

# High temperature adsorption of carbon dioxide on Cu–Al hydrotalcite-derived mixed oxides: kinetics and equilibria by thermogravimetry

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**Abstract** The effect of Cu/Al molar ratio on the high-temperature adsorption characteristics of CO<sub>2</sub> on the mixed oxides of Cu–Al hydrotalcite skeletal structure has been studied by thermogravimetry. The Cu/Al molar ratio of the hydrotalcites synthesized was varied between 1.0 and 3.0, and the adsorption temperature ranged from ambient to 600 °C. The hydrotalcite with Cu/Al molar ratio of 2.0 was found to be the most suitable adsorbent for high-temperature CO<sub>2</sub> adsorption, in both the capacity and the rate of adsorption. The activation energy values suggested that the physical adsorption dominates at low temperatures (<400 °C) and the chemisorption dominates at high temperatures (>400 °C).

**Keywords** Activation energy of adsorption · Adsorption capacity · Adsorption kinetics · CO<sub>2</sub> adsorption · Hydrotalcite · Mixed oxide sorbents · Thermogravimetry

## Introduction

Separation of carbon dioxide from liquids and gases by adsorption on solids becomes increasingly important in many applications, such as controlling CO<sub>2</sub> emissions from

fossil-fueled power plants, natural gas treatment and purification of hydrocarbons, production of hydrogen gas by steam reforming, and environmental control and life support systems in space vehicles [1–5]. The recovered CO<sub>2</sub> can be used in other applications such as CO<sub>2</sub>-enhanced oil recovery, production of dry ice, supercritical CO<sub>2</sub> extraction, dry reforming, and conversion to other chemicals and fuel.

However, some of the applications need adsorbents that can separate the CO<sub>2</sub> right at the high temperatures of the carrier gas, without first cooling it to ambient temperature. To achieve this, the adsorbent must have (a) high adsorption capacity and selectivity at high temperatures, (b) satisfactory adsorption/desorption kinetics, (c) moderate heat of adsorption, and (d) stable adsorption capacity for repeated adsorption cycles [6–8].

Some materials for high-temperature CO<sub>2</sub> adsorption have been known, such as CaO, MgO, Al<sub>2</sub>O<sub>3</sub>, and their mixtures [7–14]. Recently, high capacity and stability of CO<sub>2</sub> adsorption on hydrotalcite-like compounds (HTLcs) at elevated temperature have been reported [15–19]. The high-temperature CO<sub>2</sub> adsorption capacity of the HTLcs can be attributed to high thermodynamic stability of CO<sub>3</sub><sup>2-</sup> ion in the interlayer and the shape memory effect of the HTlc structure. This makes the HTLcs suitable as CO<sub>2</sub>-adsorbents in separation-enhanced steam reforming of methane for hydrogen production [4–6].

HTLcs are a class of layered compounds known as layered double hydroxides (LDHs), consisting of positively charged brucite (MgOH)-like layers balanced by hydrated anions in the interlayers [20, 21]. Most of the HTLcs that have previously been studied for high-temperature CO<sub>2</sub> adsorption were Mg–Al–CO<sub>3</sub> HTLcs [16–19]. This is because the Mg–Al–CO<sub>3</sub> is the most common naturally occurring form of HTlc and can readily and inexpensively

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be synthesized [20, 21]. The CO<sub>2</sub> adsorption capacities and the qualitative information about adsorption rates of these materials were obtained by both static and dynamic volumetric and gravimetric methods.

There are two objectives in this work. The first is to describe a dynamic thermogravimetric method to evaluate quantitatively the kinetics as well as the equilibrium of CO<sub>2</sub> adsorption. The second objective is to use the Cu–Al HTlc-derived mixed oxides as adsorbents for CO<sub>2</sub>. Copper has been chosen here as a constituent metal of the HTlc in view of using such material as an adsorbent with integrated catalytic sites for separation-enhanced steam reforming reactions. The temperature for the adsorption study, however, ranged from room temperature to 600 °C in order to determine the kinetics of adsorption.

## Experimental

### Preparation of Cu–Al hydrotalcite-like compounds

The Cu–Al HTlcs were prepared by coprecipitation of copper and aluminum hydroxycarbonates from their nitrate precursors using sodium carbonate as precipitant. The method has been described elsewhere [22]. Three samples of precipitates with theoretical Cu/Al molar ratios of 1.0, 2.0, and 3.0, respectively, were prepared. The presence of Cu–Al HTlc as the main compound in the dried precipitates was confirmed by powder X-ray diffraction (XRD) analysis. Here onward, the dried adsorbent precursors will be designated as CuAl-*x* which represents the Cu–Al HTlc with nominal Cu/Al molar ratio of *x*.

### Determination of adsorption capacity

The studies of CO<sub>2</sub> adsorption on the HTlc samples were carried out in a Perkin-Elmer TGA-7 thermogravimetric analyzer. A 20-mg each of the HTlc samples was introduced into the sample holder. First, the sample was pretreated by heating at a rate of 10 °C/min up to 600 °C under the nitrogen flow at 30 mL/min, and held at 600 °C for 15 min. The nitrogen flow was then switched to CO<sub>2</sub> flow to start adsorption at 600 °C. The sample was held under CO<sub>2</sub> flow at 600 °C for 15 min to reach a steady state at which no appreciable change of mass occurred. Next, the temperature was reduced at the rate of 15 °C/min down to 450 °C. At 450 °C, the sample was held for 10 min to reach a steady state. The procedure was repeated consecutively to other holding temperatures of 300, 150 °C, and finally room temperature. The steady-state CO<sub>2</sub> adsorption capacities at respective temperatures were recorded by the corresponding mass levels in the thermal gravimetric (TG) curve.

### Determination of rate of adsorption

First, a 20 mg of HTlc sample was introduced into the sample cell and heated at a controlled temperature ramp of 10 °C/min up to 600 °C under a nitrogen flow at 30 mL/min. The sample was held at 600 °C for 10 min under nitrogen flow. The temperature was then reduced at the rate of 15 °C/min down to 450 °C. The sample was held at 450 °C for 2 min. Finally, the nitrogen flow was switched to CO<sub>2</sub> flow and the sample was continuously held at 450 °C for 5 min to reach a steady state.

The procedure was repeated for other holding temperatures of 300 and 150 °C, respectively. The rates of adsorption on the fresh adsorbent at different temperatures were then obtained from the corresponding derivative thermal gravimetric (DTG) curves.

## Results and discussion

### Adsorbents pretreatment

In the pretreatment stage, physically adsorbed moisture, intercalated water, bonded hydroxyls, and intercalated CO<sub>2</sub> of the HTlc were removed by thermal decomposition, before the sample was subjected to CO<sub>2</sub> flow. The thermal decomposition behavior of the Cu–Al HTlc compounds has been reported in the literature [22, 23]. The pretreatment was to provide fresh adsorbents without entities that can hinder the CO<sub>2</sub> adsorption. It was also to give mixed oxides with HTlc skeletal structure for CO<sub>2</sub> adsorption. It was expected that after heating at 600 °C, almost all of the carbonates in the interlayer could have been removed [22, 23], except small amounts of amorphous hydroxycarbonate or oxycarbonate phase [24, 25]. The mass of the sample at the end of the pretreatment stage represents the mass of the fresh adsorbent. The masses of the fresh adsorbents so obtained were in the order CuAl-3.0 > CuAl-2.0 > CuAl-1.0, since the equal-mass of the initial sample with higher Cu/Al ratio contains higher mass of nonvolatile residue or mixed oxides. However, the differences in mass were only within 15% of the initial sample mass.

### Carbon dioxide adsorption capacity

The CO<sub>2</sub> adsorption occurred when the pretreated sample was cooled from 600 °C under the CO<sub>2</sub> flow. The TG curve of the adsorption stage for CuAl-2.0 sample is enlarged in Fig. 1. The pattern shows a rapid adsorption at 600 °C when the CO<sub>2</sub> was first introduced to the fresh adsorbent. The steady-state adsorption capacities at 600, 450, 300, 150, and 30 °C are given by the mass levels a, b, c, d, and e, respectively, along the cooling path.

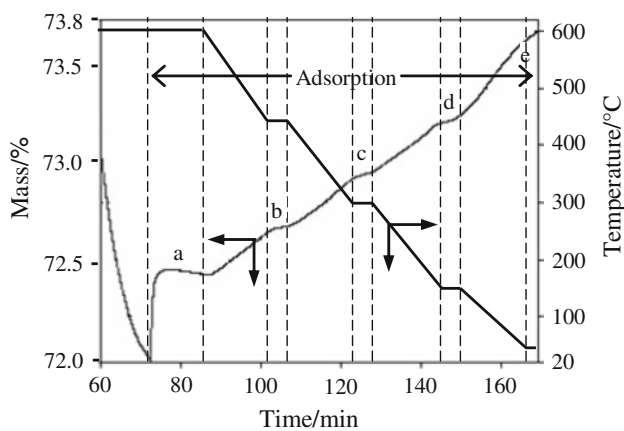


Fig. 1 TG curve for CO<sub>2</sub> adsorption on CuAl-2.0 sample

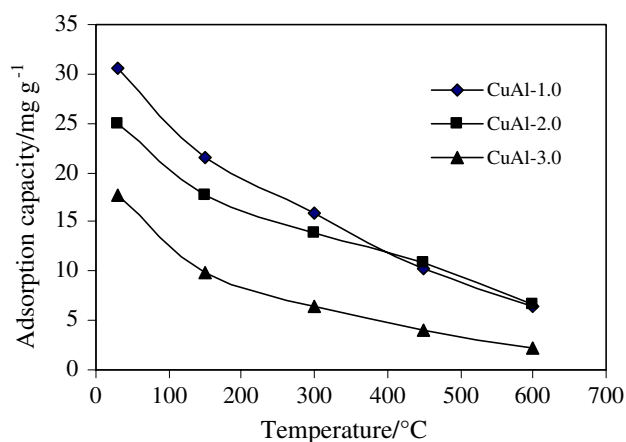


Fig. 2 Adsorption capacities of the samples at different temperatures

The adsorption capacities of the fresh adsorbent samples are compared in Fig. 2. It can be seen that the adsorption capacities are high at low temperatures and decrease as the temperature increases, in consistent with the exothermicity of the adsorption. CuAl-1.0 shows the highest adsorption capacity at low temperatures up to about 400 °C. At this temperature range, the adsorption capacities are in the order CuAl-1.0 > CuAl-2.0 > CuAl-3.0, with similar adsorption capacities for CuAl-1.0 and CuAl-2.0. Above 400 °C, the adsorption capacity of CuAl-2.0 slightly exceeds that of CuAl-1.0. Thus, the optimum Cu/Al molar ratio for maximum adsorption capacity probably lies between 1.0 and 2.0.

Mao et al. [26] have found that the maximum adsorption capacity occurs at an optimum Al<sup>3+</sup> substitution in the brucite-like layer of the HTlc, and this optimum depends on the type of interlayer anion. The same group of authors [27] has also reported that the optimum Al<sup>3+</sup> substitution for CO<sub>3</sub><sup>2-</sup> HTlc treated at low temperatures is 0.44, which corresponds to Cu/Al atomic ratio of 1.27 in the current investigation. As the M<sup>2+</sup>/M<sup>3+</sup> ratio increases, the interlayer

spacing initially increases, reaching the maximum, and then decreases, resulting in the reduction of basic sites for adsorption at higher M<sup>2+</sup>/M<sup>3+</sup> ratios [19, 27–29]. The decrease in adsorption sites, and the possible remnants of carbonates in the samples with high Cu/Al ratio even after heat treatment at 600 °C [24, 25], are the cause of reduction in CO<sub>2</sub> adsorption capacity at higher Cu/Al ratios. Thus, the adsorption capacity is intricately dependent on temperature, layer charge density, type of interlayer anion, interlayer spacing, stability of the HTlc skeletal structure, and the extent of prior decarbonation.

The adsorption capacities at 300 °C and 1 atm of CuAl-1.0 and CuAl-2.0 are comparable to those of Mg–Al–CO<sub>3</sub> HTlcs previously reported [18, 19], but about five times lower than those of Ca–Al–CO<sub>3</sub> HTlc recently reported by Hutson and Attwood [17]. At higher temperatures (>350 °C), the adsorption capacities of CuAl-2.0 HTlc are 30–50% lower than the reported capacities of potassium carbonate-promoted Mg–Al HTlcs [4, 5]. However, since the CO<sub>2</sub>-capacity of CuAl-1.0 and CuAl-2.0 at 300 °C is greater than 0.3 mmol/g, the minimum requirement for sorption-enhanced reaction process [6], they can be used as adsorbent-catalyst for low-temperature (<300 °C) steam-methanol reforming reaction.

Adsorption kinetics

The initial rates of adsorption on the fresh adsorbents at 600 °C can be determined from the slopes of the corresponding adsorption TG curves. Alternatively, the rates can be directly determined from the corresponding derivative thermal gravimetric (DTG) curves. The results are displayed in Fig. 3. It can be seen that the initial specific adsorption rate

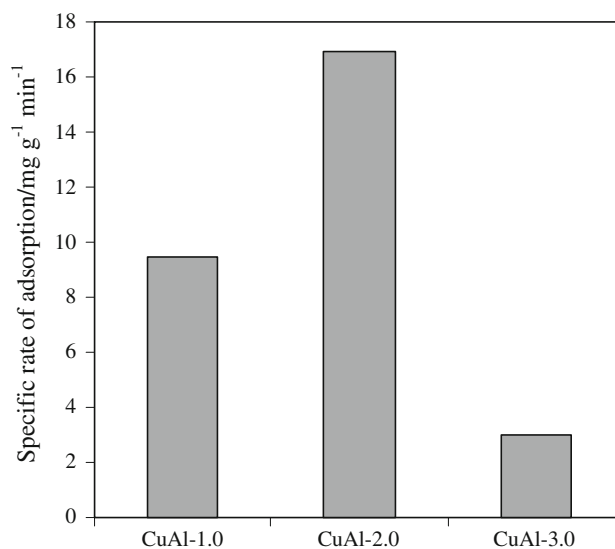
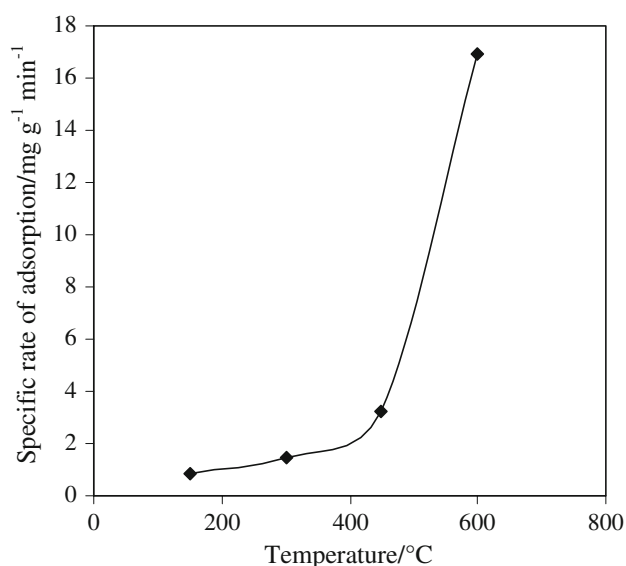


Fig. 3 Initial specific adsorption rates of samples at 600 °C



**Fig. 4** The initial rate of adsorption versus temperature for CuAl-2.0 adsorbent

of CuAl-2.0 is significantly higher than those of the other two adsorbents. Thus, the Cu/Al ratio that is thermodynamically the most favorable for CO<sub>2</sub> adsorption is also favored by kinetics. In this case, CuAl-2.0 adsorbent presents the highest rate as well as the highest capacity of adsorption, especially at high temperatures. Thus, the adsorption kinetics of this adsorbent was subsequently determined.

The specific rates of CO<sub>2</sub> adsorption on the fresh CuAl-2.0 adsorbent at different temperatures were obtained from the peak values of the corresponding DTG curves, and are plotted in Fig. 4. It can be seen that at low temperatures (<400 °C) the rate of adsorption only steadily increases with temperature. However, above 400 °C, the adsorption rate increases rapidly with temperature.

#### Apparent activation energy of adsorption

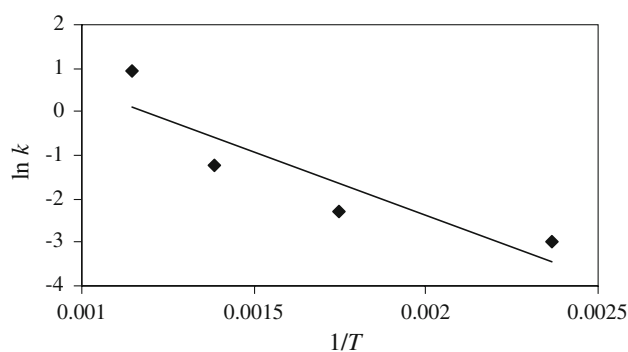
If the linear driving force model for the adsorption is considered,

$$\text{rate} = \frac{dw}{dt} = k(w^* - w) \quad (1)$$

where  $w$  is the CO<sub>2</sub> loading (mg/g),  $w^*$  is the steady-state CO<sub>2</sub> loading (adsorption capacity) (mg/g),  $k$  is the adsorption rate constant (min<sup>-1</sup>), and  $t$  is the time in min. Thus, the initial rate of adsorption corresponds to the maximum driving force,  $w^*$ . Consequently, the adsorption rate constant can be calculated by:

$$k = \frac{\text{initial rate of adsorption}}{\text{adsorption capacity}} \quad (2)$$

The Arrhenius equation can then be used to estimate the apparent activation energy.



**Fig. 5** Linear regression of  $\ln k$  versus  $1/T$  for adsorption on CuAl-2.0

$$\ln k = \ln k_0 - \frac{E}{RT} \quad (3)$$

where  $k_0$  is the pre-exponential factor (min<sup>-1</sup>),  $E$  is the apparent activation energy of adsorption (kJ/mol),  $R$  is the universal gas constant ( $8.314 \times 10^{-3}$  kJ/mol K), and  $T$  is the temperature in K.

The linear regression of  $\ln k$  versus  $1/T$  for the CO<sub>2</sub> adsorption on CuAl-2.0 adsorbent is shown in Fig. 5. The apparent activation energy of adsorption as calculated from the slope of the line is 24 kJ/mol for the whole range of temperature. A close inspection of Fig. 5 reveals that there can be two mechanisms of adsorption, one for temperatures below 400 °C and the other for temperatures above 400 °C. For the low temperature region, the activation energy is 10 kJ/mol, which represents physical adsorption. For the high temperature region, it is 75 kJ/mol, showing that the rapid chemisorption occurs in this region.

#### Conclusion

Among the adsorbents considered, the CuAl-1.0 HTlc showed the highest adsorption capacity at low temperatures up to about 400 °C. The optimum composition of the Cu–Al HTlc to be used as CO<sub>2</sub> adsorbent at high temperatures is Cu/Al molar ratio of 2.0, since it showed the highest capacity and rate of CO<sub>2</sub> adsorption at high temperatures. The Cu–Al HTlcs of Cu/Al molar ratios ranging from 1.0 to 2.0 are suitable to be used as adsorbent-integrated catalysts for low-temperature steam reforming of methanol. At low temperatures (<400 °C), the physical adsorption dominates, while at high temperatures (>400 °C), the chemisorption is the dominating mechanism.

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