Catalysis Today 158 (2010) 393–400

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

SO_2-promoted reduction of NO with NH_3 over vanadium molecularly anchored on the surface of carbon nanotubes

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ARTICLE INFO

Article history:
Available online 9 June 2010

Keywords:
SO_2
Promoting effect
NO
SCR
V_2O_5
Carbon nanotubes

ABSTRACT

Being a major poison, SO_2 is often avoided for selective catalytic reduction (SCR) of NO with ammonia at low temperatures. In the present work, we report a V_2O_5/CNT catalyst with high NO catalytic activities tolerant to SO_2, moreover, whose SCR activity is promoted by the SO_2 at proper low temperatures. When the reacting temperature is higher than 200 °C, SO_2 improves the SCR activity, while it is lower than 200 °C, SO_2 deactivates the V_2O_5/CNT catalysts. It seems that the reacting temperature behaves like a switch, capable of turning on and off the poisoning reactions. Furthermore, the promoting effect of SO_2 exhibits a magnified tendency with decreasing V_2O_5 loadings. TEM and EDS results indicate that the vanadium oxides should molecularly anchor on the surface of CNTs. X-ray photoelectron spectroscopy, ammonia temperature-programmed desorption, temperature-programmed decomposition and temperature-programmed surface reaction results show that the promoting effect of SO_2 on SCR activity originates from the formation of sulfate species on the catalyst surface. Based on these findings, a promoting process is also proposed. More importantly, the V_2O_5/CNTs catalysts show a great stability under the SO_2-containing conditions after being operated for 100 h.

1. Introduction

Nitrogen oxides (NO_x) have become a major source of air pollution which result in photochemical smog, acid rain and ozone depletion, and have strong respiratory toxicity endangering human health [1]. Selective catalytic reduction (SCR) of NO with NH_3 is an effective and economical method to remove NO_x. The general reaction for SCR of NO is as follows: $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$, in which the common catalysts (TiO_2-supported V_2O_5) used are always operated at high temperatures above 350 °C to avoid SO_2 poisoning [2,3]. The key problem for developing low-temperature SCR catalysts is to improve their resistance to SO_2 present in the flue gas after a desulfurizer. Many previously reported catalysts, such as MnO_2/Al_2O_3, CuO/AC and Fe_2O_3/AC, show high activities for the SCR reaction at 120–250 °C, but they are prone to SO_2 deactivation due to the formation of sulfate salts [4–6].

We had reported that activated carbon-supported vanadium oxide (V_2O_5/AC) catalysts exhibit high activities for the SCR reaction in a low-temperature range (180–250 °C). More importantly, the V_2O_5/AC catalysts are not poisoned but significantly promoted by SO_2 [7,8]. Previous studies suggest that the promoting effect of SO_2 on SCR activity of V_2O_5/AC catalyst stems from the formation of certain sulfur-containing species on catalyst surface, and the sulfate species is linked to carbon surfaces [9,10]. Nevertheless, some important aspects of SO_2 promotion effect remain unclear because AC includes many oxygen-containing groups and mineral impurities. Oxygen-containing groups can improve the adsorption of NH_3 on the V_2O_5/AC catalysts, which is one of the key steps in the SCR process, thus promote the catalytic activity [11]. Mineral materials have an influence on the catalytic performance of the catalysts in the presence of SO_2 [12]. Due to the "impure" surface of AC, we are still lack of definitely basic knowledge on the nature of carbon acting as a support during the SCR reaction in the presence of SO_2. Moreover, from a technical point of view, the reaction-released heat (−1627.48 kJ/mol) [1] and the fluctuation of flue gas temperature often lead to a burning of the AC support since the AC exhibits high reactivities with oxygen. It is thus necessary to develop new carbon catalysts more resistant to oxygen.

It is well-known that the unique one-dimensional tubular structure and accessible surface make carbon nanotubes (CNTs) an intriguing candidate for wide applications in catalysis [13–15]. CNTs have more stable structures and are more resistant to burning, thus expectedly exhibit better properties in the SCR reaction. Moreover, CNTs have relatively uniform structures and clear surfaces, which might be helpful for understanding the catalytic functions of carbons. Then, for the CNT support, is the SCR activity still promoted by SO_2? If yes, it is also important to clarify why the carbon support, unlike TiO_2 support, is not deactivated by SO_2 at low tem-

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doi:10.1016/j.cattod.2010.05.002

Table 1
BET surface area and pore structure analyses of CNTs.

CNT	BET SA (m^2/g)	Micropore area (m^2/g)	Tota pore volume (ml/g)	Micropore volume (ml/g)	Average pore diameter (Å)
Original	171.68	–	1.17	–	27.28
Oxidized by nitric acid	220.84	5.19	0.74	0	12.96

peratures. How does SO_2 switch from a poison to a promoter at carbon surfaces at low temperatures? More detailed and reliable information is expected to be obtained over a pure carbon surface using CNTs as support for SCR reaction.

In the present work, CNT-supported V_2O_5 catalysts (V_2O_5/CNT) are studied for the low-temperature SCR of NO in the presence of SO_2, which is an important step toward understanding both SO_2 effect on the carbon-based catalyst and the role of carbon as a support in other catalytic systems.

2. Experimental

2.1. Pretreatment of CNT and preparation of catalyst

The raw CNT samples (home-made) were refluxed and oxidized with concentrated HNO_3 under stirring for 10 h to remove the metal species pre-existed, and so as to eliminate their possible interferences on catalytic test. After the treatment, the CNTs were separated by filtration, washed fully with deionized water and ethanol, and dried at 110 °C in air for 12 h. Such a treatment also introduces carboxyl and hydroxyl groups onto the CNT surfaces, which are helpful for anchoring and dispersing uniformly vanadium oxide species on the CNT surfaces. Physical characteristics of the CNTs are presented in Table 1.

The V_2O_5/CNT catalysts were prepared by pore volume impregnation of the pre-treated CNTs with an aqueous solution of ammonium metavanadate in oxalic acid, followed by drying at 60 °C overnight and then at 110 °C for 5 h. Afterwards, the catalysts were calcined in argon stream at 500 °C for 5 h, and pre-oxidized in air at 250 °C for 5 h. A V_2O_5/TiO_2 catalyst is used for comparison with the V_2O_5/CNT catalysts, which was prepared by pore volume impregnation of TiO_2 (ISK, Japan) (particle size, 60–90 mesh) with an aqueous solution of ammonium metavanadate in oxalic acid, followed by the same drying-treated process as the V_2O_5/CNT catalysts.

2.2. Activity tests

The SCR activity tests were carried out in a fixed-bed glass reactor (6 mm in inner diameter and 510 mm in 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 reductive gas. All the gases were controlled by mass flow controllers and, before entering the reactor, were pre-mixed in a chamber filled with glass wool. For experiments involving SO_2, NH_3 in Ar was allowed to bypass the mixing chamber and directly fed into the reactor to avoid possible SO_2–NH_3 reaction in front of the catalyst bed. Concentration of NO, NO_2, SO_2 and O_2 at the inlet and the outlet of the reactor were simultaneously monitored by an online combustion gas analyzer equipped with NO, NO_2, SO_2 and O_2 sensors.

2.3. TPD of NH_3

Temperature-programmed desorption (TPD) experiments were performed in a fixed-bed reactor to determine the effect of adsorbed SO_2 on NH_3 adsorption. 1 wt% V_2O_5/CNT catalyst was employed in the reactor and was pre-treated in Ar stream (50 ml/min) at 500 °C for 1 h, and then cooled to 30 °C in the same stream. The pre-treated sample was then exposed to a gas mixture containing 2000 ppm NH_3 in Ar at a flow rate of 100 ml/min. After an adsorption equilibrium reached (about 1 h), the sample was purged with Ar of 50 ml/min for 1 h to remove the physically adsorbed NH_3. Finally, TPD experiment was carried out in Ar of 50 ml/min from 30 to 800 °C at a heating rate of 10 °C/min. During the TPD, exiting NH_3 was continuously analyzed online by combined thermogravimetric analysis (Setaram, TGA92)/mass spectrometer (Balzers, Omnistar 200) (TG–MS). To understand the effect of sulfate species loaded on the V_2O_5/CNT catalysts on the NH_3 adsorption, the sample was presulfated before the NH_3 adsorption process (following the 500 °C pretreatment of the sample). The presulfation was performed in a gas mixture containing 1000 ppm SO_2 + 5 vol% O_2 in Ar at a flow rate of 100 ml/min and a temperature of 30 °C for 2 h, followed by Ar purge of 1 h to remove physically adsorbed SO_2. For comparison, the 1 wt% V_2O_5/TiO_2 catalyst was characterized by the same TPD experiments.

2.4. Reactivity and decomposition of NH_4HSO_4 deposited on catalyst surface

Temperature-programmed decomposition (TPDC) of NH_4HSO_4 deposited on the catalysts was carried out in a fixed-bed quartz reactor (6 mm in inner diameter and 480 mm in length). The reactor, containing 0.2 g of NH_4HSO_4-deposited catalyst, was heated from 30 to 650 °C at a rate of 10 °C/min. Exiting SO_2 was monitored during the process for diagnosing the NH_4HSO_4 decomposition.

The 1 wt% V_2O_5/CNT catalyst was selected to investigate the reactivity of NH_4HSO_4, which may be formed on the catalyst surface at the reaction temperature. NH_4HSO_4 was pre-deposited by pore volume impregnation of the catalysts with NH_4HSO_4 aqueous solution, followed by overnight drying at 110 °C. An amount of 0.2 g NH_4HSO_4-deposited catalyst was exposed to a mixture stream containing about 1000 ppm NO, 5 vol% O_2 in Ar, at a total flow rate of 100 ml/min and with programmed heating from 30 to 480 °C at heating rate of 10 °C/min. During the reaction, exiting NO and SO_2 were continuously analyzed using the flue gas analyzer, and the amount of NO removed was used to estimate the reactivity of ammonium ions in NH_4HSO_4. For comparison, the 1 wt% V_2O_5/TiO_2 catalyst was performed in the same experimental process.

2.5. XPS analyses

X-ray photoelectron spectroscopy (XPS) was used to determine the nature of the vanadium-, sulfur- and nitrogen-containing species adsorbed on the catalyst surface. XPS spectra were measured with a Perkin-Elmer PHI-5300 X-ray photoelectron spectrometer, using MgKa as the radiation source. The 0.1 wt% V_2O_5/CNT catalyst was subjected to a SCR reaction at 250 °C in the presence or absence of SO_2 for 10 h. After that, the catalyst sample was in situ purged at 250 °C in Ar for 1 h to remove the physically adsorbed SO_2, cooled in Ar to room temperature, and then kept in a sealed vessel. The 5 wt% V_2O_5/CNT catalyst and the reacted catalyst were crushed and pressed into a sample holder on a double-sided glue tape, respectively. The preparation chamber was degassed at ca. 1×10^{-6} Torr and maintained at 6×10^{-9} Torr for sample analysis. The charging effect of the sample was calibrated by the C (1s) line at 284.6 eV.

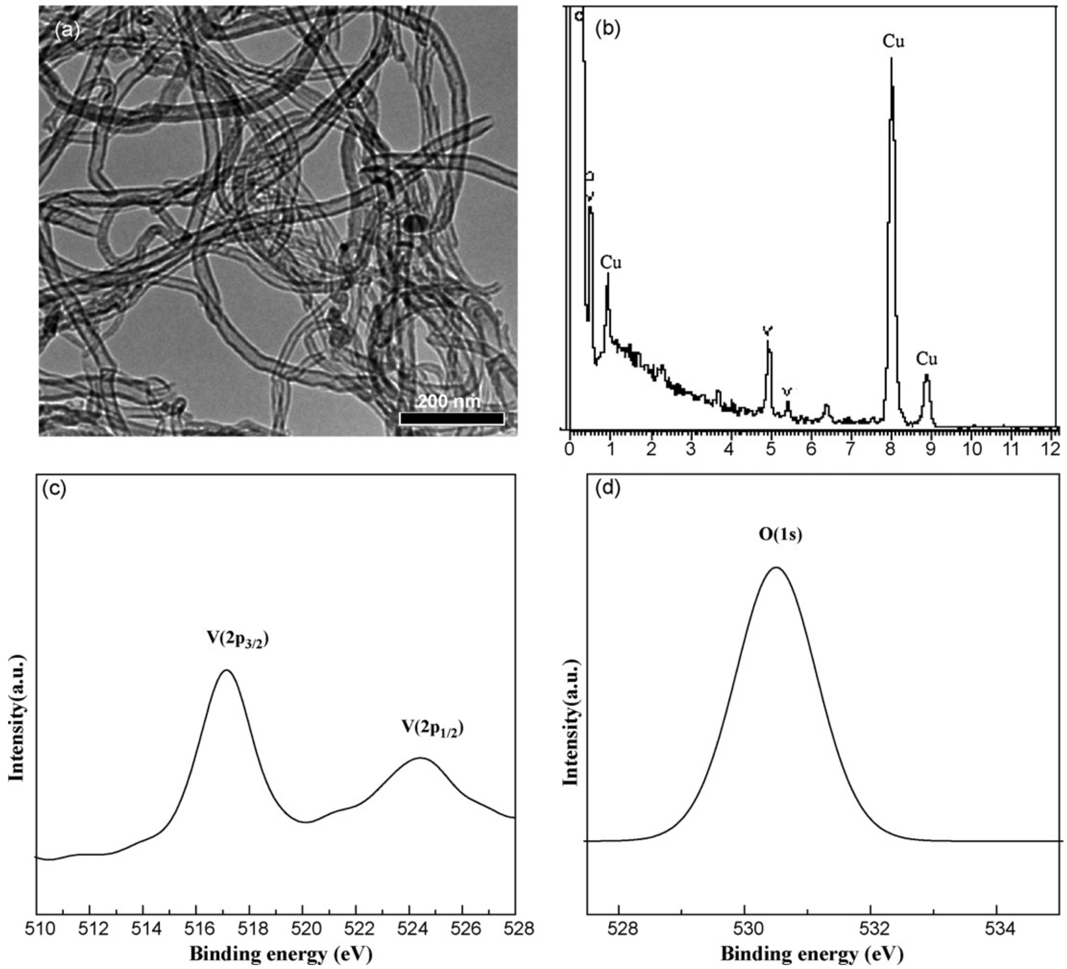

Fig. 1. TEM image (a), EDS analysis focused on the catalyst surface (b), and V 2p and O 1s XPS spectra (c and d) of the 5 wt% V_2O_5/CNT catalyst.

2.6. EDS elemental analysis

Energy dispersive X-ray spectroscopy (EDS) analysis was performed on the transmission electron microscopy (TEM, JEOL JEM-2010) equipped with energy dispersive X-ray spectrometer analyzer, using an accelerating voltage of 200 kV. During the EDS analysis, TEM image of the sample (5 wt% V_2O_5/CNTs) was first obtained. On the basis of the TEM, many areas on the catalyst surface were selected for elemental composition analysis by EDS.

3. Results and discussion

3.1. V_2O_5/CNT catalysts

Fig. 1a shows the TEM image of 5 wt% V_2O_5/CNT catalyst. It is clear that there are no vanadium species on the surface of CNTs. However, EDS for the 5 wt% V_2O_5/CNTs catalyst exhibits the presence of vanadium species (Fig. 1b), indicating that the vanadium species should be molecularly modified on the surface of CNTs. XPS analysis provides further information on the structure of vanadium-containing species, the results (Fig. 1c and d) clearly display that the vanadium-containing species are V_2O_5 [16,17].

3.2. Promoting effect of SO_2 on SCR activity over V_2O_5/CNT catalysts

Fig. 2 shows that the SO_2 promotion behavior on the V_2O_5/CNT catalysts is dependent on the reaction temperature. In the case of 0.1 wt% V_2O_5/CNT catalyst, the catalytic activity increases constantly with increasing reaction temperatures when SO_2 is absent. Note that under this condition, the catalytic activity changes indistinctively between 200 and 220 °C. After SO_2 introduction,

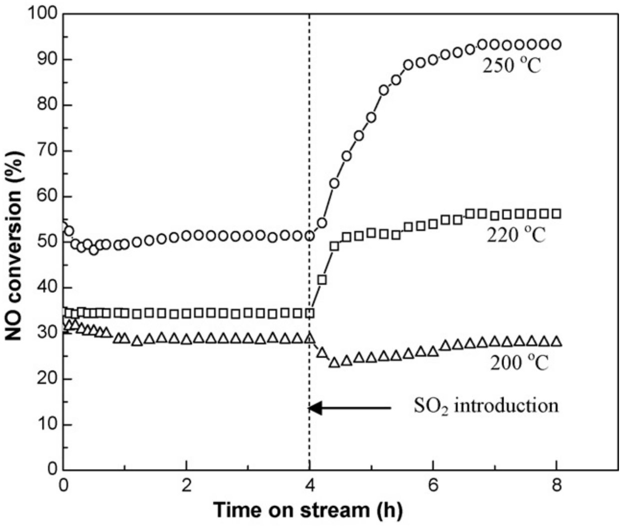

Fig. 2. Effect of SO_2 on the activity of 0.1 wt% V_2O_5/CNT catalyst at temperatures of 200–250 °C. Reaction conditions: 450 ppm NO, 500 ppm NH_3, 5.0 vol% O_2, 400 ppm SO_2 (when used), balance Ar, and WHSV of 30,000 h^{-1}.

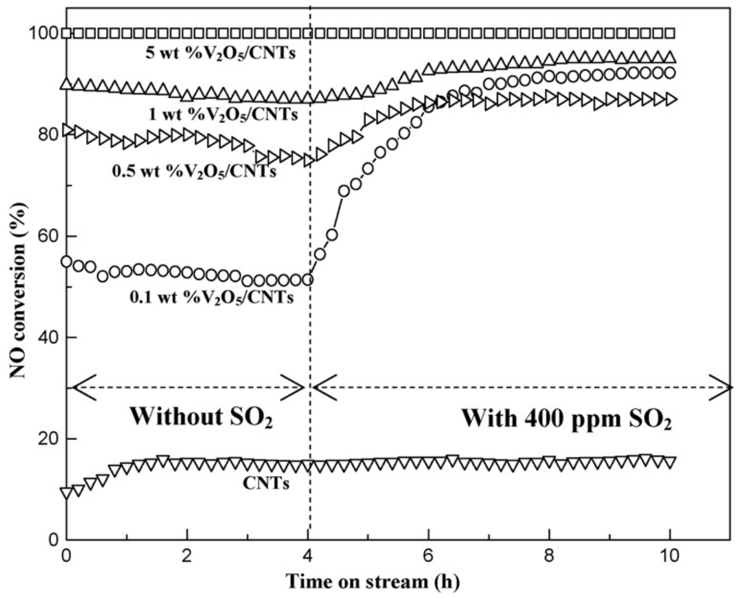

Fig. 3. Effect of SO_2 on the activities of V_2O_5/CNT catalysts with V_2O_5 loadings of 0–5 wt%. Reaction conditions: 450 ppm NO, 500 ppm NH_3, 5.0 vol% O_2, 400 ppm SO_2 (when used), balance Ar, WHSV of 30,000 h^{-1}, and reaction temperature of 250 °C.

however, the SO_2 promotion behavior is largely different at different temperatures although the catalytic activity still enhances with increasing reaction temperatures. At 200 °C, the catalyst is somewhat deactivated when SO_2 is introduced (see that the catalytic activity of 0.1 wt% V_2O_5/CNT catalyst is lower in the presence of SO_2 than that in the absence of SO_2), while the catalytic activities are greatly promoted at 220 °C, and most significantly enhanced at 250 °C. These results indicate that the temperature can controllably switch the SO_2 from a poison to a promoter for the V_2O_5/CNT catalysts. At higher temperatures, SO_2 plays a promoting role, but at lower temperatures, it acts as a poison. These observations are likely associated with the abilities of adsorbed ammonium sulfate species to react with NO at different temperatures, as we previously observed for the V_2O_5/AC catalysts [9].

Effect of SO_2 on the CNT-supported V_2O_5 catalysts with varying vanadium loading was determined at 250 °C (Fig. 3). It is clear that the catalytic activity shows no visible change with or without SO_2 in reaction stream for CNTs alone. But interestingly, it exhibits significant increase in the presence of SO_2 for the V_2O_5/CNT catalysts with V_2O_5 loading of 0.1–1 wt% although the increase becomes weaker with the enhancing of V_2O_5 loading. These results indicate that SO_2 plays a magnified promoting role at lower V_2O_5 loadings, while the promoting effect exhibits weaker at higher V_2O_5 loadings. The dependence of SO_2 promotion effect on V_2O_5 loading suggests that the effect is associated with the vanadium species. However, it has been proved that the sulfate species formed on the TiO_2 surface can also lead to a similar promoting effect of SO_2 on the SCR activity of the V_2O_5/TiO_2 [2] and TiO_2 [3]. Thus, combined with the fact that SO_2 shows no promotion function on the activity of CNTs alone, one can deduce that the SO_2 promotion effect on the activities of V_2O_5/CNT catalysts should be a synergistic cooperation between carbon nanotubes and vanadium species.

3.3. Mechanism of the promoting effect of SO_2

To understand the mechanism of the promoting role of SO_2 on the V_2O_5/CNT catalyst, SO_2 transient response experiments consisting of six consecutive parts (Fig. 4) were carried out at 250 °C using the 0.1 wt% V_2O_5/CNT catalyst. In the experiments, the outlet NO and SO_2 concentrations were all monitored. In part I without SO_2, the NO conversion is about 51%. It increases to a steady-state value of 92% after the introduction of SO_2 in part II, concomitantly, SO_2 concentration increases following the same pattern. Then, removing SO_2 from the feed, there is no decline in the NO conversion (as shown in part III). Afterwards, the catalyst was heated in Ar at 350 °C for 1.5 h (part IV) followed by cooling the reactor to the original temperature of 250 °C. Then, the reaction gas was refed under the conditions similar to part I, the NO conversion reduces back to a steady-state value of 55% (part V), which is much lower than that in part III and is just slightly higher than that in part I. When SO_2 was re-introduced in the feed, the NO conversion increases again as expected, and finally reaches a steady value the same as that in part II. This observation suggests that the promoting effect of SO_2 on the V_2O_5/CNT catalyst is relevant to some sulfur-containing species formed and deposited on the catalyst surface, but not to the gas phase SO_2. Such a conclusion is well agreed with our previous observation on the basis of V_2O_5/AC catalysts at low temperatures [8,9], and also with the results of Chen and Yang

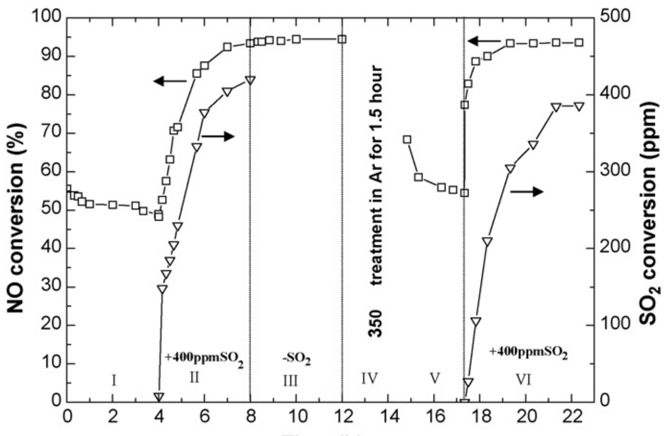

Fig. 4. SO_2 transient response experiments on the 0.1 wt% V_2O_5/CNT catalyst at 250 °C. Reaction conditions: 450 ppm NO, 500 ppm NH_3, 5.0 vol% O_2, 400 ppm SO_2 (when used), and WHSV of 30,000 h^{-1}. (I) NO–NH_3–O_2 reaction; (II) adding SO_2 into feed gas; (III) removal of SO_2 from feed gas; (IV) treating the catalyst at 350 °C (100 ml/min) for 1.5 h and cooling to 250 °C; (V) and (VI) the same as (I) and (II), respectively.

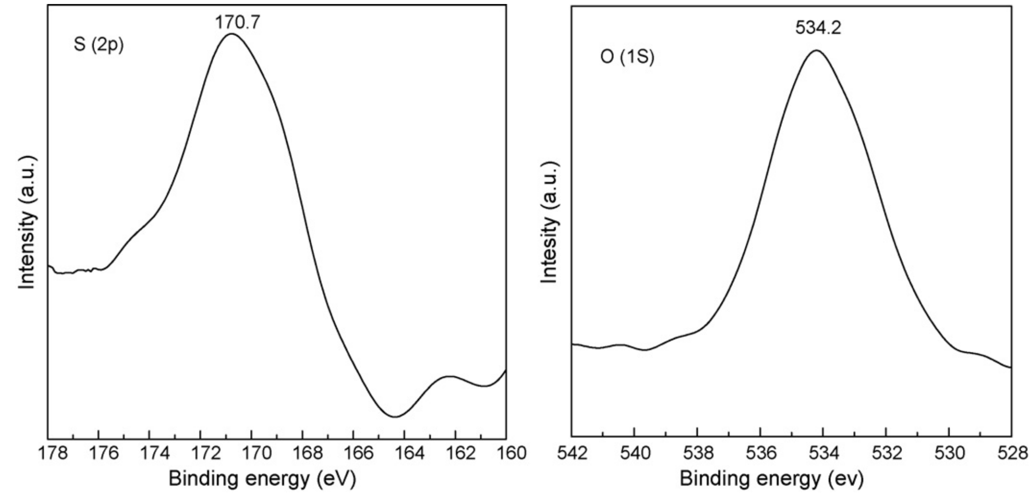

Fig. 5. S 2p and O 1s XPS spectra of the 0.1 wt% V_2O_5/CNT catalyst after SCR reaction in the presence of SO_2.

obtained on the V_2O_5/TiO_2 and TiO_2 catalysts at high temperatures (>350 °C) [2,3].

3.3.1. Effect of adsorbed SO_2 on the adsorption state of NH_3

The formation of SO_4^{2-} species on the catalyst surface through SO_2 adsorption and oxidation can generally act as new acidic sites, thus improving NH_3 adsorption and promoting the SCR activity of catalysts [2,3,8,9]. Therefore, further investigations were performed to examine the structure of sulfur-containing species possibly formed on the V_2O_5/CNT catalysts after reaction. The 0.1 wt% V_2O_5/CNT catalyst after SCR reaction in the presence of SO_2 was measured by XPS measurements (Fig. 5). Signals of V 2p of the sample are very weak (not shown), possibly due to the low vanadium content in the catalysts. S 2p and O 1s spectra are shown in Fig. 5a and b, respectively. The S 2p spectrum of the sample exhibits a peak with a binding energy of 170.7 eV, which is attributed to S^{6+} species such as sulfate in $Al_2(SO_4)_3$, $CaSO_4$ and H_2SO_4 [18–20]. The O 1s spectrum shows a main peak at 534.2 eV, wide and with a half-height width above 3.8 eV, indicating that there is complicated circumstance related to oxygen. Generally, three oxygen-containing species exist on the V_2O_5/CNT catalyst, viz. metal oxides (V_2O_5), carbon–oxygen functional groups, and

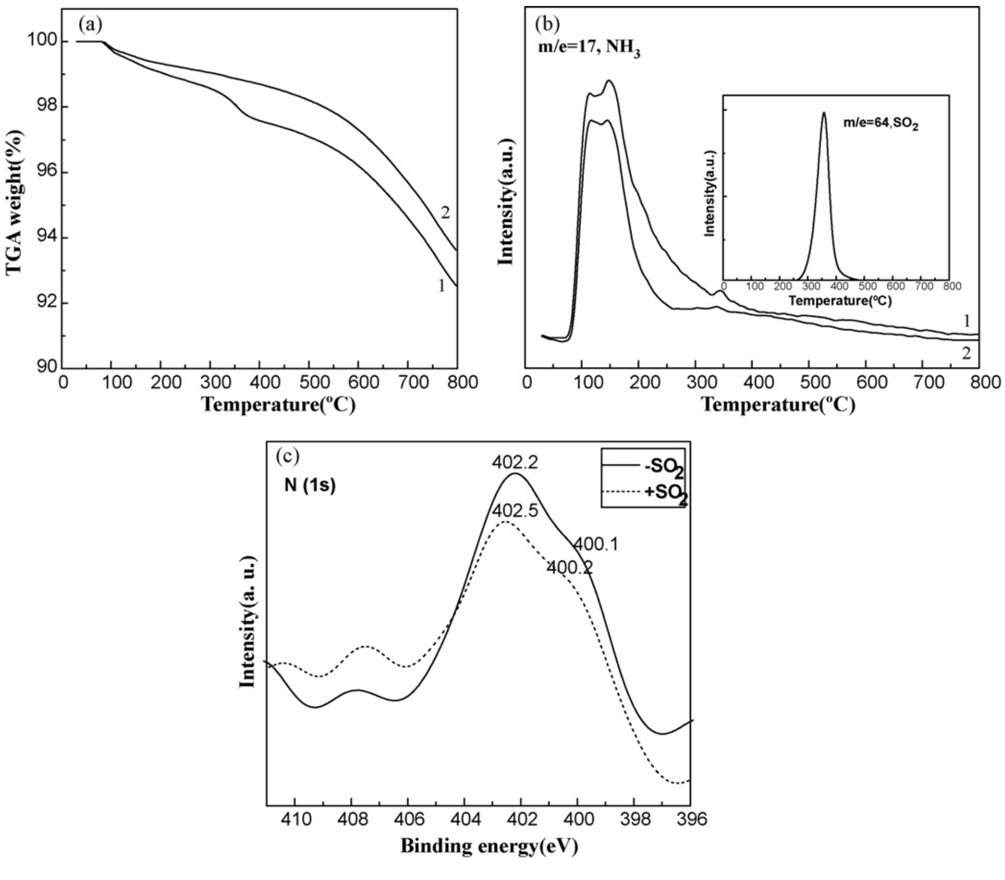

Fig. 6. TG curves (a) and NH_3-TPD profiles (b) of 1 wt% V_2O_5/CNT catalyst: (1) NH_3 desorption on catalyst pre-treated by $SO_2 + O_2$, (2) NH_3 desorption on fresh catalyst. The inset shows SO_2-TPD profiles. (c) N 1s XPS spectra of the 0.1 wt% V_2O_5/CNT catalyst after SCR reaction in the presence or absence of SO_2.

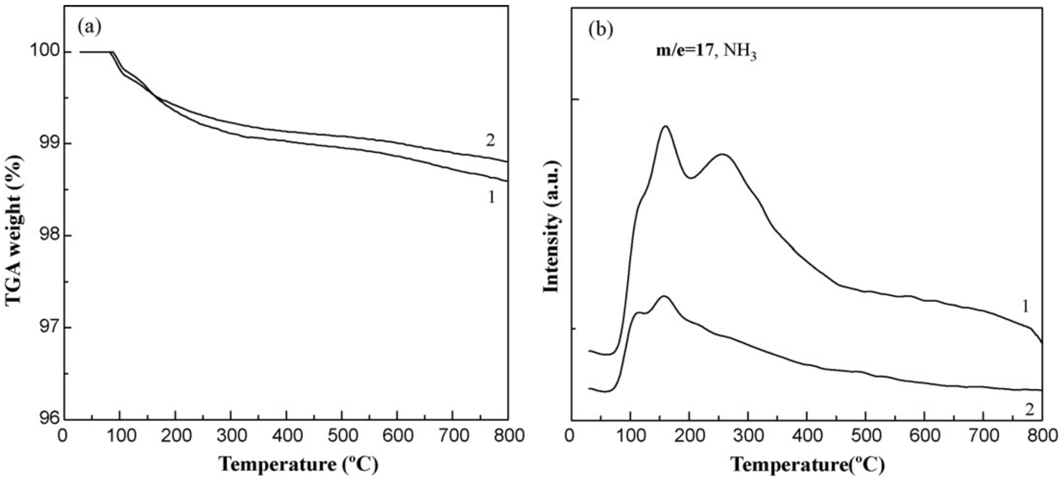

Fig. 7. TG curves (a) and NH_3-TPD profiles (b) of 1 wt% V_2O_5/TiO_2: (1) NH_3 desorption on catalyst pre-treated by $SO_2 + O_2$, (2) NH_3 desorption on fresh catalyst.

sulfur–oxygen species. The binding energy of O 1s in V_2O_5 is in the range of 529.8–530.9 eV [21,22], and that for carbon–oxygen is above 534.0 eV [23–25]. The main peak of the present sample locates at about 534.2 eV, attributed to sulfate oxygen [19,20,26]. Therefore, the XPS results show that the sulfur-containing species on the V_2O_5/CNT catalysts is SO_4^{2-}.

It is recognized that the SCR reaction proceeds between adsorbed ammonia and gas phase or weakly adsorbed NO [1,27], and we also confirmed this opinion in previous studies on the V_2O_5/AC catalysts [9]. Similarly, to observe the effect of SO_4^{2-} species formed on the catalyst surface on the adsorbed state of NH_3, TPD measurements were carried out on the non-sulfated and sulfated samples which pre-adsorbed with NH_3 at 30 °C. The normalized TPD profiles (MS signals) of NH_3 adsorbed on the 1 wt% V_2O_5/CNT catalyst before and after SO_2 adsorption are shown in Fig. 6b. It is clear that NH_3 desorption on the fresh 1 wt% V_2O_5/CNT catalyst shows two strong peaks centered at about 115 and 150 °C (LT) and a very weak peak centered at about 340 °C (HT), suggesting that there are at least two distinct NH_3 species on the catalyst surface. These species might be associated with the ammonium ions adsorbed on Brønsted acid V^{5+}–OH sites and the molecularly adsorbed ammonia through a Lewis-type interaction on coordinatively unsaturated cations, respectively, well identified by IR spectroscopy for other vanadia-based catalysts [28–32]. Since the Lewis-type NH_3 species is more thermally stable than the Brønsted-type ammonium ions [32], it can be deduced that the LT peaks are associated with NH_4^+ relating to the Brønsted acid sites, while the HT peak is attributed to molecular NH_3 corresponding to Lewis acid sites. The LT peaks are much larger than the HT peak, indicating that the main form of NH_3 adsorbed on fresh V_2O_5/CNT catalyst is NH_4^+. More importantly, the NH_3 desorption profiles of pre-sulfated V_2O_5/CNT catalyst (line 1) changes significantly in comparison with the curves of fresh catalyst (line 2). All the LT and HT peaks of NH_3 desorption increase highly, suggesting that the sulfate species on the pre-sulfated V_2O_5/CNT catalyst provide more acid sites (including Brønsted and Lewis acid sites) in favor of increasing the surface NH_3 species.

Thermogravimetric (TG) curves (Fig. 6a) corresponding to the MS curves in Fig. 6b provide quantitative information of the above conclusions. Weight loss of the pre-sulfated V_2O_5/CNT catalyst below 300 °C is about 1.4%, much higher than that (about 0.8%) of the fresh V_2O_5/CNT, suggesting that there are more NH_3 adsorbed on the pre-sulfated V_2O_5/CNT catalyst. Another significant weight loss of the pre-sulfated V_2O_5/CNT catalyst in 300–400 °C is attributed to the large amount of SO_2 released (confirmed by SO_2 desorption curve shown in inset of Fig. 6b). These results clearly indicate that the presence of surface sulfate species significantly increases the amount of NH_3 adsorption, which is the benefit to enhancing the SCR activity of the V_2O_5/CNT catalyst. TG (Fig. 7a) and MS (Fig. 7b) curves of V_2O_5/TiO_2 catalyst exhibit the NH_3 desorption behavior similar to that of the V_2O_5/CNT catalyst, except that the HT peak of NH_3 desorption centered at about 280 °C is greatly enhanced on the pre-sulfated catalyst (line 1 in Fig. 7b). The results suggest that on the V_2O_5/TiO_2 catalyst, surface sulfate species formed on catalyst surfaces also improve the adsorption of NH_3 significantly.

To further obtain the nature of the adsorbed NH_3 on catalyst surface, the reacted 0.1 wt% V_2O_5/CNT catalyst in the presence and absence of SO_2 were measured for XPS spectra (Fig. 6c). The N 1s spectra of both samples exhibit a main peak at 402.5 eV with a shoulder peaked at 400.1 eV. Since the binding energy of N 1s in NH_3 is in the range of 398.6–399.6 eV [33,34], while which in NH_4^+ of NH_4NO_3 is about 402.3 eV [35], the XPS results suggest that the nitrogen-containing species adsorbed on the V_2O_5/CNT catalysts are mainly NH_4^+ whether SO_2 is present or not in the reaction gas, only a small amount of molecularly ammonia adsorbed on catalyst surface. This is in agreement with the above NH_3-TPD conclusion. Moreover, the results provide further information that there are ammonium sulfate salts formed over the catalyst surface after SCR reaction in the presence of SO_2 [10].

3.3.2. *Behavior of NH_4HSO_4 on carbon surfaces*

The above results show that the sulfur species formed on catalysts can promote the adsorption of NH_3, forming ammonium sulfate salts, thus improving the SCR activity. A concomitant question is how to avoid the accumulation of ammonium sulfate salts, otherwise the deposited salts can block and deactivate the catalyst. There are two ways to avoid ammonium sulfate salts accumulation. One is to decompose the salts continuously, and the other is to consume the salts through reaction with other reactants. Since the fact is that SO_2 can promote the SCR activity of V_2O_5/CNT catalyst to a steady state, it means that the formed ammonium sulfate salts can be expended in a continuous way. Then, what is it?

TPDC investigations were first performed on the pure NH_4HSO_4 (a kind of ammonium sulfate species generally formed during SCR reaction) pre-deposited CNTs, V_2O_5, 1 wt% V_2O_5/CNT and 1 wt% V_2O_5/TiO_2 (for comparison) catalysts in order to explore the decomposition behaviors of the ammonium sulfate salts (Fig. 8). It is clear that the decomposition of pure NH_4HSO_4 starts at about 390 °C and reaches the highest rate at about 500 °C. When NH_4HSO_4

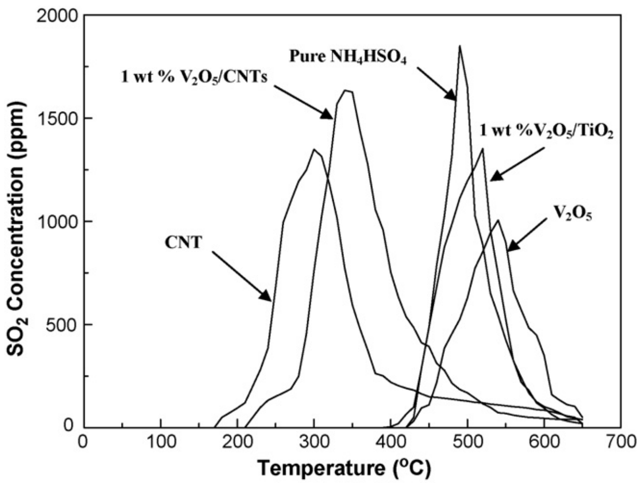

Fig. 8. TPDC profiles of NH_4HSO_4 deposited on various catalysts. Conditions: 100 ml/min Ar, heating rate of 10 °C/min, and 0.2 g catalysts with 0.086 mmol NH_4HSO_4.

is supported on V_2O_5, its decomposition temperature increases to 420 °C with a peak at 540 °C. NH_4HSO_4 decomposition on 1 wt% V_2O_5/TiO_2 catalyst starts at about 420 °C, and the peak temperature is at about 520 °C. In contrast, the decomposition temperature greatly decreases when NH_4HSO_4 is supported on CNTs, on which the SO_2 starts to evolve at about 170 °C with a peak at 300 °C. On the 1 wt% V_2O_5/CNT catalyst, the decomposition temperature is either low, with a peak temperature of 340 °C, which is only a little higher than that on the CNTs. These results indicate that the decomposition of NH_4HSO_4 is promoted by CNTs but inhibited by V_2O_5. Such a phenomenon is similar to our previous report on V_2O_5/AC catalysts after a SCR reaction in the presence of SO_2 [10], and has also been well established by Knoblauch et al. over activated cokes [36]. Since carbon materials can act as a reducing agent to reduce NH_4HSO_4 into SO_2 [10,36], the promoting effect of CNTs should also originate from their reducibility to NH_4HSO_4 at low temperatures. Moreover, the decomposition of NH_4HSO_4 on the V_2O_5/CNTs catalyst is much easier than that on the V_2O_5/TiO_2 catalyst. It can explain the different behaviors of the two catalysts in SCR reaction in the presence of SO_2. However, more importantly, the NH_4HSO_4 pre-adsorbed on the V_2O_5/CNT catalysts is not decomposed at the reaction temperature (250 °C), indicating that the decomposition of ammonium sulfate salts is not the real reason for the SCR behavior of the catalysts in the presence of SO_2 at low temperatures.

Another possible way is to consume the ammonium sulfate salts through reacting with the NO in the flue gas. What about it? Fig. 9 shows the temperature-programmed surface reaction (TPSR) of NO and NH_4SO_4 pre-deposited on the 1 wt% V_2O_5/CNT catalyst and the 1 wt% V_2O_5/TiO_2 catalyst, in which the change of NO concentration is used to express the reaction process and the reactivity of NH_4HSO_4. Clearly, the reaction of NO and NH_4HSO_4 starts slowly at about 100 °C, and dominantly at about 160 °C, then the reaction gets faster with increasing temperature for the V_2O_5/CNT catalyst. NO concentration becomes zero when the temperature increases at about 260 °C, indicating that the NO in the feed is fully reacted by the ammonium ions. Above 350 °C, NO concentration gradually increases with increasing temperature due to an insufficient amount of ammonium ions left on the catalyst surface. As for the quick decrease of NO concentration at temperatures above 420 °C, it may originate from the reaction of NO with CO (or carbon), which is based on an observation that the concentration of O_2 and CO quickly decrease and increase at temperature above 400 °C, respectively (not shown). This result clearly indicates that the ammonium sulfate salts on the V_2O_5/CNT catalyst surface can react with NO at low temperatures. For comparison, the reaction of NO and NH_4HSO_4 on 1 wt% V_2O_5/TiO_2 catalyst needs higher temperatures (fast reacting >310 °C), clearly indicating that the NH_4HSO_4 reacts with NO more easily on the V_2O_5/CNTs surface than on the V_2O_5/TiO_2 surface. It explains well the fact that the V_2O_5/TiO_2 catalyst must be operated at temperatures above 330 °C to avoid catalyst deactivation caused by the deposition of ammonium sulfate salts, while the V_2O_5/CNTs catalyst is stable at 200–250 °C, but is deactivated by SO_2 at temperatures below 200 °C.

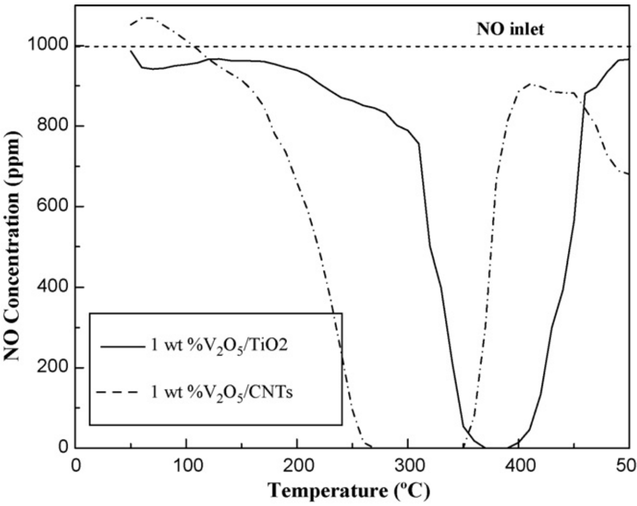

Fig. 9. TPSR profiles of NO reacting with NH_4HSO_4 deposited on 1 wt% V_2O_5/CNT and 1 wt% V_2O_5/TiO_2 catalysts. Reaction conditions: 1000 ppm NO + 5.0 vol% O_2 in Ar at 100 ml/min, heating rate of 10 °C/min, and 0.2 g samples containing 0.085 mmol NH_4HSO_4.

Therefore, it is believed that during the SCR reaction on the V_2O_5/CNTs surface in the presence of SO_2 at 220–250 °C, the formed sulfate species stays on the V_2O_5/CNT catalyst surface and acts as new acid sites for NH_3 adsorption and activation. Meanwhile, the ammonium ion reacts continuously with NO to avoid the formation and accumulation of excess ammonium sulfate salts on the catalyst surface, thus prohibiting the deactivation of the catalysts. This process effectively ensures that the V_2O_5/CNTs will be promoted but not poisoned by SO_2. The results are in agreement with our previous report on V_2O_5/AC catalysts [9]. For the V_2O_5/TiO_2 catalyst, however, the ammonium sulfate salts formed on the surface are not decomposed or react with NO at low temperatures (<350 °C), so are poisoned by SO_2.

3.4. Longevity of the V_2O_5/CNT catalyst in the presence of SO_2

Studies on the stability of the V_2O_5/CNT catalysts are very important from the theoretical and technical point of view. Fig. 10 shows the longevity of the 0.1 wt% V_2O_5/CNT catalyst in the presence of SO_2. It is clear that under the SO_2-containing conditions, the catalyst shows a high catalytic activity with a NO conversion maintaining at ca. 92% during a 100 h continuous running duration. More importantly, the catalyst deactivation was not observed in the entire operation time. This result indicates that the catalysts have a fairly well stability and SCR activity in the presence of SO_2, predicting an attractive prospect of the V_2O_5/CNT catalyst for practical applications.

4. Conclusions

Based on the above fact that SO_2 can be switched from a poison to a promoter on SCR activity for the V_2O_5/CNT catalyst at low temperatures, deep investigations on the mechanism of the SO_2 effect

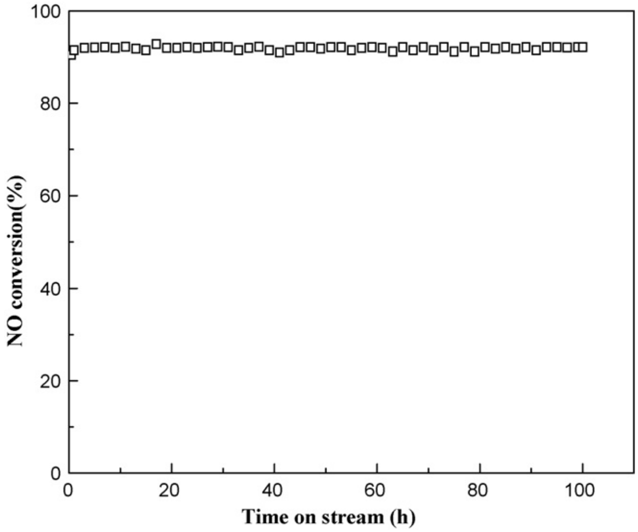

Fig. 10. A test of the stability of 0.1 wt% V_2O_5/CNT catalyst for the SCR reaction in the presence of SO_2. Reaction conditions: 450 ppm NO, 500 ppm NH_3, 5.0 vol% O_2, 400 ppm SO_2 (when used), balance Ar, and WHSV of 30,000 h^{-1}.

and the nature of carbon-based catalysts in the presence of SO_2 are studied in this work, and several major conclusions can be drawn as follows:

(1) The promoting effect of SO_2 on SCR activity of the V_2O_5/CNT catalyst depends both on the reaction temperature and the V_2O_5 loading. The reaction temperature acts as a switch that can turn on and off the poisoning reactions. SO_2 does not poison the catalysts but significantly promotes their activities when V_2O_5 loading is lower than 1 wt%.

(2) The promoting effect of SO_2 on the SCR activity of the V_2O_5/CNT catalyst is due to the formation of sulfate species on the catalyst surface, and the ammonium ions exist on the catalysts surface mainly as NH_4^+ adsorption state, hence promote the SCR activity of the catalyst.

(3) The decomposition of NH_4HSO_4 is significantly promoted by the CNTs but slightly inhibited by V_2O_5, thus the decomposition of NH_4HSO_4 is easier on the V_2O_5/CNTs catalyst than on the V_2O_5/TiO_2 catalyst.

(4) NH_4HSO_4 on the V_2O_5/CNT catalyst surface can react with NO continuously to avoid the formation and accumulation of excess ammonium sulfate salts on catalyst surface at low temperatures (<250 °C), which effectively leads the V_2O_5/CNT catalyst to being promoted but not poisoned by SO_2. For the V_2O_5/TiO_2 catalysts, however, the formed ammonium sulfate salts on the catalyst cannot react with NO at low temperature (<330 °C), so are poisoned by SO_2.

Acknowledgement

This work is supported by Nature Science Foundation of China under grant Nos. 20673135 and 20473109.

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