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Catalysis Today 62 (2000) 319–328

CATALYSIS TODAY

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Investigation of simultaneous adsorption of SO_2 and NO_x on Na-γ-alumina with transient techniques

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Abstract

The simultaneous adsorption of SO_2 and NO_x on Na-γ-alumina was studied by means of step experiments in a fixed bed plug flow reactor at 387 K and atmospheric pressure. Typically the molar composition of the feed gas was 1.5% SO_2, 1% O_2, 4000 ppm NO, 500 ppm NO_2, and Ar. First the adsorption behavior of the pure components was measured. SO_2 and NO_2 adsorb easily, whereas NO and O_2 do not adsorb. Moreover there is no influence of O_2 on the adsorption behavior of the pure components.

NO and O_2 adsorption require the simultaneous presence of SO_2, NO, and O_2. The NO and O_2 adsorption rate is enhanced by an increasing SO_2/NO ratio. The total amount of SO_2 adsorbed is not affected by the simultaneous adsorption of NO and O_2. However, NO_2 adsorption increases the SO_2 adsorption capacity. In the presence of NO_2 most of the adsorbed NO_x is released as NO. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: SO_2; NO_x; Adsorption; Alumina; Transient techniques

1. Introduction

The current technology option for the removal of SO_2 and NO_x from flue gas is the two step process consisting of SO_2 sorption in water, followed by selective catalytic reduction (SCR) of NO_x [1]. This process is wet, multistep, costly, and sometimes induces the difficulty of product disposal. Therefore a single step, dry process for the removal of SO_2 and NO_x is highly desirable. FLS-miljø-Denmark has developed a new process based on the simultaneous adsorption of SO_2 and NO_x on Na-γ-alumina in a circulating dilute phase riser reactor. The process is dry and compact and has a high removal efficiency of SO_2 and NO_x [2]. The process was derived from the NOXSO process which makes use of larger sorbent particles and a dense fluidized bed reactor [3,4].

The adsorption of SO_2 on γ-alumina is well documented [5,6] and the influence of Na-impregnation on the SO_2 adsorption on γ-alumina was investigated by Mohammed Saad et al. [7] and Mitchell et al. [8]. On the simultaneous adsorption of SO_2 and NO_x, however, not much information is available in literature. This paper reports on an investigation of the simultaneous adsorption of SO_2 and NO_x on Na-γ-alumina.

2. Experimental technique and set-up

A fixed bed plug flow reactor is used for the experiments. This allows to focus on the reaction mechanism at well defined flow conditions, but requires a non-steady state operation.

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PII: S0920-5861(00)00433-8

Nomenclature

S	reactor cross section surface area (m^2_{reac})
u_{sup}	superficial gas velocity ($m^3_g\, m^{-2}_{reac}\, s^{-1}$)
C	concentration ($mol\, m^{-3}_{gas}$)
r	adsorption rate ($mol\, kg^{-1}$ sorbent s^{-1})
t	time (s)
V	reactor volume (m^3_{reac})
W	amount sorbent (kg)

The step response technique is used [9,10]. Fig. 1 shows a schematic representation of the experimental set-up used. First an inert gas (Ar) is flowing through the boro-silicate glass reactor while a gas mixture containing all components of interest (SO_2, NO, NO_2, O_2, Ar) is sent to the vent. Flow rate and pressure of both the flows have to be equal. By switching a four-way valve, the gas mixture is sent to the reactor and the inert gas to the vent. The induced step is measured at the inlet of the reactor immediately upstream of the sorbent bed and the step response is measured immediately downstream of the sorbent bed. A Balzers Thermostar mass spectrometer is used for the measurements.

Table 1 summarizes the range of experimental conditions.

The sorbent is Na-γ-alumina powder with a mean particle size of 64 μm. To avoid high pressure drops over the sorbent bed, the sorbent is pelletized and then crushed to a mean particle diameter of 200–250 μm. The particle diameter is still small enough to avoid diffusional limitations and to guarantee plug flow conditions in the reactor. Next the sorbent is dried for 5 h at 110°C and calcined for 15 h at 600°C.

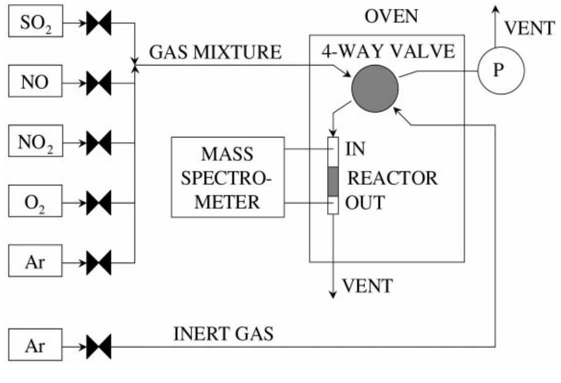

Fig. 1. Experimental set-up.

Table 1
Range of the experimental conditions

Reactor diameter (mm)	3.5
Mean particle diameter (μm)	200–250
Amount sorbent (g)	0.045
Bed height (mm)	10
Temperature (K)	387
Total flow rate ($mol\, s^{-1}$)	2.088×10^{-4}
Concentration (mol%)	
SO_2	0.86–2.3
NO	0.29–2.0
NO_2	0.0–0.43
O_2	0.0–1.0

Results are shown as inlet step and outlet responses and in terms of conversion versus time curves. The time is starting with the beginning of the adsorption. Conversion is defined as:

$$\text{Conversion} = \frac{(C_{in} - C_{out})}{C_{in}} \tag{1}$$

The specific adsorption capacity for a certain component is defined as the total amount of the component adsorbed per mass unit of the sorbent:

$$\text{Specific capacity} = \frac{S}{W} u_{sup} \int_{t=0}^{t_{end}} (C_{in} - C_{out})\,dt \tag{2}$$

The upper integration limit is typically 35 s.

3. Results and discussion

3.1. Separate adsorption of SO_2 and NO_x

The separate adsorption behavior of SO_2, NO, and NO_2 was investigated first in the absence and then in the presence of O_2.

3.1.1. SO_2 or SO_2/O_2

Fig. 2 shows the measured inlet step and outlet response for a mixture of SO_2, O_2 and Ar. SO_2 is adsorbed while O_2 is not adsorbed. No SO_3 is detected. However, it is seen that H_2O is desorbed from the sorbent surface. As all the physically adsorbed H_2O had already been removed by the calcination, the H_2O peak observed in Fig. 2 results from the adsorption of SO_2. This explains the delay in the H_2O appearance. The H_2O response shows a maximum that coincides

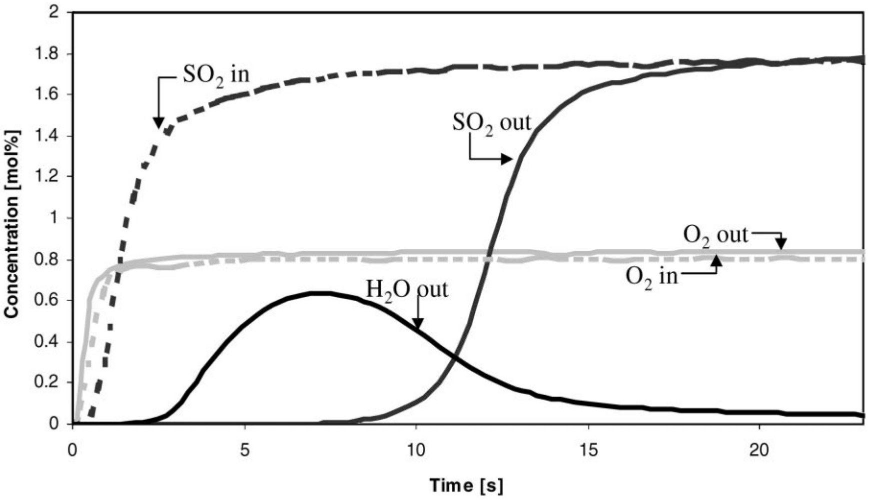

Fig. 2. Measured inlet step (- - -) and outlet response (—) of the concentrations of SO_2, O_2, and H_2O. Adsorption experiment starting from a fresh sorbent bed. Inlet concentrations: 1.7434 mol% SO_2, 0.8936 mol% O_2.

with the SO_2 breakthrough. One possible source of the H_2O released are the OH groups on the sorbent surface.

The adsorption of SO_2 in the absence of O_2 shows identical SO_2 and H_2O responses as seen in Fig. 2. No influence of the presence of O_2 is seen on the SO_2 and H_2O response.

Introducing the active site * the adsorption mechanism for SO_2 is written as:

$$SO_2 + * \rightarrow SO_2* \tag{3}$$

3.1.2. NO or NO/O₂

Experiments were performed with a NO/Ar mixture and a NO/O_2/Ar mixture.

No NO is adsorbed, independently of the presence of O_2. If O_2 is in the feed, again no adsorption of O_2 is observed.

3.1.3. Mixture of NO₂, NO, and O₂

To investigate the NO_2 behavior a mixture of NO_2, NO, and O_2 is sent to the reactor. Fig. 3 shows the measured inlet step and outlet responses for the concentrations of the different components. NO_2 is completely adsorbed. Part of the adsorbed NO_2 appears in the outlet stream as NO. This explains why the NO outlet response goes beyond the NO inlet concentration. The O_2 inlet and outlet response are identical. A possible mechanism for the above phenomena is:

$$NO_2 + * \rightarrow NO_2* \tag{4}$$

$$NO_2* \rightarrow NO + O* \tag{5}$$

While part of the adsorbed NO_2 is released as NO, the oxygen atoms do not desorb associatively to a significant extent.

3.2. Simultaneous adsorption of SO₂ and NO

3.2.1. In the absence of O₂

An experiment was performed with SO_2, NO, and Ar in the feed. SO_2 is adsorbed as fast as in the absence of NO (Fig. 2), but no NO is adsorbed. Simultaneous adsorption of SO_2 and NO is not possible in the absence of O_2.

3.2.2. In the presence of O₂

When a mixture of SO_2, NO, and O_2 is fed, all three components are adsorbed. Fig. 4 shows the measured inlet step and outlet response of the concentrations of SO_2, NO, and O_2 for a typical experiment. The NO and O_2 adsorption behavior is quite similar. The adsorption of SO_2, NO, and O_2 results in desorption of H_2O from the sorbent surface. As the physically adsorbed H_2O was already removed by the calcination, the H_2O released is related to the adsorption of SO_2,

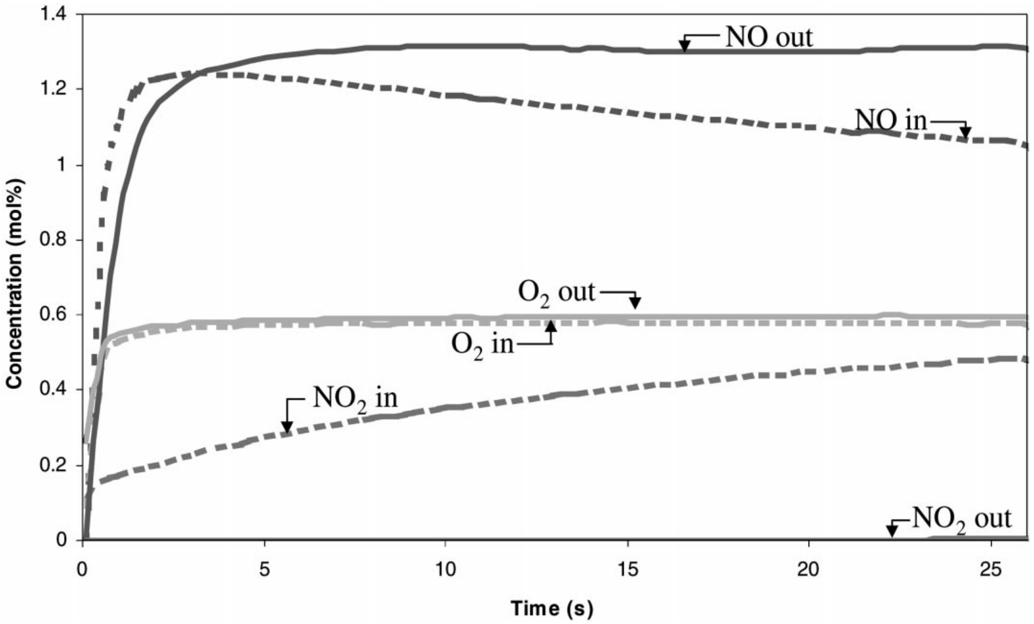

Fig. 3. Measured inlet step (- - -) and outlet response (—) of the concentrations of NO, NO_2, and O_2. Adsorption experiment starting from a fresh sorbent bed. Inlet concentrations: 0.5 mol% NO_2, 1.1 mol% NO, and 0.6 mol% O_2.

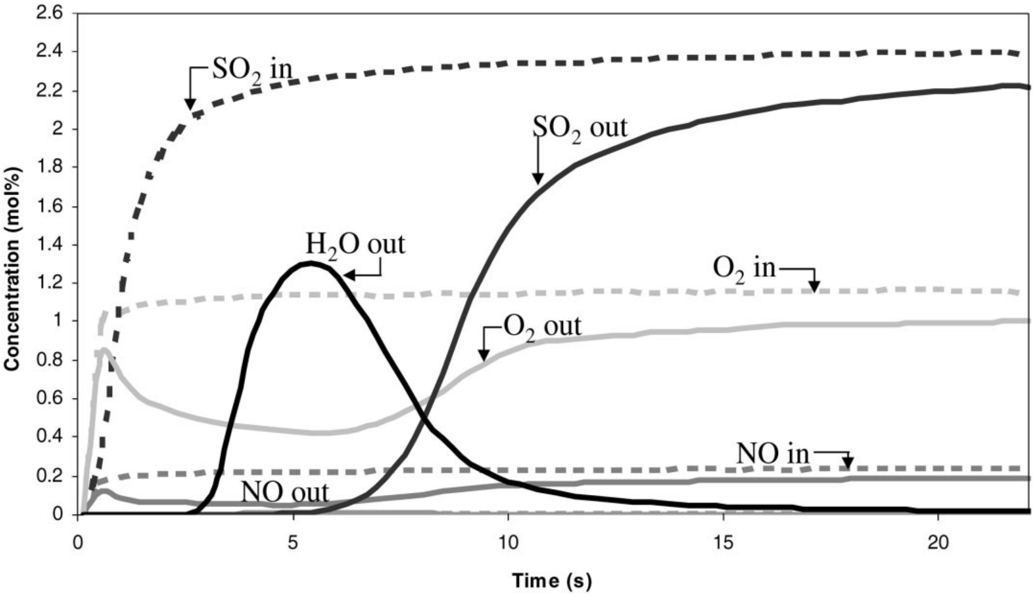

Fig. 4. Measured inlet step (- - -) and outlet response (—) of the concentrations of SO_2, NO, O_2, and H_2O. Adsorption experiment starting from a fresh sorbent bed. Inlet concentrations: 2.3 mol% SO_2, 0.2875 mol% NO, 1.0 mol% O_2.

NO, and O_2. Compared to the H_2O response observed in case of adsorption of pure SO_2 (Fig. 2), the H_2O response peak is more intense. This could be due to the interaction of SO_2* with another free active site *, involving a OH group, in the presence of NO and O_2. Again the maximum of the H_2O response coincides with the breakthrough of SO_2 and with the minima in the NO and O_2 response. No SO_3 is detected. The response of NO and O_2 first go through a maximum before adsorption takes place. This indicates that an intermediate site SO_2* is required for the simultaneous adsorption to happen. In other words, only when SO_2* is sufficiently present on the sorbent, NO and O_2 start adsorbing. The total amount of SO_2 adsorbed is not influenced by the NO and O_2 adsorption. This suggests that NO and O_2 adsorption do not consume free active sites for SO_2 adsorption.

To investigate the effect of the presence of SO_2* on the adsorption of NO and O_2 further, an experiment was performed on a bed that was first saturated with SO_2. Fig. 5 shows the corresponding adsorption behavior. The time between the saturation of the sorbent bed with SO_2 and imposing the step of the gas mixture is about 30 min, which is necessary for the stabilization of the set-up. Although less, still some SO_2 adsorption is observed. This may be due to desorption of SO_2 in the time between the saturation of the sorbent bed with SO_2 and the experiment. More important is that NO and O_2 adsorb as fast as on a fresh sorbent bed (Figs. 4 and 5). The NO and O_2 adsorption are even faster in the beginning of the adsorption. Indeed, it is seen from Figs. 4 and 5 that the maximum in the beginning of the NO and O_2 response is far less pronounced on the bed saturated with SO_2. From this it can be concluded that for the adsorption of NO and O_2, the presence of SO_2* is first of all necessary and that the rate of the NO and O_2 adsorption increases with increasing SO_2* concentration. The adsorption capacities of NO and O_2 are not influenced by the saturation of the bed with SO_2 first. This suggests that there is no competition between SO_2 and NO and O_2 for free active sites which is consistent with the absence of NO or O_2 adsorption when feeding separately NO or NO/O_2.

In Fig. 5 the H_2O response is seen to be far less pronounced as when starting from a fresh sorbent bed

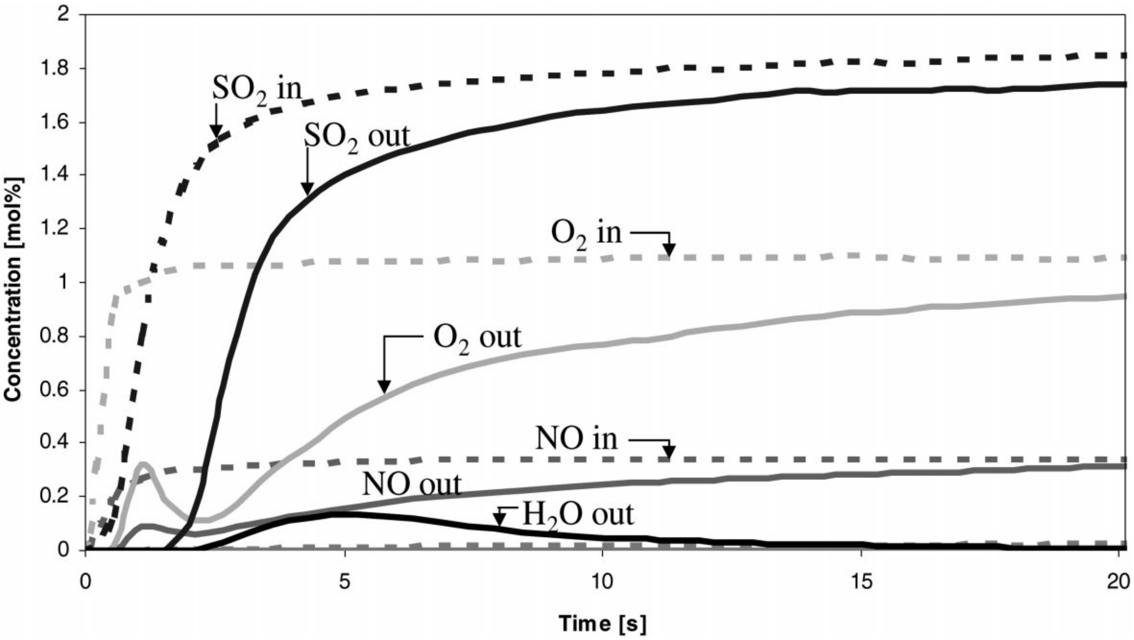

Fig. 5. Measured inlet step (- - -) and outlet response (—) of the concentrations of SO_2, NO, O_2, and H_2O. Adsorption experiment starting from a sorbent bed saturated with SO_2. Inlet concentrations: 1.8 mol% SO_2, 0.35 mol% NO, 0.01 mol% NO_2, 1.0 mol% O_2.

Table 2
Specific sorbent capacities for SO_2, NO, NO_2, and O_2 in case of (a) inlet concentrations: 2.3 mol% SO_2, 0.2875 mol% NO, 1.0 mol% O_2 (Fig. 4), (b) inlet concentrations: 2.3 mol% SO_2, 0.18 mol% NO, 0.27 mol% NO_2, 1.35 mol% O_2 (Fig. 9)[a]

Feed	Capacity ($mol\,kg^{-1}$ sorbent)			
	SO_2	NO	NO_2	O_2
(a) SO_2, NO, O_2	1.12	0.127	0.0084	0.484
(b) SO_2, NO, NO_2, O_2	1.754	−0.284	0.3	0.132

[a] Both adsorption experiments starting from a fresh sorbent bed.

(Fig. 4). The H_2O desorption is also delayed. This is due to the preceding removal of H_2O by the saturation of the bed with SO_2 first, as observed in Fig. 2.

As shown in Table 2, the adsorption capacities for SO_2, NO, and O_2 are related as $10SO_2$ for 1NO and $4O_2$. The large amount of O_2 and SO_2 adsorbed per mole of NO can only be explained by oxidation of the adsorbed SO_2 to SO_3 on the surface. Therefore, SO_2* is first associated with a second free active site * to form an unstable intermediate which is stabilized by consecutive association steps with NO, O_2 and SO_2. The second free active site is regenerated in the following association steps, resulting in NO and O_2 adsorption without consumption of free active sites. The global reaction may be written as follows:

$$\mathrm{NO} + 4\,\mathrm{O_2} + 10\,\mathrm{SO_2}* + * \rightarrow [(\mathrm{NO_2})(\mathrm{SO}_x)_{10}*_{10}] + * \qquad (6)$$

The appearance of the H_2O peak suggests that during reaction (6) dehydroxylation of the surface occurs.

The SO_x species in the complex that is formed, are either sulfite or sulfate species, dependent on the stoichiometry of the reaction. The global reaction can be divided into elementary steps in several possible ways. One possibility is that adsorbed SO_2* is first to be oxidized before associating with NO. From the pure component adsorption data it is however clear that NO and O_2 will not adsorb on free active sites *, but on SO_2* or on one of the intermediates. Further refinement of the mechanism is only possible on a quantitative basis, by modeling of the data. The latter requires deriving the continuity equations for the gas phase components and the surface species [11].

3.2.3. *Effect of the SO_2/NO ratio on the simultaneous adsorption of SO_2, NO, and O_2*

The effect of the SO_2/NO ratio on the simultaneous adsorption of SO_2, NO, and O_2 is further studied by maintaining the NO and O_2 concentration constant while varying the SO_2 concentration.

In Figs. 6 and 7 the SO_2 and the NO conversion is shown as a function of the time for three SO_2/NO ratios. The conversion is defined by (1). All three experiments were performed starting from a fresh sorbent bed. With increasing SO_2 concentration, the SO_2 breakthrough occurs faster. This is expected as the sorbent bed will be saturated faster. More interesting is the effect of the SO_2 concentration on the NO adsorption behavior. Increasing SO_2 concentration causes an increase in the NO conversion as shown in Fig. 7. The maximum in the NO conversion also occurs faster due to the faster build-up of SO_2* at higher SO_2/NO ratio. This confirms that increasing SO_2 concentration has a positive influence on the NO adsorption, again indicating SO_2* as an intermediate involved in the NO and O_2 adsorption.

3.3. *Adsorption of SO_2/NO_2/NO mixture*

3.3.1. *In the absence of O_2*

An experiment was performed with SO_2, NO, and NO_2 in the feed. Fig. 8 shows the measured inlet step and outlet responses. NO_2 is completely adsorbed. It is seen that the outlet response of NO is beyond the inlet concentration. This is explained by desorption of the adsorbed NO_2 as NO. No O_2 is detected. The SO_2 adsorption capacity has increased by more than 70% compared to the experiments done in the absence of NO_2 (Fig. 4), even for a lower SO_2 inlet concentration. Per mole of NO_2, one mole of NO is released and 3 moles of SO_2 are adsorbed and no O_2 is formed. The enhanced SO_2 capacity is explained by the fact that NO_2 adsorbed sites are acting as new sites for multiple SO_2 adsorption by the following global reaction

$$3\mathrm{SO_2} + \mathrm{NO_2}* \rightarrow \mathrm{NO} + (\mathrm{SO}_x)_3* \qquad (7)$$

The SO_x species in the complex that is formed, are either sulfite or sulfate species.

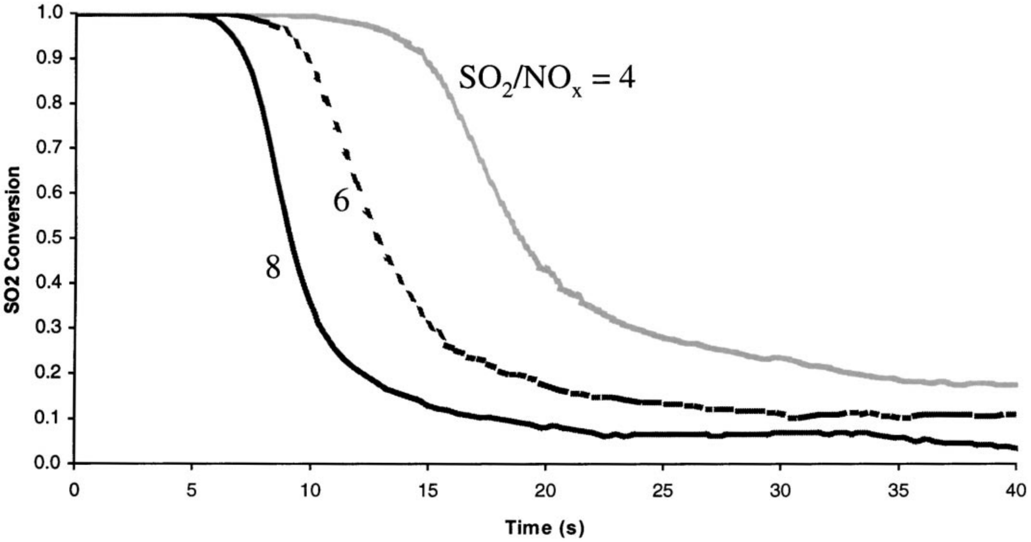

Fig. 6. SO_2 conversion as a function of time: effect of SO_2/NO_x ratio. Conversion defined by (1). Constant inlet concentrations: 0.2875 mol% NO, 0.8936 mol% O_2; varying SO_2 inlet concentration. All three adsorption experiments were starting from a fresh sorbent bed.

3.3.2. In the presence of O_2

A mixture of SO_2, NO, NO_2, and O_2 was admitted to a fresh bed. The inlet step and outlet responses are shown in Fig. 9.

It is interesting to note that the NO concentration increases and goes beyond the inlet concentration in the beginning and then comes down. This is due to the combination of the formation of NO from adsorbed

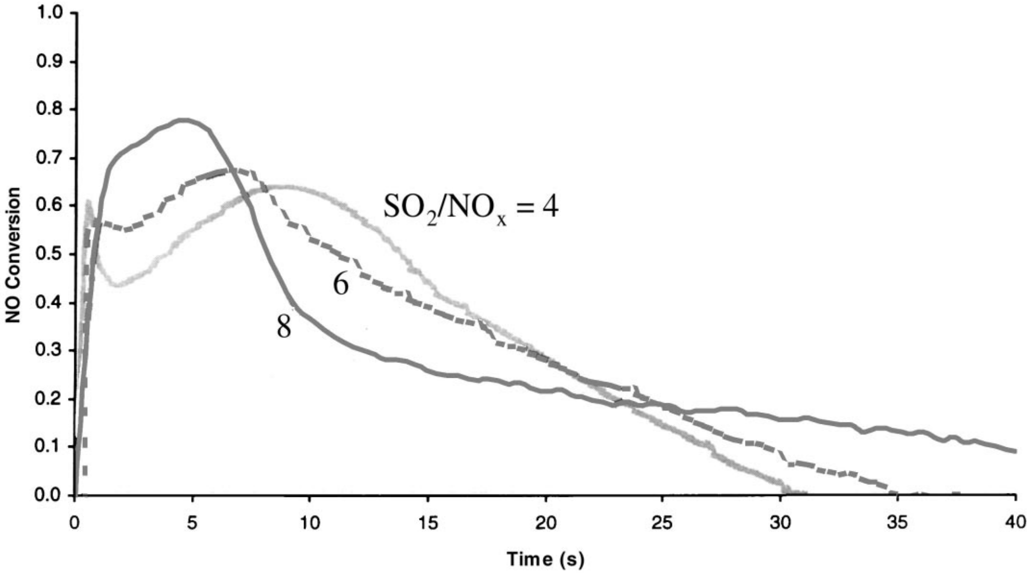

Fig. 7. NO conversion as a function of time: effect of SO_2/NO_x ratio. Conversion defined by (1). Constant inlet concentrations: 0.2875 mol% NO, 0.8936 mol% O_2; varying SO_2 inlet concentration. All three adsorption experiments were starting from a fresh sorbent bed.

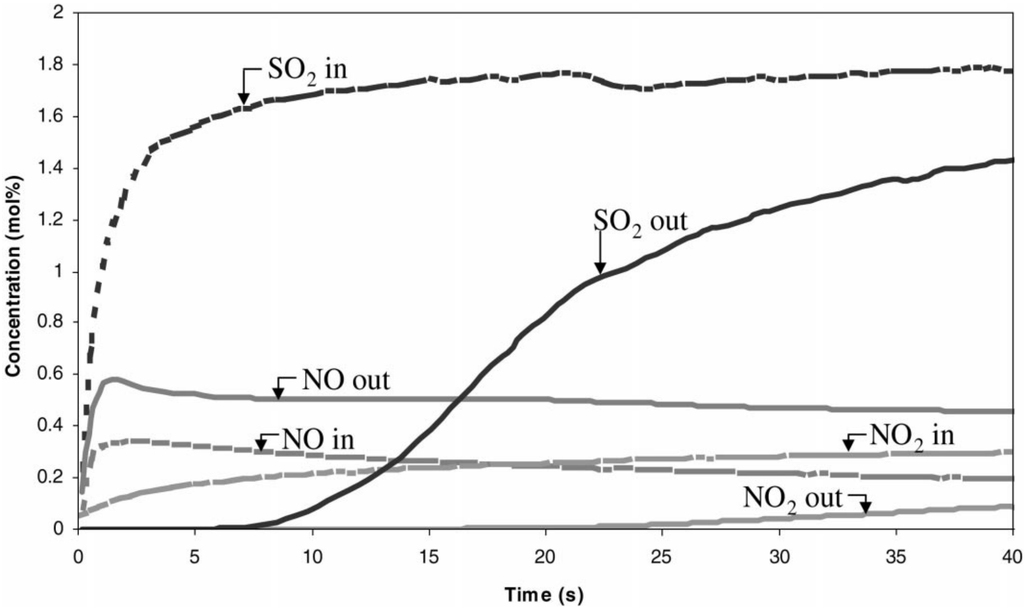

Fig. 8. Measured inlet step (- - -) and outlet response (—) of the concentrations of SO_2, NO, and NO_2. Adsorption experiment starting from a fresh sorbent bed. Inlet concentrations: 1.8 mol% SO_2, 0.2875 mol% NO, 0.39 mol% NO_2.

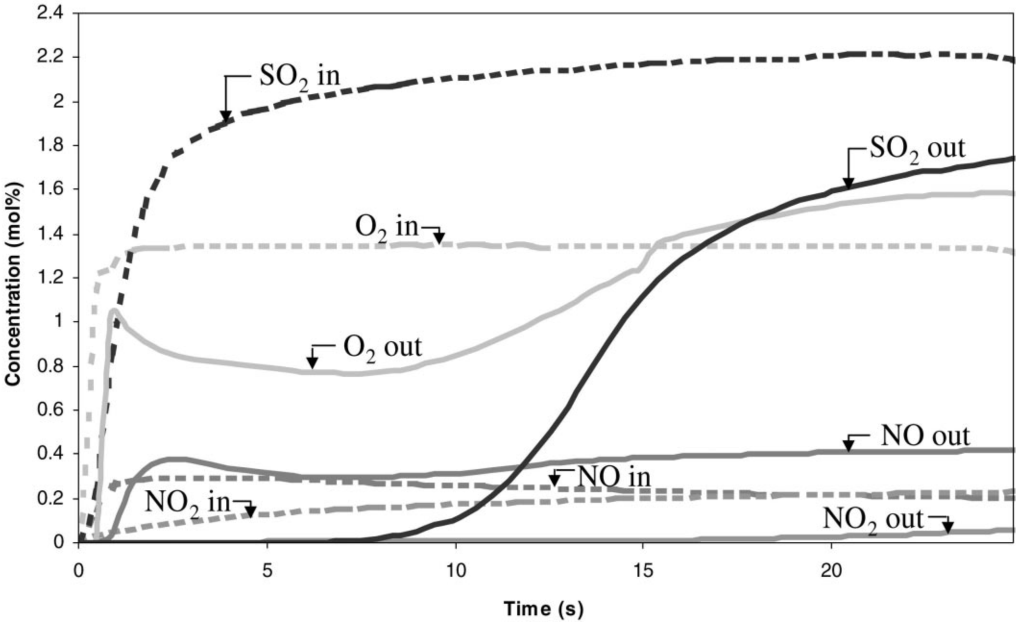

Fig. 9. Measured inlet step (- - -) and outlet response (—) of the concentrations of SO_2, NO, NO_2, and O_2. Adsorption experiment starting from a fresh sorbent bed. Inlet concentrations: 2.3 mol% SO_2, 0.18 mol% NO, 0.27 mol% NO_2, 1.35 mol% O_2.

NO_2 by reactions (5) and (7) and the simultaneous adsorption of NO with O_2 and SO_2 by reaction (6). As expected from reactions (5) and (7) no extra O_2 is formed from NO_2 adsorption in the beginning. From Table 2 it is seen that again the adsorption capacity for SO_2 has significantly increased compared to cases where SO_2 is adsorbed in the absence of NO_2 (Figs. 2 and 4).

Remarkably after a certain period and coinciding with NO_2 breakthrough around 25 s, all the adsorbed NO, NO_2, and most of the adsorbed O_2 is released, as seen in Fig. 9. It is seen in Table 2 case b) that the specific sorbent capacity for NO as calculated from (2) becomes negative and that the magnitude of the NO production equals the magnitude of the NO_2 adsorption capacity. All the NO_2 adsorbed was released as NO by reaction (5), but more important all the NO adsorbed by reaction (6) is desorbed in the presence of NO_2. This is explained by the reaction of NO_2 with the $[(NO_2)(SO_x)_{10}\ {*}_{10}]$ complex

$$[(NO_2)(SO_x)_{10}{*}_{10}] + NO_2 \rightarrow 2NO + 4O_2 + [(SO_x)_{10}{*}_{10}] \qquad (8)$$

To confirm the possibility of reaction (8), an experiment was performed where the sorbent bed was first saturated with NO_2, before admitting a mixture of SO_2, NO, NO_2, and O_2. The measured inlet step and outlet responses are shown in Fig. 10. Almost right from the beginning the adsorbed NO_2 is released as NO, leading to a sharp increase of NO in the NO outlet response. This is explained by reaction (7). Simultaneously with NO_2 breakthrough, O_2 and NO are released by reaction (8).

4. Practical consequences

The SNAP process is a riser reactor application. The sorbent powder and the flue gas move cocurrently upwards through the reactor. This reactor type is seen to make the SNAP process very effective.

Flue gas typically contains 1000 ppm SO_2, 500 ppm NO, 50 ppm NO_2, and an excess of O_2. NO_2 is adsorbed first on the free active sites (reaction (4)) and will be removed completely from the flue gas immediately in the bottom part of the reactor. SO_2 also adsorbs on free active sites (reaction (3)) from the

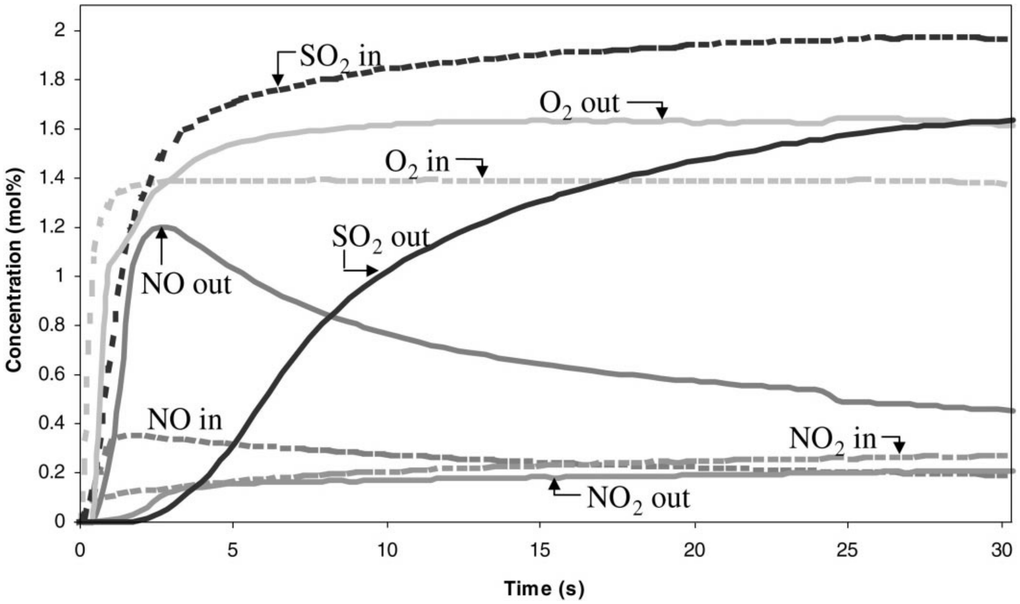

Fig. 10. Sequential to Fig. 3: measured inlet step (- - -) and outlet response (—) of the concentrations of SO_2, NO, NO_2, and O_2. Adsorption experiment starting from a sorbent bed saturated with NO_2 (from Fig. 3). Inlet concentrations: 1.9 mol% SO_2, 0.25 mol% NO, 0.2 mol% NO_2, and 1.3 mol% O_2.

reactor inlet on. NO and O_2 adsorption however require the presence of adsorbed SO_2* (reaction (6)) and take place more downstream in the riser reactor. The sorbent capacity is such that there are still free active sites available for reaction (6) more downstream.

As NO_2 is adsorbed in the bottom part of the riser reactor and no NO_2 is left in the flue gas, decomposition of the $[(NO_2)(SO_x)_{10} *_{10}]$ complex by NO_2 (reaction (8)) cannot occur in a riser reactor. This explains the effectiveness of the commercial SNAP process [2].

5. Conclusions

Simultaneous adsorption of SO_2 and NO_x is possible on Na-γ-alumina. SO_2 and NO_2 adsorb easily, even separately and in the absence of NO and O_2. NO and O_2 adsorption, however, require the simultaneous presence of SO_2, NO, and O_2.

The large influence of the SO_2 presence on the simultaneous adsorption of NO and O_2 is explained by the necessity of adsorbed SO_2 as an intermediate in the NO and O_2 adsorption. The significant increase of the SO_2 adsorption capacity and decrease of the NO and O_2 adsorption capacity in the presence of NO_2 is caused by multiple SO_2 adsorption on an active site oxidized by NO_2.

Acknowledgements

This work was financed by the European Commission within the frame of the Non-Nuclear Energy Programme, Joule III under Contract JOF3-CT95–0012 (project partners: Laboratorium voor Petrochemische Techniek-Universiteit Gent, FLS miljØ-Denmark). The authors thank Niels Thulstrup of FLS-milj∅ and Mr. Das for the helpful discussions.

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