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Theoretical and experimental study of the interaction between NO_x reduction and SO_2 oxidation over $DeNO_x$-SCR catalysts

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Abstract

The interaction between NO_x reduction and the undesired SO_2 oxidation over $DeNO_x$-SCR catalysts is investigated experimentally during catalyst conditioning and by transient and steady-state activity tests, as well as by means of model simulations in order to evaluate possible methods to minimize formation of SO_3.

Keywords: NO_x; Sulphur dioxide; Reduction; Oxidation; $DeNO_x$-SCR catalysts

1. Introduction

The selective catalytic reduction (SCR) of nitrogen oxides with ammonia is based on the main reaction:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (1)$$

However, in the case of sulfur-bearing fuels, reaction (1) occurs simultaneously with the undesired oxidation of SO_2:

$$SO_2 + 1/2O_2 \rightarrow SO_3 \qquad (2)$$

Typical $DeNO_x$-SCR process specifications include NO_x reduction efficiencies ≥ 80% with an ammonia slip of 1–5 ppm and SO_2 conversions lower than 1–2%. The low levels imposed to NH_3 slip and SO_2 conversion are intended to prevent SO_3, NH_3 and H_2O from forming ammonium sulfates which may deposit in the cold equipments downstream from the reactor, causing severe corrosion and pressure drop problems [1,2].

In this work the interaction between SO_2 oxidation and NO_x reduction over commercial and home-made V_2O_5-WO_3/TiO_2 $DeNO_x$ing catalysts has been studied, both experimentally and theoretically. The catalyst conditioning during SO_2 oxidation and NO_x reduction under SO_2 containing atmospheres is investigated to elucidate the effect of catalyst sulfation in reactions (1) and (2). To further clarify the kinetic interaction between the two reactions, already mentioned in [3], specifically designed experiments were performed under transient and steady state conditions. In particular the oxidation of SO_2 was performed in the presence of both reagents of NO_x reduction and the NO_x reduction was measured under the same conditions employed for SO_2 oxidation. The results of catalytic tests are discussed

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on the basis of the information provided by the characterization study performed over the home-made catalysts. Finally the possibility to take advantage of this interaction to minimize SO_2 conversion to SO_3 is explored by means of a complete mathematical model of the $DeNO_x$-SCR monolith reactor.

2. Experimental

Different commercial (honeycomb) and home-made (powder) V_2O_5-WO_3/TiO_2 catalysts have been used. Their characteristics are listed in Table 1. The honeycomb commercial-type SCR catalysts differ in the V_2O_5 content and the pitch. The home-made catalysts have been prepared from a paste consisting of WO_3/TiO_2 powder (ca. 10% w/w), previously impregnated with a solution of NH_4VO_3, an organic binder, a plasticizer and water. In some preparations silico-aluminates and glass fibres were added to the paste. The paste was dried at 110°C overnight, calcined at 550°C for 2 h and finally grounded to 8–14 mesh. The surface area of fresh home-made catalysts A and B is 88 m^2/g and 77 m^2/g respectively.

The apparatus and the procedures employed in the catalytic tests have been described elsewhere [3,4]. Standard conditions for SO_2 oxidation measurements included AV = 10 Nm/h (for honeycomb catalysts) or the corresponding contact time (for powder catalysts), and feed composition 1000 ppm SO_2, 2% O_2, 10% H_2O, N_2 balance. In the case of NO_x reduction standard test conditions included AV = 33 Nm/h, and feed composition 500 ppm NO_x, 550 ppm NH_3, 500 ppm SO_2, 2% O_2, 10% H_2O, N_2 balance.

Table 1
Characteristics of the tested catalysts

Catalyst	V_2O_5 content (% w/w)	Pitch (mm)
Home-made A	0.50	powder
Home-made B	0.45	powder
Commercial C	low	ca. 7
Commercial D	medium	ca. 5
Commercial E	medium	ca. 7
Commercial F	high	ca. 6

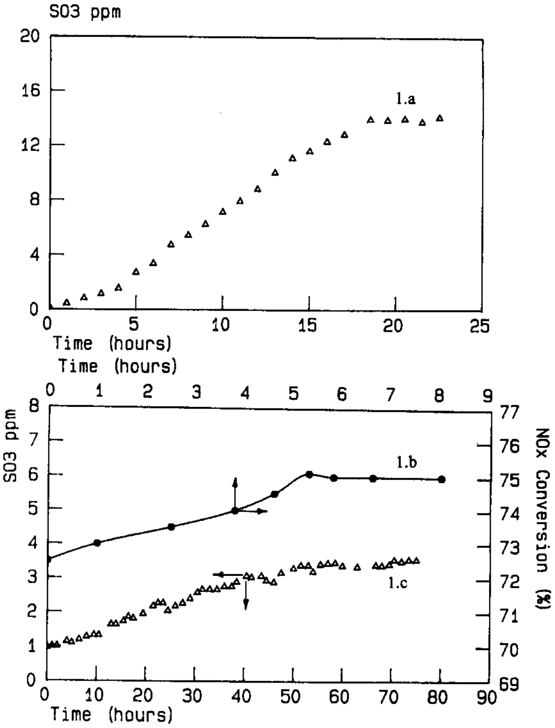

Fig. 1. (a) SO_2 conditioning of catalyst C (standard conditions); $T = 380°C$. (b) $DeNO_x$ conditioning of catalyst C; $T = 360°C$, AV = 25 Nm/h; inlet gas composition: 200 ppm NO_x; 250 ppm NH_3; 500 ppm SO_2; 2% O_2; 10% H_2O; N_2 balance. (c) SO_2 conditioning of catalyst C after $DeNO_x$; ; T = 360°C, AV = 10 Nm/h; inlet gas composition: 500 ppm SO_2; 2% O_2; 10% H_2O; N_2 balance.

Fresh and used home-made catalysts have been characterized by means of XRD, surface area and pore size distribution measurements, FTIR, TG, and chemical analysis. Details on the experimental techniques can be found elsewhere [5].

3. Results

3.1. Conditioning of the catalysts

Significant and reproducible steady state results for SO_2 oxidation and NO_x reduction are obtained only after the catalysts have been conditioned.

In the case of SO_2 oxidation the catalyst is conditioned after operation under standard conditions for several hours. As shown in Fig. 1a the concentration of SO_3 at the reactor exit is nil at time zero and increases slowly with time until the steady state concentration is attained. The catalyst conditioning is faster when the reaction is operated at higher SO_2 and O_2 concentrations, higher temperatures and lower area velocities (AV) and H_2O concentrations. This indicates that the process is controlled by the kinetics of SO_2 oxidation.

In the case of NO_x reduction the conversion of NO_x measured under standard conditions is already high at time zero, but increases further with time on stream until a stationary value is achieved after few hours (Fig. 1b). It is worth noting that under the experimental conditions of Fig. 1b the reaction is controlled by intraparticle and gas-solid diffusional limitations [4,6,7]. Accordingly a more conspicuous change of 11–12% is calculated for k_c, the pseudo first-order apparent rate constant of the chemical reaction, as compared to the change of 7–8% observed for k_{NO_x}, the first order overall activity constant, that is related to the NO_x conversion (x_{NO_x}) according to the following equation:

$$k_{NO_x} = -AV \times \ln(1 - x_{NO_x}) \qquad (I)$$

It has been observed that the catalysts already conditioned for NO_x reduction for a few hours may be not yet fully conditioned for SO_2 oxidation. Indeed smaller SO_3 concentrations are measured in this case at the beginning of the conditioning procedure for SO_2 oxidation and several hours are required to achieve a final stable SO_2 conversion level (Fig. 1c).

3.2. Characterization of fresh and used home-made catalysts

The FTIR spectra of the used home-made samples show more intense absorptions at 1050, 1135 and at 1210 cm^{-1}, that are attributed to ν(S–O) stretchings of surface anchored SO_4^{2-} species [8,9]. This indicates that sulfates have been accumulated onto the catalyst surface in the course of SO_2 oxidation. The FTIR spectra also show that the absorption observed at 980 cm^{-1} in the fresh samples and associated with V=O and W=O stretchings in isolated vanadyl and wolframyl groups [10,11] is shifted to slightly higher frequencies and is better resolved in the used catalyst. This has been explained by Busca and coworkers for V_2O_5/TiO_2 in terms of the increased V=O bond strength due to the weaker basic character of SO_4^{2-}, that act as ligand for coordinatively unsaturated vanadyl centres in sulfated catalysts with respect to oxide species of sulfate-free catalysts [12].

TG measurements point out a weight loss between 630–800°C for fresh catalyst and a weight loss between 580–800°C for used catalyst. This is due to the thermal decomposition of sulfates, along the lines provided by previous investigations over sulfated titania [8,9]. This result has been confirmed by FTIR, through the disappearance of the absorptions attributed to SO_4^{2-} species after treatment at 600°C. Quantitative analysis of the TG results indicate that ca. 0.5% w/w of SO_3 have been accumulated onto the catalysts during SO_2 oxidation.

It is expected that the sulfates accumulated during SO_2 oxidation are primarily associated with titania. This conclusion is based on the comparison with reference sulfated TiO_2, WO_3/TiO_2 and V_2O_5/TiO_2 samples, on the low tendency of tungsta-titania towards sulfatation and on the small vanadia content in the sample. Sulfates may also accumulate onto other catalyst constituents, e.g., silico-aluminates.

3.3. Catalytic behaviour under steady state and transient conditions

Oxidation of SO_2

The individual effects of NO_x and NH_3, the reactants of the $DeNO_x$ reaction, on SO_2 oxidation under steady state conditions have already been investigated [3]. It has been found that the conversion of SO_2 is slightly enhanced in the presence of NO_x but strongly inhibited by NH_3.

In the course of the present work experiments were performed in the absence of the catalyst and negligible SO_2 conversions were measured under these conditions. This proves that the promoting effect of NO_x is not due to a homogeneous contri-

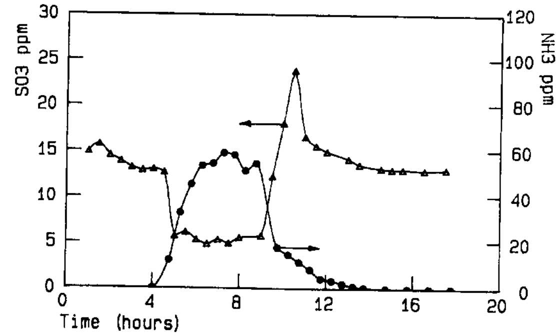

Fig. 2. Response of catalyst E to a step addition of NH_3 (standard conditions); $T = 380°C$. Time = 4 h: addition of 75 ppm NH_3. Time = 9 h: stop of NH_3 feed.

bution of NO_x to the reaction, as in the case of the commercial sulfuric acid process, but it is likely associated with overoxidation of the catalyst by NO_x. Indeed higher oxidation levels of V ions are associated with higher conversions of SO_2 to SO_3 [13].

The response of the catalyst to a step addition of NH_3 is given in Fig. 2: a drop in SO_3 concentration along with a regular increase with time of ammonia at the reactor exit is observed.

When the flow of ammonia is stopped ammonia is progressively released from the catalyst and a maximum in SO_3 concentration is observed before the original SO_2 oxidation level is restored. The amount of ammonia desorbed roughly corresponds to that originally adsorbed, which implies that the interaction of ammonia with the catalyst surface is essentially reversible in nature.

From Fig. 2 we calculate that the amount of reversibly adsorbed ammonia is in the order of 3×10^{-5} moles of NH_3/g of catalyst and that the amount of sulfates that have been accumulated due to the adsorption of ammonia is about 0.05% w/w. This last quantity corresponds to ca. 10% of the total amount of sulfates accumulated during catalyst conditioning, which in turn is comparable to the amount of adsorbed ammonia. It appears therefore that: (i) the adsorption capacity of ammonia is primarily controlled by the sulfates accumulated during catalyst conditioning: accordingly, the adsorption of ammonia under SO_2 containing atmospheres is likely due to an acid-base interaction involving sulfates; (ii) the overaccumulation of sulfates onto the catalyst is due to a similar acid-base interaction involving adsorbed ammonia and gaseous SO_3.

Reduction of NO_x

The effects of SO_2 and O_2, the reagents of the SO_2 oxidation reaction, on NO_x reduction have already been investigated in [4], where it is reported that the rate of NO_x removal increases up to 2–4% oxygen and that the addition of SO_2 does not affect appreciably the conversion of NO_x. It has also been reported that the reduction of NO_x is inhibited by water.

Oxidation of SO_2 in the presence of NO_x

The kinetic interaction between $DeNO_x$ and SO_2 oxidation reactions has been studied by performing experiments at different AV values in the presence of $NH_3 + NO_x$, where both reactions occur simultaneously. The results of SO_2 oxidation are shown in Fig. 3.

At low AV values and very low inlet NH_3/NO_x ratios ($\alpha = NH_3/NO_x \ll 1$) the SO_2 conversion is higher than in the absence of NO_x and the behaviour is dominated by the promoting effect of NO_x. On increasing the inlet NH_3/NO_x ratio ($\alpha \langle 1$) the SO_2 conversion decreases slightly due to the consumption of NO_x. For very high inlet NH_3/NO_x ratios ($\alpha \gg 1$) the SO_2 oxidation is strongly reduced due to the presence of unreacted ammonia and the SO_2 oxidation level is comparable to that

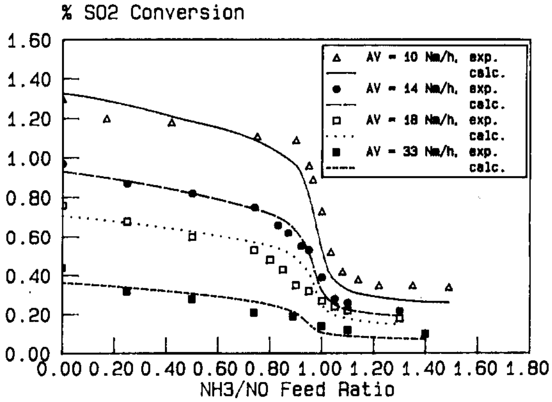

Fig. 3. Experimental and calculated SO_2 conversion over a commercial SCR monolith catalyst as function of NH_3/NO feed ratio and of the area velocity.

measured in the case of 50–100 ppm of NH_3 with no NO_x in the feed.

Inspection of Fig. 3 also indicates that the conversion of SO_2 decreases on increasing AV, as expected, and that for the different settings of AV a drop in SO_2 conversion is always observed at NH_3/NO_x values around unity.

4. Discussion

4.1. *Chemistry of the interaction between NO_x reduction and SO_2 oxidation*

FTIR and TG data prove that conditioning of the catalyst under SO_2 containing atmosphere is associated with a build-up of sulfates onto the catalyst surface. The process is accelerated by operating at conditions that favour the oxidation of SO_2 to SO_3, namely at higher temperatures, at greater SO_2 concentrations and at lower area velocities. This proves that catalyst conditioning is controlled by the kinetics of SO_2 oxidation.

The catalyst conditioning requires typically few hours in the case of NO_x reduction but it takes several hours in the case of SO_2 oxidation. The different characteristic times of catalyst conditioning for the two reactions can be explained by assuming that conditioning involves sulfatation of vanadia in the former case and of vanadia and titania (or other catalyst constituents, e.g., silico-aluminates) in the latter case. In this respect it is worth noticing that: (i) vanadia is sulfated first and the other catalyst components later on because SO_3 is formed at the vanadium sites and is kept strongly adsorbed at these sites; (ii) the surface coverage of vanadia is much lower than that of titania; (iii) tungsta shows a lower tendency towards sulfatation due to the stronger acidity of WO_3/TiO_2.

0.5% w/w of SO_3 are accumulated under standard conditions for SO_2 oxidation during catalyst conditioning. Such an amount compares well with the one estimated assuming that after few hours, corresponding to the characteristic time of conditioning for NO_x, SO_3 is already produced at the rate observed under steady state conditions but is being accumulated onto the catalyst until SO_3 adsorption–desorption equilibrium is approached. This appears to be consistent with the picture outlined above where vanadia is sulfated first and titania later on.

As for NO_x reduction the promoting effect of sulfates on this reaction is associated with the higher Lewis and Brønsted acidity of sulfated catalysts, that is known to favour the SCR reaction, possibly through an enhanced adsorption capacity of NH_3. Still the increase of k_c is limited due to the fact that V_2O_5-WO_3/TiO_2 are already characterised by remarkably strong acidity [13].

4.2. *Model analysis*

Since the rate of SO_2 oxidation depends on the local concentrations of NO and NH_3, a quantitative elucidation of the kinetic interaction between NO_x reduction and SO_2 oxidation over SCR catalysts requires a detailed description of the internal concentration gradients of NO and NH_3 originated by the diffusion-limited DeNO_x reaction throughout the porous matrix of the monolith catalyst. This point has been addressed in a previous paper [14], where a steady-state mathematical model of the SCR monolith reactor is reported, which implements a rate expression for SO_2 oxidation accounting both for inhibition by NH_3 and for promotion by NO. The adequacy of the model in reproducing the observed dependence of SO_2 conversion on the NH_3/NO feed ratio is documented in Fig. 3 by the match between the experimental data and the solid lines, which represent calculated values. As model parameters, the NO and NH_3 effective intraporous diffusivities were determined experimentally, while the rate constants were obtained by independent kinetic measurements.

The model has been applied to study practical solutions aimed at exploiting the inhibiting action of ammonia on the undesired oxidation of SO_2. Fig. 3 indicates that SO_2 conversion to SO_3 is minimized when an excess of ammonia prevails throughout the catalyst volume. Indeed, this is typical of operation with $\alpha > 1$, whereas industrial operation of SCR reactors involves substoichiometric NH_3/NO feed ratios ($\alpha < 1$). By means of model simulations we have investigated whether, under these conditions, an excess of ammonia can be still brought about within the catalyst either by appropriate modifications of the catalyst pore structure or by ad hoc reactor configurations.

Influence of catalyst pore structure

Concerning the catalyst pore size distribution, it turns out that internal NH_3 concentrations are favoured by shifting the intraporous diffusion towards the Knudsen regime, since the effective diffusivity of ammonia is higher than the diffusivity of NO in this case. This implies adoption of catalysts with large void fractions of small micropores: unfortunately, such a morphological structure is not viable, since it is also associated with very low effectiveness factors for the $DeNO_x$ reaction. In any event, it becomes impossible to effect significant internal NH_3 concentrations when $\alpha < 0.9$ due to the dominance of the stoichiometric constraints [14]. Thus, the optimal morphological configuration of SCR catalysts is one with a large fraction of macropores, favouring the diffusion-limited $DeNO_x$ reaction, and low specific surface areas, in order to moderate SO_2 oxidation.

Reactor configuration

A different way of exploiting the NH_3 inhibition to minimize SO_3 formation is based on the idea of splitting the NO_x containing feed stream to the SCR reactor so that a portion of the catalyst volume operates with an excess of ammonia, even though the overall NH_3/NO feed ratio remains a substoichiometric one. The simplest design accomplishing this purpose involves two reactors in series, with catalyst volumes V_1 and V_2. Suppose that the total gas feed is partitioned in two streams, with flow rates Q_1 and Q_2, respectively. Q_1 is fed to the first reactor after mixing with ammonia, whereas Q_2 is simply combined with the stream entering the second reactor, with no further addition of NH_3. It is easily seen that, depending on the split ratio $Q_1/(Q_1+Q_2)$, an excess of NH_3 can be attained in the first reactor with an overall $\alpha < 1$. In principle such a configuration is expected to reduce the extent of SO_3 formation while still securing low values of NH_3 slip. To test the idea, simulations have been carried out assuming: overall area velocity AV = 10 Nm/h, overall $\alpha = 0.8$, NH_3/NO feed ratio = 1 in the first reactor, feed concentrations = 500 ppm NO, 1000 ppm SO_2, kinetic parameters and catalyst morphological properties representative of commercial SCR catalysts [14]. Results showing the calculated influence of partitioning the total catalyst volume between reactors 1 and 2 are presented in Fig. 4. The reference case, corresponding to a conventional configuration with a single SCR reactor, is given by $R = V_1/(V_1+V_2) = 0$, with the total feed stream entering the second reactor. On increasing R the outlet SO_3 concentration is seen to decrease due to the enhanced inhibiting action of ammonia in the first reactor, as expected, while the NH_3 slip first slightly decreases and then grows markedly. Notice that the undesired precipitation of ammonium bisulfate is controlled by the product of the outlet concentrations of SO_3 and NH_3 due to thermodynamic reasons [15]: Fig. 4 shows that such a product goes through a minimum, too, the optimum reactor configuration ($R \cong 0.3$) securing a 20% reduction as compared to the reference conditions.

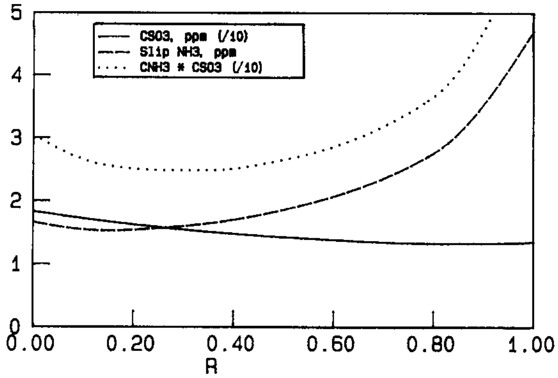

Fig. 4. Calculated effect of catalyst volume split ratio R on the outlet concentrations of SO_3 and NH_3, and on their product.

The results in Fig. 4 are by no means optimized and may be sensitive to the assumptions and parameter values adopted in our calculations. It appears however that, in principle, the inhibition of SO_2 oxidation by ammonia can be advantageously exploited by adopting a split feed configuration of the SCR reactor.

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