100°C using 10 vol% NH₃ in He with flow rate of 50 mL min⁻¹ for 60 min and then flushed with He during 1 h to remove physisorbed NH₃. Finally, the ammonia was desorbed in helium flow of 30 mL min⁻¹ from 100 to 600°C using a heating rate of 10°C min⁻¹. H₂ temperature programmed reduction (H₂-TPR) was carried out on the same PX200 apparatus (Tianjin Pengxiang Technology Co. Ltd.) with a TCD. Prior to H₂-TPR measurements, the catalyst (0.1 g) was pre-treated under Ar flow of 50 mL min⁻¹ rate at 400°C (ramp 10°C min⁻¹) for 60 min. After being cooled down to 50°C in the same atmosphere, the sample was exposed to a flow containing 10 vol% H₂ in Ar (50 mL min⁻¹) for 1 h, and then heated between 50 and 800°C with a heating rate of 10°C min⁻¹.

2.3. Catalyst performance tests

The SCR activity tests were conducted in a vertical fixed-bed quartz reactor with an internal diameter of 25 mm and heated by a tube-type electric furnace. The simulated flue gas consisted of 500 ppm NO, 500 ppm NH₃, 3 vol% O₂, and the balance gas was mixed with Ar. A total flow rate of 1000 mL/min was maintained in all the tests. The amount of catalyst was 2 g, the reaction space velocity was 30,000 h⁻¹, and the reaction temperature ranged from 100 to 300°C. The gas concentrations of NO were measured online by using a Laoying 3026 infrared flue gas comprehensive analyser. NO conversion was calculated according to the following expression:

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

where the [NO]_{in} and [NO]_{out} indicated the inlet and outlet concentration.

3. Results and discussion

3.1. Catalytic activity

Figure 1 shows the SCR activities of NO with NH₃ over all catalysts. It is clearly seen that NO conversion over all the catalysts increased with temperature rising from 100 to 300°C except P-CNTs. For P-CNTs, NO conversion slightly increases less than 150°C. Once exceeding the temperature, the NO conversion starts to decline gradually. As for V₂O₅/CNTs-I and V₂O₅/CNTs-M, the maximum efficiencies of denitration are 85% and 72% at 300°C, respectively. However, their temperature window is relatively narrow. Compared with these catalysts, those prepared by in-situ growth show better NO conversion and more wide operating temperature window. The NOₓ efficiencies of in-situ growth catalysts are more than 70%, when the operation temperature reaches 175°C. The results show that the operation temperature of catalysts prepared by in-situ growth has obviously dropped. Meanwhile, the NOₓ efficiencies slightly increase first and then decrease with increasing the weight ratio of CPC and CNTs. When the weight ratio of CPC and CNTs is 2:1, the V₂O₅/CNTs-2 catalyst exhibits the best low
Figure 1. NH$_3$-SCR performance of the catalysts. Reaction conditions: [NO] = [NH$_3$] = 500 ppm, [O$_2$] = 3 vol%, N$_2$ balance, and GHSV = 30000 h$^{-1}$.

3.2. Characteristics of the catalysts

Figure 2 shows the XRD patterns of all catalysts. It can be observed that the catalysts prepared by in-situ deposition exhibited similar XRD patterns. The broad diffraction peaks at 26.2° and 44.3° are attributable to graphite of CNTs. Besides that, there is no obvious diffraction signal related to the vanadium species, which could be attributed to the highly dispersed or amorphous vanadium oxide on the surface of CNTs. In contrast, for the V$_2$O$_5$/CNTs-I and V$_2$O$_5$/CNTs-M catalysts, some sharp diffraction peaks around 15.4°, 20.3°, 21.7°, 25.3°, and 31° are observed, ascribed to the characteristics diffraction peaks of V$_2$O$_5$ (PDF#01-085-0601). This indicates that the vanadium species of the two catalysts may be agglomerated over the surface of CNTs.
Figure 3 shows the TEM images of the catalysts prepared by different methods. \( \text{V}_2\text{O}_5/\text{CNTs}-2 \) catalyst shows the best dispersion compared to \( \text{V}_2\text{O}_5/\text{CNTs}-1 \) and \( \text{V}_2\text{O}_5/\text{CNTs}-3 \) samples. But no obvious nanoparticles anchored on the surface of CNTs can be observed. This is due to the high dispersion of VO\(_x\) on the CNTs surface. Besides that, the block \( \text{V}_2\text{O}_5 \) was found in Figures 3d and 3e, which indicates that the active components in samples \( \text{V}_2\text{O}_5/\text{CNTs}-1 \) and \( \text{V}_2\text{O}_5/\text{CNTs}-M \) are agglomerated severely. In addition, the agglomeration of \( \text{V}_2\text{O}_5/\text{CNTs}-M \) catalyst is the most serious. Good dispersion could provide more active sites, and thus improve the \( \text{NH}_3-\text{SCR} \) activities of the catalysts. EDS mapping of \( \text{V}_2\text{O}_5/\text{CNTs}-2 \) catalyst was used to further confirm the dispersion state of VO\(_x\) supported on the surface of CNTs. As shown in Figure 4, the atomic ordinal contrast of the high angle annular dark field image of the sample indicates that VO\(_x\) is successfully loaded on the surface of the CNTs. EDS-mapping indicates that V and O elements are evenly distributed on the surface of CNTs, which proves that vanadium oxide is highly dispersed on the surface of the CNTs.

The \( \text{N}_2 \) adsorption-desorption isotherms and pore size distributions of the catalysts are exhibited in Figure 5. As shown in Figure 5a, all the samples show the typical IV isotherms with H3 hysteresis loops [16]. Figure 5b shows the pore size distributions of six catalysts. It reveals that all catalysts have similar pore structure. As shown in Table 1, P-CNTs possess the largest surface area. After the vanadium oxide is supported, the specific surface area of the composite catalysts is decreased, because vanadium oxide
blocks a part of the pores of the CNTs. In addition, the catalysts prepared by in-situ growth possess a smaller surface area than those prepared by impregnation and mechanically mixed method. This indicates that in catalyst V₂O₅/CNTs-2, VOₓ more closely contacts with CNTs, thereby blocking more pores. In addition, compared with V₂O₅/CNTs-1 and V₂O₅/CNTs-3, V₂O₅/CNTs-2 catalyst has the largest specific surface area due to the best dispersion, which is beneficial to the SCR reaction.

The XPS measurements were carried out to study the valence state of elements on the surface of catalysts. The obtained XPS spectra of V2p and O1s are shown in Figure 6. As shown in Figure 6a, the V2p peaks of V₂O₅/CNTs-2 could be deconvoluted to three peaks: the peaks at 517.3, 515.8, and 514.2 eV represented V⁵⁺, V⁴⁺, and V³⁺, respectively. However, the V2p peaks of V₂O₅/CNTs-1 and V₂O₅/CNTs-M could only be deconvoluted to two peaks, which were attributed to V⁵⁺ (517.3 eV for V₂O₅/CNTs-I, 517.2 eV for V₂O₅/CNTs-M) and V⁴⁺ (515.9 eV for V₂O₅/CNTs-I, 516.0 eV for V₂O₅/CNTs-M). As shown in Table 2, the V⁴⁺+/V⁵⁺ (n = 3, 4, and 5) of the three catalysts were 44.9, 25.2, and 20.1%, respectively. According to the literature, vanadium oxides with low valence states can easily adsorb oxygen to generate active oxygen species during SCR reaction, which is important to the low temperature SCR activity [17–20].

Figure 6b shows O 1s XPS spectra of the catalysts prepared by different methods. The peak at 530 eV was assigned to the lattice oxygen species (O β) and that at 532 eV was assigned to the chemisorbed oxygen species (O α). The O α/(O α+O β) ratios of three catalysts were calculated and are shown in Table 2. It is interesting that the O α/(O α+O β) ratio of V₂O₅/CNTs-2 (40.9%) is higher than V₂O₅/CNTs-1 (35.1%) and V₂O₅/CNTs-M (23.1%). It is reported that the chemisorbed oxygen species are more active than the lattice ones, which is attributed to a higher mobility of chemisorbed oxygen. In addition, the chemisorbed oxygen species could easily oxide NO to NO₂, which could accelerate the NH₃-SCR reaction due to the occurrence of the ‘fast SCR’ [3].

The acid sites on the surface of the catalyst are closely related to the adsorption and activation of NH₃. The NH₃-TPD was performed to investigate the surface acid amount and strength of the catalysts.

**Figure 5.** N₂ adsorption-desorption isotherms (a) and pore size distributions (b) of the catalysts prepared by different methods.

**Table 1.** Surface area and pore characterization of catalysts.

| Catalysts          | BET surface area (m² g⁻¹) | Pore volume (cm³ g⁻¹) | Pore size (nm) |
|--------------------|---------------------------|-----------------------|----------------|
| P-CNTs             | 295.2                     | 1.442                 | 19.54          |
| V₂O₅/CNTs-1        | 146.7                     | 0.975                 | 26.60          |
| V₂O₅/CNTs-2        | 188.6                     | 0.969                 | 20.54          |
| V₂O₅/CNTs-3        | 138.3                     | 0.857                 | 24.78          |
| V₂O₅/CNTs-I        | 252.4                     | 1.236                 | 19.59          |
| V₂O₅/CNTs-M        | 239.4                     | 1.111                 | 18.56          |
Figure 6. XPS spectra for (a) V2p and (b) O1s of the catalyst samples.

Table 2. Some results of XPS, H$_2$-TPR, and NH$_3$-TPD.

| Catalysts        | V$^{4+}$/V$^{3+}$/V$^{n+}$ | $O_\alpha$/(O$_\alpha$+O$_\beta$) | Peaks area (H$_2$-TPR) | Peaks area (NH$_3$-TPD) |
|------------------|---------------------------|----------------------------------|------------------------|------------------------|
| V$_2$O$_5$/CNTs  | 24.9%                    | 40.9%                           | 11.55                  | 12.65                  |
| V$_2$O$_5$/CNTs-I| 25.2%                    | 35.1%                           | 8.96                   | 2.38                   |
| V$_2$O$_5$/CNTs-M| 20.1%                    | 23.1%                           | 6.55                   | 1.45                   |

As shown in Figure 7a, there are two desorption peaks of V$_2$O$_5$/CNTs-M catalyst. The weak peak centred at about 167°C is mainly caused by desorption of ammonia bounded to weak Bronsted acid sites and physically adsorbed ammonia molecules. Another peak centred at 438°C is attributed to desorbed ammonia from strong Lewis acid sites. However, a new peak centred around 358°C is appeared in the NH$_3$-TPD profile of the V$_2$O$_5$/CNTs-I sample, which is corresponded to desorbed ammonia from medium strong acid sites [21]. As for V$_2$O$_5$/CNTs-2 catalyst, in addition to the broad peak centred at 167°C, there are two strong peaks centred at 470 and 520°C, which can be attributed to desorbed ammonia from strong acid sites. The higher the temperature corresponding to the desorption peak, the stronger the acid site. So the acid sites of V$_2$O$_5$/CNTs-2 catalyst are the strongest among all the catalysts.

Figure 7. NH$_3$-TPD (a) and H$_2$-TPR (b) profiles of the catalyst samples.
In addition, the area of the peaks represents the amount of adsorbed NH$_3$, which is also equivalent to the number of acid sites on the catalyst surface. Therefore, Table 2 allows concluding that V$_2$O$_5$/CNTs-2 catalyst possesses most acid sites. The results show that V$_2$O$_5$/CNTs-2 catalyst exhibits a stronger ability to adsorb NH$_3$ than V$_2$O$_5$/CNTs-I and V$_2$O$_5$/CNTs-M, which may result in a higher SCR activity.

The redox properties of different catalyst samples were investigated by H$_2$-TPR experiments. It is commonly recognized that the redox capacity of the catalyst plays a crucial role in the SCR cycle. As shown in Figure 7b, the redox peaks in the range of 400 - 600$^\circ$C are assigned to the reduction of the VO$_x$ from V$^{V_2}$ to V$^{V_3}$. The redox peaks of V$_2$O$_5$/CNTs-2 are at about 419 and 497$^\circ$C, while the peaks of V$_2$O$_5$/CNTs-I and V$_2$O$_5$/CNTs-M are at 512, 582 and 549, 657$^\circ$C, respectively. The area of the reduction peak is positively correlated with the consumption of H$_2$. As shown in Table 2, the area of the reduction peak for V$_2$O$_5$/CNTs-2 is larger than that of the other two samples. The above results suggest that the V$_2$O$_5$/CNTs-2 possesses stronger redox properties than V$_2$O$_5$/CNTs-I and V$_2$O$_5$/CNTs-M catalysts due to interaction between the vanadium oxide and CNTs, which is associated with higher SCR activity.

4. Conclusion
A series of catalysts of in situ supported VO$_x$ on CNTs were successfully synthesized by a CPC assisted reflux route, and their performance on the NH$_3$-SCR reaction was evaluated. All the catalysts prepared by in situ growth display better NH$_3$-SCR activity and more extensive operating-temperature window than the those prepared by impregnation and mechanically mixed method. In addition, the catalyst V$_2$O$_5$/CNTs-2 shows the highest NO conversion of 97% at 250$^\circ$C. Characterization revealed that V$_2$O$_5$/CNTs-2 catalyst displays best dispersion of the active component on the surface of CNTs. Besides that, the V$_2$O$_5$/CNTs-2 catalyst possesses more vanadium oxides with lower valence states (V$^{V_4}$ and V$^{V_3}$) and chemisorbed oxygen species, which could promote NH$_3$-SCR reaction. NH$_3$-TPD result indicates that the V$_2$O$_5$/CNTs-2 catalyst possesses a stronger ability to adsorb NH$_3$, and the H$_2$-TPR result shows that it has stronger redox properties, which is critical in the SCR cycle.

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