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Sulfuric acid formation over ammonium sulfate loaded V_2O_5–WO_3/TiO_2 catalysts by DeNO$_x$ reaction with NO$_x$

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Abstract

Operating the SCR DeNO$_x$ reactor at temperatures below 200 °C results in a considerable saving in operating costs. Plant experience shows that on the catalysts in these second generation DeNO$_x$ plants, even for flue gases with SO_2 concentration below 10 mg/m^3, over 1–2 years operating time sizeable quantities of ammonium sulfates accumulate. Ammonium sulfates deposited on V_2O_5–WO_3/TiO_2 catalysts react with NO$_x$ to nitrogen and sulfuric acid. Second-order rate constants of this reaction for temperatures of 170 °C have been derived. It could be shown that the sulfuric acid formed on the catalyst is displaced by water vapour and desorbs resulting in gas phase concentrations of up to 6.5 mg acid/m^3 flue gas. Plant equipment downstream of the ammonium sulfate containing low temperature DeNO$_x$ catalysts has to be protected against the corrosive action of the sulfuric acid in the flue gases leaving the DeNO$_x$ reactor.

Keywords: V_2O_5–WO_3/TiO_2 catalyst; Sulfuric acid; Ammonium sulfate; SCR DeNO$_x$

1. Introduction

Selective catalytic reduction (SCR) of nitrogen oxides with ammonia on V_2O_5–WO_3/TiO_2 catalysts is a proven technology to abate NO$_x$ in flue gases. The structure and performance of TiO_2 supported V_2O_5-based catalysts as well as the kinetics and the reaction mechanism have been subjected to numerous investigations [1–3].

Second generation DeNO$_x$ plants are designed to be more cost efficient. The energy requirements for reheating the flue gases are often contributing a quarter of the operating cost of clean gas DeNO$_x$ plants operating at temperatures around 300 °C. In order to reduce reheating costs the second generation plants are often operated at temperatures below 200 °C, the so-called low temperature range. The DeNO$_x$ abatement efficiency of the catalysts is still sufficient in this operating regime. However, even flue gases with a SO_2 content below 10 mg/m^3 may result under this reaction condition in an accumulation of ammonium sulfate in the 10 mass% range after an operating time of only 1–2 years. Therefore these catalysts have to be regenerated in certain intervals by thermal (greater than 350 °C) or washing treatment.

The behaviour of the ammonium sulfates on the DeNO$_x$ catalyst in the low temperature regime has to the best of our knowledge not been investigated in detail so far. However, especially the mobility of the ammonium sulfate deposited on the catalyst may be of great importance for the reliability of the plants downstream of the DeNO$_x$ reactor. After all acidic ammonium sulfates as well as sulfuric acid are known strong corrosive substances, which may be released from the deposited ammonium sulfate.

Our interest in the following work was focussed on the question whether the deposited ammonium sulfate could release sulfuric acid to the flue gases leaving the reactor at temperatures below 200 °C. In this

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Table 1
Characteristics of catalysts investigated (4.5 wt.% V_2O_5)

Catalyst origin	Sample Ia industrially used $DeNO_x$ catalyst	Sample Ib industrially used $DeNO_x$ catalyst	Sample IIa industrially used $DeNO_x$ catalyst	Sample IIb industrially used $DeNO_x$ catalyst	Sample III regenerated sample II and saturated with 400 ppm NH_3 at 170 °C
Sulfate content (mg SO_4^{2-}/g)	77	115.8	35	41.8	1.6
Ammonium content at $t = 0$ (mg NH_4^+/g)	21	33.6	8.7	8.3	4.1
Ammonium content after NO_x-treatment (mg NH_4^+/g)	1.6 (87 h NO_x-treatment)	3.4 (52.5 h NO_x-treatment)	1 (28 h NO_x-treatment)	1.2 (20 h NO_x-treatment)	–

connection, we studied also the reaction of NH_3 of the ammonium sulfates on the catalyst with NO_x in the flue gas passing through the $DeNO_x$ reactor as a possible first step required for sulfuric acid release.

2. Experimental

2.1. Apparatus and test procedures

Experiments have been carried out in a micro-scale flow reactor (glass tube) heated in a tubular furnace. The applied V_2O_5–WO_3/TiO_2 honeycomb catalyst samples were derived from an industrially used catalyst. The reactor containing 42–70 g catalyst with 25 channels and a length of 13–19.2 cm was operated isothermally. If not stated otherwise, the reaction temperature was 170 °C. The total feed gas flow rate was varied between 250 and 490 l/h corresponding to an area velocity (AV) of 3.8–10 m/h. The inlet gas composition was varied in the range of 0–550 ppm NO_x, 0–20 vol.% H_2O, 10.5–21 vol.% O_2 with nitrogen as the carrier gas. The flow rates of the individual gas streams were controlled by Bronkhorst mass flowmeters. Water was dosed by a mass flowmeter for liquids into an evaporator and then mixed with the gas stream. In the outlet gas the sulfuric acid concentration was determined after condensation at 70–90 °C according to the Shell method by wet-chemical analysis. NO_x conversion was measured using an NDIR spectrometer (Fisher–Rosemount NO/NO_2 BINOS 1004).

The ammonium sulfate content of the tested catalysts was extracted by shaking for 24 h with the 10-fold quantity of pure water followed by wet ionic chromatographic and Nessler photometric determination of the respective ions in the filtrated extract.

2.2. Catalysts characterisation

The catalyst referred to in this work contained 4.5 wt.% V_2O_5. The three catalyst samples under study differ only in their sulfate content (Table 1)—samples Ia and b: high sulfate content; samples IIa and b: medium sulfate content and sample III: low sulfate content sample derived from sample II by thermal regeneration at 350 °C.

3. Results and discussion

3.1. Formation and desorption of sulfuric acid

In order to answer the question if under the conditions of the low temperature $DeNO_x$ process appreciable amounts of sulfuric acid can be formed we started with a series of screening experiments. In these laboratory experiments ammonium sulfate loaded catalysts from an industrial plant were contacted with model flue gases of a defined composition.

From the results presented in Fig. 1, the following conclusions can be derived for the low temperature (170 °C) region:

- In a NO_x-free gas stream (Fig. 1A) sulfuric acid is not desorbed from the sulfate loaded catalyst. This finding agrees with previous studies on the thermal decomposition of pure ammonium sulfates [4].
- SO_2 in the gas feed is only to a minor degree oxidized to SO_3 (Fig. 1B). Thus, SO_2 oxidation over

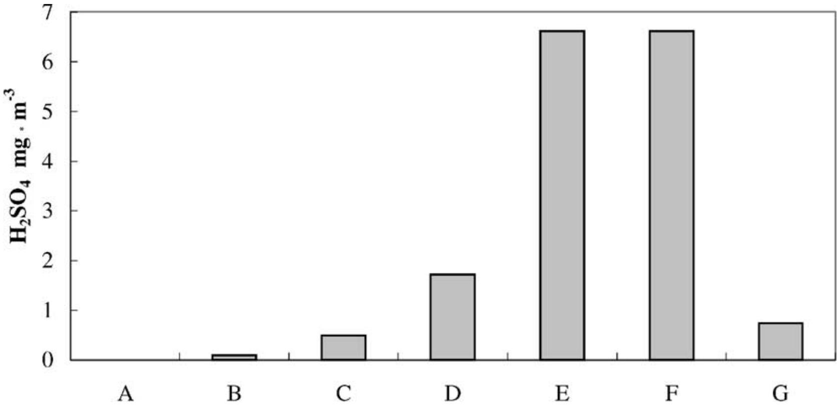

Fig. 1. Results of screening tests: H_2SO_4 concentration in the gas stream at the reactor outlet, temperature 170 °C, AV 3.8 m/h: (A) sample Ia, wet air; (B) sample III, 70 ppm SO_2 in wet air; (C) sample Ia, 500 ppm NO_x in dry air; (D) sample IIa, 410 ppm NO_x in wet air; (E) sample Ia, 410 ppm NO_x in wet air; (F) NO_x-free wet gas stream after NO_x-treatment corresponding to (E); (G) NO_x-free dry gas stream after NO_x-treatment corresponding to (E).

this catalyst can be excluded as a primary source of appreciable sulfuric acid formation.

- Ammonium sulfate loaded catalysts in a NO_x-containing gas stream result, after a lag period of several hours and in the absence of gaseous ammonia, in a pronounced release of sulfuric acid into the gas phase (Fig. 1C and E).
- The release of sulfuric acid is strongly enhanced by the presence of water (Fig. 1E vs. C).
- Sulfuric acid is also desorbed into a NO_x-free wet gas stream, provided the catalyst has been previously subjected to an extensive pretreatment in a NO_x-containing gas (Fig. 1F). However, only small sulfuric acid concentrations were observed in the gas stream after the same pretreatment, when a dry gas stream was used (Fig. 1G).

Thus, in our experiments at 170 °C, the appearance of sulfuric acid at relevant concentrations in the gas phase is bound on the presence of NO_x and water in the gas in contact with the catalyst. The results in Fig. 1C–F point to the occurrence of the $DeNO_x$ reaction as a prerequisite and as the first reaction step for the formation of gas phase sulfuric acid. The reaction between NO_x and ammonium sulfate on a $DeNO_x$ catalyst to form nitrogen has been shown earlier by Kasaoka et al. [5] without, however, proving the formation of the free acid and without referring to the fate of the sulfuric acid produced according to the following equations:

$$NO + \tfrac{1}{4}O_2 + (NH_4)_2SO_4 = N_2 + \tfrac{3}{2}H_2O + NH_4HSO_4 \qquad (1)$$

$$NO + \tfrac{1}{4}O_2 + NH_4HSO_4 = N_2 + \tfrac{3}{2}H_2O + H_2SO_4 \qquad (2)$$

We studied the reaction between NO_x and ammonium on the catalyst surface by following the NO_x conversion as a function of time and compared the behaviour of the ammonium sulfate loaded catalyst with that of the same catalyst subjected to thermal desulfation followed by saturation with ammonia previous to the reduction (Fig. 2). In all cases the $DeNO_x$ reaction is observed until almost all ammonia on the catalyst surface is consumed.

The amount of reacted ammonia derived from the integral of the curve of sample IIb (for calculation, cf. Fig. 2), assuming a reaction stoichiometry NO_x:NH_4^+ = 1:1, agrees well with the ammonium content of the studied catalyst given in Table 1 derived from wet-chemical analysis. Although the reaction rate with the sulfate loaded catalyst is lower than with the regenerated catalyst, the reactions (1) and (2) take place almost quantitatively.

As the reactions (1) and (2) take place both in wet and dry atmosphere, the decisive role of water in the release of sulfuric acid (Fig. 1) may be attributed to a

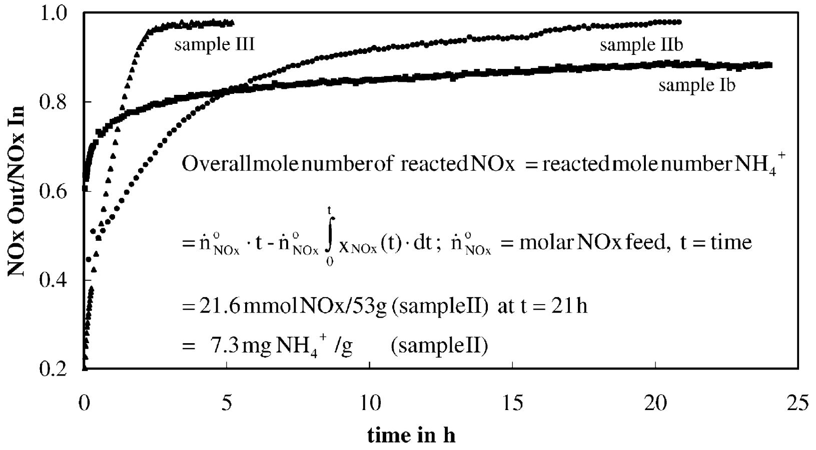

Fig. 2. NO_x reaction with surface ammonia; catalyst: regenerated and with NH_3 saturated (sample III), medium ammonium sulfate (sample IIb) and high ammonium sulfate (sample Ib) catalyst as a function of time-on-stream. Reaction conditions: AV 10 m/h, 10 vol.% H_2O, 16 vol.% O_2, 500 ppm NO_x, balance N_2.

strong enhancing effect of water on the desorption of sulfuric acid from the catalyst surface.

The time-dependency of the sulfuric acid concentration obtained with a wet gas stream (after extensive NO_x-treatment prior to this experiment) is given in Fig. 3. With the highly ammonium sulfate loaded catalyst sample Ia an almost constant sulfuric acid concentration as high as 6.5 mg/m^3 in the outlet gas was found over a period of 100 h and more. Such an acid concentration could be sufficiently high to cause severe corrosion in the downstream heat exchanger behind the catalyst bed, if it is operated below the dew point of the sulfuric acid.

3.2. DeNO$_x$ reaction with adsorbed ammonia and ammonium sulfate

The screening experiments showed in accordance with the work of Kasaoka et al. [5] that a DeNO$_x$ reaction between ammonium sulfate and gaseous NO_x takes place. The results obtained indicate further this to be the first decisive step for the formation of gas phase sulfuric acid. Therefore, in order to get a deeper understanding of this reaction, we followed the kinetics.

In an earlier work, Chen and Yang [6] found that in the reaction between NO_x and NH_3 saturated catalysts, at 400 °C only 52% of the ammonia is involved

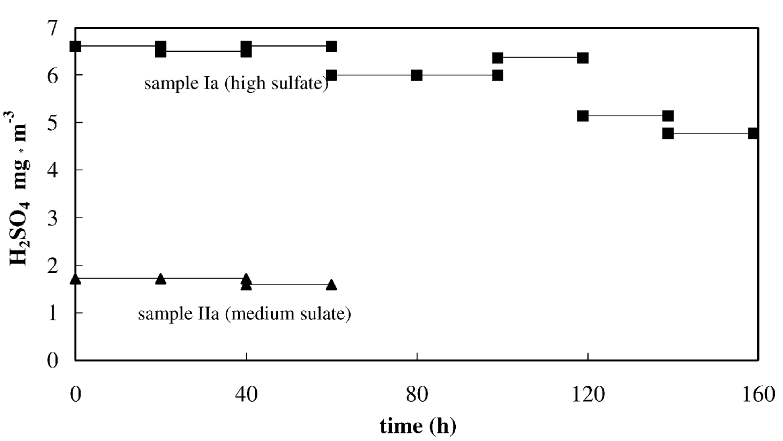

Fig. 3. Time-on-stream dependency of sulfuric acid release: AV 3.8 m/h, 20 vol.% H_2O, balance air.

in the DeNO$_x$ reaction. The remainder is desorbed or remains inactive on the surface. However, in the low temperature region the reaction can be followed more conveniently: under these reaction conditions NH$_3$ removal from the reactor by the gas flow can be neglected.

Typical NO$_x$ conversion curves for catalysts with different ammonia and ammonium sulfate contents are presented in Fig. 2. As the change of the concentration of the second reaction partner, ammonia, during a single measuring operation (about 2 min) is differentially small for every experimental value the pseudo-first-order reaction rate constant k_1 can be calculated using the following equation:

$$k_1(t) = -\mathrm{AV}\ln(x(t)) \quad \text{with} \quad x(t) = \frac{C_{\mathrm{NO}_x\,\mathrm{out}}(t)}{C_{\mathrm{NO}_x\,\mathrm{in}}} \tag{3}$$

The values of $k_1(t)$ are given in Fig. 4 as a function of the reaction time (time-on-stream) t. The initial value of k_1 significantly decreases with increasing sulfur content of the catalyst samples tested. In the case of the low sulfated sample III the reaction is almost completed after 2 h, whereas the higher sulfated catalysts are still active even after 10 h. At this reaction time the catalyst with the highest sulfate level is characterised by the highest value of k_1, corresponding to the higher ammonia surface concentration.

The general decrease of k_1 with t is mainly due to the decrease of the ammonia surface concentration. As shown above (Fig. 2), for each value of t the ammonia concentration can be derived. In this way the magnitude of the second-order rate constant k_2 can be calculated using the following equation:

$$k_2 = \frac{k_1(t)}{C_{\mathrm{NH}_{3,\mathrm{S}}}(t)} \quad \text{with} \quad C_{\mathrm{NH}_{3,\mathrm{S}}}(t) = \mathrm{mmol\,NH_3/g\,catalyst} \tag{4}$$

Values of k_2 are reported in Fig. 5a for the initial reaction time up to $t = 3$ h, and in Fig. 5b k_2 is given for the overall catalyst time-on-stream period.

Three characteristic regions can be distinguished in the k_2 over time curves.

In the *first reaction period* (0.3 h with sample IIb, 2.2 h with sample III: Fig. 5a) generally a rapid decrease of k_2 with t is observed. The variation of k_2 with t in this period, especially pronounced with sample III (low sulfate high free ammonia content), may reflect the presence of differently bound species—ammonia adsorbed on Lewis and Brönsted site—may also be due to energetic inhomogeneities of the surface bound species. As the ammonia on this sample is consumed almost completely during the reaction, many different species must have been involved in the reaction.

The *second reaction period* characterised by constant k_2 values starts at a stoichiometric NH$_3$:SO$_4{}^{2-}$ ratio in the catalyst of about unity, which is achieved with sample III after 2.2 h and with sample IIb after 0.3 h of reaction. This period may be attributed to the reaction of ammonia associated with the sulfate at the catalyst surface. This assumption is in line with the observed direct correlation between the sulfate

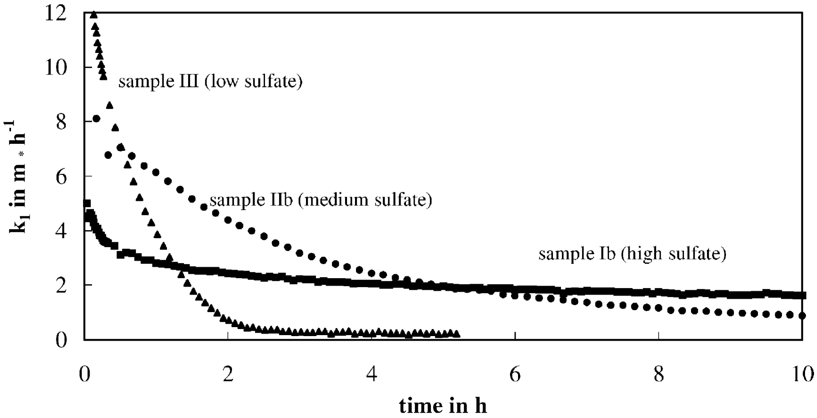

Fig. 4. Time-on-stream dependency of the first-order rate constant k_1 (for catalyst and reaction condition compare Fig. 2).

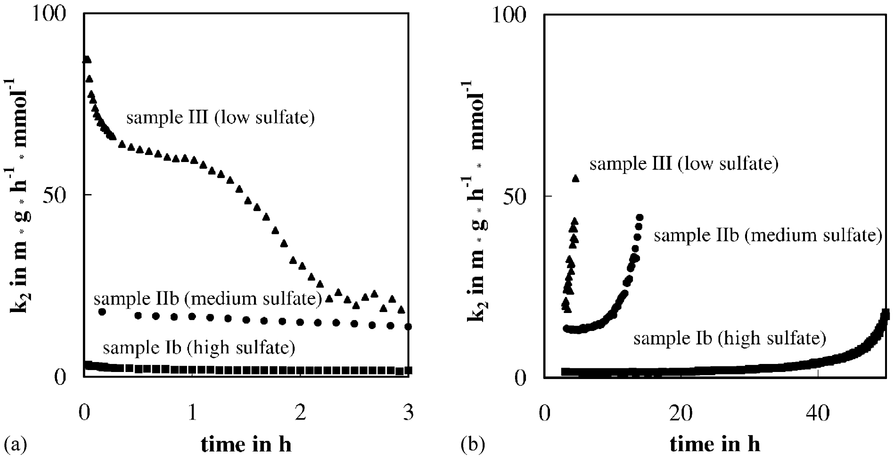

Fig. 5. Time-on-stream dependency of the second-order rate constant k_2 (for catalyst and reaction condition compare Fig. 2): (a) first 3 h; (b) 3–50 h.

content and the length of the second period but also with the (indirect) correlation of the value of k_2 with the sulfate content (Fig. 5a and b). The higher the sulfate content (sample I > sample II > sample III) the lower the reactivity of the ammonia on the catalyst in the second reaction period. This indirect correlation between k_2 and sulfur content may be either due to a reduced intrinsic catalyst activity or to a reduced accessibility of ammonia with increased sulfate content. The temperature dependence of k_2 in the second reaction period was determined for sample II in the temperature range between 150 and 210 °C. The dependency obeys the Arrhenius equation with an activation energy of 42 kJ/mol, which is in good agreement with data reported for the DeNO$_x$ reaction in the literature [7,8].

Towards the end of the reaction, in the *third reaction period* an increase of k_2 with time-on-stream is observed for all catalyst samples (Fig. 5b). This increase corresponds to a low actual surface concentration of ammonia (about 0.8 mg/g catalyst in the sulfated samples). At the same time, in the third reaction period enhanced oxidation of NO–NO$_2$ in the gas leaving the reactor is observed indicating the possibility of a new reaction pathway with participation of NO$_2$. In fact, it is well known that under DeNO$_x$ reaction conditions the rate of the reaction given in Eq. (5) is much higher than the rate of reaction (6) [9]. It is to be expected that this sequence of rate magnitudes found under ordinary DeNO$_x$ conditions also holds for the DeNO$_x$ reaction with ammonia on sulfated catalyst surfaces:

$$NO_2 + NO + 2NH_3 = 2N_2 + 3H_2O \qquad (5)$$

$$NO + NH_3 + \tfrac{1}{2}O_2 = 2N_2 + \tfrac{3}{2}H_2O \qquad (6)$$

However, an essential contribution of the path via Eq. (5) in the preceding two reaction periods can be excluded, as the consumption rate of NO$_x$ at the higher ammonia surface concentration is much higher than the rate of NO$_2$ formation.

4. Summary and conclusions

A potential scenario is revealed for the formation of sulfuric acid in the flue gas streams in contact with a V$_2$O$_5$–WO$_3$/TiO$_2$ DeNO$_x$ catalysts under conditions of the low temperature processes (below 200 °C). In the absence of ammonia in the gas stream, the ammonium of the ammonium sulfate accumulated on the catalyst during the DeNO$_x$ process is consumed by reacting with NO$_x$. The magnitude of the second-order rate constants of the reaction between NO$_x$ from the gas phase with ammonia on the surface of different catalysts reflect the different adsorption states of the ammonia together with the different sulfate contents of the catalyst samples.

The sulfuric acid produced in the DeNO_x reaction on the surface of ammonium sulfate containing catalyst is displaced by water and desorbed into the gas stream. The desorption of sulfuric acid starts only after a considerable portion of the sulfate associated ammonia has been consumed in the reaction with NO_x. Therefore, the time-on-stream required for the appearance of H_2SO_4 in the gas phase increases with increasing catalyst ammonium sulfate content. In addition, this time is further prolonged by the fact that the ammonia on highly sulfated catalysts is less reactive: the second-order rate constant of the reaction between surface bound ammonia and gas phase NO_x decreases with increasing sulfate content.

In model experiments, it was shown that the sulfuric acid concentration in the gas phase behind a low temperature DeNO_x reactor may reach several milligrams per cubic metre and may thus give rise to severe corrosion problems if the downstream equipment, like a heat exchanger, is operated below the dew point of the acid in the flue gas.

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