

Investigation of simultaneous adsorption of SO₂ and NO on γ -alumina at low temperature using DRIFTS

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ABSTRACT

The interaction mechanism between SO₂ and NO on γ -Al₂O₃ was explored by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and outlet response of the concentrations of NO, NO₂ and SO₂ under exposure of Al₂O₃ to SO₂ and/or NO in the absence or presence of oxygen at 150 °C. The results showed that SO₂ promoted NO oxidation and NO transformed weakly adsorbed SO₂ into strongly adsorbed species on γ -Al₂O₃, and the presence of O₂ facilitated this transformation. An interaction mechanism between SO₂ and NO on γ -Al₂O₃ was thus postulated. The exposure of Al₂O₃ to SO₂ and NO in the presence of O₂ resulted in the formation of at least two types of intermediates. One type was [SO₃NO], which decomposed to form NO₂, and the other type was [SO₃NO₂], which decomposed to form SO₃. The decomposition of both intermediates probably formed O vacancies replaceable by gaseous O₂.

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1. Introduction

The emission of sulphur oxides (SO_x) and nitrogen oxides (NO_x) from flue gases, causing acid rain and urban air pollution, is a major environmental issue. Normally, SO_x and NO_x in flue gases consist of more than 98% sulphur dioxide (SO₂) and over 90–95% nitric oxide (NO) [1,2]. To control SO₂ and NO_x emission, a great deal of simultaneous removal processes have been developed [3–9]. Flue gas treatment technologies are broadly classified as dry and wet techniques. The wet techniques use scrubber columns in which the flue-gas mixture is subjected to liquid wash to remove gaseous SO₂ and NO_x with high efficiency, however, the wet process induces the difficulty of product disposal. Therefore, it is highly desirable to have a suitable single-step dry process for the removal of SO₂ and NO_x from flue gas.

As a promising dry process, the NOXSO process uses a regenerable sorbent (prepared by spraying sodium carbonate on γ -Al₂O₃) to remove SO₂ and NO_x simultaneously by catalytic oxidation. The process was tested at different scales, which was still in stage of demonstration industrial plant [10]. FLS-miljø-Denmark has developed a new process derived from NOXSO process. In the process, the simultaneous adsorption of SO₂ and NO_x was performed on Na- γ -Al₂O₃ in a circulating dilute phase riser reactor. De Wilde

et al. performed simultaneous SO₂ and NO_x removal on Na- γ -Al₂O₃ at lower temperature (150 °C) [11]. The interaction of SO₂ and NO_x on Na- γ -Al₂O₃ is described. They explained the influence of the SO₂ presence on the simultaneous adsorption of NO and O₂ by the adsorbed SO₂ as an intermediate in the NO and O₂ adsorption. With respect to the role of supporter γ -Al₂O₃ and interaction of SO₂ and NO on γ -Al₂O₃ without Na-impregnation, however, not much information is available in literature. Moreover, few studies related to the sequential adsorption of SO₂ and NO_x on γ -Al₂O₃.

In this paper, the interaction among NO, SO₂ and O₂ on γ -Al₂O₃ at low temperature (150 °C) was systematically studied. Different with De Wilde's research [11] sequential adsorption experiment was carried out for better understanding the reactions occurring on γ -Al₂O₃ surface. Finally, the interaction mechanism of SO₂ and NO was proposed in this paper.

2. Experimental

The sample of γ -Al₂O₃ was obtained from Merck (Merck Co., Germany) in the form of powder with a particle size of 0.10–0.15 mm. The specific surface area was 128 m²/g, and the average pore diameter and pore volume were 7 nm and 0.2484 cm³/g, determined by ourselves. The feed gas mixture contained 0.075% NO, 0.51% SO₂, 4.5% O₂, and balance Ar.

The adsorption experiments were performed in a fixed-bed reactor apparatus. The sample (1 g) was charged in a stainless reactor (\varnothing 19 mm) and then purged under inert flow at a total flow rate

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of 100 ml/min at 600 °C for 1 h in order to remove containing oxygen compounds (H₂O and CO₂); it was then cooled to 150 °C and exposed to a mixture of NO and/or SO₂ in Ar at a total flow rate of 100 ml/min until the concentration of NO and SO₂ in the outlet gas became steady.

A series of NO and SO₂ adsorption experiments on γ -Al₂O₃ were performed by exposing the samples to NO and/or SO₂ in Ar with or without oxygen. SO₂ and NO sequential experiments were also performed (termed PreSO₂ and PreNO). PreSO₂ indicates that SO₂/O₂ was first introduced to a fresh catalyst ('clean' Al₂O₃). After saturation (sulphated Al₂O₃), the SO₂ gas flow was changed to inert gas for 5 min, followed by exposure of the sulphated Al₂O₃ to NO/O₂ in Ar. PreNO indicates that NO/O₂ was first introduced to a fresh catalyst ('clean' Al₂O₃). After saturation (nitrated Al₂O₃), the nitrated Al₂O₃ was exposed to SO₂/O₂ in Ar.

The measured outlet response curves were determined in a flow-reactor equipped with a Total Sulphur/Nitrogen Analyzer for monitoring the concentrations of NO, NO₂ and SO₂ in the outlet gas (detection limit S or N with 0.2 mg/m³). After saturation, the sample was cooled to 50 °C and then purged in Ar for 1 h. Finally, a temperature ramp of 10 °C/min from 50 to 727 °C was applied with an Ar gas rate of 20 ml/min. The diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectrum was carried out on a Bruker vector 33 spectrometer

3. Results and discussion

3.1. Adsorption of SO₂ and NO

The amounts of adsorbed SO₂ and NO under different atmospheres over γ -Al₂O₃ at 150 °C are summarised in Table 1.

3.1.1. Separate adsorption of SO₂ and NO

Comparing SO₂ with SO₂/O₂ (experiments a and b in Table 1), the amount of adsorbed SO₂ in the absence of O₂ was 0.265 mmol g⁻¹, whereas that in the presence of O₂ was 0.321 mmol g⁻¹. This demonstrated that the adsorption of SO₂ alone on γ -Al₂O₃ at 150 °C occurred, and that the presence of O₂ enhanced SO₂ adsorption (the amount of adsorbed SO₂ increased by 20%). In addition, 0.014 mmol g⁻¹ of SO₂ desorbed when sweeping with Ar at 150 °C, which indicated that some adsorbed SO₂ was unstable.

Comparing NO with NO/O₂ (experiments c and d), the amount of adsorbed NO in the absence of O₂ was 0.0298 mmol g⁻¹, whereas in the presence of O₂, it was 0.038 mmol g⁻¹. These data indicated that NO could be independently adsorbed on γ -Al₂O₃ at 150 °C. Additionally, the amount of adsorbed NO increased in the presence of O₂. In experiment c for NO in the absence of O₂, oxygen-containing compounds were removed from the γ -Al₂O₃ surface by purging with Ar at 600 °C for 1 h before adsorption. However, a trace of NO₂ still occurred in the outlet gas. This was likely that lattice oxygen of the γ -Al₂O₃ participated in the oxidation reaction [12,13].

3.1.2. Simultaneous adsorption of SO₂ and NO

Comparing the amount of adsorbed SO₂ over γ -Al₂O₃ under SO₂/NO and SO₂ atmospheres (experiments e and a in Table 1), the amount of adsorbed SO₂ for simultaneous adsorption of SO₂ and NO was higher than that in the absence of NO, which indicated that NO enhanced the adsorption of SO₂.

Comparing SO₂/NO with NO (experiments e and c in Table 1), although the amount of adsorbed NO was almost the same, NO₂ was also detected in the outlet gas for simultaneous adsorption of SO₂ and NO. Based on thermodynamics, it was unlikely that the oxygen of NO₂ was from SO₂. Thus, the oxidation of NO may be attributed to the lattice oxygen of γ -Al₂O₃ with SO₂, which promoted this oxidation reaction.

When SO₂/NO/O₂ was compared with SO₂/NO (experiments f and e in Table 1), both the amounts of adsorbed SO₂ and NO were significantly higher than in the absence of O₂. This observation revealed that O₂ facilitated the simultaneous adsorption of SO₂ and NO, whereas NO promoted the adsorption of SO₂ and vice versa.

3.1.3. Sequential adsorption of SO₂ and NO

Comparing SO₂/O₂ over "nitrated Al₂O₃" with SO₂/O₂ over "clean Al₂O₃" (experiments h and b in Table 1), the amount of adsorbed SO₂ over the "clean Al₂O₃" was 0.321 mmol g⁻¹, whereas that over the "nitrated Al₂O₃" increased to 0.377 mmol g⁻¹. Thus, pre-adsorbed NO species on Al₂O₃ promoted SO₂ adsorption. Moreover, in experiment h, SO₂/O₂ was exposed to "nitrated Al₂O₃" after NO/O₂ was saturated on the Al₂O₃ and NO and NO₂ were detected in the outlet gas. It might have been that some adsorbed NO species on the Al₂O₃ were replaced by SO₂ due to its stronger acidity, leading to the discharge of NO and NO₂ into the outlet gas.

When NO/O₂ over "sulphated Al₂O₃" was compared with "clean Al₂O₃" (experiments g and d in Table 1), the amount of adsorbed NO increased by 27%, which indicating that pre-adsorbed SO₂ species on Al₂O₃ promoted NO adsorption. In the PreSO₂ experiment (experiment g in Table 1), the desorbed SO₂ was 0.0533 mmol g⁻¹, whereas that for SO₂/O₂ over "clean Al₂O₃" was 0.014 mmol g⁻¹ (experiment b in Table 1) by sweeping with Ar. The reason for this phenomenon was probably that some pre-adsorbed SO₂ was replaced by NO. In conclusion, both the adsorption of SO₂ on nitrated Al₂O₃ (PreNO) and NO on sulphated (PreSO₂) were promoted regardless of the sequence of exposure for SO₂ or NO.

3.2. DRIFTS studies of adsorbed species

3.2.1. Separate adsorption of SO₂ and NO

The surface species formed from the reaction of SO₂ or NO on Al₂O₃ were studied by DRIFTS (Fig. 1). Fig. 1(a, b and i) shows the spectra of SO₂ or SO₂/O₂ adsorption on Al₂O₃ and the desorption after SO₂/O₂ saturation at 150 °C for 1 h.

Datta et al. [14] identified at least five different adsorption SO₂ sites on Al₂O₃: a species physically adsorbed on hydroxyl groups (Al–OH–SO₂) with bands at 1334 and 1148 cm⁻¹, a weakly chemisorbed species (Al–O–SO₂) with bands at 1322 and 1140 cm⁻¹, two species chemisorbed on acidic (positively charged aluminium ions, Al–SO₂) Al³⁺ sites with bands at 1255 and 1189 cm⁻¹, and one strongly chemisorbed species (Al–SO₃) with a broad band at approximately 1060 cm⁻¹. As seen from spectra (a) and (b), the bands at 1325 cm⁻¹ were observed and assigned to a weakly chemisorbed species (Al–O–SO₂) [15]. In addition, the bands between 1200 and 1000 cm⁻¹ might all be characteristic peaks of mixtures of the above-mentioned SO₂ surface species.

It was noted that the intensity for the bands from spectrum (b) was greater than that from spectrum (a). Additionally, the increase in intensity at 1325 cm⁻¹ indicated that O₂ had an effect on SO₂ chemisorption at 150 °C, which probably enhanced SO₂ adsorption on O²⁻ basic sites of Al₂O₃ (Al–O–SO₂). In the literature, Andersson et al. [16] reported that the amount of SO₂ adsorbed in the presence of O₂ was much higher than that adsorbed in the absence of O₂. The results (seen from experiments b and a in Table 1) were in agreement with Andersson's report. It was probable that O₂ formed new basic sites at the lattice defect-sites on Al₂O₃, thus increasing the amount of Al–O–SO₂ species present. Furthermore, compared with spectrum (b), the intensity for bands of spectrum (i) at 1325 and 1140 cm⁻¹ decreased, indicating that adsorbed SO₂ was bonded to O²⁻ basic sites through the sulphur atom (Al–O–SO₂), a weak surface species readily desorbed by sweeping in Ar at 150 °C.

Fig. 1(c and d) displays representative DRIFTS data for Al₂O₃ exposed to NO at 150 °C. The bands in the region from 1640 to 1000 cm⁻¹ were assigned to surface nitrate and nitrite species [17].

Table 1The amount of SO₂ or NO adsorbed on γ -Al₂O₃ at 150 °C.

Experimental no.	Feed gas, Ar balance	Amount adsorbed SO ₂ (mmol g ⁻¹)	Amount adsorbed NO (mmol g ⁻¹)	SO ₂ desorption rate below 600 °C (%) ^f
a	SO ₂	0.265	–	30
b	SO ₂ /O ₂ ^a	0.321	–	31
c	NO ^b	–	0.0298	–
d	NO/O ₂	–	0.0380	–
e	SO ₂ /NO ^c	0.324	0.0308	16
f	SO ₂ /NO/O ₂	0.582	0.0866	0.5
g	PreSO ₂ NO/O ₂ ^d	–	0.0484	0.6
h	PreNO SO ₂ /O ₂ ^e	0.377	–	0.5

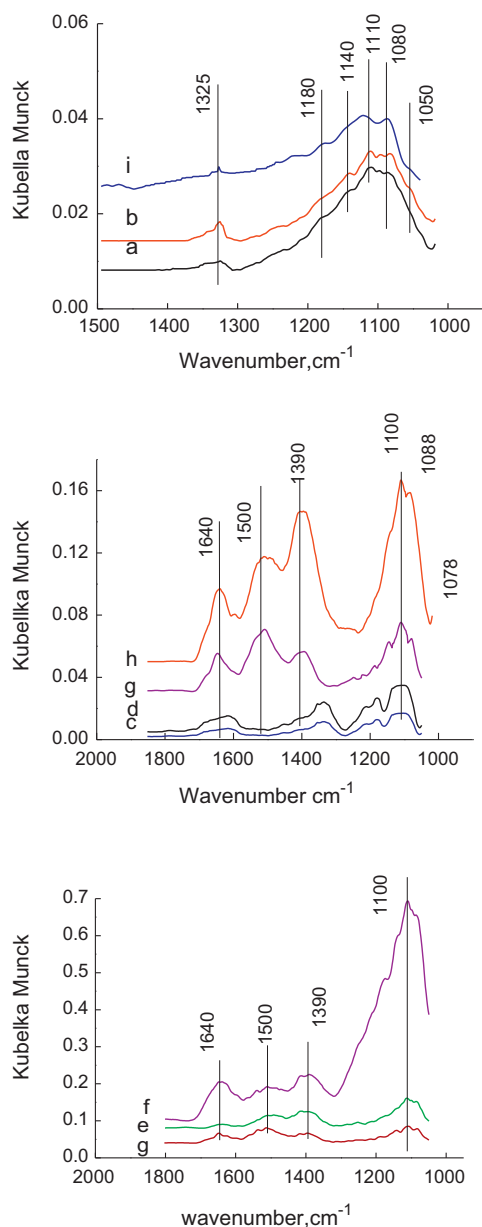
^a Sweeping with inert gas (Ar) at 150 °C after adsorption, SO₂ (0.014 mmol g⁻¹) in sweeping gas.^b NO₂ was found in outlet gas during the adsorption process.^c NO₂ was found in outlet gas during the adsorption process.^d SO₂ (0.053 mmol g⁻¹) in outlet gas during the adsorption process.^e NO₂ was found in outlet gas during the adsorption process.^f Mole ratio of SO₂ desorption below 600 °C and SO₂ adsorbed at 150 °C.

Fig. 1. DRIFT spectra of Al₂O₃ exposed to different atmospheres at 150 °C. (a) SO₂; (b) SO₂/O₂; (c) NO; (d) NO/O₂; (e) SO₂/NO; (f) SO₂/NO/O₂; (g) PreSO₂: pre-adsorbed SO₂ and NO/O₂; (h) PreNO: pre-adsorbed NO and SO₂/O₂; (i) desorption at 150 °C for 1 h after exposure to SO₂/O₂.

The bands at 1630 and 1246 cm⁻¹ were assigned to bridged nitrate, 1570 and 1249 cm⁻¹ were assigned to bidentate nitrate, 1574 and 1290 cm⁻¹ were assigned to monodentate nitrate, and the bands at 1470 and 1080 cm⁻¹ were assigned to linear nitrite. In addition, the bands at 1240 and 1180 cm⁻¹ were assigned to bidentate nitrite, whereas 1320 and 1230 cm⁻¹ were assigned to bridged nitrite. In general, the bands ranging from 1640 to 1500 cm⁻¹ were mainly assigned to surface nitrate species and bands between 1400 and 1000 cm⁻¹ were mainly assigned to surface nitrite species.

It has been reported that the exposure Al₂O₃ to NO mainly formed nitrites on basic sites, and exposure of Al₂O₃ to NO₂ primarily formed nitrates at these sites [17–19]. In Fig. 1(c and d), it can be seen that bands at 1640–1500 cm⁻¹ and 1400–1000 cm⁻¹ were again observed, indicating that surface nitrite and nitrate species might have formed. Therefore, it was suggested that NO₂ formed due to the oxidation reaction of adsorbed NO and lattice oxygen on Al₂O₃. Compared with (c) and (d) in Fig. 1, the band intensities increased in the presence of O₂, suggesting that gaseous O₂ might migrate into O vacancies to enhance adsorption of NO and NO₂ [20].

3.2.2. Simultaneous adsorption of SO₂ and NO

Compared with the result of exposure of Al₂O₃ to NO, the intensity for bands at 1640–1500 cm⁻¹ increased in the case of simultaneous adsorption of SO₂ and NO (Fig. 1(e and c)). This observation indicated that more surface nitrate species formed in the case of SO₂/NO. It thus seemed that SO₂ promoted the oxidation of NO to form NO₂ adsorbed species. In Fig. 1(e and a), the bands at 1390 cm⁻¹ and 1100 cm⁻¹ grew in intensity under conditions of simultaneous adsorption of SO₂ and NO, an effect assigned to surface sulphates (SO₄²⁻) [1,15]. This indicated that NO could enhance SO₂ oxidation and lead to the formation of surface sulphates. These data were in good agreement with results reported by Tomohiro et al. [21].

Compared with the spectra of exposure to SO₂/NO (e), all of the band intensities for exposure to SO₂/NO/O₂ (f) increased, especially the bands at 1390 cm⁻¹ and 1100 cm⁻¹, assigned to surface sulphates (SO₄²⁻). These results indicated that gaseous O₂ promoted mutual oxidation of SO₂ and NO.

3.2.3. Sequential adsorption of NO and SO₂

Fig. 1(g and h) depicts the DRIFTs results of “nitrated Al₂O₃” exposed to SO₂/O₂ (PreNO) and “sulphated Al₂O₃” exposed to NO/O₂ (Pre SO₂). It was found that both nitrate (1640–1500 cm⁻¹) and SO₄²⁻ (1390 and 1100 cm⁻¹) formed regardless of the sequence of exposure to SO₂ and NO. Compared with sulphated Al₂O₃ exposed to NO/O₂ (g in Fig. 1), the bands at 1390 and 1100 cm⁻¹ increased in intensity when nitrated Al₂O₃ was exposed to SO₂/O₂ (h in Fig. 1). In this case, more SO₄²⁻ formed. Thus, the amounts

of nitrate and SO_4^{2-} formed were correlated with the sequence of exposure.

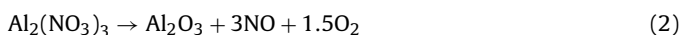
3.3. Response curve

Figs. 2 and 3 display the measured outlet responses of NO, NO_2 and SO_2 .

3.3.1. Separate adsorption of SO_2 and NO

In Chang's report [22], it was demonstrated that the desorption of weakly adsorbed SO_2 species on basic sites occurred below 600°C , whereas that of strongly adsorbed SO_2 species on acidic sites occurred above 600°C . Fig. 2(c) shows that the SO_2 response curve exhibited three desorption peaks, indicating different degrees of basicity for the surface basic sites of $\gamma\text{-Al}_2\text{O}_3$. By comparison to SO_2/O_2 and SO_2 , it appeared that the area of the SO_2 desorption peak (below 600°C) was greater in the presence of O_2 than in the absence of O_2 and that the total amount of adsorbed SO_2 increased (Table 1). It is likely that adsorbed O_2 created new basic sites on defect sites of the Al_2O_3 surface, leading to an increased number of weakly adsorbed SO_2 species.

Based on the decomposition equations for magnesium nitrate [23], aluminium nitrate decomposition equations were determined as follows:



It was noted that NO was formed by the decomposition of nitrite and nitrate and that NO_2 was formed by the decomposition of nitrate.

Because nitrite decomposed more easily than nitrate, the low temperature peaks for NO represented the decomposition of nitrite, whereas the high-temperature peaks for NO and NO_2 represented the decomposition of nitrate. Therefore, the low- and high-temperature peaks represented weakly and strongly adsorbed species, respectively. After exposure of Al_2O_3 to NO in the absence of O_2 , the high-temperature peak for NO_2 appeared, indicating that nitrate species formed on the surface of Al_2O_3 (Fig. 2(b)). The reason for this phenomenon might have been the oxidation of adsorbed NO to NO_2 by lattice oxygen to form nitrate species.

After exposure to NO/O_2 , the position of the low-temperature peak of NO shifted towards lower temperature, and the area of the low temperature peak increased within a wide range. This development indicated that new basic sites formed on the defect sites of Al_2O_3 in the presence of O_2 , increasing the amount of weakly adsorbed species. The area of the response peak at high temperature for NO_x (NO and NO_2) also greatly increased. This indicated that a considerable amount of NO was oxidized into NO_2 (i.e., more surface nitrate on $\gamma\text{-Al}_2\text{O}_3$). This observation was likely attributed to the formation of O vacancies after the lattice oxygen participated in the reaction which were subsequently replaced by gaseous O_2 for the reaction. Otherwise, the adsorbed oxygen on defect sites could also have participated in the oxidation of NO.

3.3.2. Simultaneous adsorption of SO_2 and NO

From Fig. 2(c) and Table 1 (experiments a and e), it can be seen that the area of three SO_2 response peaks below 600°C for NO/SO_2 decreased compared to SO_2 , and the rate of SO_2 desorption dropped from 30% to 16%. However, the amount of SO_2 adsorbed increased. The reason for this trend was probably that NO transformed weakly adsorbed SO_2 species into strongly adsorbed SO_2 species. It was presumed that weakly adsorbed SO_2 species ($\text{Al}-\text{O}-\text{SO}_2$) was the active species. According to the DRIFT results, the strongly adsorbed species were most likely $\text{Al}-\text{O}-\text{SO}_3$ or SO_4^{2-} .

By comparing the SO_2/NO and $\text{SO}_2/\text{NO}/\text{O}_2$ cases, the SO_2 response peaks nearly disappeared (the rate of SO_2 desorption decreased from 16% to 0.5%, experiments a and e) below 600°C . However, the amount of SO_2 adsorbed greatly increased. Thus, the weakly adsorbed SO_2 species were likely transformed into more strongly adsorbed species (surface sulphates) in the presence of O_2 . It also seemed that gaseous O_2 promoted this transformation process. These results were in accordance with DRIFT results where the bands at 1390 cm^{-1} and 1100 cm^{-1} , characteristic of surface sulphates, were found to be greatly increased.

Compared with the results of response peaks for NO alone, the low-temperature response peak of NO disappeared in the case of NO/SO_2 . Meanwhile, the area of the NO_x response peaks increased and the position for the high-temperature peaks of NO_x both shifted towards lower temperatures. It was thus presumed that lattice oxygen participated in the oxidation of weakly adsorbed NO species and that the presence of SO_2 enhanced the transformation of NO to NO_2 on Al_2O_3 . As for the shift towards lower temperatures, it was concluded that SO_2 promoted nitrate decomposition [21].

Compared with the response peaks for NO/SO_2 , the area for the NO_x response peaks at high temperature were significantly larger than in the absence of O_2 . This indicated that O_2 could facilitate the oxidation NO by SO_2 .

3.3.3. Sequential adsorption of NO and SO_2

In Fig. 3(c), it can be seen that the response peak of SO_2 disappeared over a wide range of temperatures ($90\text{--}600^\circ\text{C}$). In addition, less SO_2 was desorbed from the sulphated or nitrated Al_2O_3 compared to the 'clean' Al_2O_3 . This indicated that weakly adsorbed SO_2 could be converted into strongly adsorbed species on Al_2O_3 in both cases (pre SO_2 and preNO), regardless of the sequence of exposure to SO_2 and NO.

The NO and NO_2 response peaks of sulphated Al_2O_3 exposed to NO/O_2 (pre SO_2) and nitrated Al_2O_3 exposed to SO_2/O_2 (preNO) were shown in Fig. 3(a and b). Compared with 'clean' Al_2O_3 exposed to NO/O_2 , the area of the low-temperature peak for NO decreased and the area of the high-temperature peak for NO_2 increased. It therefore seemed that the surface species associated with NO low-temperature desorption took part in oxidative reactions to form surface nitrate as long as SO_2 existed, regardless of the sequence of NO exposure. From Fig. 3(a and b), it was also noted that the position of the high-temperature peaks shifted towards lower temperatures. It is known that when the amount of acidic species (surface sulphates) increases on Al_2O_3 , the desorption of NO_x species occurs more easily [19]. Therefore, compared with sulphated Al_2O_3 exposed to NO/O_2 (pre SO_2), a greater shifting towards lower temperatures indicated that more SO_4^{2-} formed on the Al_2O_3 in the case of nitrated Al_2O_3 exposed to SO_2/O_2 (preNO).

According to the results of DRIFTS and response curve (Fig. 3), it was determined that at least two intermediates formed when SO_2 and NO interacted on Al_2O_3 and that the sequence of SO_2 and NO exposure to Al_2O_3 had a significant effect on the amount of intermediates. Furthermore, the decomposition of some intermediates in this scenario proceeded more easily, leading to more surface sulphates in the case of nitrated Al_2O_3 exposed to SO_2/O_2 (preNO).

Based on the discussion of separate, simultaneous and sequential adsorption of SO_2 and NO on Al_2O_3 , five main conclusions could be drawn:

- (1) The adsorption and oxidation of SO_2 and NO on the Al_2O_3 was promoted by each other.
- (2) The lattice oxygen of Al_2O_3 may have lower activity but probably could participate in oxidation reactions. Adsorbed O_2 on defect sites of the Al_2O_3 could also participate in oxidation reactions. Gaseous O_2 facilitated the replacement of O vacancies.

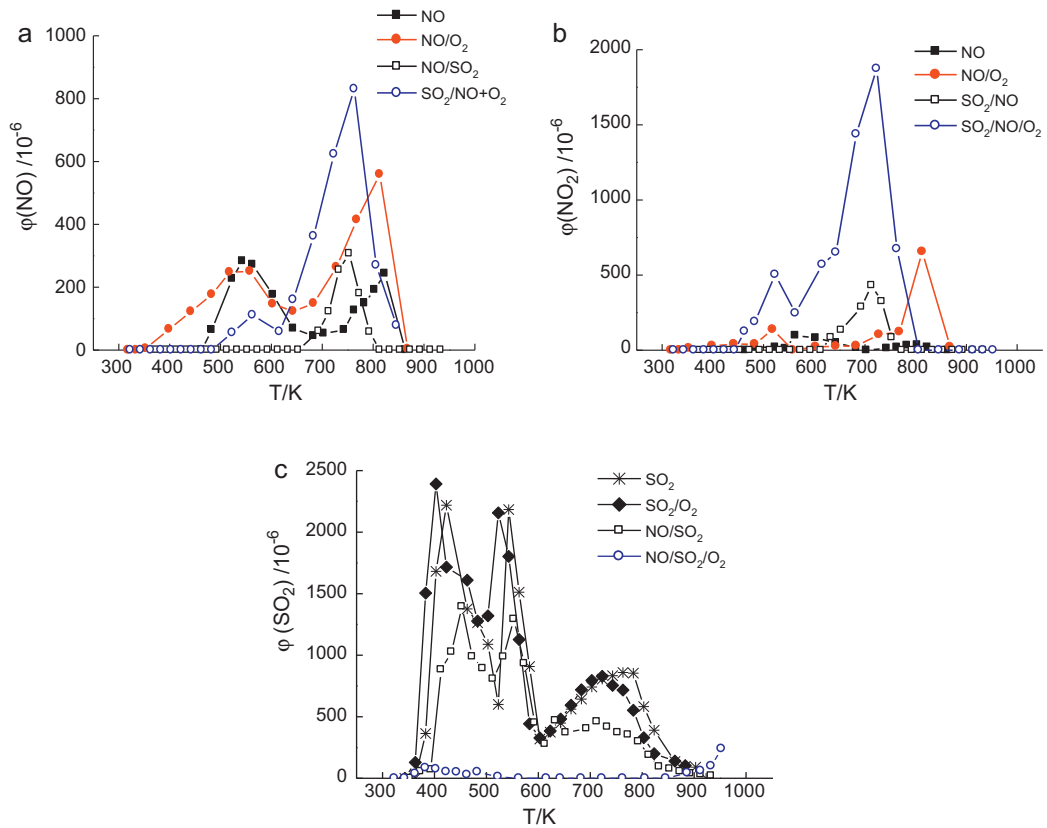


Fig. 2. Measured outlet response of NO, NO₂ and SO₂ in different atmospheres. (a) NO; (b) NO₂; and (c) SO₂.

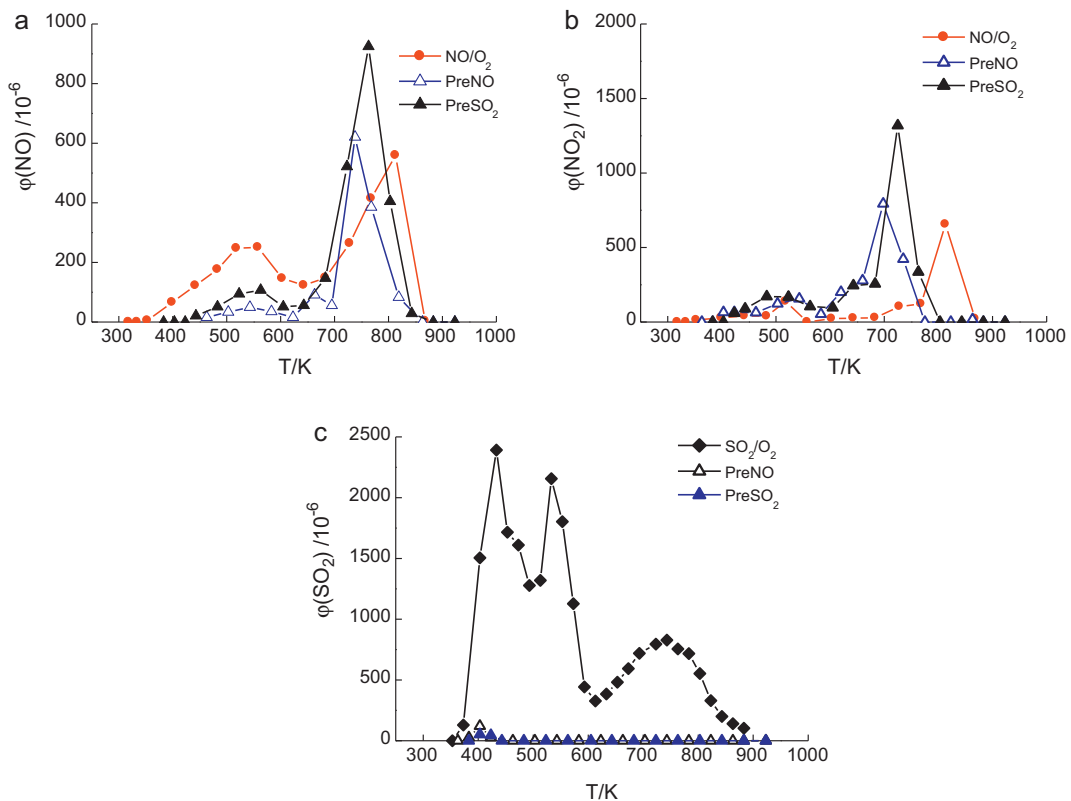


Fig. 3. Measured outlet response of NO, NO₂ and SO₂ on sulphated (preSO₂) and nitrated (preNO) Al₂O₃ at 150 °C. (a) NO; (b) NO₂; and (c) SO₂.

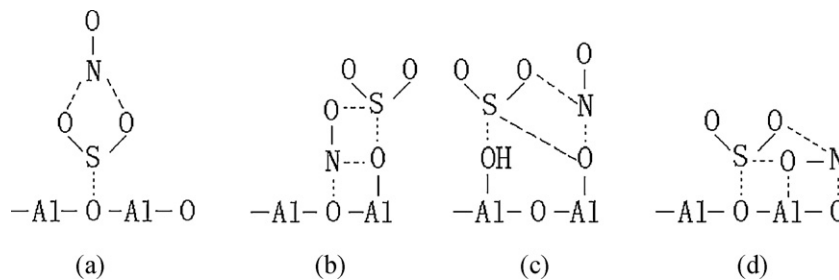


Fig. 4. Intermediates formed for SO_2 and NO interactions on an Al_2O_3 surface.

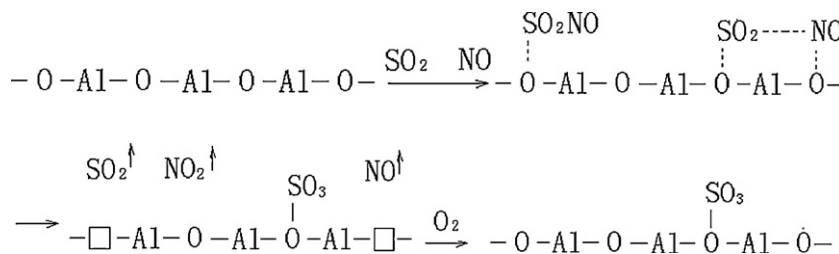


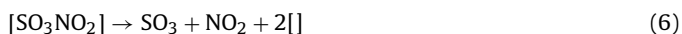
Fig. 5. Possible modes of interacting for $\text{SO}_2/\text{NO}/\text{O}_2$ on an Al_2O_3 surface.

- (3) The weakly absorbed NO and SO_2 species ($\text{Al}-\text{O}-\text{SO}_2$ and $\text{Al}-\text{O}\cdots\text{NO}$) associated with low-temperature desorption might have activity.
- (4) The weakly absorbed NO and SO_2 species could be partly replaced with each other on sulphated and nitrated Al_2O_3 (pre SO_2 and pre NO). The adsorptions of SO_2 and NO were also promoted by each other regardless of the sequence of exposure to SO_2 and NO .
- (5) At least two intermediates formed when SO_2 and NO interacted on Al_2O_3 , and the amount of intermediates was affected by the amount of surface SO_2 and NO_x species. Some intermediates decomposed more easily to form surface sulphates (SO_4^{2-}) in the case of SO_2 exposure to nitrated Al_2O_3 (pre NO) rather than NO exposure to sulphated Al_2O_3 (pre SO_2).

3.4. Mechanism

Wilde et al. [24] proposed several intermediates, as shown in Fig. 4(a). Apparently, more NO adsorbed species were favoured in the formation of intermediate $[\text{SO}_3\text{NO}_2]$. For the Pre NO process, when the nitrated Al_2O_3 was exposed to SO_2/O_2 , the basic sites of the Al_2O_3 were mostly occupied by NO_x (NO or NO_2). The amount of $[\text{SO}_3\text{NO}_2]$ formed was then much higher than $[\text{SO}_3\text{NO}]$ due to a considerable amount of NO adsorbed species ($\text{Al}-\text{O}\cdots\text{NO}$).

The decomposition process for intermediates $[\text{SO}_3\text{NO}]$ and $[\text{SO}_3\text{NO}_2]$ are shown in Eqs. (4)–(8), where $[]$ represents O vacancies.



The intermediate $[\text{SO}_3\text{NO}]$ decomposed according to Eqs. (4) and (5). However, for the pre SO_2 process, the predominant intermediate formed was $[\text{SO}_3\text{NO}]$. It was therefore concluded that (5) was the main process for decomposition of $[\text{SO}_3\text{NO}]$.

The other intermediate $[\text{SO}_3\text{NO}_2]$ decomposed according to Eqs. (6)–(8). For the pre NO process, the main intermediate formed with more SO_4^{2-} on the Al_2O_3 was $[\text{SO}_3\text{NO}_2]$. It could therefore be concluded that (6) and (8) were possible decomposition pathways. However, in Eq. (6), as the lattice oxygen is inactive and two lattice oxygens are consumed in the formation of $[\text{SO}_3\text{NO}_2]$, there was little chance that decomposition occurred via Eq. (6). Thus, (8) was the main process for decomposition of $[\text{SO}_3\text{NO}_2]$.

In the following, two modes were proposed for the interaction of SO_2 and NO on Al_2O_3 .

Mechanism I: $\text{Al}-\text{O}\cdots\text{SO}_2$ reacting with gaseous NO in the presence of O_2 formed intermediate $[\text{SO}_3\text{NO}]$, which decomposed to form NO_2 , SO_2 and an O vacancy. The lattice oxygen and defect-site oxygen was assumed to be regenerated by gaseous O_2 .

Mechanism II: $\text{Al}-\text{O}\cdots\text{SO}_2$ or $\text{Al}-\text{OH}\cdots\text{SO}_2$ interacting with adjacent $\text{Al}-\text{O}\cdots\text{NO}$ formed intermediate $[\text{SO}_3\text{NO}_2]$, which decomposed to form NO , an O vacancy and SO_4^{2-} (or NO_2 , two O vacancies and SO_4^{2-}). The lattice oxygen and defect site oxygen on Al_2O_3 was assumed to be regenerated by gaseous O_2 .

The possible interacting modes of SO_2 and NO on Al_2O_3 are illustrated in Fig. 5.

4. Conclusions

The interaction of adsorbed SO_2 and NO on $\gamma-\text{Al}_2\text{O}_3$ at low temperature (150°C) was studied by DRIFT and measured outlet response curves. The adsorptions of SO_2 and NO on Al_2O_3 were promoted by each other, especially in the presence of O_2 . The weakly absorbed species of NO ($\text{Al}-\text{O}\cdots\text{NO}$) and SO_2 ($\text{Al}-\text{O}\cdots\text{SO}_2$) might have activity and could be transformed into strongly absorbed species. In addition, the lattice oxygen of Al_2O_3 likely had a low activity, but could directly participate in oxidation reactions. At least two types of intermediates formed when SO_2 and NO interacted on Al_2O_3 . One type was $[\text{SO}_3\text{NO}]$, which decomposed to form NO_2 , and $[\text{SO}_3\text{NO}_2]$, which decomposed to form SO_3 . The decomposition of both intermediates could form O vacancies, which could then be replaced by gaseous O_2 .

References

- [1] I. Dahlan, K.T. Lee, A.H. Kamaruddin, A.R. Mohamed, Sorption of SO₂ and NO from simulated flue gas over rice husk ash (RHA)/CaO/CeO₂ sorbent: evaluation of deactivation kinetic parameters, *J. Hazard. Mater.* 185 (2011) 1609–1613.
- [2] K.C. Pillai, S.J. Chung, T. Raju, Experimental aspects of combined NO_x and SO₂ removal from flue-gas mixture in an integrated wet scrubber–electrochemical cell system, *Chemosphere* 76 (2009) 657–664.
- [3] D.S. Jin, B.R. Deshwal, Y.S. Park, H.K. Lee, Simultaneous removal of SO₂ and NO by wet scrubbing using aqueous chlorine dioxide solution, *J. Hazard Mater.* B135 (2006) 412–417.
- [4] I. Dahlan, K.T. Lee, A.H. Kamaruddin, A.R. Mohamed, Selection of metal oxides in the preparation of rice husk ash (RHA)/CaO sorbent for simultaneous SO₂ and NO removal, *J. Hazard. Mater.* 166 (2009) 1556–2155.
- [5] W.Y. Sun, S.L. Ding, S.S. Zeng, W.J. Jiang, Simultaneous absorption of NO_x and SO₂ from flue gas with pyrolusite slurry combined with gas-phase oxidation of NO using ozone, *J. Hazard. Mater.* 192 (2011) 124–130.
- [6] G.Y. Xie, Z.Y. Liu, Z.P. Zhu, Q.Y. Liu, J. Ge, Z.G. Huang, Simultaneous removal of SO₂ and NO_x from flue gas using a CuO/Al₂O₃ catalyst sorbent I. Deactivation of SCR activity by SO₂ at low temperatures, *J. Catal.* 224 (2004) 36–41.
- [7] G.Y. Xie, Z.Y. Liu, Z.P. Zhu, Q.Y. Liu, J. Ge, Z.G. Huang, Simultaneous removal of SO₂ and NO_x from flue gas using a CuO/Al₂O₃ catalyst sorbent II: promotion of SCR activity by SO₂ at high temperatures, *J. Catal.* 224 (2004) 42–49.
- [8] A.K. Das, J. De. Wilde, G.J. Heynderickx, G.B. Marin, CFD simulation of dilute phase gas–solid riser reactors: part II–simultaneous adsorption of SO₂–NO_x from flue gases, *Chem. Eng. Sci.* 59 (2004) 187–200.
- [9] S. Sumathi, S. Bhatia, K.T. Lee, A.R. Mohamed, Cerium impregnated palm shell activated carbon (Ce/PSAC) sorbent for simultaneous removal of SO₂ and NO—process study, *Chem. Eng. J.* 162 (2010) 51–57.
- [10] W.T. Ma, A.M. Chang, J.L. Haslbeck, L.G. Neal, NOXSO₂/NO_x flue gas treatment process adsorption chemistry and kinetics: novel adsorbents and their environmental applications, *AIChE Symp. Ser.* 309 (1995) 18–31.
- [11] J. De. Wilde, G.B. Marin, Investigation of simultaneous adsorption of SO₂ and NO_x on Na–(–)alumina with transient techniques, *Catal. Today* 62 (2000) 319–328.
- [12] S. Blonski, S.H. Garofalini, Molecular dynamics simulations of γ -alumina and γ -alumina surfaces, *Surf. Sci.* 295 (1993) 263–274.
- [13] I. Levin, D. Brandon, Metastable alumina polymorphs: crystal structures and transition sequences, *J. Am. Ceram. Soc.* 81 (1998) 1995–2012.
- [14] A. Datta, R.G. Cavell, R.W. Tower, Z.M. George, Claus catalysis. 1. Adsorption of sulfur dioxide on the alumina catalyst studied by FTIR and EPR spectroscopy, *J. Phys. Chem.* 89 (3) (1985) 443–449.
- [15] S.W. Nam, G.R. Gavalas, Adsorption and oxidative adsorption of sulfur dioxide on (–)alumina, *Appl. Catal.* 55 (1989) 193–213.
- [16] S. Andersson, R. Pompe, N. Vannerberg, SO_x adsorption/desorption processes on (–)alumina for SO_x transfer catalyst, *Appl. Catal.* 16 (1985) 49–58.
- [17] B. Westerberg, E. Fridell, A transient FTIR study of species formed during NO_x storage in the Pt/BaO/Al₂O₃ system, *J. Mol. Catal. A: Chem.* 165 (2001) 249–263.
- [18] R. Burch, E. Halpin, J.A. Sullivan, A comparison of the selective catalytic reduction of NO_x over Al₂O₃ and sulphated Al₂O₃ using, CH₃OH and C₃H₈ as reductants, *Appl. Catal. B: Environ.* 17 (1998) 115–129.
- [19] P. Li, G.Z. Lu, Effect of SO₂ on NO catalytic oxidation (V): the mechanism of SO₂ over NiO/ γ -Al₂O₃, *Acta Chim. Sin.* 61 (2003) 660–665.
- [20] N. Apostolescu, T. Schröder, S. Kureti, Study on the mechanism of the reaction of NO₂ with aluminium oxide, *Appl. Catal. B: Environ.* 51 (2004) 43–50.
- [21] I. Tomohiro, K. Hajime, Y. Tsutomu, Initial step of flue gas desulfurization—an IR study of the reaction of SO₂ with NO_x on CaO, *Environ. Sci. Technol.* 34 (2000) 2799–2803.
- [22] C.C. Chang, Infrared studies of SO₂ on γ -alumina, *J. Catal.* 53 (1978) 374–385.
- [23] W.S. Epling, L.E. Campbell, A. Yezerets, Overview of the fundamental reactions and degradation mechanisms of NO_x storage/reduction catalysts, *Catal. Rev.* 46 (2) (2004) 163–245.
- [24] J. De. Wilde, A.K. Das, G.H. Heynderickx, G.B. Marin, Development of a transient kinetic model for the simultaneous adsorption of SO₂–NO_x over Na/ γ -Al₂O₃ sorbent, *Ind. Eng. Chem. Res.* 40 (2001) 119–130.