

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

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Abstract

Deactivating effect of SO₂ on selective catalytic reduction of NO by NH₃ over a CuO/Al₂O₃ catalyst sorbent was examined in a fixed-bed reactor. Transient experiment, DRIFT, elemental analysis, temperature-programmed techniques, and physical adsorption were used to evaluate the deactivation mechanism. Results show that SO₂ greatly deactivates SCR activity of CuO/Al₂O₃ catalyst sorbent at temperatures of 200–300 °C, and the deactivation is dependent on reaction temperature. The deactivating agents are ammonium sulfate salt and copper sulfate, formed during the reaction of NO–NH₃–O₂–H₂O in the presence of SO₂. Ammonium sulfate salt reduces the SCR reaction through pore filling and/or plugging, but can be removed by heat treatment at around 400 °C. Copper sulfate deactivates the SCR either by pore filling and/or plugging or by its low SCR activity compared to CuO at low temperatures. Copper sulfate decomposes at temperatures greater than 660 °C but can be converted back to CuO in NH₃ at about 400 °C.

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1. Introduction

Elimination of SO₂ and NO_x emitted from stationary sources is important. Various processes have been developed for the purpose [1]. Among them, CuO/Al₂O₃ catalyst sorbents have received much attention due to its capability of simultaneous removal of SO₂ and NO_x from flue gases because (i) they readily adsorb SO₂ in the presence of O₂ to form CuSO₄ in a wide range of temperatures [2,3], (ii) they are relatively easy to be regenerated under reducing conditions [4,5], and (iii) copper compounds (CuO and CuSO₄) are active for selective catalytic reduction (SCR) of NO_x to N₂ with NH₃ as a reducing agent [6,7].

Research works in the literature on sulfation, regeneration, and effect of SO₂ on NO_x removal of CuO/Al₂O₃ catalyst sorbents showed that SO₂ has very different effects on NO_x removal in different temperature ranges [6–8]. Specifically, it promotes SCR activity in the temperature range of 350–450 °C, but reduces the SCR activity at temperatures

below 300 °C. However, few studies have been made on the detailed mechanism of this dual SO₂ effect.

The deactivation effect of SO₂ on NO_x removal was also found for other SCR catalysts such as V₂O₅/TiO₂ [9], MnO_x/Al₂O₃ [10], V₂O₅/Al₂O₃ [11], CuO/AC [12], V₂O₅/AC [13,14], and CuHM [15]. Clearly, surface property change of the support and/or chemical transformation of active sites are important in the determination of NO_x removal activity at different temperatures. In the case of V₂O₅/Al₂O₃ [11], formation of aluminum sulfate during SCR reaction in the presence of SO₂ reduces surface area of the catalyst sorbents, which results in severe deactivation of SCR activity. Ammonium (bi)sulfate was also found to form and accumulate on the surface of V₂O₅/TiO₂ [9], V₂O₅/AC [13,14], and CuHM [15] at temperatures below 280 °C and strongly deactivate SCR activity due to pore filling and/or plugging. Additionally, it was reported that chemical transformation of MnO to MnSO₄ was the main reason for deactivation of SCR over MnO_x/Al₂O₃ [10].

The purpose of this work is to systematically study the deactivation of a CuO/Al₂O₃ catalyst sorbent by SO₂ at the temperature range of 200–300 °C and to evaluate the deacti-

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vation mechanism. Transient experiment, diffuse reflectance infrared Fourier transform (DRIFT), XRD, elemental analysis, temperature-programmed techniques, and physical adsorption are used. With the deactivation mechanism gained, the relevant regenerative treatments of the deactivated catalyst sorbent are discussed.

2. Experimental

2.1. Preparation of CuO/Al₂O₃

The CuO/Al₂O₃ catalyst sorbent was prepared by pore volume impregnation of pure γ -Al₂O₃ pellets (30–40 mesh, BET surface area of 185 m² g⁻¹, Fushun Petrochemical Co.) with an aqueous solution of copper(II) nitrate. After drying at 50 °C for 8 h and 120 °C for 5 h, the pellets were calcined at 400 °C for 8 h in a muffle furnace. The calcined catalyst sorbent contains 8.0 wt% of Cu, which is confirmed by ICP analysis and is termed Cu8 in the text. The Cu8 catalyst sorbent shows a BET surface area of 149.6 m² g⁻¹ and no crystalline materials in XRD except the alumina support. Two sulfated Cu8 catalyst sorbents were also prepared. One was saturated in a stream containing 1600 ppm SO₂, 3 vol% H₂O, 5.5 vol% O₂, and balance Ar at 250 °C and termed Cu8(250S); another one was saturated in a stream containing 620 ppm NO, 620 ppm NH₃, 1600 ppm SO₂, 3 vol% H₂O, 5.5 vol% O₂, and balance Ar at 250 °C and termed Cu8(250SN). Cu8(250S) represents a composition after SO₂ removal and Cu8(250SN) after simultaneous SO₂ and NO removal.

2.2. Activity measurements

Effect of SO₂ on SCR activity of the catalyst sorbents was studied in a fixed-bed quartz reactor (16 mm i.d.). The catalyst sorbent was placed between two quartz wool plugs held in the reactor, which was heated by a vertical electrical furnace. A thermocouple was inserted inside the reactor for actual temperature measurement. A simulated flue gas (620 ppm NO, 620 ppm NH₃, 3 vol% H₂O, 5.5 vol% O₂, and balance Ar) flowed through the reactor. The catalyst sorbent in the reactor was preheated in Ar (460 ml min⁻¹) at 400 °C for 1 h and then was cooled down to a lower temperature between 200 to 300 °C. The feed of the reactor was switched to the simulated flue gas for activity measurement. The catalyst sorbents were kept at the temperature until a stable NO conversion region was reached. Subsequently, 1600 ppm SO₂ was added to the feed to replace the same volume of Ar and hence to maintain the initial concentrations of NO, NH₃, and O₂. The concentrations of NO, NO₂, SO₂, and O₂ at the inlet and outlet of the reactor were simultaneously monitored online by a flue gas analyzer (KM9006 Quintox, Kane international Limited) equipped with NO, NO₂, SO₂, and O₂ sensors.

2.3. Characterization of the catalyst sorbent

2.3.1. Diffuse reflectance infrared Fourier transform (DRIFT) analysis

DRIFT spectra were collected using an infrared spectrometer (Equinox55, Bruker, Germany), equipped with KBr optics and a MCT D316 detector which works at the liquid-nitrogen temperature (77 K). Ex situ treated samples were ground into powder and placed inside a diffuse reflectance cell without packing or dilution. All spectra were obtained by accumulating 100 scans at a resolution of 4 cm⁻¹.

2.3.2. Surface area and pore structure analysis

The textural properties of the catalyst sorbent were measured through nitrogen adsorption at the liquid-nitrogen temperature (77 K) (ASAP2000, Micromeritics, USA). Before the measurements, the sample was degassed at 150 °C for 12 h. The total surface area was evaluated by the BET method.

2.3.3. Elemental analysis

Sulfur, nitrogen, and hydrogen analyses of the catalyst sorbents were conducted on a Vario EL from Elementar Analysensysteme GmbH Germany.

2.3.4. Temperature-programmed decomposition (TPDC)

TPDC was carried out in Ar on a thermogravimetric analyzer (TGA92 thermoanalyzer, SETARAM, France) with a continuous analysis of product stream by an on-line mass-quadrupole detector (OmniStar 200, Blazers).

2.3.5. Temperature-programmed reduction (TPR)

The redox property of the fresh and sulfated Cu8 was studied by H₂-TPR on the same thermogravimetric analyzer equipped with the same mass-quadrupole detector. In the experiment, 30 mg of sample was pretreated at 400 °C in a flow of Ar for 1 h to remove adsorbed species. After the sample was cooled down to room temperature in Ar, TPR was carried out up to 800 °C in a flow of 5 vol% H₂/Ar (40 ml min⁻¹) at a rate of 10 °C min⁻¹. The weight change of the sample with time was recorded on a personal computer. The hydrogen consumption was monitored on-line by the mass-quadrupole detector.

3. Results and discussion

3.1. Effect of SO₂ on SCR activity

Fig. 1 shows the effect of SO₂ on the SCR activity (expressed as a fraction of NO conversion at steady state) of Cu8 at temperatures of 200–300 °C and a space velocity (GHSV) of 14000 L kg⁻¹ h⁻¹. In the absence or presence of SO₂, the catalytic activity increases monotonously with increasing temperature. NO conversions in the presence of

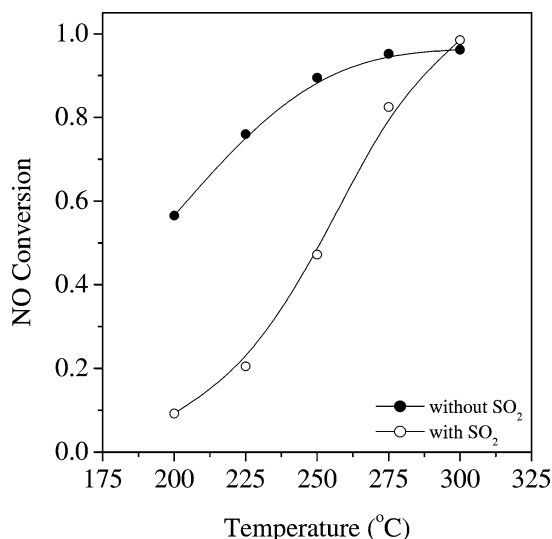


Fig. 1. Effects of SO₂ on the SCR activity of Cu8 catalyst sorbent as a function of temperature. Reaction conditions: 620 ppm NO, 620 ppm NH₃, 1600 ppm SO₂ (when used), 4.3 vol% O₂, 3 vol% H₂O, GHSV of 14000 L kg⁻¹ h⁻¹.

SO₂ are much lower than those in the absence of SO₂ except at 300 °C. This indicates that SO₂ greatly deactivates the SCR activity of the CuO/Al₂O₃ catalyst sorbent at temperatures below 300 °C.

To investigate the deactivation mechanism by SO₂ on the SCR activity, a transient experiment, consisting of seven consecutive parts, as shown in Fig. 2, was carried out. At the first stage (section a), at 250 °C, NO conversion is about 92% under the employed conditions. Upon admission of SO₂ into the feedstream (section b), NO conversion decreases with time on stream. When SO₂ (open symbols) breakthrough begins at about 270 min, NO conversion decreases to a stable

level of 52%. When SO₂ is cut off from the feedstream (section c), NO conversion recovers little, suggesting that the deactivation is irreversible. In section d, all of the reactants, such as NO, NH₃, and O₂, are removed from the feedstream, leaving only Ar to purge the catalyst sorbent surface. After 30 min, temperature-programmed desorption (TPD) is performed from 250 to 500 °C at a heating rate of 5 °C min⁻¹ in an Ar stream of 460 ml min⁻¹. During the TPD, a large amount of SO₂ is released starting at about 390 °C and peaking at 415 °C. After the TPD, the catalyst sorbent is cooled to the reaction temperature of 250 °C, and NO, NH₃, and O₂ are resumed in the feed (section e) at the same flow rate as that in section a. During this process, the catalytic activity recovers as indicated by the increase in NO conversion from 52% to 72%. However, the steady-state NO conversion of 72% is much lower than that in section a, 92%. In section f, the catalyst sorbent goes through a reductive treatment with 5% NH₃/Ar at 400 °C for 1 h and then the conditions of section e are repeated in section g. The NO conversion of the NH₃-treated catalyst sorbent recovers to that of the fresh sample, showing that the deactivation can be completely removed by the reduction process with NH₃. These experimental results clearly indicate that SO₂ significantly deactivates the CuO/Al₂O₃ catalyst sorbent for the reaction of NO–NH₃–O₂–H₂O at 250 °C and that the deactivation may result from the changes in catalyst form and/or structure other than from the gas-phase SO₂. Comparisons of NO conversions in sections a, c, e, and g show that there are at least two kinds of sulfur compounds formed during the reaction of NO–NH₃–O₂–H₂O in the presence of SO₂, which deactivates the catalyst sorbent. One is thermally decomposable at around 400 °C, and another one is thermally stable up to 500 °C but removable by NH₃ at 400 °C. However, one may also propose that there is only one sulfur compound

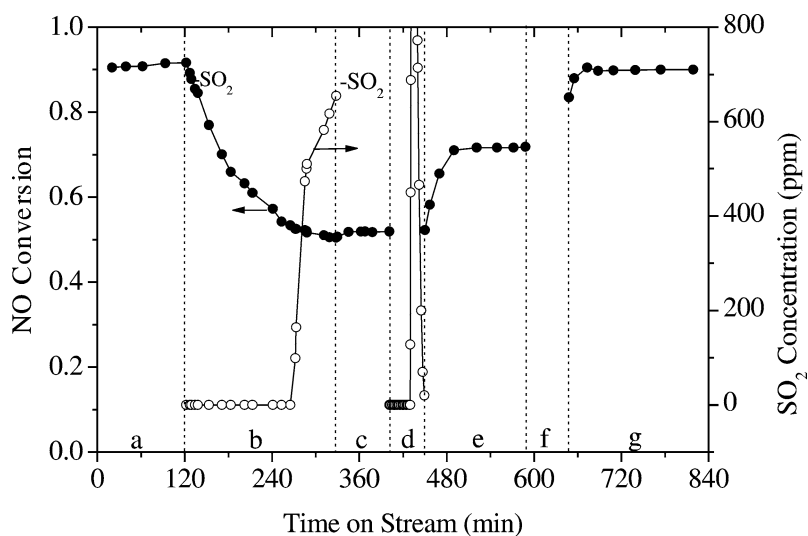


Fig. 2. Effect of SO₂ on SCR activity of Cu8 catalyst sorbent. (a) NO–NH₃–O₂–H₂O reaction at 250 °C; (b) with 1600 ppm SO₂; (c) without SO₂ in the feed; (d) Ar purge and then TPD from 250 to 500 °C; (e) cooling from 500 to 250 °C and then NO–NH₃–O₂–H₂O reaction; (f) 1 h at 400 °C in 5% NH₃/Ar; (g) NO–NH₃–O₂–H₂O reaction at 250 °C. The initial reaction conditions: 620 ppm NO, 620 ppm NH₃, 4.3 vol% O₂, 3 vol% H₂O, GHSV of 14000 L kg⁻¹ h⁻¹.

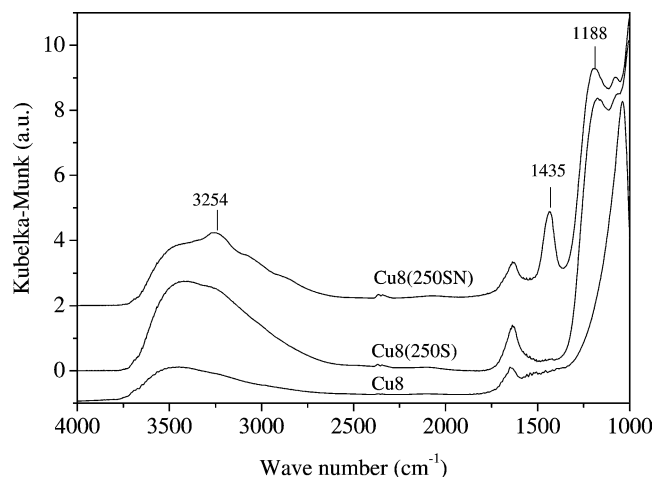


Fig. 3. DRIFT spectra of Cu8, Cu8(250S), and Cu8(250SN).

formed in the presence of SO₂, which undergoes a two-stage decomposition, one occurs thermally at 400 °C, and another one occurs at 400 °C in NH₃. But the results presented below show that this is not the case for the catalyst sorbent studied here.

3.2. Catalyst-sorbent characterization

3.2.1. DRIFT analysis

It is important to identify the actual form of the deactivating agents on the catalyst sorbent to understand the mechanism of SCR deactivation by SO₂. Fig. 3 shows DRIFT analyses of the catalyst sorbent deactivated at 250 °C in simultaneous SO₂ and NO removal (Cu8(250SN)) and in SO₂ removal (Cu8(250S)), as well as the catalyst sorbent itself (Cu8). Due to the strong absorption of skeletal vibrations of the alumina support in frequencies below 1000 cm⁻¹, spectra in the range of 1000–4000 cm⁻¹ is only shown in the figure. Cu8(250S) exhibits a band at 1188 cm⁻¹, which may be attributed to the vibration of surface sulfate. The literature [16] indicates that SO₄²⁻ ion shows two infrared peaks at 1104 (ν₁) and 613 (ν₂), and when SO₄²⁻ is bound to the catalyst-sorbent surface, the symmetry may be lowered to either C_{3v} or C_{2v} and the ν₁ may split into two peaks. The band at 1188 cm⁻¹ may result from the ν₁ splitting. Compared to Cu8(250S), the spectra of Cu8(250SN) also exhibits a similar band at 1188 cm⁻¹, but with a stronger intensity than that of Cu8(250S). In addition, it also shows two more bands at 1435 and 3254 cm⁻¹. The band at 1435 cm⁻¹ is due to the asymmetric bending vibration of NH₄⁺ species, whereas the band at 3254 cm⁻¹ is assigned to the corresponding N–H stretching vibration of NH₄⁺ ions [17,18]. These indicate that ammonium sulfate salt is deposited on Cu8(250SN). The spectrum of Cu8 shows the absence of either SO₄²⁻ or NH₄⁺. These observation are supported by elemental analysis shown in Table 1, where sulfur and hydrogen contents in Cu8(250SN) are higher than those in Cu8(250S), and nitrogen presents only in Cu8(250SN).

Table 1
Elemental analysis results of Cu8 catalyst sorbent after different treatments

Sample	S (wt%)	N (wt%)	H (wt%)
Cu8(250S)	2.52	0	0.98
Cu8(250SN)	3.91	1.01	1.17

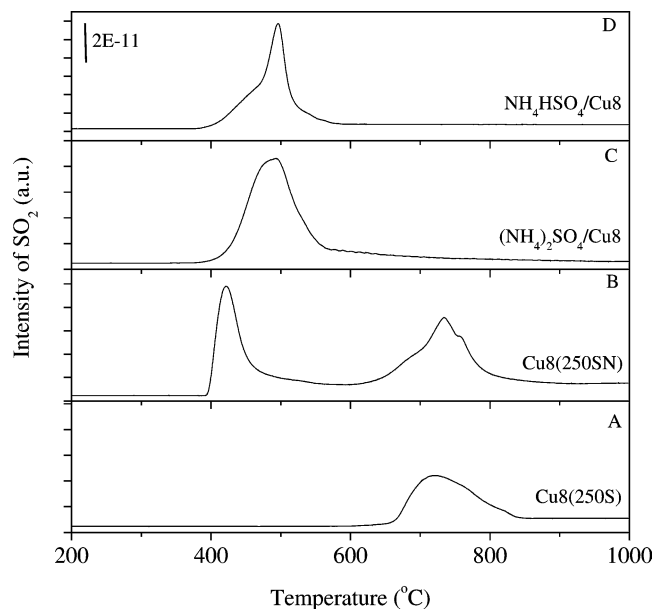


Fig. 4. TPDC patterns of (A) Cu8(250S), (B) Cu8(250SN), (C) (NH₄)₂SO₄/Cu8, and (D) NH₄HSO₄/Cu8. Conditions: Ar of 50 ml min⁻¹, heating rate of 10 °C min⁻¹.

3.2.2. Temperature-programmed decomposition (TPDC)

The TPDC curve of the deactivated catalyst sorbent (Cu8(250SN)) is shown in Fig. 4B. Two major SO₂ release peaks are observed in the temperature ranges of 390–500 and 660–810 °C, which can be attributed to the decomposition of sulfate species formed during the SCR reaction in the presence of SO₂. A review of the decomposition temperatures of possible sulfate compounds formed in the catalytic system shows that the low-temperature SO₂ release fits the decomposition of ammonium sulfate salt. The literature [9, 13–15] reported strong deactivation by SO₂ at temperatures below 280 °C for a variety of SCR catalysts and attributed the deactivating agents to ammonium sulfate salt such as (NH₄)₂SO₄ and NH₄HSO₄, which decompose at temperatures of 250–450 °C. TPDC of (NH₄)₂SO₄ and NH₄HSO₄ impregnated on Cu8, presented in Fig. 4C ((NH₄)₂SO₄/Cu8) and Fig. 4D (NH₄HSO₄/Cu8), show SO₂ releases in the temperature range of 390–570 °C, which is a little wider toward the high-temperature side than the SO₂ release in Fig. 4B for Cu8(250SN). This indicates that the ammonium sulfate salt formed on this catalyst sorbent are likely to be in the form of NH₄HSO₄ and/or (NH₄)₂SO₄. The wider temperature range of curves C and D may result from the higher ammonium sulfate loadings than that in curve B. The SO₂ release at temperatures of 660–810 °C may result from decomposition of copper sulfate, as supported by the TPDC

curve of Cu8(250S) in Fig. 4A, since the sample Cu8(250S) contains only copper sulfate and aluminum sulfate [19,20], and the decomposition temperatures of pure copper sulfate and aluminum sulfate are around 750 and 920 °C [21,22], respectively.

3.2.3. Characterization in surface properties

Table 2 presents surface area and pore volume data of the catalyst sorbent after different treatments. Sulfation of the catalyst sorbent at 250 °C (Cu8(250S)) results in a decrease in both surface area and pore volume, from 149.6 m² g⁻¹ and 0.23 cm³ g⁻¹ to 116.8 m² g⁻¹ and 0.18 cm³ g⁻¹, respectively. This suggests that the conversion of CuO to CuSO₄ fills some of the pores in the catalyst sorbent. The reaction of NO + O₂ + NH₃ + SO₂ at 250 °C (Cu8(250SN)) further reduces the surface area and pore volume of the catalyst sorbent to 77.1 m² g⁻¹ and 0.14 cm³ g⁻¹, respectively. This suggests that the formation of ammonium sulfate salt on the catalyst sorbent also fills and plugs some of the pores of the catalyst sorbent. The heat treatment at 500 °C in Ar for 1 h (Cu8(250SN500H)) increases the surface area and pore volume to the value of the sulfated sample (Cu8(250S)), which suggests that 500 °C is high enough for the complete decomposition of ammonium sulfate salt. The treatment in 5% NH₃/Ar at 400 °C (Cu8(250SN400R)) increases the surface area and pore volume further to the values of the fresh sample, which suggests that the NH₃ treatment is capable to convert the CuSO₄ back to CuO and to remove the ammonium sulfate salt. These results along with those presented earlier, especially those in Fig. 2, indicate that the deactivation behavior of the catalyst sorbent by SO₂ is closely associated with the reduction in surface area and pore volume due to the formation of sulfate compounds, ammonium sulfate salt, and CuSO₄. It should be pointed out at this stage that Fig. 2 shows that the deactivation caused by the formation of sulfate compounds has limits, such as in section b where the decrease in NO conversion stops when SO₂ breakthrough begins. It is understandable that CuSO₄ will not form if there is no CuO available on the catalyst sorbent. However, the system always contains NH₃ and SO₂ due to the constant feeding. This indicates that stopped formation of ammonium sulfate salt is resulted from the stopped formation of SO₃. This may further indicate that the formation of SO₃ from SO₂ is catalyzed by CuO, and the conversion of CuO to CuSO₄ terminates the oxidation of SO₂ to SO₃.

3.2.4. Temperature-programmed reduction in H₂ (H₂-TPR)

It is worth pointing out that activation of adsorbed ammonia is a key step for SCR, which is directly related to redox property of the catalyst sorbent. H₂-TPR, as shown in Fig. 5, was performed to evaluate redox property change of the CuO/Al₂O₃ catalyst sorbent through sulfation. The H₂ consumption peaks in the figure may reflect the oxidation ability of the catalyst sorbents to convert H₂ to H₂O. The maximum H₂ consumption occurs at about 200 °C for Cu8 and 320 °C for sulfated Cu8 (Fig. 5A), which corresponds to obvious

Table 2
Surface area and pore structure of Cu8 catalyst sorbent after different treatments

Sample	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
Cu8	149.6	0.23
Cu8(250S)	116.8	0.18
Cu8(250SN)	77.1	0.14
Cu8(250SN500H)	113.6	0.16
Cu8(250SN400R)	148.3	0.22

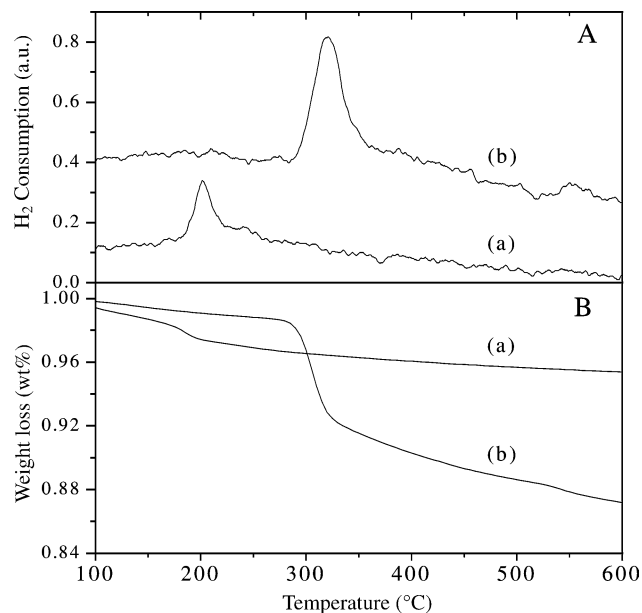


Fig. 5. H₂-TPR profiles of (a) Cu8 and (b) sulfated Cu8. (A) MS spectrum of H₂ consumption; (B) TG data.

weight loss of the samples (Fig. 5B). These data point to a major decrease in oxidation ability of the CuO/Al₂O₃ catalyst sorbent by sulfation, indicating that the reduced SCR reactivity by sulfation may also be due to chemical transformation of the active site from CuO to CuSO₄.

4. Conclusions

SO₂ deactivates the SCR activity of CuO/Al₂O₃ catalyst sorbent at temperatures of 200–300 °C. The main deactivating substances are ammonium sulfate salt and copper sulfate, formed during the reaction of NO–NH₃–O₂–H₂O in the presence of SO₂. Ammonium sulfate salt deactivates the SCR through pore filling and/or plugging, but it decomposes at around 400 °C. Copper sulfate deactivates the SCR by either pore filling and/or plugging or by its low SCR activity compared to CuO. Copper sulfate decomposes at temperatures greater than 660 °C but can be converted back to CuO in 5 vol% NH₃/Ar at about 400 °C. CuO may have catalytic activity to catalyze the oxidation of SO₂ to SO₃, which initiates the formation of sulfate compounds, but CuSO₄ may not have this catalytic activity.

Acknowledgments

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