

Article

High Temperature Adsorption of SO₂ on Mixed Oxides Derived from CaAl Hydrotalcite-Like Compounds

Hailin Wang ¹, Run Hao ^{1,*}, Meiping Gao ¹, Zhongshen Zhang ² and Zhengping Hao ²
¹ Beijing Key Laboratory for VOCs Pollution Prevention and Treatment Technology and Application of Urban Air, Beijing Municipal Research Institute of Environment Protection, Beijing 100037, China; wanghailin@cee.cn (H.W.); gaomeiping@cee.cn (M.G.)

² National Engineering Laboratory for VOCs Pollution Control Material & Technology, Research Center for Environmental Material and Pollution Control Technology, University of Chinese Academy of Sciences, Beijing 101408, China; zszhang@gucas.ac.cn (Z.Z.); zphao@ucas.ac.cn (Z.H.)

* Correspondence: haorun@cee.cn

Abstract: SO₂ which is usually emitted at high temperature is one of the most important air pollutants. It is of great significance to develop high temperature SO₂ adsorbent with high efficiency and low cost. In this work, a series of hydrotalcite-like compound-derived CaAlO and CaXAlO (X = Ce, Co) were prepared by coprecipitation and calcination method, and were employed as adsorbents for SO₂ adsorption at high temperature (700 °C). The structure and surface properties of these adsorbents were characterized by XRD, Brunauer–Emmett–Teller (BET), Derivative thermogravimetric analysis (DTG) and CO₂-TPD (temperature programmed desorption) measurement. Addition of a minor amount of Ce, Co (5 wt%) could significantly increase the number of weak alkalinity sites. CaO in CaCeAlO showed the best SO₂ adsorption capacity of 1.34 g/g, which is two times higher than that of CaO in CaAlO (0.58 g/g).

Keywords: hydrotalcite-like compounds; SO₂; CaAlO; high temperature adsorption



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1. Introduction

SO₂ is regarded as one of the most important air pollutants due to its contribution to acid rain formation and direct threat to public health. Therefore, restricting SO₂ emissions from coal/oil combustion sources is of great importance. In most cases, SO₂ emitted from such sources is accompanied with high temperature, for instance the temperature of SO₂ emitted from power plant does not exceed 200 °C. During the fluid catalytic cracking (FCC) process in the oil refining enterprises, about 5–10% of feed sulfur originated with crude oil is converted to SO_x (SO₂ ≥ 90%) and emitted with high temperature (650–700 °C) and high concentration (around 2000 ppmv, in China), which accounts for about 5% or even higher of total SO₂ emission [1]. At present, with the increase in throughput of FCC units and sulfur content in crude oil, the problem of SO₂ pollution is becoming more and more prominent. It is urgent to control SO₂ emitted from such sources characterized with high temperature and high concentration.

Materials such as activated carbons, activated carbon fibers, and fly ash were usually employed in previous studies [2–5]. However, SO₂ storage capacity on these materials is limited and those studies were often carried out at low temperature, and these physical adsorption methods are often inapplicable at high temperature. Thus, it is important to develop efficient and inexpensive adsorbents for high temperature SO₂ adsorption and storage.

Hydrotalcite-like compounds (HTLcs) are known as anionic clay or layered double hydroxides and could be expressed as M_{1-x}²⁺ M_x³⁺ (OH)₂ A_x·nH₂O [6,7], where M²⁺ and M³⁺ represent most divalent and trivalent metal ions, respectively. Owing to the considerable selection of M and A, a wide variety of HTLcs could be synthesized and used

for different application [8]. For SO₂ control at higher temperatures like in the FCC process, MgAlO is widely used with the addition of other elements at laboratory scale [9–13].

In our previous studies, we found that the addition of Ca led to a notable increase in pollutant adsorption capacity [14,15]. Here, based on the fact that CaO is widely used for SO₂ emission control, and that Ca and Mg belong to the same group but the alkalinity of Ca is stronger than that of Mg, it can be concluded that the Ca replacing MgAlO will have excellent SO₂ adsorption performance.

In this article, to test the adsorption capacity of Ca-based mixed metal oxides at high temperature, HTlcs-derived CaAlO was prepared and employed as adsorbent for the SO₂ adsorption experiments at 700 °C. Moreover, high temperature SO₂ adsorption is a chemical adsorption process involving chemical oxidation, so the absorption process could be effectively improved by increasing the amount of reactive oxygen species on the adsorbent surface. Ce and Co are two commonly used transition metal elements in catalytic reactions, which can promote the improvement of oxygen storage capacity of metal oxide materials. Therefore, typical metals like Ce and Co were added to CaAlO to study their effect during the SO₂ adsorption process.

2. Materials and Methods

Materials preparation: CaAl and CaXAl-HTlcs (X = Ce, Co) were synthesized using the coprecipitation method. As for the CaAl-HTlcs, a mixed salt solution containing Ca(NO₃)₂·4H₂O (>99%), Al(NO₃)₃·9H₂O (>99%), and a solution of NaOH (>96%) and NaNO₃ (>99.8%) were prepared separately with distilled water. After dissolution, the mixed Ca-Al salt solution was added dropwise into the NaOH-NaNO₃ solution under vigorous mechanical stirring with N₂ protection. The precipitate was aged at 80 °C for 24 h, and then the precipitate was thoroughly washed and filtered. The filter cakes of precipitate were dried at 100 °C overnight. The synthesized CaXAl-HTlcs (X = Ce, Co, 5 wt%) were calcined at 800 °C for 4 h to obtain the corresponding HTlcs-derived mixed oxides, which are denoted as CaAlO and CaXAlO (X = Ce, Co). The oxides were then crushed and sized in 20–40 meshes for SO₂ adsorption measurement.

Material characterization: The X-ray diffraction (XRD) patterns of precursors and the derived mixed oxides were recorded on a Rigaku TTR2 powder diffractometer by using Cu K α radiation (λ = 0.154 nm) with a 2 θ range of 5–70° at a scanning rate of 4°/min. The tube voltage and current were set at 40 kV and 20 mA, respectively. Thermal decomposition behaviors of as-prepared HTlcs were investigated with Derivative thermogravimetric analysis (DTG) (Setaram, Labsys). In a typical measurement, 20–30 mg of HTlcs sample was heated in a ceramic crucible at a heating rate of 10 °C/min from room temperature to 800 °C, with N₂ purging at a flow rate of 30 mL/min. Textural properties of derived mixed oxides were analyzed by N₂ adsorption/desorption at liquid-nitrogen temperature (77 K) using a gas adsorption analyzer (Quantachrome NOVA-1200). The specific surface area (SSA) was calculated by the Brunauer–Emmett–Teller (BET) equation. The pore volume and pore size distribution were obtained with the Bopp–Jancso–Heinzinger (BJH) method. CO₂-TPD (temperature programmed desorption) was taken by a chemical adsorption instrument (Micromeritics 2720) to characterize the alkalinity adsorption sites of these mixed metal oxides. A total of 50 mg of mixed metal oxide sample was put into a U-type quartz tube, after pretreatment, a stream of 20% CO₂/He (*v/v*) was introduced for 2 h to reach adsorption saturation, and then the sample was heated at a heating rate of 10 °C/min from room temperature to 800 °C with He purging at a flow rate of 50 mL/min.

SO₂ adsorption test: Thermal SO₂ adsorption experiments were carried out in a quartz fixed-bed flow-reactor (i.d. = 6 mm and L = 600 mm) using 0.5 g oxide sorbent (20–40 mesh powder) at atmospheric pressure. The oxide sorbent was pretreated from room temperature to 700 °C with N₂ flowing at 40 mL/min. After stabilizing for 30 min, N₂ flow was shut off and a stream mixture of SO₂ and air with 0.5% SO₂ at a total flow rate of 50 mL/min was passed through the fixed bed. The sorbent bed was heated by a tubular furnace, and the temperature was monitored with a thermocouple which was inserted into the

bed. The concentration of SO₂ at the outlet was monitored online by an auto-sampling gas chromatograph (GC) which equipped with a Flame photometric detector (FPD), until the concentration reached the origin inlet level of 0.5%. The SO₂ adsorbed on the sample was calculated by the following formula

$$W_{\text{SO}_2} = \int_0^t k c_i dt \quad (1)$$

where c_i means the SO₂ concentration at i minutes, and k is the constant, which is calculated by the flow volume, M_{SO_2} , and the mole volume constant.

The saturated adsorption was calculated as

$$W = W_{\text{SO}_2} / W_{\text{sorbent}} \text{ (g/g)} \quad (2)$$

3. Results and Discussion

Structure of HTLcs and Derived Oxides

Figure 1a shows the X-ray diffraction patterns of CaAl-HTLcs and CaXAl-HTLcs (where X = Ce, Co) which was obtained by drying the filter cake at 100 °C. All the precursors exhibited the typical X-ray diffractogram of hydrotalcite. The peaks at $2\theta = 10^\circ$, 21° , 39° corresponding to the (003), (006), and (009) crystal planes indicate the well-formed crystalline layered structure with a rhombohedral symmetry (3R) [16]. The in-plane X-ray diffractions from planes (110) and (113) at 31° and 32° reveal a good dispersion of metal ions in the hydroxide layers [14]. Compared with CaAl-HTLcs, the peaks of CaXAl-HTLcs become stronger, which indicates the better crystallinity. In this study, to avoid the formation of CaCO₃, the metal nitrates were employed instead of the carbonates and the N₂ protection was also introduced during the titration. Therefore, these HTLcs were synthesized successfully and no CaCO₃ (JCPDS 85-1108) were found [17,18].

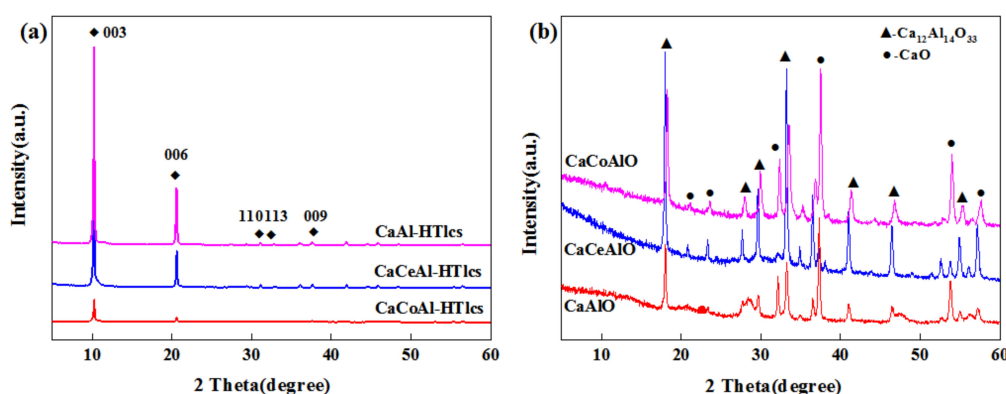


Figure 1. XRD patterns of (a) prepared hydrotalcite-like compounds (HTLcs) and (b) derived metal oxide sorbents.

Figure 1b describes the XRD patterns of the obtained mixed metal oxides which were derived from the corresponding HTLcs by the calcination process, which mainly contains dehydration, dehydroxylation, and loss of compensating anions, and leads to acidic or basic mixed oxides. No spinel phase was observed; it can be inferred that during the dehydroxylation and loss of compensating anions processes, Ca could not be melt with Al to form the spinel phase. In fact, CaO (JCPDS 48-1467), marked with • in Figure 1b and Ca₁₂Al₁₄O₃₃ (JCPDS 09-0413), marked with ▲ in Figure 1b were observed in those samples. Here, it can be deduced that Ca₁₂Al₁₄O₃₃ acts a support/binder to disperse the CaO. Among those samples, no obvious peaks single X oxide (where X = Ce, Co) were found, indicating the good dispersion of these metal oxides. The specific surface area, mean pore diameter, and total pore volume were tabulated in Table 1. Obviously, the slight addition of other metals affects the SSA, pore size, and pore volume. Compared with CaAlO, these parameters values of CaXAlO (X = Ce, Co) samples are lower. Generally,

the interparticle pore diameter calculated fell in the range of 15.6–20.2 nm. According to a previous study [19], gas molecule diffusion in such pores could not be the rate-determining step for the gas adsorption.

Table 1. Textual property and SO₂ adsorption amount of CaO in oxide sorbents.

Sample	SSA(m ² /g)	Pore Size (nm)	Pore Volume (cm ³ /g)	Adsorption Amount (g/g)
CaAlO	30.8	20.2	0.16	0.28
CaCoAlO (Co = 5 wt%)	19.9	15.6	0.08	0.40
CaCeAlO (Ce = 5 wt%)	24.4	19.3	0.12	0.67

In Figure 2, DTG curves present the weight loss rate of these HTlcs during heating in the air. In general, thermo-gravimetric loss during heating involves two or three steps [20]. The first step occurs at 50–200 °C, mainly ascribed to the loss of surface-adsorbed and interlayer water molecules. The second stage takes place at 200–500 °C, including the dehydroxylation of layer hydroxyl groups and decomposition of interlayer nitrate, causing collapse of the layer structure. In this study, there were three observed peaks of CaAl-HTlcs and CaXAl-HTlcs samples under 600 °C, falling in the range of 50–180 °C, 240–330 °C, and 450–600 °C, respectively. Considering that the loss of OH[−] usually occurred under 200–500 °C and the anion removal temperature of nitrate is higher than 500 °C, it is concluded that the peaks in the range of 50–180 °C, 240–330 °C, and 450–600 °C refer to the loss of H₂O, OH[−], and NO₃[−], respectively. Compared with CaAlO, the addition of Ce and Co promotes the dehydroxylation temperature (about 5–20 °C higher) and facilitates the decomposition of NO₃[−] (about 10–40 °C lower). It is noted that for the CaCeAlO sample, an obvious peak at 663 °C was observed. We assume that the addition of Ce could remarkably promote the condensation during the transformation from CaAl-HTlc to CaAlO.

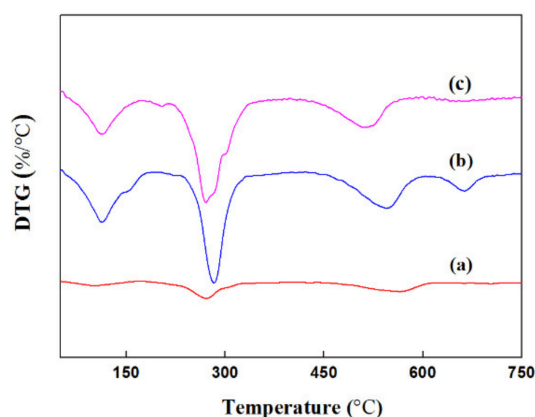


Figure 2. DTG profiles of the precursors HTlcs: (a) CaAl-HTlc, (b) CaCeAl-HTlc, and (c) CaCoAl-HTlc.

CO₂-TPD tests were conducted to characterize the alkalinity of those samples and shown by Figure 3. There were four peaks observed for CaAlO and CaXAlO samples, the first peak represents the weak alkaline sites (<200 °C), the second peak corresponds to the mid-strong alkaline sites (200–400 °C), and the third and the fourth belong to the high temperature peaks, referring to the strong alkaline sites (>400 °C). Compared with CaAlO, the alkalinity of strong alkaline sites of CaCeAlO and CaCoAlO are weaker in that the peak temperature decreased from 628 °C (CaAlO) to 595 °C (CaCeAlO) and 602 °C (CaCoAlO) and the sites numbers characterized by integration area also decrease about 8% and 33% for CaCeAlO and CaCoAlO, respectively. The similar pattern was also observed for the strong alkaline sites in the range of 350–500 °C. As for the weak alkaline sites, the site numbers of CaCeAlO and CaCoAlO were at the same level, about two times those of CaAlO. The peaks of those weak alkaline sites appeared around 100 °C, indicating the adsorption of SO₂ over

CaCeAlO and CaCoAlO samples, which would favor further chemical adsorption at high temperature. The adsorption of SO_2 is generally a chemical adsorption process, which includes a series of steps, such as surface diffusion and pore diffusion of SO_2 and chemical reaction occurring on active sites, to form products of sulfate finally [15].

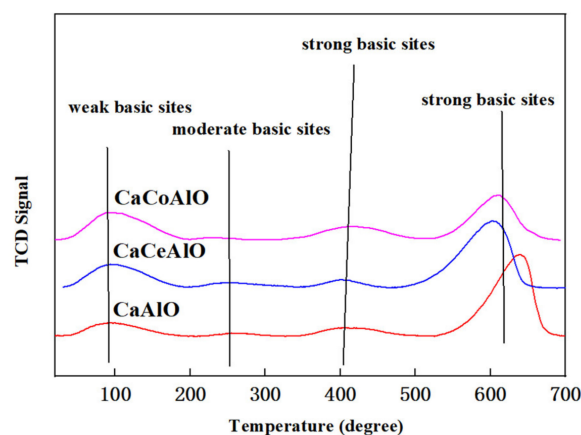


Figure 3. CO_2 -TPD profiles of the oxide sorbents.

Figure 4 shows the typical adsorption breakthrough curves of SO_2 over the oxide sorbents. All oxide sorbents seemingly follow a similar sorption pattern. As shown in Figure 4, SO_2 adsorption mainly could be divided into three stages. In the initial stage, 5000 ppm SO_2 was completely adsorbed, lasting about 70, 90, and 150 min, for the CaAlO, CaCoAlO and CaCeAlO, respectively. After the initial stage, the SO_2 concentration increases rapidly in the next 60–90 min. Afterward, the increase of SO_2 slows down and finally reaches the initial level of 5000 ppm, indicating that SO_2 is no longer adsorbed on those adsorbents.

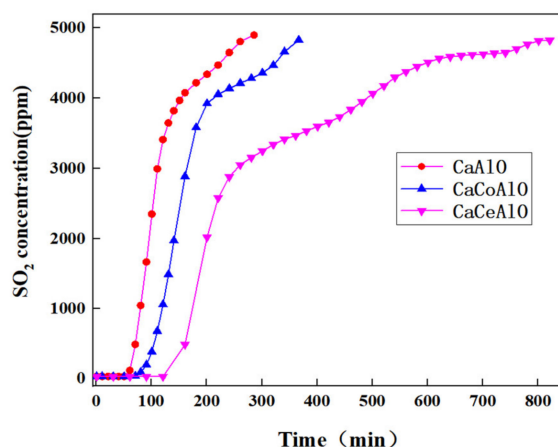


Figure 4. SO_2 adsorption on CaAlO, CaCoAlO and CaCeAlO at 700 °C.

Table 1 lists the SO_2 sorption amounts of all oxides. It is well-known that CaO can quickly capture and strongly hold SO_2 in the calcium sulfate form. It is assumed that the active sites and SO_2 affinity of the oxide sorbent are determinant. In CaAlO and CaXAlO samples, the CaO content was calculated by titration method. Where the mixed samples were resolved by ethylene glycol together with bromocresol green-methyl red mixed indicator solution and determined by HCl titration. The results show that CaO is about 50 wt% of CaAlO and CaXAlO samples. Considering CaO and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ are formed in the same process, the dispersion of CaO in CaXAlO might be better than that of CaAlO, which could lead to the better contact with SO_2 and result in better adsorption.

Theoretically, 1.14 g SO_2 could be absorbed on 1 g CaO at 100% conversion. In this study, CaO (50 wt%) was mixed with $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ in CaAlO and CaXAlO samples. There-

fore, the theoretical maximum SO₂ absorption capacity of CaO will be two times that of these samples. For CaAlO, CaCoAlO, and CaCeAlO samples, the SO₂ absorption capacity is 0.28 g/g, 0.40 g/g, and 0.67 g/g, respectively, which correspond to 0.56 g/g, 0.80 g/g, and 1.34 g/g for the adsorption capacity of contained CaO, respectively. It is noted that the SO₂ adsorption in CaCeAlO is higher than the maximum value of 1.14 g/g, suggesting that in the surface of CaCeAlO, one CaO molecule might not absorb only one SO₂ molecule, it might absorb two or even more SO₂ molecules. Addition of a minor amount of Ce, Co (5 wt%) could lead to good dispersion of metal oxide and obviously increase the SO₂ adsorption. In this study, the SO₂ adsorption of CaAlO, CaCoAlO, and CaCeAlO was carried out on fixed-bed flow-reactor, which is closer to the actual situation.

4. Conclusions

CaAl-HTlcs and CaXAlO (X = Ce, Co) were prepared by metal nitrates through coprecipitation method, and the corresponding mixed metal oxide XCaAlO, CaXAlO (X = Ce, Co) were obtained after calcination. The samples were characterized by XRD, BET, DTG, and CO₂-TPD, and the high temperature SO₂ adsorption capacity was measured at 700 °C. The results indicated that Ca was successfully introduced into HTlcs system and CaO was well mixed with Ca₁₂Al₁₄O₃₃ in the CaAlO samples. Introduction of Ce and Co into CaAlO could significantly increase the number of weak alkalinity sites, which have an important effect on the SO₂ adsorption rather than the pore structure parameters. The adsorption of SO₂ by CaCeAlO was 0.67 g/g, and the adsorption of SO₂ by CaO in the CaCeAlO showed a maximum value of 1.34 g/g, suggesting the super adsorption capacity.

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