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Investigation of simultaneous adsorption of SO_2 and NO on γ-alumina at low temperature using DRIFTS

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ABSTRACT

The interaction mechanism between SO_2 and NO on γ-Al_2O_3 was explored by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and outlet response of the concentrations of NO, NO_2 and SO_2 under exposure of Al_2O_3 to SO_2 and/or NO in the absence or presence of oxygen at 150 °C. The results showed that SO_2 promoted NO oxidation and NO transformed weakly adsorbed SO_2 into strongly adsorbed species on γ-Al_2O_3, and the presence of O_2 facilitated this transformation. An interaction mechanism between SO_2 and NO on γ-Al_2O_3 was thus postulated. The exposure of Al_2O_3 to SO_2 and NO in the presence of O_2 resulted in the formation of at least two types of intermediates. One type was [SO_3NO], which decomposed to form NO_2, and the other type was [SO_3NO_2], which decomposed to form SO_3. The decomposition of both intermediates probably formed O vacancies replaceable by gaseous O_2.

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 (SO_2) and over 90–95% nitric oxide (NO) [1,2]. To control SO_2 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 SO_2 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 SO_2 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-Al_2O_3) to remove SO_2 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 SO_2 and NO_x was performed on Na-γ-Al_2O_3 in a circulating dilute phase riser reactor. De Wilde et al. performed simultaneous SO_2 and NO_x removal on Na-γ-Al_2O_3 at lower temperature (150 °C) [11]. The interaction of SO_2 and NO_x on Na-γ-Al_2O_3 is described. They explained the influence of the SO_2 presence on the simultaneous adsorption of NO and O_2 by the adsorbed SO_2 as an intermediate in the NO and O_2 adsorption. With respect to the role of supporter γ-Al_2O_3 and interaction of SO_2 and NO on γ-Al_2O_3 without Na-impregnation, however, not much information is available in literature. Moreover, few studies related to the sequential adsorption of SO_2 and NO_x on γ-Al_2O_3.

In this paper, the interaction among NO, SO_2 and O_2 on γ-Al_2O_3 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-Al_2O_3 surface. Finally, the interaction mechanism of SO_2 and NO was proposed in this paper.

2. Experimental

The sample of γ-Al_2O_3 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 m^2/g, and the average pore diameter and pore volume were 7 nm and 0.2484 cm^3/g, determined by ourselves. The feed gas mixture contained 0.075% NO, 0.51% SO_2, 4.5% O_2, and balance Ar.

The adsorption experiments were performed in a fixed-bed reactor apparatus. The sample (1 g) was charged in a stainless reactor (Ø19 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 (H_2O and CO_2); it was then cooled to 150 °C and exposed to a mixture of NO and/or SO_2 in Ar at a total flow rate of 100 ml/min until the concentration of NO and SO_2 in the outlet gas became steady.

A series of NO and SO_2 adsorption experiments on γ-Al_2O_3 were performed by exposing the samples to NO and/or SO_2 in Ar with or without oxygen. SO_2 and NO sequential experiments were also performed (termed PreSO_2 and PreNO). PreSO_2 indicates that SO_2/O_2 was first introduced to a fresh catalyst ('clean' Al_2O_3). After saturation (sulphated Al_2O_3), the SO_2 gas flow was changed to inert gas for 5 min, followed by exposure of the sulphated Al_2O_3 to NO/O_2 in Ar. PreNO indicates that NO/O_2 was first introduced to a fresh catalyst ('clean' Al_2O_3). After saturation (nitrated Al_2O_3), the nitrated Al_2O_3 was exposed to SO_2/O_2 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, NO_2 and SO_2 in the outlet gas (detection limit S or N with 0.2 mg/m^3). 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 SO_2 and NO

The amounts of adsorbed SO_2 and NO under different atmospheres over γ-Al_2O_3 at 150 °C are summarised in Table 1.

3.1.1. Separate adsorption of SO_2 and NO

Comparing SO_2 with SO_2/O_2 (experiments a and b in Table 1), the amount of adsorbed SO_2 in the absence of O_2 was 0.265 mmol g^{-1}, whereas that in the presence of O_2 was 0.321 mmol g^{-1}. This demonstrated that the adsorption of SO_2 alone on γ-Al_2O_3 at 150 °C occurred, and that the presence of O_2 enhanced SO_2 adsorption (the amount of adsorbed SO_2 increased by 20%). In addition, 0.014 mmol g^{-1} of SO_2 desorbed when sweeping with Ar at 150 °C, which indicated that some adsorbed SO_2 was unstable.

Comparing NO with NO/O_2 (experiments c and d), the amount of adsorbed NO in the absence of O_2 was 0.0298 mmol g^{-1}, whereas in the presence of O_2, it was 0.038 mmol g^{-1}. These data indicated that NO could be independently adsorbed on γ-Al_2O_3 at 150 °C. Additionally, the amount of adsorbed NO increased in the presence of O_2. In experiment c for NO in the absence of O_2, oxygen-containing compounds were removed from the γ-Al_2O_3 surface by purging with Ar at 600 °C for 1 h before adsorption. However, a trace of NO_2 still occurred in the outlet gas. This was likely that lattice oxygen of the γ-Al_2O_3 participated in the oxidation reaction [12,13].

3.1.2. Simultaneous adsorption of SO_2 and NO

Comparing the amount of adsorbed SO_2 over γ-Al_2O_3 under SO_2/NO and SO_2 atmospheres (experiments e and a in Table 1), the amount of adsorbed SO_2 for simultaneous adsorption of SO_2 and NO was higher than that in the absence of NO, which indicated that NO enhanced the adsorption of SO_2.

Comparing SO_2/NO with NO (experiments e and c in Table 1), although the amount of adsorbed NO was almost the same, NO_2 was also detected in the outlet gas for simultaneous adsorption of SO_2 and NO. Based on thermodynamics, it was unlikely that the oxygen of NO_2 was from SO_2. Thus, the oxidation of NO may be attributed to the lattice oxygen of γ-Al_2O_3 with SO_2, which promoted this oxidation reaction.

When $SO_2/NO/O_2$ was compared with SO_2/NO (experiments f and e in Table 1), both the amounts of adsorbed SO_2 and NO were significantly higher than in the absence of O_2. This observation revealed that O_2 facilitated the simultaneous adsorption of SO_2 and NO, whereas NO promoted the adsorption of SO_2 and vice versa.

3.1.3. Sequential adsorption of SO_2 and NO

Comparing SO_2/O_2 over "nitrated Al_2O_3" with SO_2/O_2 over "clean Al_2O_3" (experiments h and b in Table 1), the amount of adsorbed SO_2 over the "clean Al_2O_3" was 0.321 mmol g^{-1}, whereas that over the "nitrated Al_2O_3" increased to 0.377 mmol g^{-1}. Thus, pre-adsorbed NO species on Al_2O_3 promoted SO_2 adsorption. Moreover, in experiment h, SO_2/O_2 was exposed to "nitrated Al_2O_3" after NO/O_2 was saturated on the Al_2O_3 and NO and NO_2 were detected in the outlet gas. It might have been that some adsorbed NO species on the Al_2O_3 were replaced by SO_2 due to its stronger acidity, leading to the discharge of NO and NO_2 into the outlet gas.

When NO/O_2 over "sulphated Al_2O_3" was compared with "clean Al_2O_3" (experiments g and d in Table 1), the amount of adsorbed NO increased by 27%, which indicating that pre-adsorbed SO_2 species on Al_2O_3 promoted NO adsorption. In the PreSO_2 experiment (experiment g in Table 1), the desorbed SO_2 was 0.0533 mmol g^{-1}, whereas that for SO_2/O_2 over "clean Al_2O_3" 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 SO_2 was replaced by NO. In conclusion, both the adsorption of SO_2 on nitrated Al_2O_3 (PreNO) and NO on sulphated (PreSO_2) were promoted regardless of the sequence of exposure for SO_2 or NO.

3.2. DRIFTS studies of adsorbed species

3.2.1. Separate adsorption of SO_2 and NO

The surface species formed from the reaction of SO_2 or NO on Al_2O_3 were studied by DRIFTS (Fig. 1). Fig. 1(a, b and i) shows the spectra of SO_2 or SO_2/O_2 adsorption on Al_2O_3 and the desorption after SO_2/O_2 saturation at 150 °C for 1 h.

Datta et al. [14] identified at least five different adsorption SO_2 sites on Al_2O_3: a species physically adsorbed on hydroxyl groups (Al–OH–SO_2) with bands at 1334 and 1148 cm^{-1}, a weakly chemisorbed species (Al–O–SO_2) with bands at 1322 and1140 cm^{-1}, two species chemisorbed on acidic (positively charged aluminium ions, Al–SO_2) Al^{3+} sites with bands at 1255 and 1189 cm^{-1}, and one strongly chemisorbed species (Al–SO_3) 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–SO_2) [15]. In addition, the bands between 1200 and 1000 cm^{-1} might all be characteristic peaks of mixtures of the above-mentioned SO_2 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 O_2 had an effect on SO_2 chemisorption at 150 °C, which probably enhanced SO_2 adsorption on O^{2-} basic sites of Al_2O_3 (Al–O–SO_2). In the literature, Andersson et al. [16] reported that the amount of SO_2 adsorbed in the presence of O_2 was much higher than that absorbed in the absence of O_2. The results (seen from experiments b and a in Table 1) were in agreement with Andersson's report. It was probable that O_2 formed new basic sites at the lattice defect-sites on Al_2O_3, thus increasing the amount of Al–O–SO_2 species present. Furthermore, compared with spectrum (b), the intensity for bands of spectrum (i) at 1325 and 1140 cm^{-1} decreased, indicating that adsorbed SO_2 was bonded to O^{2-} basic sites through the sulphur atom (Al–O–SO_2), a weak surface species readily desorbed by sweeping in Ar at 150 °C.

Fig. 1(c and d) displays representative DRIFTS data for Al_2O_3 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].