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# Formation and reaction of ammonium sulfate salts on $V_2O_5/AC$ catalyst during selective catalytic reduction of nitric oxide by ammonia at low temperatures

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## Abstract

The formation rate and reaction rate of ammonium sulfate salts on $V_2O_5/AC$ catalyst during selective catalytic reduction (SCR) of NO with $NH_3$ at low temperatures were studied using elemental analysis, transient response, and TPR methods. In the presence of $SO_2$ and $H_2O$, ammonium sulfate salts deposit on the surface of the $V_2O_5/AC$ catalyst, block the pores of the catalyst, and cause catalyst deactivation. Moreover, the deactivation rate increases with increasing $H_2O$ content in the flue gas. The deposition rate of the ammonium sulfate salts is governed by the rate difference between its formation and reaction with NO. In the presence of $H_2O$, the formation rate of the ammonium sulfate salts is higher than that in the absence of $H_2O$, and the reaction rate between the formed ammonium sulfate salts and NO is lower than that in the absence of $H_2O$. $SO_2$ does not affect the reaction rate of the ammonium sulfate salts with NO. FT-IR and XRD analysis show that the ammonium sulfate salts formed in the presence of $SO_2$ and $H_2O$ on the catalyst surface at 250 °C is mainly $(NH_4)_3H(SO_4)_2$.

*Keywords:* Ammonium sulfate salts; Formation and reaction; $V_2O_5/AC$ catalyst; SCR reaction; Nitric oxide

## 1. Introduction

Nitrogen oxides ($NO_x$) emitted from stationary sources are considered to be major pollutants in air. Selective catalytic reduction (SCR) of NO with $NH_3$ has been proven to be the most effective in removal of $NO_x$ from flue gases [1]. Commercial catalysts, $V_2O_5/TiO_2$ or $V_2O_5$–$WO_3/TiO_2$, must be used at temperatures higher than 350 °C to avoid deactivation by $SO_2$ [1,2]. However, low-temperature SCR processes are preferable because of low energy consumption and better economy in retrofitting into existing systems for flue gas cleaning [3,4]. In many cases, however, SCR catalysts employed at lower temperatures are prone to $SO_2$ deactivation due to the formation of solid sulfate salts on the catalyst surface [5,6].

Recently it was reported that an activated carbon-supported vanadium oxide catalyst ($V_2O_5/AC$) showed high SCR activity. $SO_2$, in the absence of $H_2O$, promoted catalytic activity for catalysts with $V_2O_5$ loadings of less than 5 wt% at temperatures higher than 180 °C [4,7,8], which was attributed to the high catalytic activity for the reactions between the ammonium sulfate salts, formed on the catalyst surface, and NO [9]. However, in the presence of both $SO_2$ and $H_2O$, deactivation of the $V_2O_5/AC$ catalyst is significant, especially at temperatures lower than 250 °C and space velocities greater than 9000 $h^{-1}$ [10]. The deactivation was attributed to accumulation of the ammonium sulfate salts on the catalyst surface [11], which is different from deactivation of other catalysts in the presence of both $SO_2$ and $H_2O$ [12,15–17], where the reduced desorption rate of $H_2O$ from the catalyst surface was considered to be the reason.

Our previous study suggested that the accumulation of the ammonium sulfate salts is determined by the combined effects of its formation and its consumption. It is important, therefore, to decouple these effects and evaluate the influence of $H_2O$ and other SCR conditions on these individual reactions. Furthermore, the specific forms of the ammonium sulfate salts need to be determined.

In this work, the rate of formation of the ammonium sulfate salts is studied and analyzed using elemental analysis and the reaction between the ammonium sulfate salts and

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NO is investigated through transient response and TPR. The forms of the ammonium sulfate salts formed on the catalyst surface in the presence of $SO_2$ and $H_2O$ are also analyzed by FT-IR and XRD.

## 2. Experimental

### 2.1. Catalyst preparation

The activated carbon (AC), as the catalyst support, was prepared from a commercial coal-derived semicoke through steam (92% in Ar) activation at 900 °C for 1.5 h. The AC was then grounded to 30–60 mesh and preoxided with concentrated $HNO_3$ at 60 °C for 1 h, followed by filtration, washing with deionized water, and drying at 120 °C for 4 h.

$V_2O_5/AC$ catalyst was prepared through conventional pore volume impregnation using an aqueous solution of ammonium metavanadate in oxalic acid ($m(AC)/V(NH_4VO_3) = 1.5$ g/ml), as described in detail elsewhere [11]. After the impregnation, the catalyst was dried at 50 °C for 12 h and then at 120 °C for 5 h and subsequently calcined in Ar at 500 °C for 5 h and preoxidized in air at 250 °C for 5 h. The $V_2O_5$ loading of the catalyst was confirmed to be 1 wt% by ICP analysis and termed 1 wt% $V_2O_5/AC$.

### 2.2. Catalytic activity measurement

The activity measurement of the 1 wt% $V_2O_5/AC$ catalyst was conducted in a fixed bed glass reactor. Mass flow meters were used to control the flow rates of $NH_3/Ar$ and $NO/Ar$, whereas rotameters were used to measure the flow rates of Ar, $SO_2/Ar$, and $O_2$. To prevent formation of ammonium sulfate salts [1] in the inlet tubing of the reactor, the tubing was heated by heating tapes.

The feed contained 500 ppm NO, 600 ppm $NH_3$, 500 ppm $SO_2$ (when used), 3.4% $O_2$, different amounts of $H_2O$ (when used), and the balance Ar. In all the runs, the total flow rate and the reaction temperature were 300 ml/min and 250 °C. $H_2O$ was generated by passing Ar, $O_2$, and NO/Ar through a heated gas-wash bottle containing deionized water. During the activity measurement, the concentrations of NO, $SO_2$, and $O_2$ in the inlet and the outlet of the reactor were measured simultaneously by an on-line flue gas analyzer (KM9006 Quintox, Kane–May International Limited).

### 2.3. Temperature-programmed decomposition (TPDC)

Catalyst 0.5 g was loaded into the reactor and exposed to the reaction gases in the absence and presence of 2.5% $H_2O$. After about 10 h of SCR reaction at 250 °C, the catalyst was purged with Ar at 100 ml/min for 1 h at the same temperature to remove the physically adsorbed $SO_2$ and then cooled to 30 °C in the same stream. TPDC was then carried out in Ar of 300 ml/min at a heating rate of 10 °C/min from 30 to 650 °C. During the TPDC, the effluent $SO_2$ concentration was monitored continuously using a KM9006 flue gas analyzer to estimate the amount of ammonium sulfate salt decomposed on the catalyst surface.

### 2.4. Transient response experiment of $NH_3$

Transient response experiments were carried out with 0.5 g catalyst at a temperature of 250 °C and a space velocity of 36,000 $h^{-1}$. The SCR activity of the catalyst in the presence of $SO_2$ was initially measured in the absence and presence of 2.5% $H_2O$. After about 330 min, $NH_3$ was removed from the feed. NO concentration at the outlet of the reactor was measured during the whole process.

### 2.5. Reactivity of ammonium sulfate salts with NO

The reactivity of ammonium sulfate salts with NO, in the presence of $H_2O$ or $SO_2$, was studied in temperature-programmed reaction (TPR). First, the SCR reaction was carried out at 250 °C and a feed gas concentration of 500 ppm NO, 600 ppm $NH_3$, 3.4% $O_2$, 500 ppm $SO_2$, 2.5% $H_2O$, and the balance Ar to allow deposition of ammonium sulfate salts on the catalyst surface as indicated by the decrease in NO conversion to about 67%. The sample was then purged with Ar at the same temperature for 1 h to remove the physically adsorbed reactants. After cooling down in Ar, the sample was then divided into three parts for reactivity measurement under conditions shown in Table 1.

### 2.6. FT-IR analysis

Fourier transform infrared (FT-IR) spectra were recorded on a Bio-Rad FTS 165 FT-IR spectrometer. Before the measurement, the 1 wt% $V_2O_5/AC$ catalysts were subjected to SCR reaction at 250 °C in the presence of 2.5% $H_2O$ for different time periods. After the SCR reaction, the catalyst samples were purged at the same temperature in Ar for 1 h to remove the physically adsorbed $SO_2$ and cooled in Ar to room temperature. The samples were then mixed with potassium bromide, ground, and pelletized. The weight ratio of the sample to potassium bromide is 1:300. Thirty-two scans were made and averaged to yield a spectrum with resolution of 4 $cm^{-1}$ over the spectral range 4000–400 $cm^{-1}$.

Table 1
Reaction conditions between ammonium sulfate salts formed on the catalyst and NO

| | First part | Second part | Third part |
|---|---|---|---|
| NO (ppm) | 600 | 600 | 600 |
| $O_2$ (%) | 3.4 | 3.4 | 3.4 |
| $SO_2$ (ppm) | – | 500 | 500 |
| $H_2O$ (%) | – | – | 2.5 |
| Ar | balance | balance | balance |
| Total flow rate (ml/min) | 300 | 300 | 300 |
| Catalyst loading (g) | 0.2 | 0.2 | 0.2 |
| Temperature (°C) | 30–250 | 30–250 | 30–250 |

### *2.7. Elemental and XRD analysis*

The sulfur, nitrogen, hydrogen, and carbon contents of the catalyst samples were measured on a Vario EL from Elementar Analysensysteme GmbH. X-ray powder diffraction (XRD) spectra of the catalyst samples were measured on a Rigaku D/Max 2500 system. Diffraction patterns were recorded with Cu-$K_\alpha$ ($\lambda = 0.1542$ nm) radiation. The X-ray tube was operated at 40 KV and 100 mA. The step scans were taken over the range of $2\theta$ from 10° to 80°.

## 3. Results and discussion

### *3.1. Effect of $H_2O$ content on the SCR reaction*

Fig. 1 shows the effect of $H_2O$ content on the SCR activity of the 1 wt% $V_2O_5/AC$ catalyst. NO conversion increases from about 61 to 91% upon addition of $SO_2$. This $SO_2$ promoting effect is similar to our earlier reports [9,18] and is attributed to the formation of sulfate species on the catalyst surface, which results in increased catalyst surface acidity and $NH_3$ adsorption. Introduction of $H_2O$, at time on stream 12 h, results in immediate decreases and subsequent "slow" decreases in NO conversion for all the $H_2O$ concentrations used. The rates of the "slow" decrease are proportional to the $H_2O$ concentration in the flue gas. Although the actual mechanism for the catalyst deactivation is unknown at the present time, it is likely that the immediate decrease in NO conversion upon the introduction of $H_2O$ is caused by adsorption of $H_2O$ on the active sites of the catalyst, as reported in the literature [12–14], as well as by lose of pore surface area resulted from capillary $H_2O$ condensation in some of the micropores. As previously reported [11], the relatively "slow" deactivation of the catalyst is resulted from the deposition of ammonium sulfate salts on the catalyst surface, which blocks the pores of the catalyst. The increased deactivation rate of the catalyst with increasing $H_2O$ content suggests that $H_2O$ promotes the deposition of ammonium sulfate salts. This is confirmed by a TPDC experiment for used catalyst (Fig. 2), where the sample that experienced $H_2O$ during the SCR releases more $SO_2$ than the one that experienced no $H_2O$ during the SCR reaction.

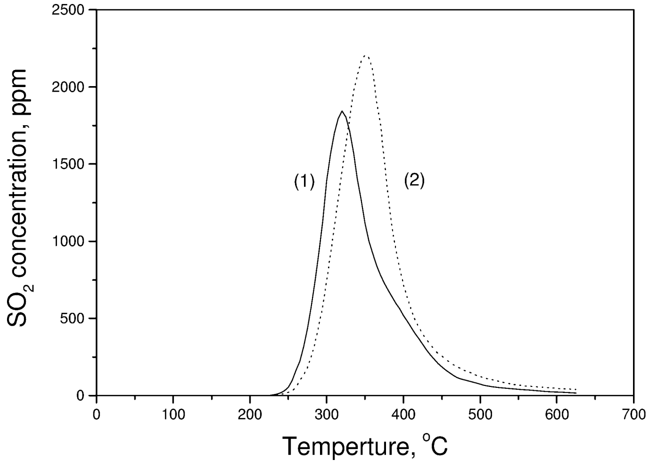

Fig. 2. The decomposition of the ammonium sulfate salts formed on the surface of the 1 wt% $V_2O_5/AC$ catalyst at 250 °C for 10 h (1) in the absence of $H_2O$, (2) in the presence of $H_2O$. Conditions: 300 ml/min Ar, heating rate 10 °C/min, 0.5 g sample.

It is important to note that ammonium sulfate salts form on the catalyst surface in the presence of $SO_2$ regardless the presence of $H_2O$, and the amount of ammonium sulfate salts on the catalyst surface determines its effect on the SCR activity. A small amount of ammonium sulfate salts promotes the SCR activity [4,18] and large amounts of

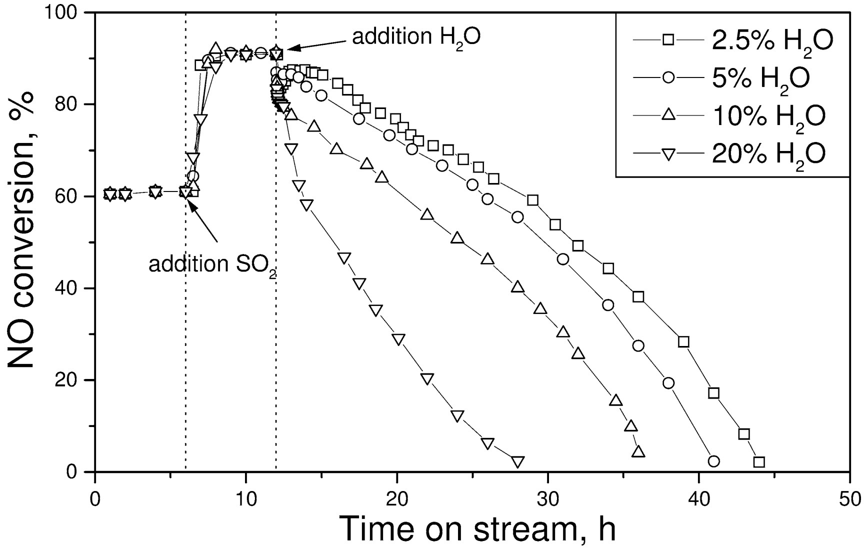

Fig. 1. Effect of $H_2O$ content on the activity of the 1 wt% $V_2O_5/AC$ catalyst. Reaction conditions: 500 ppm NO, 600 ppm $NH_3$, 500 ppm $SO_2$ (when used), 3.4% $O_2$, balance Ar, space velocity 90,000 $h^{-1}$, reaction temperature 250 °C.

Table 2
Formation of ammonium sulfate salts in the absence and presence of $H_2O$

| Samples | S (wt%) | N (wt%) | H (wt%) | C (wt%) | S/V (mol/mol) |
|---|---|---|---|---|---|
| Fresh catalyst | 0.44 | 0.83 | 0.64 | 83.30 | 1.25 |
| Catalyst[a] | 3.91 | 5.15 | 1.77 | 62.92 | 11.11 |
| Catalyst[b] | 6.33 | 6.29 | 1.97 | 55.59 | 17.98 |

[a] The 1 wt% $V_2O_5/AC$ catalyst after SCR reaction for 6 h. Reaction conditions: 500 ppm NO, 600 ppm $NH_3$, 3.4% $O_2$, 500 ppm $SO_2$, balance Ar, 36,000 $h^{-1}$, 250 °C.

[b] The 1 wt% $V_2O_5/AC$ catalyst after SCR reaction for 6 h. Reaction conditions are the same as (a) with 2.5% $H_2O$.

ammonium sulfate salts deactivates the catalyst [11]. The promoting effect of $H_2O$ on the deposition of ammonium sulfate salts may result from an increase in its formation rate and/or from a decrease in its reaction rate with NO.

### *3.2. Formation and reaction of the ammonium sulfate salts*

To evaluate the effect of $H_2O$ on the formation rate of the ammonium sulfate salts, two experiments were carried out at 250 °C with 600 ppm $NH_3$, 500 ppm $SO_2$, and 3.4% $O_2$ with and without 2.5% $H_2O$. NO was not included in the feed to eliminate consumption of the ammonium sulfate salts (through reaction with NO). After a 6-h reaction, the catalyst samples were subjected to elemental analysis. Sulfur, nitrogen, hydrogen, and carbon contents of the samples are shown in Table 2. The sample obtained in the presence of $H_2O$ has higher sulfur, nitrogen, and hydrogen content than the sample obtained in the absence of $H_2O$. The fresh catalyst contains the least amount of sulfur, nitrogen, and hydrogen. This indicates that $H_2O$ promotes the formation of ammonium sulfate salts on the catalyst surface, possibly through conversion of adsorbed $SO_3$ to $H_2SO_4$ [19]. The data also confirm the formation of small amounts of ammonium sulfate salts on the catalyst surface in the absence of $H_2O$.

Fig. 3 shows the response of NO conversion to removal of $NH_3$ from the feed in the absence and presence of $H_2O$. In the first 330 min, before the removal of $NH_3$, NO conversion is stable at 98% in the absence of $H_2O$ (open symbol), but continually decreases to 90% in the presence of $H_2O$ (solid symbol). This suggests that more ammonium sulfate salts deposit on the catalyst surface in 330 min in the presence of $H_2O$. When $NH_3$ is removed from the feed, NO conversions decrease from 98 to 8% in 60 min in the absence of $H_2O$ and from 90 to 8% in 500 min in the presence of $H_2O$. Since the removal of $NH_3$ from the feed terminates the formation of ammonium sulfate salts on the catalyst surface, the conversion of NO after 330 min only results from the reaction between the formed ammonium sulfate salts and NO. If $H_2O$ had no effect on the reaction between the salts and NO, the decrease in NO conversion should be slower in the presence of $H_2O$ than in the absence of $H_2O$, simply because more ammonium sulfate salt is on the catalyst surface at time on stream 330 min in the presence of $H_2O$. If $H_2O$ inhibits the reaction between the salts and NO, however, it may also give similar result.

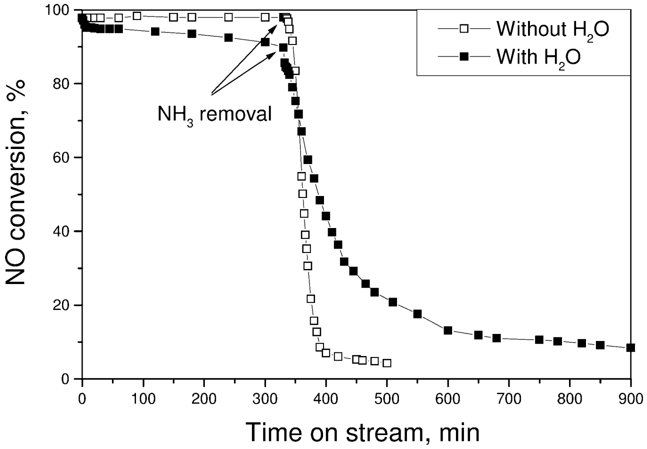

Fig. 3. The response of NO conversion to removal of $NH_3$ from the feed in the absence or presence of 2.5% $H_2O$. Reaction conditions: 500 ppm NO, 600 ppm $NH_3$ (when used), 500 ppm $SO_2$, 3.4% $O_2$, balance Ar, space velocity 36,000 $h^{-1}$, reaction temperature 250 °C.

To eliminate the ambiguity on the $H_2O$ effect, TPR experiments were made under the conditions listed in Table 1 using a fresh catalyst and catalyst samples in situ deposited with the same amount of ammonium sulfate salts. Since there is no $NH_3$ in the feed, the decrease in NO concentration, from the feed concentration, can only be caused by adsorption and/or by reaction with the ammonium sulfate salts. If the reaction stoichiometric ratio of $NH_4^+/NO$ (or $NH_3/NO$) is 1 as measured by many authors on vanadia-based catalysts [1,20], the amount of NO consumed can be used directly to estimate the amount of reactive $NH_4^+$ (or $NH_3$) on the catalyst surface [9]. The effect of $H_2O$ on the reaction of the ammonium sulfate salts with NO is shown in Fig. 4. In the case of the fresh catalyst, NO concentration increases quickly from zero to the inlet value (600 ppm) when temperature increases from room temperature to 150 °C. The amount of NO adsorbed is about 0.0285 mmol/g (Table 3).

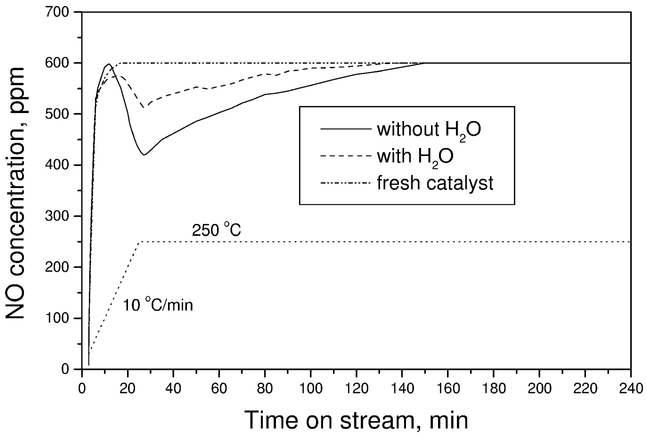

Fig. 4. Effect of $H_2O$ on the reaction of the ammonium sulfate salts with NO. Reaction conditions: 600 ppm NO, 3.4% $O_2$, 2.5% $H_2O$ (when used), balance Ar, space velocity 90,000 $h^{-1}$, reaction temperature 250 °C.

Table 3
Reactivity of ammonium sulfate salts formed on the catalyst surface with NO

| Reaction conditions | Amount of reacted $NH_4^+$ (mmol/g) | Reaction nitration temperature (°C) |
|---|---|---|
| Fresh catalyst | 0.0285[a] | – |
| After TPR without $SO_2$ and $H_2O$ | 0.6333 | 110 |
| After TPR with $SO_2$ | 0.6300 | 110 |
| After TPR with $H_2O$ | 0.3018 | 160 |

[a] This datum represents the amount of NO adsorbed.

For the catalyst deposited with ammonium sulfate salts, significant decreases in NO concentration were observed at temperature above 110 °C for the case without $H_2O$, 160 °C for the case with $H_2O$, indicating occurrence of a reaction between NO and the deposited ammonium sulfate salts. The higher starting temperature in the presence of $H_2O$ (160 °C) than in the absence of $H_2O$ (110 °C) suggests an inhibition effect of $H_2O$ on the reaction. It is interesting to note that the NO concentration reaches to a minimum at about 250 °C and then starts to increase until it reaches an inlet value of 600 ppm at about 150 min for both cases, with and without $H_2O$. It seems that $H_2O$ has no effect on the shape of the NO concentration. It is very surprising that the amount of ammonium sulfate salts reactable with NO is very different, 0.633 mmol/g without $H_2O$, 0.3018 mmol/g with $H_2O$ (Table 3). It is even more surprising that the sulfur content of the catalyst samples after 240 min of the TPR process is about 6% of with 2.5% $H_2O$ and 5% without $H_2O$ (Table 4), suggesting a large amount of unreactable sulfur on the catalyst in both cases and the promoting effect of $H_2O$ on the sulfur retention.

Experiments similar to these in Fig. 4 were made in the absence of $H_2O$, with and without $SO_2$, as shown in Fig. 5. The shapes of the curves in Fig. 5 are similar to those in Fig. 4, and no effect of $SO_2$ on the reaction between NO and the ammonium sulfate salts is observed. The reaction between ammonium sulfate salts and NO starts at a temperature of about 110 °C without and with $SO_2$, and the amount of ammonium sulfate salts reactable with NO is about 0.63 mmol/g (Table 3). After 240 min of the TPR process, the sulfur content is also similar, about 5% without and with $SO_2$ (Table 4).

Table 4
Elemental analysis of ammonium sulfate salts before and after TPR with NO

| Reaction conditions | S (wt%) | N (wt%) | H (wt%) | C (wt%) |
|---|---|---|---|---|
| Before TPR | 6.80 | 7.61 | 1.87 | 48.38 |
| After TPR without $SO_2$ and $H_2O$ | 4.95 | 5.65 | 1.54 | 49.71 |
| After TPR with $SO_2$ | 5.01 | 5.56 | 1.68 | 48.87 |
| After TPR with $H_2O$ | 6.01 | 5.79 | 1.69 | 48.31 |

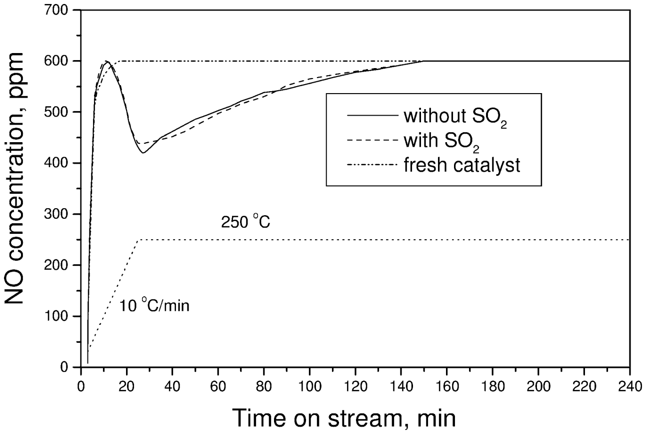

Fig. 5. Effect of $SO_2$ on the reaction of the ammonium sulfate salts with NO. Reaction conditions: 600 ppm NO, 500 ppm $SO_2$ (when used), 3.4% $O_2$, balance Ar, space velocity 90,000 $h^{-1}$, reaction temperature 250 °C.

### 3.3. FT-IR spectra

The solid deposited on the catalyst has been termed ammonium sulfate salts throughout this paper and in the literature, without indicating its actual formulation. To understand its actual form, the catalyst samples before and after SCR reaction at 36,000 $h^{-1}$ and 250 °C in the presence of $SO_2$ and $H_2O$ were analyzed by FT-IR, the results are shown in Fig. 6. For the fresh catalyst, a broad band in the range 950–1250 $cm^{-1}$ is found. This phenomenon is similar to but noticeably different from others in the literature [21,22]. Tarama et al. [21] showed that $V_2O_5/\gamma\text{-}Al_2O_3$ and $V_2O_5/SiO_2$ exhibit a sharp absorption at 1023 $cm^{-1}$. Frederickson et al. [22] showed stretching vibration of $V^{5+}{=}O$ occurred at 1020 $cm^{-1}$ for bulk $V_2O_5$. The broad band of the $V_2O_5$/AC catalyst possibly resulted from the lowered symmetry of vanadium species or the existence of some different species [18].

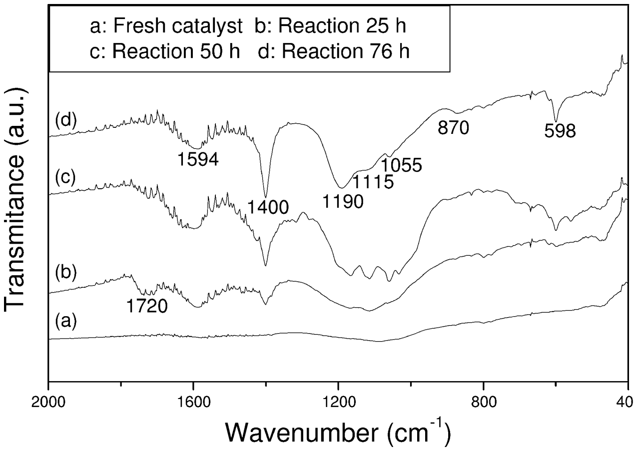

Fig. 6. FT-IR spectra obtained under different deactivation times of the 1 wt% $V_2O_5$/AC catalyst. The samples were obtained in the reaction conditions 500 ppm NO, 600 ppm $NH_3$, 500 ppm $SO_2$, 3.4% $O_2$, 2.5% $H_2O$, balance Ar, space velocity 36,000 $h^{-1}$, reaction temperature 250 °C.

The FT-IR spectra of the used $V_2O_5/AC$ catalyst exhibit similar bands in the range of 950–1250 $cm^{-1}$, much stronger than the fresh catalyst. The phenomenon shows that the symmetry of vanadium species is higher than that of fresh catalyst. The used catalyst samples show other absorption peaks as well, such as 1720, 1594, 1400, 1190, 1115, 1055, and 598 $cm^{-1}$. The bands at 1720 and 1400 $cm^{-1}$ are close to the vibration frequency of $NH_4^+$ chemically adsorbed on Brønsted acid sites [23,24], and the band intensity increases with increasing time on stream. Long and Yang [25] showed, for a Fe-ZSM-5 catalyst absorbed with $NH_3$, that the bands at 1705 and 1473 $cm^{-1}$ were due to the symmetric and asymmetric bending vibration, respectively, of $NH_4^+$ that was chemisorbed on the Brønsted acid sites, while the bands at 1587 and 1276 $cm^{-1}$ were attributed to asymmetric and symmetric bending vibrations, respectively, of N–H bonds in $NH_3$ coordinately linked to Lewis acid sites. The decreasing band intensity at 1720 $cm^{-1}$ and the increasing band intensity at 1400 $cm^{-1}$ with increasing time on stream indicates a decrease in the symmetric vibration and an increase in the asymmetric vibration of the surface $NH_4^+$ ions resulted from $H_2O$ and $SO_2$. The 1594 $cm^{-1}$ peak is assigned to $NH_3$ adsorption on Lewis acid sites. The bands at 1115 and 598 $cm^{-1}$ may be attributed to the vibration of the $SO_4^{2-}$ ions. $SO_4^{2-}$ ions show two infrared peak at 1104 ($\nu_1$) and 613 ($\nu_2$) [23]. When $SO_4^{2-}$ is bound to the catalyst surface, the symmetry can be lowered to either $C_{3\nu}$ or $C_{2\nu}$ and the $\nu_1$ would split into two peaks [23]; the bands at 1190 and 870 $cm^{-1}$ may result from the $\nu_1$ splitting. The band at 1055 $cm^{-1}$ may be attributed to the $V^{5+}{=}O$ stretching vibration. The catalysts after SCR reaction are showed to contain $SO_4^{2-}$ and $NH_4^+$ by FT-IR, which suggests ammonium sulfate salts deposited on the catalyst surface during the SCR reaction.

### 3.4. XRD analysis

In the present study, FT-IR shows sulfate species existed on the catalyst surface. It is important to identify the ammonium sulfate salts deposited on the catalyst surface. Bosch and Janssen [1] suggested that the deactivation materials, deposited on the catalyst surface, were $NH_4HSO_4$ and/or $(NH_4)_2S_2O_7$ at lower temperatures. The deactivation materials are presumed to be $(NH_4)_2SO_4$ and/or $NH_4HSO_4$ from the results of TGA and ion chromatography measurement in the absence of $H_2O$ [26].

XRD patterns of the catalyst samples used for FT-IR study in Fig. 6 are shown in Fig. 7. For the fresh catalyst and the catalyst sample used for 25 h in the presence of $H_2O$ and $SO_2$, only $SiO_2$ peaks are visible. For the samples used for 50 and 76 h, $(NH_4)_3H(SO_4)_2$ are identified on the catalyst surface and the content of the $(NH_4)_3H(SO_4)_2$ increases with time on stream. The peak at 26.3° ($d = 0.339$ nm) is the summation of *hkl* indices of (111). The diffraction at 17.9° ($d = 0.496$ nm) may be the summation of *hkl* indices of (020) and $(1\bar{1}0)$; the diffraction at 30.6° ($d = 0.293$ nm) is the summation of *hkl* indices of $(1\bar{3}0)$; and the diffraction at 23.6° ($d = 0.378$ nm) is the summation of *hkl* indices of (002). The nonpresence of a $(NH_4)_3H(SO_4)_2$ peak for the sample used for 25 h is likely due to small crystals on the catalyst surface. The main peaks of the *d* value of $(NH_4)_2SO_4$ should be 0.434, 0.439, and 0.305 nm; the main diffraction of the *d* value of $NH_4HSO_4$ should be 0.475, 0.390, and 0.369 nm; and the main diffraction of the *d* value of $(NH_4)_2S_2O_7$ should be 0.502, 0.337, and 0.314 nm, which indicates that the deactivation material formed on the $V_2O_5/AC$ catalyst is different with the formulation as before literatures [1,26]. For the catalyst after reaction in the absence of $H_2O$ for 76 h, except the $SiO_2$, there is no diffraction by XRD, which is due to the lesser $(NH_4)_3H(SO_4)_2$ deposition on the catalyst surface and results in the higher stability of the 1 wt% $V_2O_5/AC$ catalyst.

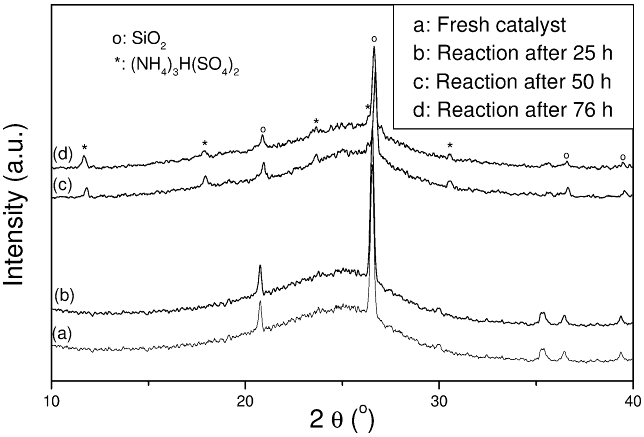

Fig. 7. XRD patterns of the fresh 1 wt% $V_2O_5/AC$ catalyst and different deactivation level of the catalyst. The samples obtained in the reaction conditions: 500 ppm NO, 600 ppm $NH_3$, 500 ppm $SO_2$, 3.4% $O_2$, 2.5% $H_2O$, balance Ar, space velocity 36,000 $h^{-1}$, reaction temperature 250 °C.

## 4. Conclusions

The effect of $H_2O$ content on the 1 wt% $V_2O_5/AC$ catalyst for NO reduction with $NH_3$ is studied. In the presence of $SO_2$ and $H_2O$, the reasons that the $V_2O_5/AC$ catalyst is deactivated are analyzed through the elemental analysis, transient response of $NH_3$ and TPR method. The solid materials deposited on the catalyst surface are observed using FT-IR and XRD. The main results obtained are as follows:

1. The deactivation of the 1 wt% $V_2O_5/AC$ catalyst in the presence of $SO_2$ and $H_2O$ is caused by the deposition of the ammonium sulfate salts on the catalyst surface. Higher $H_2O$ content results in a higher deactivation rate of the catalyst.
2. $H_2O$ addition into the reaction stream increases the formation rate of the ammonium sulfate salts; furthermore, it decreases the reaction rate between the ammonium

sulfate salts and NO. $SO_2$ does not affect the reaction rate. These functions result in the deactivation of the $V_2O_5/AC$ catalyst in the presence of $SO_2$ and $H_2O$.

3. In the presence of $SO_2$ and $H_2O$, the ammonium sulfate salts deposited on the surface of the $V_2O_5/AC$ catalyst during the SCR reaction at 250 °C is $(NH_4)_3H(SO_4)_2$.

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