Catalysis, Kinetics and Reaction Engineering

Carbon nanotubes loaded with vanadium oxide for reduction NO with NH$_3$ at low temperature ☆

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ABSTRACT

The catalytic activity of carbon nanotubes-supported vanadium oxide (V$_2$O$_5$/CNTs) catalysts in the selective catalytic reduction (SCR) of NO with NH$_3$ at low temperatures ($\leq$250 °C) was investigated. The effects of V$_2$O$_5$ loading, reaction temperature, and presence of SO$_2$ on the SCR activity were evaluated. The results show that V$_2$O$_5$/CNTs catalysts exhibit high activity for NO reduction with NH$_3$ at low-temperatures. The catalysts also show very high stability in the presence of SO$_2$. More interestingly, their activities are significantly promoted instead of being poisoned by SO$_2$. The promoting effect of SO$_2$ is distinctly associated with V$_2$O$_5$ loading, particularly maximized at low V$_2$O$_5$ loading, which indicated the role of CNTs support in this effect. The promoting effect of SO$_2$ at low temperatures suggests that V$_2$O$_5$/CNTs catalysts are promising catalytic materials for low-temperature SCR reactions.

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1. Introduction

Carbon nanotubes (CNTs) possess many excellent properties, including high thermal stability and the accessibility of outer and inner surfaces, making them highly attractive as catalysts or catalyst supports [1,2]. CNTs-supported catalysts [3–8] exhibit excellent catalytic activity and selectivity in 1-octene hydroformylation, selective cinnamaldehyde hydrogenation to hydrocinnamaldehyde, NH$_3$ decomposition, selective H$_2$S oxidation, selective hydrogenation of nitrobenzene and NO decomposition.

Selective catalytic reduction (SCR) of NO with NH$_3$ is one of the most important industrial processes in environmental catalysis. The general reaction is as follows: $4NO + 4NH_3 + O_2 \rightarrow 4 N_2 + 6H_2O$. However, SO$_2$ poisoning is a key problem in the development of SCR catalysts. Several reported catalysts [9–13], such as MnO$_2$/Al$_2$O$_3$, CuO/AC and Fe$_2$O$_3$/AC, show high activities in SCR reactions at 120 °C to 250 °C, but they are prone to deactivation by SO$_2$ because of the formation of solid SO$_4^{2-}$ salts on the catalyst surfaces, which block the catalyst pores. Others reported that catalysts, such as V$_2$O$_5$/TiO$_2$ or V$_2$O$_5$–WO$_3$/TiO$_2$ must be used at temperatures above 350 °C to avoid catalyst deactivation [14,15]. Thus, developing catalysts that resist SO$_2$ poisoning at low temperatures is necessary for practical applications.

Activated carbon-supported vanadium oxide (V$_2$O$_5$/AC) catalysts [16–19] exhibit high activities in SCR reactions within the low-temperature range (180 °C to 250 °C). The V$_2$O$_5$/AC catalysts are not poisoned, moreover are significantly promoted by SO$_2$. The excellent property of V$_2$O$_5$/AC catalysts is attributed to the special carbon surfaces. However, the unique catalytic functions remain unclear because of the complex composition and structure of ACs. Unlike ACs, CNTs have relatively uniform structures and can be rationally functioned, which may be helpful for the understanding of its catalytic functions. The reaction-released heat and the fluctuation of the flue gas temperature often lead to the burning of the AC support because of the high reactivity of AC with oxygen. In contrast, CNTs have more stable structures and are more resistant to burning, thus, they exhibit better properties in SCR reactions [20,21].

In the present work, CNTs-supported V$_2$O$_5$ catalysts (V$_2$O$_5$/CNTs) were prepared and investigated for their catalytic activities in low-temperature SCR reactions. The effects of the V$_2$O$_5$ loading, reaction temperatures, and performance of the catalysts in the presence SO$_2$ were also studied.

2. Experimental

2.1. Catalysts preparation

The raw CNTs samples prepared by our research group were refluxed and oxidized with concentrated HNO$_3$ under stirring for 10 h to remove pre-existing metal species and eliminate the possible interferences. The CNTs were then collected *via* filtration, washed fully

with deionized water and ethanol, and dried at 110 °C in air for 12 h. The treatment also introduced carboxyl and hydroxyl groups onto the CNTs surfaces, which are helpful for the anchoring and uniform dispersion of vanadium oxide species on the CNTs surfaces.

The V_2O_5/CNTs catalysts were prepared through pore volume impregnation of HNO_3-oxidized CNTs using an aqueous solution of ammonium metavanadate in oxalic acid. The catalysts were then dried overnight at 60 °C and at 110 °C for 5 h, calcinated under an argon stream at 500 °C for 5 h, and pre-oxidized in air at 250 °C for 3 h. The weight V_2O_5 of V_2O_5/CNTs catalysts was measured by the inductively coupled plasma (ICP) atomic emission spectrometer (AtomScan 16, TJA, USA).

2.2. Catalyst characterization

Temperature-programmed desorption (TPD) experiments were performed in a fixed-bed reactor to determine the effect of different catalysts surface on SO_2 adsorption. CNTs, V_2O_5 and 0.1%(by mass) V_2O_5/CNTs catalysts were employed in the reactor and pre-treated in Ar stream (100 ml·min^{-1}) at 500 °C for 1 h, respectively, and then cooled to 250 °C in the same stream. The pre-treated samples were then exposed to a gas mixture 1000 μl·L^{-1} SO_2 + 5.0% O_2 (by volume) in Ar at a flow rate of 100 ml·min^{-1}. After adsorption equilibrium was reached (about 2 h), the sample was purged with Ar of 100 ml·min^{-1} for 1 h to remove the physically adsorbed SO_2. Finally, TPD experiment was carried out in Ar of 100 ml·min^{-1} from 250 to 640 °C at a heating rate of 8 °C·min^{-1}. During the TPD, exiting SO_2 was continuously analyzed online by flue gas analyzer (ZR-3100TZ) equipped with NO, NO_2, SO_2 and O_2 sensors.

The morphology and structure of the as-prepared catalysts were characterized *via* transmission electron microscopy (TEM JEOL JEM-2010), and X-ray diffraction (XRD) patterns were obtained on a D8 ADVANCE BRUKER diffractometer equipped with a CuK$_\alpha$ radiation (wavelength 0.15406 nm) at 2.2 kW. The specific surface areas of the samples were determined through nitrogen adsorption at 77 K on the basis of Brunner–Emmet–Teller (BET) equation using a micrometrics Tristar 3000.

2.3. Activity test

The SCR activity of the catalysts in NO reduction was evaluated in a fixed-bed glass reactor (6 mm inner diameter, 510 mm length). NO in Ar, SO_2 in Ar (when used), pure O_2 and pure Ar were used to mimic the flue gas, and NH_3 in Ar was used as the reductive gas. All gases were controlled by mass flow controllers, and pre-mixed in a chamber filled with glass wool before entering the reactor. For experiments involving SO_2, NH_3 in Ar was allowed to bypass the mixing chamber and was directly fed into the reactor to avoid possible SO_2–NH_3 reactions in front of the catalyst bed. The concentration of NO, NO_2, SO_2 and O_2 at the inlet and outlet of the reactor was simultaneously monitored using an online flue gas analyzer (ZR-3100TZ) equipped with NO, NO_2, SO_2 and O_2 sensors.

3. Results and Discussion

TEM images of the treated CNTs sample and 20% (by mass) V_2O_5/CNTs catalysts are shown in Fig. 1(a) and (b). The diameter of the nanotubes ranges from 12 nm to 50 nm and the length reaches tens of micrometers. No vanadium species is observed on the 20% (by mass) V_2O_5/CNTs catalyst surface [Fig. 1(b)]. The catalysts with different V_2O_5 loadings were characterized *via* XRD. The three distinctive peaks in Fig. 1(c) are mainly assigned to the graphite of CNTs [20]. The crystalline vanadium is difficult to be observed due to some of the crystalline vanadium at 2θ of 20°–30° that coincides with the 002 diffraction of graphite. TEM and XRD results indicate that the vanadium species on CNTs may be very small or highly

dispersed [21]. The V_2O_5 mass of the 20% (by mass) V_2O_5/CNTs catalysts (about 18.7%) was measured by ICP and the result shows that vanadium species are loaded on the surface of the catalysts.

The catalytic activity of the V_2O_5/CNTs catalyst is much higher than that of the V_2O_5/AC catalyst under the same reaction conditions (Fig. 2). In the experiment, the Brunauer–Emmett–Teller (BET) surface of the selected CNTs (220 m^2·g^{-1}) is lower than that of AC (615 m^2·g^{-1}), suggesting that the CNTs exhibit better catalytic properties than AC when used as catalyst supports for the NO reduction reaction because of its structure and specifically surface.

Fig. 3 shows NO conversion over the V_2O_5/CNTs catalysts with different V_2O_5 loadings at 250 °C. Each result is obtained through a 4 h reaction after NO concentration is nearly unchanged. The V_2O_5-unloaded CNTs sample shows very low activity under the experimental conditions. The 0.1% (by mass) V_2O_5 loading on the CNTs only results in a significant improvement of the catalytic activity, thereby enhancing NO conversion to approximately 51%. Further increase in V_2O_5 loading from 0.1% (by mass) to 5% (by mass) leads to a continuous increase in NO conversion from 51% to 100% until it subsequently decreases to approximately 88% at a V_2O_5 loading of 20% (by mass). The catalysts with lower V_2O_5 loadings [0.1%–1% (by mass)] exhibit lower activity, which may be attributed to the lower V coverage on the CNTs surface. However, the nearly constant activity at V_2O_5 loadings of 5% to 15% (by mass) and the decreased activity of the 20% (by mass) V_2O_5/CNTs catalyst are not easy to explain because the XRD results of these catalysts show no diffraction peaks for vanadium compounds and no vanadium compound particles are observed *via* TEM. These results suggest that the vanadium species particles in the catalysts are small size and highly dispersed on the CNTs surface. In addition, all the catalysts show good stability within the tested time range.

The effect of SO_2 on the activities of the V_2O_5/CNTs catalysts with different V_2O_5 loadings at 250 °C is shown in Fig. 4. For CNTs alone, the degree of NO conversion in the reaction stream with and without SO_2 shows no significant difference. However, for the V_2O_5/CNTs catalysts at V_2O_5 loadings of 0.1% to 1% (by mass), NO conversion in the presence of SO_2 increases significantly and then becomes nearly constant at high levels as the reaction proceeds. These results suggest that the presence of SO_2 increases NO reduction over the V_2O_5/CNTs catalysts at low temperature. The effect of SO_2 promotion is associated with V_2O_5 loading, that is, SO_2 promotion increases as the V_2O_5 loading decreases (Fig. 4), indicating the importance of the CNTs support surface. Thus, a synergistic relationship between the CNTs and the vanadium species is implied. However, the mechanism behind this cooperation remains unknown, hence, further investigations are recommended.

In addition, the promoting effect of SO_2 revealed in this study, instead of the expected poisoning effect in the presence of the V_2O_5/CNTs catalyst must be understood. The promoting effect of SO_2 on the V_2O_5/CNTs catalyst is likely associated with SO_2 adsorption and oxidation and the formation of SO_4^{2-} species on the catalyst surfaces. These SO_4^{2-} species act as new acidic sites and improve NH_3 adsorption, thereby promoting the activity of the catalyst. The results agree with previous observation on the V_2O_5/AC catalyst at low temperatures [19] and those of Chen and Yang [22,23] on V_2O_5/TiO_2 and TiO_2 catalysts at high temperatures (>350 °C).

Fig. 5 shows the profiles of the temperature-programmed desorption (TPD) of SO_2 adsorbed on the CNTs, V_2O_5, and 0.1% (by mass) V_2O_5/CNTs catalysts during the oxidation of SO_2 by O_2. The SO_2 adsorption on the V_2O_5 surface under the given adsorption conditions is very limited. A negligible amount of SO_2 is desorbed during TPD from 250 °C to 640 °C. The TPD of SO_2 on the CNTs catalyst shows a peak at approximately 340 °C, however, the amount desorbed is very low. In addition, the 0.1% (by mass) V_2O_5/CNTs catalyst exhibits a desorption peak at a temperature similar to that of the CNTs, which further supports the suggestion that the formed SO_4^{2-} species is primarily associated with the carbon surface rather than the vanadium surface. Furthermore, the amount desorbed from the 0.1% (by mass) V_2O_5/CNTs
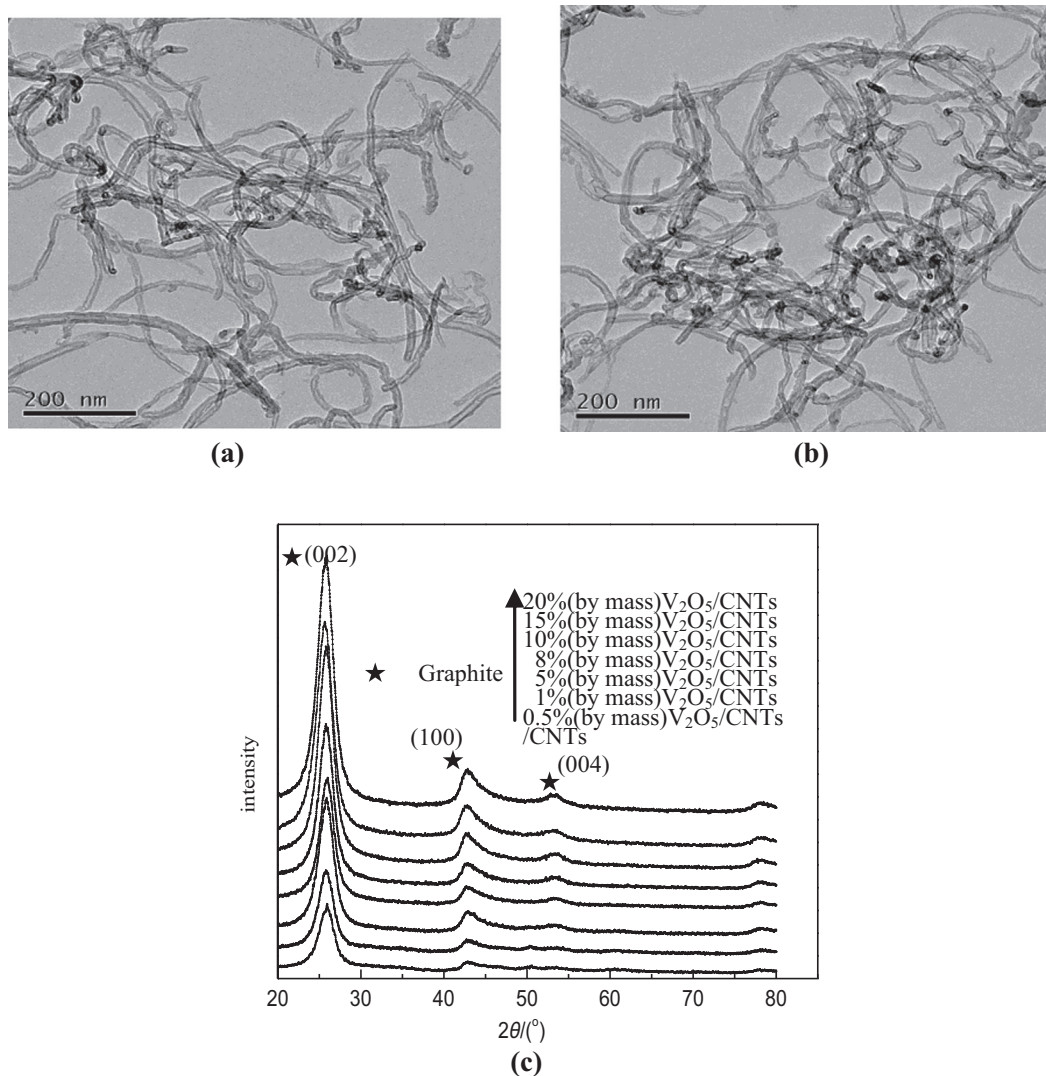
Fig. 1. TEM of the treated CNTs (a), 20% (by mass) V_2O_5/CNTs catalysts (b) and X-ray diffractograms of vanadium oxide catalyst support on carbon nanotubes (c).

catalyst is significantly higher than that from the CNTs. The increased adsorption of SO_2 on the V_2O_5/CNTs catalyst under the given conditions may be attributed to a synergistic interaction between carbon and V_2O_5, wherein SO_2 is initially oxidized into SO_3 on the V_2O_5 surface, and SO_3 then migrates and attaches to the carbon surface. Furthermore, the adsorbed SO_3 is converted into SO_4^{2-} *via* reaction with H_2O, which is
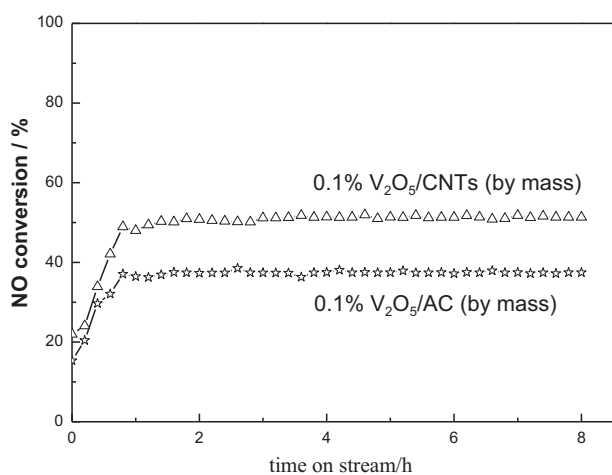

Fig. 2. Comparison of catalytic activity of 0.1% (by mass) V_2O_5/CNTs and 0.1% (by mass) V_2O_5/AC at 250 °C. Reaction conditions: 450 μl·L^{-1} NO, 500 μl·L^{-1} NH$_3$, 5% O$_2$ (by volume), WHSV, 30000 h^{-1}, reaction temperature, 250 °C.

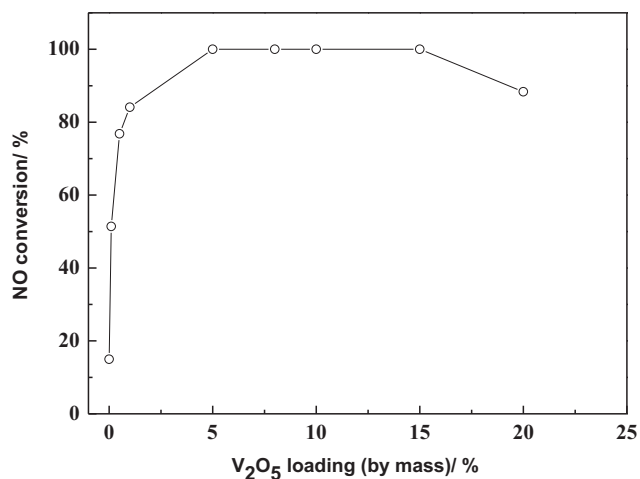**Fig. 3.** Effect of V_2O_5 loading on the activity of V_2O_5/CNTs catalysts. Reaction conditions: 450 μl·L^{-1} NO, 500 μl·L^{-1} NH$_3$, 5% O$_2$ (by volume), WHSV, 30000 h^{-1}, reaction temperature, 250 °C.
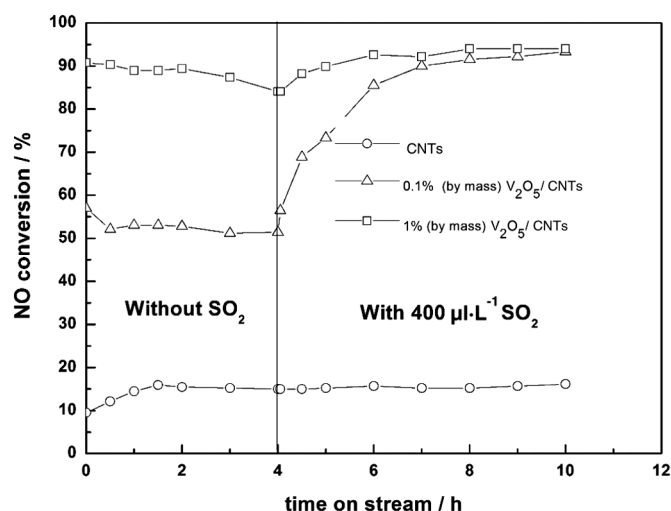
Fig. 4. Effect of SO$_2$ on the activity of V$_2$O$_5$/CNTs and CNTs catalysts. Reaction conditions: 450 μl·L^{-1} NO, 500 μl·L^{-1} NH$_3$, 5% (by volume) O$_2$, 400 μl·L^{-1} SO$_2$ (when used), WHSV, 30000 h^{-1}, reaction temperature, 250 °C.

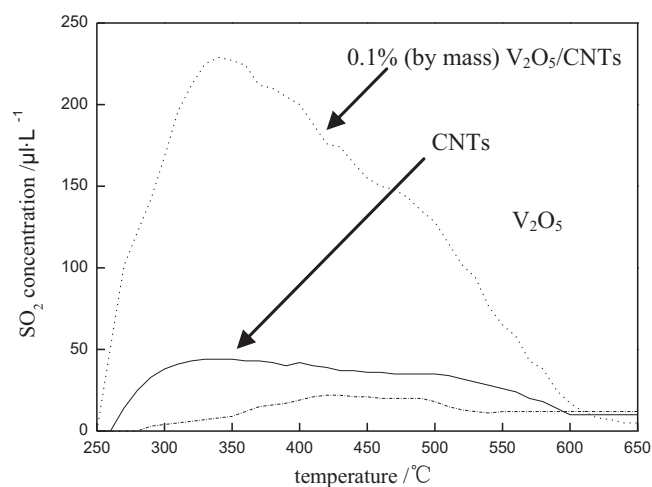**Fig. 5.** TPD patterns of SO$_2$ on different catalysts after a SO$_2$ + O$_2$ treatment. The treatment was performed at 250 °C in 1000 μl·L^{-1} SO$_2$ + 5%O$_2$ (Ar balance) for 2 h, followed by a purge with Ar for 1 h. The TPD was carried out in Ar of 100 ml·min^{-1} at a heating rate of 8 °C·min^{-1}.

formed during the SCR reaction. The SO$_4^{2-}$ species then acts as a new acid sites and increases NH$_3$ adsorption. Thus, SO$_2$ induces a promoting effect on the V$_2$O$_5$/CNTs catalysts during SCR at low temperatures.

4. Conclusions

In this work, CNTs loaded with vanadium oxide for catalytic reduction NO with NH$_3$ at low temperatures are investigated. The results show that the V$_2$O$_5$/CNTs catalysts exhibit a high SCR activity at 250 °C. Interestingly, SO$_2$ does not poison the catalysts but instead significantly promotes their activities when the V$_2$O$_5$ loading is below

1% (by mass). The SO$_2$ promoting effect on the activities of the V$_2$O$_5$/CNTs is attributed to the synergistic relationship between the CNTs and the vanadium species. This unique promoting effect of SO$_2$ at low temperatures suggests that the V$_2$O$_5$/CNTs catalyst system is a promising catalytic material for low-temperature SCR reactions. Further investigations on the function of CNTs are of significant scientific interest.

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