Decomposition and Reactivity of NH_4HSO_4 on V_2O_5/AC Catalysts Used for NO Reduction with Ammonia

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The decomposition and reactivity of NH_4HSO_4 deposited or *in situ* formed on various V_2O_5/AC and V_2O_5/TiO_2 catalysts are studied in detail using a temperature-programmed method. The results are correlated directly with the behavior of the catalysts in the NO reduction with NH_3 in the presence of SO_2. The decomposition and reaction of NH_4HSO_4 are easier on the V_2O_5/AC catalysts than on the V_2O_5/TiO_2 catalysts. On the V_2O_5/AC catalysts, the decomposition and reactivity of NH_4HSO_4 are greatly dependent upon V_2O_5 loading, the temperatures for the decomposition, and reaction increase with increasing V_2O_5 loading. Most of the NH_4HSO_4 deposited on the V_2O_5/AC can react with NO at 250°C when V_2O_5 loading is below 5 wt%. The reactivity of NH_4HSO_4 with NO, other than its decomposition, is associated with the behavior of the catalysts for the SCR reaction in the presence of SO_2. During the SCR reaction on the V_2O_5/AC catalysts of low V_2O_5 loading in the presence of SO_2, the formed sulfate species stay on the catalyst surface and act as acid sites for NH_3 adsorption. Simultaneously, the ammonium ions react continuously with NO to avoid the surface deposition of excess ammonium–sulfate salts. Such a process effectively ensures the catalyst being promoted but not poisoned by SO_2. The interaction between the AC and vanadium species results in synergism in the activation and reaction of ammonium ions linked to sulfate species. A bridge-type activated ammonia species is proposed and discussed. © 2000 Academic Press

INTRODUCTION

Commercial V_2O_5/TiO_2 or V_2O_5–WO_3/TiO_2 catalysts for selective catalytic reduction (SCR) of NO with NH_3 must be used at temperatures above 330°C to avoid pore plugging from the deposition of ammonium–sulfate salts such as NH_4HSO_4 and $(NH_4)_2S_2O_7$ on the catalyst surface (1), which are formed by SO_2 oxidation and subsequent reaction with NH_3 and H_2O at lower temperatures. A low-temperature SCR process is believed to have low-energy consumption and to be economical for retrofitting into the existing units for flue gas cleaning (2, 3). The key to development of the low-temperature SCR process is SCR catalysts

of high resistance to SO_2 poisoning because the formation of the ammonium–sulfate salts on the catalyst surface is serious at low temperatures.

We recently reported an activated carbon supported vanadium oxide (V_2O_5/AC) catalyst that shows high activities for the SCR reaction and good tolerance to SO_2 poisoning at temperatures of 180–250°C (4–7). The catalytic activity is significantly promoted by SO_2, and the promoting effect and the catalyst stability in the presence of SO_2 are critically dependent upon V_2O_5 loading and reaction temperature (5, 6). At V_2O_5 loadings of less than 5 wt% and temperatures of higher than 180°C, the promoting effect of SO_2 is significant and the catalyst is stable. But at higher V_2O_5 loadings and lower temperatures, the promoting effect of SO_2 disappears, and the catalyst deactivation becomes serious with increasing V_2O_5 loading and decreasing temperature. FTIR, XPS, XAFS, and EDX studies (7) have shown that the promoting effect of SO_2 is due to the formation of sulfate species on the carbon surface (other than vanadium surface), which may provide new sites for NH_3 adsorption and activation.

However, some crucial aspects of the V_2O_5/AC catalyst behavior remain unclear. (a) It is believed that the sulfate species formed on the V_2O_5/AC catalyst surface will react with NH_3 to form ammonium–sulfate salts during the SCR reaction. Since the pure salts are difficult to decompose at the reaction temperatures used (180–250°C), it is important to clarify why the ammonium–sulfate salts do not deactivate the V_2O_5/AC catalyst and whether the support AC promotes their decomposition or reaction. (b) If the ammonium–sulfate salts decompose through carbon catalysis during the SCR reaction, then what is the role of the sulfate species in improving the catalytic activity? (c) The cause of the effects of V_2O_5 loading and reaction temperature on the SO_2 promotion and catalyst stability needs to be understood.

These questions will be studied and discussed in this work. At present, little information is available in the literature on the decomposition or reaction of the ammonium–sulfate salts on the SCR catalyst, even in the abundant studies on the V_2O_5/TiO_2 and V_2O_5–WO_3/TiO_2 catalysts (8, 9).

Shikada *et al.* (8) reported that NH$_4$HSO$_4$ reacts with NO in a molten salt of NH$_4$HSO$_4$/NaHSO$_4$ and V$_2$O$_5$. Kasaoka *et al.* (9) showed that NH$_4$HSO$_4$ and (NH$_4$)$_2$SO$_4$ mechanically mixed with V$_2$O$_x$/TiO$_2$ (4 < x < 5) can react with NO at about 130°C. However, there was no detailed information on the effect of reaction temperature and the behavior of the added sulfate species in the reaction, which may be very important for understanding the deactivation of the V$_2$O$_5$/TiO$_2$ catalyst poisoned by SO$_2$ at temperatures below 330°C. Therefore, the V$_2$O$_5$/TiO$_2$ catalyst is also studied and discussed in this work for better understanding of the V$_2$O$_5$/AC catalyst.

For the purposes mentioned above, NH$_4$HSO$_4$ was deposited on the surfaces of V$_2$O$_5$/AC and V$_2$O$_5$/TiO$_2$ catalysts, and its decomposition and reaction with NO were studied in detail using a temperature-programmed method. The decomposition of sulfate species *in situ* formed on the V$_2$O$_5$/AC surface during the SCR reaction or SO$_2$ oxidation was also studied to see whether the deposited NH$_4$HSO$_4$ represents those formed in the actual reaction. These studies are also useful for evaluation of NH$_4$HSO$_4$ or other ammonium salts deposited on the V$_2$O$_5$/AC catalyst as a replacement for NH$_3$ as the reducing agent for NO removal from flue gases.

EXPERIMENTAL

Catalyst Preparation and NH$_4$HSO$_4$ Deposition

The support, activated carbon (AC), was prepared from a commercial coal-derived semicoke (Datong Coal Gas Co., China) through steam activation at about 900°C. The burn-off during the activation was about 37 wt%. Before use or catalyst preparation, the AC was preoxidized with concentrated HNO$_3$ (3 ml/g of AC) at 60°C for 1 h, followed by filtration, complete washing with distilled water, and drying at 120°C for 5 h. The physical characteristics of the AC before and after HNO$_3$ oxidation were measured by N$_2$ adsorption at 77 K and are presented in Table 1. The V$_2$O$_5$/AC catalysts were prepared by pore volume impregnation of the HNO$_3$-oxidized AC (particle size, 28–60 mesh) with an aqueous solution of ammonium metavanadate in oxalic acid. The V$_2$O$_5$ loadings in the catalysts were determined

TABLE 1

The Physical Characteristics of the Different Catalysts

Catalyst	BET surface area (m^2/g)	Micropore area (m^2/g)	Pore volume (ml/g)	Micropore volume (ml/g)
Original AC	647	486	0.338	0.229
HNO$_3$–oxidized AC	560	432	0.287	0.204
5 wt% V$_2$O$_5$/AC	545	411	0.265	0.182
5 wt% V$_2$O$_5$/TiO$_2$	95			

Note. Measured by N$_2$ adsorption at 77 K.

by the amount of ammonium metavanadate used. The impregnated catalysts were dried at 50°C overnight and then at 120°C for 5 h followed by calcination in Ar at 500°C for 8 h and preoxidization in air at 250°C for 5 h. For the 5 wt% V$_2$O$_5$/AC catalyst, BET surface area and the pore volume were measured and are listed in Table 1.

A 5 wt% V$_2$O$_5$/TiO$_2$ catalyst is used for comparison with the V$_2$O$_5$/AC catalysts. It was prepared by combustion of mixed TiCl$_4$, NH$_4$VO$_3$, and urea, having a BET surface area of about 95 m^2/g. The catalyst showed high activity and stability for the SCR reaction in the presence of SO$_2$ at 350°C (10).

The NH$_4$HSO$_4$-deposited catalysts were prepared by impregnation of 1 g of catalyst with 1 ml of 0.86 mol/L aqueous solution of NH$_4$HSO$_4$, followed by drying in air at 110°C for 5 h.

Measurements of Decomposition and Reactivity of NH$_4$HSO$_4$ Deposited on the Catalysts

Temperature-programmed decompositions (TPDC) of NH$_4$HSO$_4$ deposited on the catalysts were carried out in a tubular quartz reactor with 8-mm i.d. and 300-mm length in an Ar stream of 300 ml/min. The reactor, containing 0.2 g of NH$_4$HSO$_4$-deposited catalyst, was heated from 30 to 650°C at a rate of 10°C/min. Exiting SO$_2$ was monitored during the process and for diagnosing the NH$_4$HSO$_4$ decomposition.

The reactivity of NH$_4$HSO$_4$ deposited on the catalysts was measured using a temperature-programmed surface reaction (TPSR) with NO. First, 0.2 g of NH$_4$HSO$_4$-deposited catalyst was exposed to a stream containing about 1000 or 540 ppm NO, 3.3 vol% O$_2$, and balance Ar at a total flow rate of 300 ml/min. Then the temperature was ramped from 30 to 480°C at a heating rate of 10°C/min or kept constant at 250°C. Exiting NO and SO$_2$ were monitored during the TPSR. The amount of NO removed was used to estimate the reactivity of ammonium ions in NH$_4$HSO$_4$.

During the TPDC and TPSR processes, effluent gases were continuously analyzed using an on-line flue gas analyzer (KM9006 Quintox, Kane-May International Limited Co.). The analyzer was equipped with NO, NO$_2$, SO$_2$, CO, and O$_2$ sensors and thus makes it possible to analyze these gases simultaneously (this analyzer was also used in all the experiments mentioned below.) It should be pointed out that the detected SO$_2$ signal includes also that of SO$_3$.

Decomposition of in Situ Formed Ammonia and Sulfate Species

To understand the real behavior of the sulfate species formed, the SCR reaction in the presence of SO$_2$ or SO$_2$ oxidation (or adsorption) was performed at 250°C. First, 0.2 g of catalyst was exposed to feed gases containing 500 ppm NO, 560 ppm NH$_3$, 3.3 vol% O$_2$, and 400 ppm SO$_2$ in Ar for the SCR reaction or 1000 ppm SO$_2$ and 3.3 vol% O$_2$ in Ar

for SO_2 oxidation. The total flow rate was 300 ml/min for both experiments. When the SCR reaction or SO_2 oxidation reached steady states or equilibrium, reactive gases were then removed from the feed; Ar flow was kept to purge the physically adsorbed SO_2 at the same temperature for 1 h. After this, the TPDC of the *in situ* formed sulfate species was performed in an Ar stream of 300 ml/min from 250 to 650°C for an SCR reaction or to 580°C for SO_2 oxidation, at a heating rate of 10°C/min.

Transient Response Experiment of NH_3

To understand whether the sulfate species formed can improve ammonia adsorption or activation, transient response experiments were carried out at 220°C in the absence or presence of SO_2. First, 0.2 g of 1 wt% V_2O_5/AC catalyst was initially exposed to a stream containing 500 ppm NO, 560 ppm NH_3, and 3.3 vol% O_2 in Ar with or without 400 ppm SO_2, at a total flow rate of 300 ml/min. At steady state, NH_3 was then removed from the feed. NO concentration was continuously monitored during the subsequent process until a new steady state was reached. The amount and reactivity of ammonia species adsorbed on the catalyst surface could be estimated from the variation of NO concentration in the effluent.

RESULTS AND DISCUSSION

Decomposition of NH_4HSO_4 Deposited

Figure 1 shows the TPDC profiles of pure NH_4HSO_4 and that deposited on the support AC, V_2O_5, 5 wt% V_2O_5/AC,
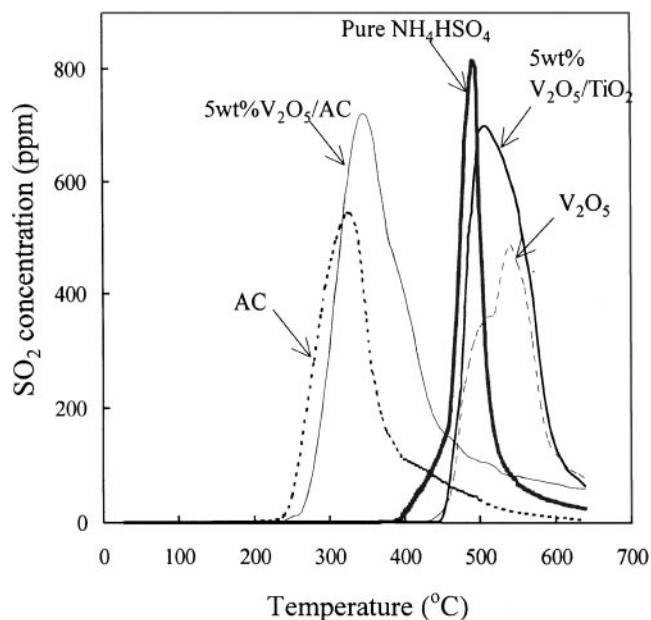

FIG. 1. TPDC profiles of NH_4HSO_4 deposited on various catalysts. Conditions: 300 ml/min Ar; heating rate of 10°C/min; 0.2 g catalysts with 0.17 mmol NH_4HSO_4.

and 5 wt% V_2O_5/TiO$_2$ catalysts. The SO_2 released during the TPDC is used to express the decomposition behavior of NH_4HSO_4. The decomposition of pure NH_4HSO_4 starts at about 390°C and reaches the highest rate at about 490°C. When NH_4HSO_4 is supported on V_2O_5, the decomposition temperature increases, and the evolved SO_2 shows a main peak at about 540°C and a shoulder at about 490°C. The latter may be attributed to the decomposition of NH_4HSO_4 not attached to V_2O_5. Similarly, on 5 wt% V_2O_5/TiO$_2$ catalyst, NH_4HSO_4 decomposition starts at about 450°C and peaks at about 510°C. In contrast, when NH_4HSO_4 is supported on the AC, the decomposition temperature greatly decreases, starts at 250°C, and peaks at 325°C. On the 5 wt% V_2O_5/AC catalyst, the decomposition temperature is also low, with a peak temperature of 345°C, which is only slightly higher than that on the AC.

These results indicate that the decomposition of NH_4HSO_4 is promoted by carbon but inhibited by V_2O_5. Carbon may act as a reducing agent to reduce NH_4HSO_4 into SO_2. Such a process has been well established (11–13). The AC, or activated coke, has been used as the catalyst and adsorbent for simultaneous removal of SO_x and NO_x from flue gas. During this process, NH_4HSO_4 (and/or $(NH_4)_2SO_4$ or H_2SO_4) is formed on the AC and is reduced by carbon into SO_2 in the AC regeneration step. In addition, the TPDC profile of NH_4HSO_4 deposited on the AC is similar to that observed by Knoblauch *et al.* (11) after a SCR reaction over activated coke in the presence of SO_2.

The decomposition of NH_4HSO_4 on the V_2O_5/AC is much easier than that on the V_2O_5/TiO$_2$ catalyst. It may be related to the different behaviors of the two catalysts in the SCR reaction in the presence of SO_2. The V_2O_5/TiO$_2$ catalyst gradually deactivates by the formation of ammonium–sulfate salts on the surface at temperatures below 330°C (1), although it shows high SCR activities in the absence of SO_2 at lower temperatures (1, 10). Indeed, the V_2O_5/TiO$_2$ catalyst can also be promoted by SO_2, but the reaction temperature must be more than 350°C (14, 15). On the other hand, the V_2O_5/AC catalyst, with low V_2O_5 loading, shows good SCR stability in the presence of SO_2 in the temperature range 180–250°C and is significantly promoted by SO_2 at the same temperatures (4–6).

Effect of V_2O_5 Loading on the Decomposition of Sulfate Species

Figure 2 shows the TPDC profiles of NH_4HSO_4 deposited on V_2O_5/AC catalysts with different V_2O_5 loadings. NH_4HSO_4 decomposition is greatly influenced by the amount of V_2O_5 on the carbon surface, and the decomposition temperature significantly increases with increasing V_2O_5 loading. In the cases of 1 and 3 wt% V_2O_5 on the AC, the TPDC show a single SO_2 release peak at about 340°C. For 5 wt% V_2O_5, in addition to the main peak at 345°C, a shoulder appears at about 400°C, which becomes a
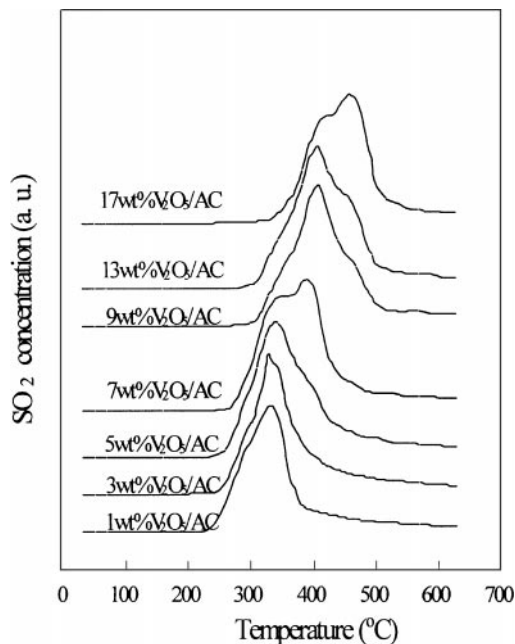
FIG. 2. Effect of V_2O_5 loading on the decomposition of NH_4HSO_4 deposited on the V_2O_5/AC catalysts. Experimental conditions are the same as in Fig. 1.

dominant decomposition peak for V_2O_5 loadings of 7 to 13 wt%. Moreover, at V_2O_5 loading of 17 wt%, the TPDC exhibits a main peak at about 460°C and a relatively weak peak at about 400°C.

To determine whether the sulfate species of the deposited NH_4HSO_4 is representative of those actually formed on the
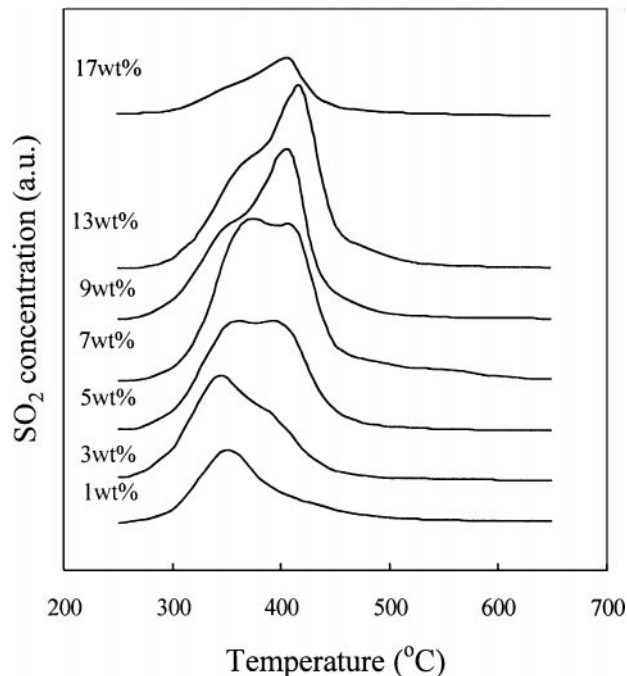
TABLE 2

SCR Activity[a] and BET Surface Area of Various V_2O_5/AC Catalysts

	V_2O_5 loading		TOF^b (NO conversion (%))	
wt%	BET SA (m^2/g)	$(\mu mol$ of $V^{5+}/m^2)$	without SO_2	with SO_2^c
0	560	0.00	(12.7)	(12.5)
1	576	0.19	2.72 (58.7)	4.32 (93.0)
3	564	0.58	1.15 (74.4)	1.35 (87.0)
5	545	1.01	0.74 (79.7)	0.80 (86.0)
7	519	1.48	0.52 (78.5)	0.51 (77.4)
9	433	2.28	0.41 (78.7)	0.38 (74.2)
13	446	3.20	0.29 (80.9)	0.25 (69.2)
17	396	4.72	0.18 (64.8)	0.16 (57.8)

[a] Test conditions: 500 ppm NO + 560 ppm NH_3 + 3.3% O_2 + 400 ppm SO_2 (when used), Ar balance, WHSV of 90,000 h^{-1}, 250°C.
[b] TOF: the turnover frequency of the V_2O_5/AC catalysts, expressed in units of moles of NO reacted per mole of V per second, [(mol of NO)/(mol of V)(s)] $\times 10^{-3}$.
[c] The values were collected after 4 h of reaction since the catalytic activity reaches a steady state in the period for the catalysts with low V_2O_5 loadings but decreases continuously with time for the catalysts with high V_2O_5 loadings.
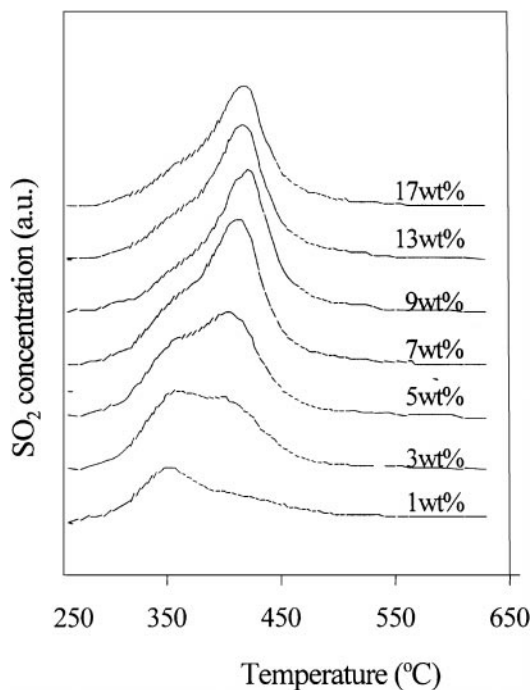

FIG. 3. TPDC profiles of sulfate species formed during the SCR reaction over the V_2O_5/AC catalysts in the presence of SO_2 at 250°C. Conditions: 300 ml/min Ar; heating rate of 10°C/min; 0.2 g sample.

catalyst, the SCR reaction in the presence of SO_2 and the SO_2 oxidation were carried out separately on the V_2O_5/AC catalysts with different V_2O_5 loadings at 250°C. Table 2 presents the SCR activities of the catalysts in the absence and presence of SO_2. After the SCR reaction in the presence of SO_2 and the SO_2 oxidation, TPDC of the sulfate species *in situ* formed on the catalyst surface were studied, and the results are shown in Figs. 3 and 4 for the SCR reaction and SO_2 oxidation, respectively. For the catalysts with V_2O_5/AC loadings of 1–5 wt%, the TPDC profiles of sulfate species formed during both the SCR reaction and the SO_2 oxidation are similar to that of NH_4HSO_4 deposited on them (Fig. 2). For the catalysts with V_2O_5/AC loadings of above 5 wt%, there are some differences in the SO_2-evolving temperatures, possibly as a result of the somewhat different chemical surroundings of the sulfate species, especially for SO_2 oxidation (no NH_4^+ links to sulfate species, and no H_2O exists during the oxidation.) However, in both situations, the overall dependence of the sulfate species decomposition on V_2O_5 loading is similar to that shown in Fig. 2. That is, the decomposition of the sulfate species formed on the V_2O_5/AC catalysts becomes more difficult with increasing V_2O_5 loading. This suggests that the sulfate species in the deposited NH_4HSO_4 can represent, to a good extent, those actually formed. These results confirm that the decomposition of the sulfate species is inhibited by V_2O_5. The oxidative property of V_2O_5 may depress the reduction of sulfate species by carbon.

FIG. 4. TPDC profiles of sulfate species formed during the SO₂ oxidation over the V₂O₅/AC catalysts in the presence of SO₂ at 250°C. Experimental conditions are the same as in Fig. 3.

We previously reported (5, 6) (Table 2) that the V_2O_5/AC catalysts with low V_2O_5 loadings (<5 wt%) are stable in the SCR reaction in the presence of SO_2 and significantly promoted by SO_2, while those with higher V_2O_5 loadings are deactivated by SO_2, and the deactivation becomes severe with increasing V_2O_5 loading. These observations seem to be associated with the dependence of NH_4HSO_4 (or other sulfate species) decomposition upon V_2O_5 loading. In other words, during the SCR reaction in the presence of SO_2, ammonium–sulfate salts formed on the catalysts of high V_2O_5 loading are difficult to decompose, resulting in a plugging catalyst pore structure and thus reduction in catalytic activity and stability. In contrast, those formed on the catalysts of low V_2O_5 loading are easy to decompose; thus, the catalyst surface is renewed continuously for constant activity.

However, this explanation cannot explain the following facts. (a) The decomposition of sulfate species deposited (or formed) on the 1 wt% V_2O_5/AC catalyst starts at about 250°C (see Figs. 2–4), but the catalyst activity is stable at lower temperatures such as 200°C for the SCR reaction in the presence of SO_2 (6). In a similar way, the V_2O_5/TiO₂ catalyst is stable in the presence of SO_2 at 350°C (1), although the decomposition of NH_4HSO_4 on the catalyst starts at about 425°C (see Fig. 1). (b) Previous studies (6, 7) showed that the promoting effect of SO_2 on the activities of the V_2O_5/AC catalysts with low V_2O_5 loadings is due to the formation of sulfate species on the carbon surface. Then, how

do we correlate the promoting effect based on the decomposition of the sulfate species. It may be that the decomposition of the sulfate species is not the actual reason for the behavior of the V_2O_5/AC catalysts in the presence of SO_2 at low temperatures. There may be other reasons associated with it.

Reactivity of Deposited NH₄HSO₄ with NO

Figure 5 shows the TPSR profiles of NO with NH_4HSO_4 in the pure state or deposited on AC or V_2O_5. The variation of NO concentration reflects the reactivity of NH_4HSO_4 in a different state. The reaction of pure NH_4HSO_4 with NO starts at about 390°C, as indicated by the decrease of NO concentration. The increasing reaction rate with increasing temperature shows that NH_4HSO_4 (0.2 g) is not consumed under the reaction conditions used. NH_4HSO_4 deposited on V_2O_5 shows complicated reaction behavior, including three distinguishable reaction stages, with a start at temperatures of about 200, 285, and 350°C. The former two reaction stages may be associated with the reactions of NH_4HSO_4 located at different sites of V_2O_5. The last reaction stage may be attributed to the reaction of NH_4HSO_4 in poor contact with V_2O_5 since the reaction temperature is somewhat similar to that in the case of pure NH_4HSO_4. This agrees with the results of NH_4HSO_4 decomposition on V_2O_5 in Fig. 1. NH_4HSO_4 deposited on the AC shows a two-staged reaction, with a start at about 180 and 260°C. Unlike the situation with V_2O_5, no additional reaction is observed, possibly due to complete dispersion of NH_4HSO_4 on the AC surface. Note that the decrease in NO concentration
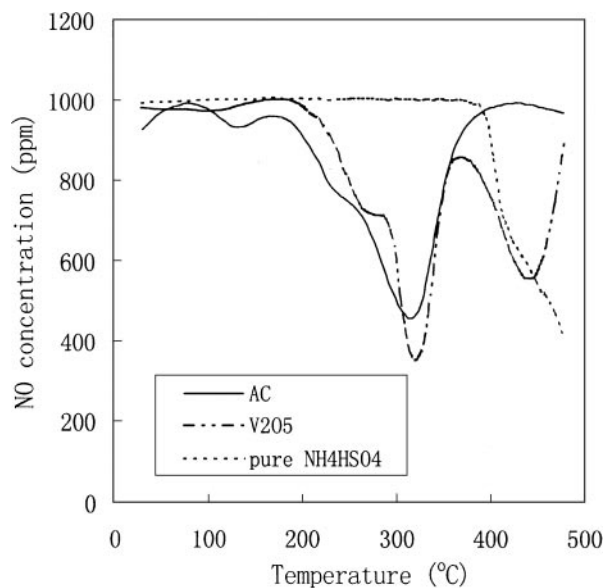

FIG. 5. TPSR profiles of NO with NH_4HSO_4 deposited on the AC and V_2O_5 with NO. Conditions: 1000 ppm NO + 3.3% O_2 in Ar at 300 ml/min; heating rate of 10°C/min; 0.2 g sample containing 0.17 mmol NH_4HSO_4 except for pure NH_4HSO_4.
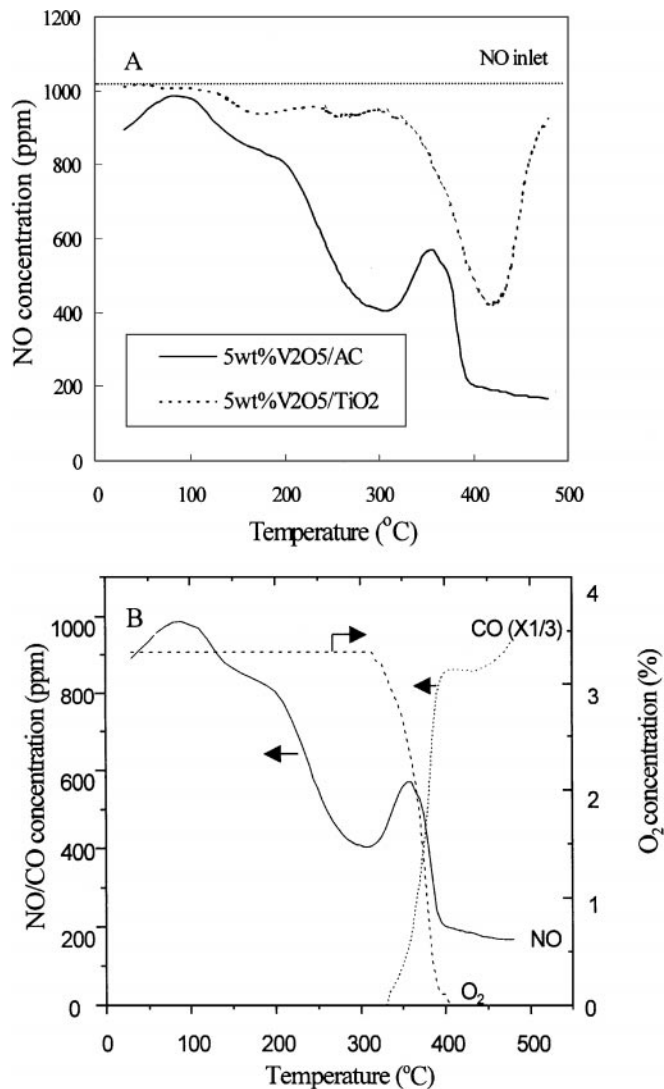
FIG. 6. (A) TPSR profiles of NO with NH$_4$HSO$_4$ deposited on 5 wt% V$_2$O$_5$/AC and 5 wt% V$_2$O$_5$/TiO$_2$ catalysts with NO. Reaction conditions are the same as those in Fig. 5. (B) O$_2$ and CO releases during the TPSR on 5 wt% V$_2$O$_5$/AC catalyst in (A).

below 100°C is attributed to NO adsorption on the AC surface. The change in the range of 100–180°C may be from NO adsorption on the vacant sites left by the evaporation of H$_2$O, which is expected to remain on the AC surface after the impregnation of NH$_4$HSO$_4$ and drying. A similar phenomenon is observed in the cases of V$_2$O$_5$/AC catalysts as shown below. Conclusively, these results suggest that both the AC and the V$_2$O$_5$ promote the reaction of NH$_4$HSO$_4$ and NO and that NH$_4$HSO$_4$ deposited on the AC is more active than that on V$_2$O$_5$.

Figure 6A shows the TPSR profiles of NO and NH$_4$HSO$_4$ deposited on the 5 wt% V$_2$O$_5$/TiO$_2$ and 5 wt% V$_2$O$_5$/AC catalysts. For the 5 wt% V$_2$O$_5$/TiO$_2$ catalyst, with increasing temperature, NO concentration is initially close to the inlet level and starts to decrease at about 120°C, but the

decrease is very small up to about 320°C. Above 320°C, the decrease is significant and yields a minimum value of NO concentration at about 425°C, which is followed by a gradual increase in NO concentration due to an insufficient amount of ammonium ions left on the catalyst surface. This suggests that on the 5 wt% V$_2$O$_5$/TiO$_2$ surface most of the ammonium ions in NH$_4$HSO$_4$ react with NO only at temperatures above 320°C. For the 5 wt% V$_2$O$_5$/AC catalyst, NO concentration is initially lower than the inlet level and gradually increases with increasing temperature up to 100°C, which may result from NO adsorption on the catalyst surface. From 100 to 480°C, there are three stages in the NO concentration profile. In the first stage (100–190°C), similar to the case of the AC (see Fig. 5), the gradually decreased NO concentration may be attributed to NO adsorption on the vacant sites left by the evaporation of H$_2$O. In the second stage (190–350°C), the decrease and then the increase of NO concentration show progressive reaction and consumption of ammonium ions on the catalyst surface. In the final stage (>350°C), the rapid decrease of NO concentration may result from additional NO reduction by CO (and/or directly by carbon at a higher temperature). This is strongly supported by the observation shown in Fig. 6B. When the temperature is increased to about 330°C, exiting O$_2$ concentration quickly decreases concomitant with a large amount of CO release. NO reduction with CO into nitrogen has been frequently studied on other catalysts (16–18). The TPSR profile of the support AC also shows the reaction between NO and NH$_4$HSO$_4$ at relatively low temperatures, although the peak temperature is slightly higher than that for the 5 wt% V$_2$O$_5$/AC catalyst. Moreover, unlike the 5 wt% V$_2$O$_5$/AC catalyst, the AC shows no obvious oxidation (or burning) by O$_2$ below 480°C. This suggests that the AC oxidation by O$_2$ for the 5 wt% V$_2$O$_5$/AC catalyst (and other catalysts studied below) is catalyzed by vanadium species and that the V$_2$O$_5$/AC catalyst should be used at temperatures below 330°C to avoid burning of the support AC.

Conclusively, the reaction of NO and NH$_4$HSO$_4$ on the 5 wt% V$_2$O$_5$/AC catalyst mainly starts at about 190°C, much lower than the 320°C for the 5 wt% V$_2$O$_5$/TiO$_2$ catalyst. This clearly indicates that the ammonium ion in NH$_4$HSO$_4$ reacts with NO more easily on the V$_2$O$_5$/AC surface than on the V$_2$O$_5$/TiO$_2$ surface. It explains well the fact that the V$_2$O$_5$/TiO$_2$ catalyst must be operated at temperatures above 330°C to avoid catalyst deactivation caused by deposition of ammonium sulfate salts (1), while the V$_2$O$_5$/AC catalyst is stable at 180–250°C, but is deactivated by SO$_2$ at temperatures below 180°C (6).

To understand the behavior of sulfate species in NH$_4$HSO$_4$ during the reactions shown in Fig. 6A, exiting SO$_2$ was also analyzed; the results are presented in Fig. 7. SO$_2$ release on the 5 wt% V$_2$O$_5$/AC catalyst starts at a much lower temperature than that on the 5 wt% V$_2$O$_5$/TiO$_2$ catalyst, which is similar to the observation of

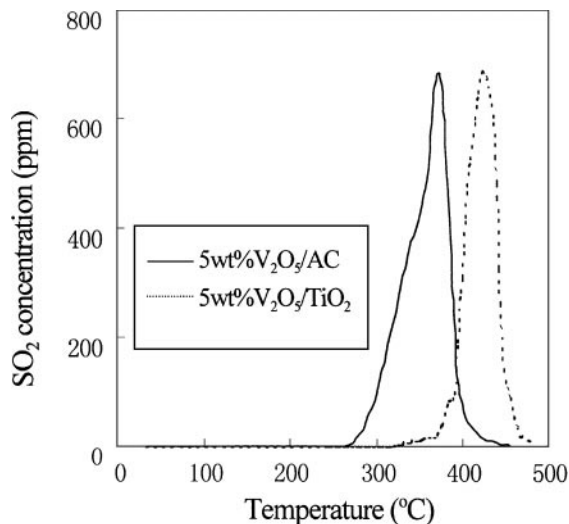**FIG. 7.** SO$_2$ release during the TPSR of NH$_4$HSO$_4$ deposited on 5 wt% V$_2$O$_5$/AC and 5 wt% V$_2$O$_5$/TiO$_2$ catalysts in Fig. 6A.

NH$_4$HSO$_4$ decomposition shown in Fig. 1. However, the SO$_2$ release on the V$_2$O$_5$/AC catalyst starts at a temperature (280°C) much higher than that (190°C) required by the reaction of NO and the deposited NH$_4$HSO$_4$ (see Fig. 6A). Similar results were also observed for other V$_2$O$_5$/AC catalysts with different V$_2$O$_5$ loadings. Therefore, it is believed that the sulfate species, formed on the V$_2$O$_5$/AC catalysts during the SCR reaction in the presence of SO$_2$ and at 180–250°C, stay on the catalyst surface and act as new acid sites for NH$_3$ adsorption and activation. At the same time, the ammonium ions react continuously with NO to prevent the formation and deposition of excess ammonium–sulfate salts on the catalyst surface. Such a process can effectively ensure the V$_2$O$_5$/AC catalyst being promoted but not poisoned by SO$_2$ as previously reported (6). This finding is further confirmed by the following observations.

Figure 8 shows a transient response of the SCR reaction on 1 wt% V$_2$O$_5$/AC catalyst in the presence and absence of SO$_2$, where NH$_3$ is removed from the feed at steady state. The steady state NO conversion is much higher in the presence of SO$_2$ than that in the absence of SO$_2$, which shows the promoting effect of SO$_2$ on the catalytic activity. When NH$_3$ is removed from the feed, NO conversion decreases from 63 to 8% in 30 min in the absence of SO$_2$ and from 85 to 8% in 60 min in the presence of SO$_2$. This indicates that more NH$_3$ is adsorbed on the catalyst surface during the SCR reaction in the presence of SO$_2$, which can be attributed to the contribution of the formed sulfate species. It also suggests that the ammonium ions linked to sulfate species can react with NO at temperatures as low as 220°C.

Effect of V$_2$O$_5$ Loading on the NH$_4$HSO$_4$ Reactivity

Figure 9 shows the effect of V$_2$O$_5$ loading on the reactivity of NH$_4$HSO$_4$ deposited on the V$_2$O$_5$/AC catalysts. It is

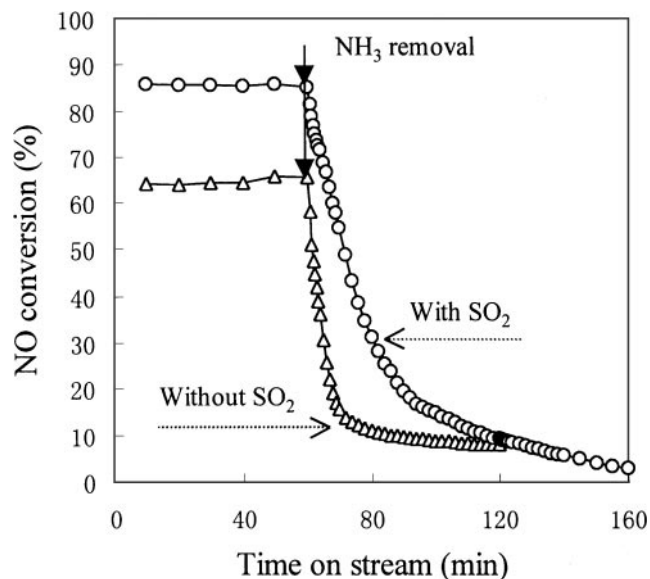**FIG. 8.** NH$_3$ transient response of the SCR reaction on 1 wt% V$_2$O$_5$/AC catalyst in the absence or presence of SO$_2$. Conditions: 500 ppm NO + 560 ppm NH$_3$ + 3.3% O$_2$ + 400 ppm SO$_2$ (when used); Ar balance; WHSV of 90,000 h^{-1}; 220°C, NH$_3$ removal from the feed at 60 min.

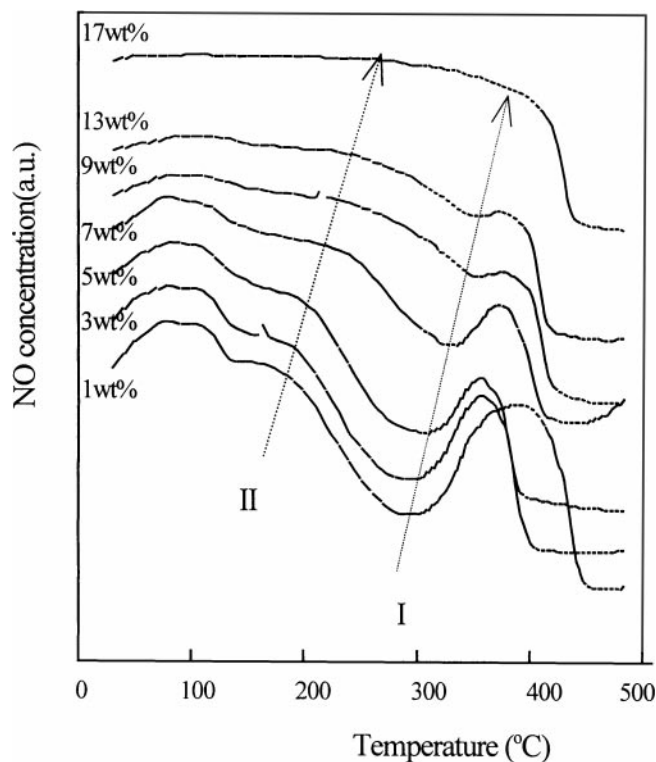**FIG. 9.** TPSR profiles of NH$_4$HSO$_4$ deposited on the V$_2$O$_5$/AC catalysts of different V$_2$O$_5$ loadings. Conditions: 1000 ppm NO + 3.3% O$_2$ in Ar at 300 ml/min; heating rate of 10°C/min; 0.2 g samples containing 0.17 mmol NH$_4$HSO$_4$.

found that the reactivity of NH_4HSO_4 is highly dependent on V_2O_5 loading. The NO consumption by ammonium ions, as shown by the arrow I, obviously decreases with increasing V_2O_5 loading, although the same amount of NH_4HSO_4 was deposited on these catalysts. Actually, on the 17 wt% V_2O_5/AC catalyst, only a little NO is removed by the deposited ammonium ions at temperatures below 400°C. The sharp decrease in NO concentration above 400°C (and the corresponding ones for the other catalysts) may result from the reaction between NO and CO as described above because CO is produced by carbon oxidation in this stage. For all the catalysts, the temperatures for the reaction initiation and the maximum reaction rate, as shown by arrows II and I, respectively, increase significantly with increasing V_2O_5 loading, from about 180 and 290°C for 1 wt% V_2O_5 to about 270 and 350°C for 13 wt% V_2O_5. These observations clearly indicate that the ammonium ions linked to the sulfate species react with NO more easily on the V_2O_5/AC catalysts at low V_2O_5 loadings than at high V_2O_5 loadings.

It is useful to estimate the amount of NH_4^+ ions that participated in the reaction with NO, but it is difficult based on the data in Fig. 9 because of the influence of CO–NO reaction in the temperature range. A special experiment was performed on 1 wt% V_2O_5/AC catalyst at a constant temperature of 250°C. The result is shown in Fig. 10 and compared with a blank experiment. The blank experiment was performed over a NH_4HSO_4-free 1 wt% V_2O_5/AC catalyst (actually a NO adsorption pattern), and the results showed that NO concentration reaches the inlet value at about
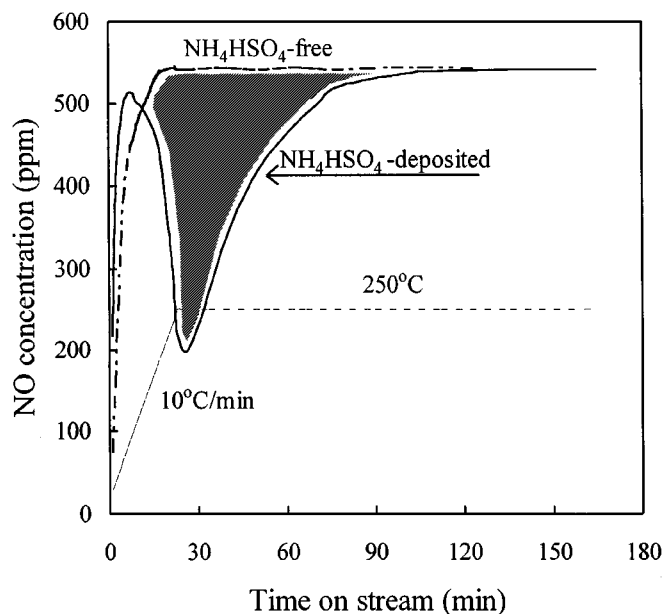
TABLE 3

Amount of NH₄HSO₄ Reacted on Various Catalysts during the Reaction with NO at 250°C

Catalyst		Amount of deposited NH_4HSO_4 (mmol)	Amount of reacted NH_4^+		
			(mmol)	(mmol/m²) × 10⁻³	%
1 wt %					
V_2O_5/AC	(0.2 g)	0.17	0.140	1.22	82.4
AC	(0.2 g)	0.17	0.053	0.47	31.2
V_2O_5	(0.2 g)	0.17	0.037	—	21.8

Note. Procedure and conditions are the same as those in Fig. 10.

145°C and that the amount of NO adsorbed in the period is about 0.025 mmol/g. In the case of the NH_4HSO_4-deposited catalyst, NO concentration increases more quickly in the initial temperature-raised period, indicating that NO adsorption decreases possibly due to some sites for NO adsorption being covered by the deposited NH_4HSO_4. These results are in agreement with those from isothermal NO adsorption (19), which showed that the presence of 1 wt% V_2O_5 greatly reduces NO adsorption on the AC surface and that the NO adsorption is further reduced when the sulfate species is present on the 1 wt% V_2O_5/AC catalyst surface. When the temperature reaches about 90°C, the reaction between NH_4HSO_4 and NO starts over and this results in decreased NO concentration. Calculation of the shaded area reveals that the amount of NO consumed is 0.14 mmol (Table 3). If the stoichiometric ratio of NH_4^+/NO (or NH_3/NO) is 1 as measured by many authors on vanadia-based catalysts (1, 20, 21), the amount of NH_4^+ that participated in the reaction is 0.14 mmol. This value is somewhat close to the amount (0.17 mmol) of NH_4HSO_4 deposited on the catalyst. The difference may arise from experimental errors and/or the escape of NH_3 from reacting with NO. This result suggests that on the V_2O_5/AC catalysts with low V_2O_5 loadings, nearly all ammonium ions linked to the sulfate species can participate in the reaction with NO.

Previously, we reported that during the SCR reaction, in the presence of SO_2 and at 250°C, the V_2O_5/AC catalysts with V_2O_5 loadings of 1–5 wt% show stable and high activities, while those with V_2O_5 loadings above 7 wt% are gradually deactivated with reaction time, and the deactivation rate increases with increasing V_2O_5 loading (5, 6) (Table 2). These observations are consistent with the findings described above. For the V_2O_5/AC catalysts with low V_2O_5 loadings (1–5 wt%), the ammonium ions that formed on the catalyst surface are continuously removed through reaction with NO, which effectively restricts the formation and deposition of excess ammonium–sulfate salts and thus results in stable activity. For the V_2O_5/AC catalysts with high V_2O_5 loadings (>7 wt%), however, the ammonium–sulfate salts formed are difficult to react with NO, which

FIG. 10. Reaction of NO and NH_4HSO_4 deposited on 1 wt% V_2O_5/AC catalyst at 250°C. Conditions: 540 ppm NO + 3.3% O_2 in Ar at 300 ml/min; heating rate of 10°C/min; 0.2 g catalyst with or without 0.17 mmol NH_4HSO_4.

results in accumulation of the salts on the catalyst surface and deactivation of the catalysts. The reaction (or deactivation) mechanism presented so far can be further extended to explain the deactivation of the V_2O_5/AC catalysts of high V_2O_5 loadings at high temperatures. Although NH_4HSO_4 can react with NO at 250°C on 7 wt% V_2O_5/AC catalyst, as shown in Fig. 9, the reaction rate may still be lower than its formation rate. In addition, the oxidation rate of SO_2 over V_2O_5 and dispersed vanadium species should be quite different and this should have an impact on the formation rate of the ammonium–sulfate salts. To delineate whether the influence is respondent to the distinguished activity and stability of the V_2O_5/AC catalysts with different V_2O_5 loadings, XRD analyses were performed on the catalysts but the results showed no signal about any form of vanadium species, even that of the 17 wt% V_2O_5/AC catalyst.

Role of the AC and Vanadia in the Reaction of NH_4HSO_4 with NO

It is important to understand the roles of the AC and vanadium species in the activation and reaction of ammonium ions linked to sulfate species on the V_2O_5/AC catalyst surface. As shown in Fig. 5, both the AC and V_2O_5 promote the reaction of NH_4HSO_4 and NO, but the reaction profiles exhibit turning points at about 260 and 285°C, respectively. This suggests that there are at least two types of ammonium ions on both AC and V_2O_5, and one is more active than the other. To verify this, reaction of NO and NH_4HSO_4 deposited on the AC and V_2O_5 was performed at 250°C under the same conditions as those shown in Fig. 10. The results (see Table 3) showed that only 31 and 22% of NH_4HSO_4 deposited on the AC and V_2O_5, respectively, participated in the reaction with NO at 250°C. On the other hand, as shown in Fig. 9, the TPSR profiles for the V_2O_5/AC catalysts with V_2O_5 loadings of 1–5 wt% exhibit no turning point in the range of 180–300°C. The temperatures at the maximum reaction rates (280–300°C) are slightly lower than those for both the AC and V_2O_5 (315°C and 320 respectively; see Fig. 5.) Moreover, about 82% of NH_4HSO_4 deposited on the 1 wt% V_2O_5/AC catalyst is consumed in the reaction with NO as shown in Fig. 10 and Table 3.

These results suggest synergism between the AC and vanadium species in the activation and reaction of ammonium ions linked to sulfate species on the V_2O_5/AC catalyst at low V_2O_5 loadings. The synergism may result from the formation of specific activated ammonia species, which is associated with both AC (carbon) and vanadium species as proposed in Fig. 11a. The ammonium ion is linked to both sulfate species and adjacent vanadium species (such as V=O) in a bridge-type structure in which the sulfate species is located at the carbon site. Therefore, the ammonium ion is activated indirectly by carbon and directly by vanadium, and thus shows high reactivity with NO. This proposition is supported by suggestions of other au-
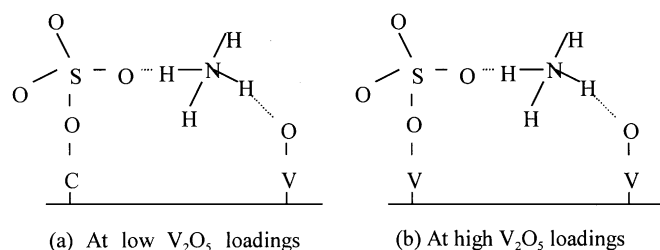

(a) At low V_2O_5 loadings   (b) At high V_2O_5 loadings

FIG. 11. Proposed structures of activated ammonia–sulfate species on the V_2O_5/AC catalyst with different V_2O_5 loadings.

thors. Wachs and co-workers (22, 23) proposed that on the V_2O_5/TiO_2 catalyst a couple of nearby sites are needed for the adsorption and reaction of ammonia. Inomata and co-workers (21, 24, 25) suggested that during the SCR reaction on the V_2O_5/TiO_2 catalyst in the presence of oxygen, an activated ammonia complex, $V-O-H-NH_3\cdots O=V$, is formed. On the basis of *in situ* FTIR studies, Topsøe and co-workers (26–28) proposed an activated ammonia complex of $V^{5+}-O^-\cdots{}^+H_3N\cdots H-O-V^{4+}$. Similarly, in both the activated ammonia complexes, two vanadium sites are linked to an ammonium ion. In the present proposition for the V_2O_5/AC catalyst, sulfate species linked to carbon replaces the V–OH and acts as a Brønsted acid site for NH_3 adsorption and activation. Additionally, such a proposition is in agreement with some other experimental observations. (a) The activities of the V_2O_5/AC catalysts with low V_2O_5 loadings (1–5 wt%) are significantly promoted by SO_2 (5, 6) (Table 2), and the SO_2 promotion is associated with the formation of sulfate species on the carbon site rather than on vanadium site (7). (b) Sulfuric acid modification greatly enhances NH_3 adsorption and SCR activity on activated carbon (or coke) (29) (Table 4), but the resulting activity is much lower than that on the V_2O_5/AC catalyst in the presence of SO_2 (Table 4). (c) The decomposition of NH_4HSO_4 deposited or *in situ* formed on the V_2O_5/AC catalysts of low V_2O_5 loadings (1–5 wt%) is rather similar to that on the AC (Figs. 1–3).

TABLE 4

SCR Activities of Various Catalysts at 250°C

Catalyst	WHSV (h^{-1})	NO conversion (%)	
		without SO_2	with SO_2
AC	36,000	31.2	—
	90,000	12.7	12.5
Sulfate-modified AC[a]	36,000	73.6	—
	90,000	36.1	—
1 wt%V_2O_5/AC	36,000	98.3	100
	90,000	58.7	93

Note. Feed: 500 ppm NO + 560 ppm NH_3 + 3.3% O_2 + 400 ppm SO_2 (when used), Ar balance.

[a] Sulfate modification by pore volume impregnation of 2 mol/l H_2SO_4 solution followed by drying at 120°C for 5 h, 2 mmol of H_2SO_4/g of AC.

On the other hand, when V$_2$O$_5$ loading is 7 wt% or more, most of the sulfate species deposited may locate on vanadium sites instead of on carbon sites. The resulting ammonia species, as shown in Fig. 11b, may be less active than that shown in Fig. 11a at low temperatures (<250°C). This is supported by some experimental facts. (a) The V$_2$O$_5$/AC catalysts with high V$_2$O$_5$ loadings (>7 wt%) are not promoted but deactivated by SO$_2$ during the SCR reaction at 250°C (5, 6) (Table 2). (b) The decomposition of NH$_4$HSO$_4$ is promoted by AC but inhibited by V$_2$O$_5$ (Fig. 1). With increasing V$_2$O$_5$ loading, NH$_4$HSO$_4$ deposited on the V$_2$O$_5$/AC catalysts becomes difficult to decompose (Fig. 2) and to react with NO (Fig. 9), especially when the V$_2$O$_5$ loading is over 7 wt%. (c) Most of the NH$_4$HSO$_4$ deposited on V$_2$O$_5$ is not reactive with NO at 250°C (Table 3).

Note that the results and discussions presented above seem to suggest that the AC surface is completely covered by vanadium species at a V$_2$O$_5$ loading of 7 wt%. This disagrees with the results of other authors. On the basis of density calculation, Roozeboom *et al.* (30) showed that a surface density of vanadia is about 9.5 V^{5+}/nm^2 for vanadia crystals. For a catalyst with a surface area of 400 m^2/g this would correspond to a monolayer V$_2$O$_5$ loading of 56 wt%. However, compared with this value, the V$_2$O$_5$ loadings of the studied catalysts are rather low (see Table 2). A possible reason for the great difference may be that only small fractions of the AC surface (or carbon sites) contribute to supporting vanadia. This fraction of the surface may be completely covered by vanadium species at V$_2$O$_5$ loading of 7 wt%. This is supported by the data presented in Table 1. The AC was prepared by stream activation and shows a large fraction of micropore, which might not contribute to supporting vanadia since the precursor of vanadia, a complex of ammonium metavanadate and oxalic acid, is very large in size.

In addition, for the different reactivity of NH$_4$HSO$_4$ with NO over the AC, V$_2$O$_5$, V$_2$O$_5$/AC, and V$_2$O$_5$/TiO$_2$, one could question whether it may not be due to the difference in the chemical properties of the supports but due to the difference in the surface areas since a large surface area support may be able to better disperse NH$_4$HSO$_4$. This conjecture is consistent with some of the results described above but is contrary to the others as follows. (a) The surface areas of the AC and the 1 wt% V$_2$O$_5$/AC catalyst are quite close (see Table 2), but the reactivity of NH$_4$HSO$_4$ supported on them is significantly different. The amount of the reacted NH$_4$HSO$_4$ per square meter for 1 wt% V$_2$O$_5$/AC is about 2.5 times larger than that for the AC (see Table 3). (b) NH$_4$HSO$_4$ supported on V$_2$O$_5$ is more active than that supported on the 5 wt% V$_2$O$_5$/AC catalyst at low temperatures (see Figs. 5 and 6A), but the surface area of V$_2$O$_5$ (chemical reagent) is estimated to be lower than that of the 5 wt% V$_2$O$_5$/TiO$_2$ catalyst. (c) Although the AC has a large surface area (560 m^2/g), the SCR reaction rate over it shows a progressive decrease with time in the presence of SO$_2$ (6),

suggesting pore plugging by the formed ammonium–sulfate salts (12). Therefore, the different reactivities of NH$_4$HSO$_4$ with NO over the catalysts are believed to originate mainly from the difference in the chemical properties of the catalysts, although a contribution of surface area is also possible.

The high reactivity of NH$_4$HSO$_4$ on the V$_2$O$_5$/AC catalysts of low V$_2$O$_5$ loadings (Figs. 9 and 10) also suggests that NH$_4$HSO$_4$ or other ammonium salts deposited on a catalyst surface perhaps could replace NH$_3$ as a reductive reagent in the reduction of NO. This could be realized by alternating between the impregnation of ammonium salts and the reaction with NO. However, since the sulfate species remains on the catalyst surface after the consumption of ammonium ions, a selection of other ammonium salts with easily decomposing anions such as ammonium carbonate is needed.

CONCLUSIONS

The decomposition and reaction of NH$_4$HSO$_4$ deposited on various V$_2$O$_5$/AC and V$_2$O$_5$/TiO$_2$ catalysts are studied in detail using the temperature-programmed method. As a comparison, the decomposition and reaction of ammonium–sulfate salts or sulfate species *in situ* formed on the V$_2$O$_5$/AC catalysts during the SCR reaction or SO$_2$ oxidation are also studied. The results are correlated directly with the behavior of the catalysts in NO reduction with NH$_3$ in the presence of SO$_2$. Important findings obtained are as follows.

1. The decomposition of NH$_4$HSO$_4$ is significantly promoted by the AC but slightly inhibited by V$_2$O$_5$. Both the AC and V$_2$O$_5$ promote the reaction of NH$_4$HSO$_4$ with NO. The reaction exhibits two-stage behavior with increasing temperature; only a small portion of NH$_4$HSO$_4$ participates in the reaction at temperatures below 250°C.

2. The decomposition and reaction of NH$_4$HSO$_4$ are easier on the V$_2$O$_5$/AC catalyst than on the V$_2$O$_5$/TiO$_2$ catalyst. On the V$_2$O$_5$/AC catalysts, the temperatures of the decomposition and reaction of NH$_4$HSO$_4$ increase with increasing V$_2$O$_5$ loading. Most of the NH$_4$HSO$_4$ deposited can react with NO at 250°C when the V$_2$O$_5$ loading is below 5 wt%.

3. The reactivity of NH$_4$HSO$_4$ with NO, other than its decomposition, is well associated with the behavior of the catalysts in the SCR reaction in the presence of SO$_2$. The deactivation of the V$_2$O$_5$/TiO$_2$ catalyst by SO$_2$ at low temperatures (<330°C) is due to the low reactivity of the formed ammonium–sulfate salts with NO in the temperature range. A similar mechanism occurs on the V$_2$O$_5$/AC catalysts of high V$_2$O$_5$ loadings. The high stability and the SO$_2$-promoted activity of the V$_2$O$_5$/AC catalyst of low V$_2$O$_5$ loadings at low temperatures (180–250°C) result from the high reactivity of ammonium–sulfate salts with NO in the temperature range.

4. During the SCR reaction on the V_2O_5/AC catalysts of low V_2O_5 loadings in the presence of SO_2 at low temperatures, the formed sulfate species stay on the catalyst surface and act as new acid sites for NH_3 adsorption and activation. At the same time, ammonium ions react continuously with NO to avoid the formation and deposition of excess ammonium–sulfate salts on the catalyst surface. Such a process effectively ensures the catalyst being promoted but not poisoned by SO_2.

5. Interaction of AC and vanadium species results in synergism in the activation and reaction of ammonium ions linked to the sulfate species on the V_2O_5/AC catalyst of low V_2O_5 loadings. A bridge-type activated ammonia species is proposed in which the ammonium ion is linked to both sulfate species and adjacent vanadium species, and the sulfate species is located at the carbon site.

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