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Breakthrough analysis for CO_2 removal by activated hydrotalcite and soda ash

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Abstract

Carbon dioxide sorption rate parameters and sorption capacities on two different regenerable sorbents, namely hydrotalcite and activated trona, were investigated in a fixed bed flow adsorber, in the temperature range of 400–527 °C and 80–152 °C, respectively. Hydrotalcite, which was activated at 550 °C, was shown to give total and breakthrough CO_2 sorption capacities as high as 1.16 and 0.70 mmol/g, respectively, at 452 °C, in the absence of water vapor. In the presence of excess water vapor, the total CO_2 sorption capacity was not affected much, however a decrease in the breakthrough capacity and on the sorption rate constant was observed, especially at lower temperatures. In the presence of water vapor, activated trona was shown to give comparable total and breakthrough CO_2 sorption capacities, at much lower temperatures ($T < 100$ °C). The deactivation model gave good predictions of the CO_2 breakthrough curves and it was successfully used for the evaluation of the adsorption and the deactivation rate constants.

Keywords: CO_2 removal; Hydrotalcite; Trona; Soda ash; Deactivation model

1. Introduction

Removal of carbon dioxide from the fuel gas produced in steam reforming of natural gas or other light hydrocarbons and in a shift converter is a critical step to enhance hydrogen production. Adsorptive reactors, in which the steam reforming reaction and the carbon dioxide separation are carried out together in the reformer, are proposed to enhance hydrogen production by the elimination of equilibrium limitations and to make these processes more cost efficient [1–5]. Success of such a sorption enhanced reaction process depends upon the development of effective regenerable sorbents for the high temperature removal of CO_2. Since physical adsorption processes are exothermic, the high temperature removal of CO_2 can be achieved by chemisorption or through a gas–solid chemical reaction. Balasubramanian et al. [4] proposed a single step hydrogen production process, in which a calcium based CO_2 acceptor was added to the commercial methane steam reforming catalyst.

Recently, hydrotalcite like compounds attracted the attention of researchers for high temperature removal of CO_2 [6–9]. Hydrotalcite is a basic clay, composed of positively charged brucite-like layers. A typical composition of this layered double hydroxide is $Mg_6Al_2(CO_3)(OH)_{16}\cdot 4H_2O$. As a result of the calcination of hydrotalcite, it is activated by the removal of H_2O and CO_2 from its structure.

Due to the environmental and the economical considerations, removal of carbon dioxide from the process and the combustion gasses at relatively milder temperatures also attracted the attention of researchers working on pressure swing adsorption and temperature swing adsorption processes. Also for these dry CO_2 recovery processes, development of high capacity regenerable sorbents are needed. In number of cases, gas streams contain some water vapor in addition to CO_2. Consequently, effect of water vapor on the sorption rate, as well as on the sorption capacity of CO_2, is also an important factor to be investigated. In the present study, we investigated the sorption rate and capacity of CO_2 on two different sorbents, namely hydrotalcite for high temperature removal (400–527 °C) and activated trona (soda ash) for medium temperature removal (80–152 °C).

2. Experimental work

Carbon dioxide sorption experiments were performed in a tubular flow adsorber, which was placed into a tubular furnace. Carbon dioxide is mixed with an inert gas (He in our case) and water vapor (produced in an evaporator), at predetermined

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Nomenclature

a	Activity of the solid reactant
k_0	Initial sorption rate constant ($cm^3\ min^{-1}\ g^{-1}$)
k_d	Deactivation rate constant (min^{-1})
Q	Volumetric flow rate ($cm^3\ min^{-1}$)
W	Catalyst mass (g)

Table 2
Physical properties of fresh and calcined hydrotalcite

Physical property	Hydrotalcite	Calcined hydrotalcite
Porosity		0.70
BET surface area (m^2/g)	8.1	172.9
Hg porosimeter surface area (m^2/g)	12.6	23.5
Bulk density (g/cm^3)	0.86	0.50
Average pore diameter (nm)	10	4

compositions. The total flow rate of the gas mixture was kept at 50 cm^3/min. The CO_2 mole fraction was kept at about 0.15, at atmospheric pressure. The exact values of CO_2 mole fractions are reported in Tables 3 and 4. Experiments were carried out in the presence as well as in the absence of water vapor. In the experiments carried out in the presence of water vapor, mole fraction of H_2O was adjusted to 0.20. Carbon dioxide composition was measured by a gas chromatograph connected on line to the adsorber outlet, by injecting successive pulses of gas samples from the reactor exit stream.

As the sorbent, hydrotalcite with a chemical structure of $Mg_6Al_2(CO_3)(OH)_{16}\cdot 4H_2O$ and trona (natural soda) with a structure of $Na_2CO_3\cdot NaHCO_3\cdot 2H_2O$ were used. Compositions of hydrotalcite and trona are given in Table 1. Trona was obtained from Beypazari region of Turkey. Two grams of sorbent was packed into a stainless steel tubular reactor and supported by quartz wool from both sides. In order to minimize pressure drop in the adsorber, hydrotalcite was first pelletized and the particles with an average diameter of 1.4 mm were used in the sorption experiments. Trona is used in powder form. The sorbent was first calcined in the adsorber under the flow of an inert gas (He in our case). In the case of hydrotalcite, sorbent was heated at a heating rate of 70 °C/min until 550 °C and the calcination was continued at this temperature for about 30 min, until the evolution of CO_2 from the hydrotalcite was finished. The removal of CO_2 from the hydrotalcite structure was observed at temperatures higher than about 380 °C. In the case of trona, calcination was carried out at 200 °C. Calcination temperatures of these two sorbents were determined from the TGA analysis of the fresh samples.

3. Results and discussions

3.1. Characterization of the sorbents

Some physical properties of the fresh and the calcined hydrotalcite are reported in Table 2. As seen in this table, BET surface area of the hydrotalcite was increased from 8.1 to 172.9 m^2/g as a result of calcination, while the increase in surface area measured by a mercury porosimeter was much less. Since mercury porosimeter can measure only the pores having diameters higher than about 100 nm, this result indicated the formation of mesopores by the calcination of the hydrotalcite, at 550 °C. In fact, the average pore diameter of the calcined hydrotalcite was found 4 nm, from the nitrogen adsorption isotherms. In the case of trona, increase of the surface area by calcination was much less. The surface area of the trona was found to increase from 2.6 to 8.9 m^2/g, after calcination at 200 °C. The porosity and the average pore diameter of the activated trona were found to be 0.75 and 6 nm, respectively.

Table 1
Chemical compositions of hydrotalcite and trona

Hydrotalcite		Trona	
Compound	%	Compound	%
MgO	40.04	$NaHCO_3$	30.1
Al_2O_3	16.88	Na_2CO_3	48.8
H_2O	35.79	H_2O	17.9
CO_2	7.29	Impurities	3.2

The thermogravimetric analysis (TGA) of the hydrotalcite showed three desorption peaks at 260.5, 337 and 456.9 °C (Fig. 1). Interlayer water and some H_2O formed by the decomposition of aluminum hydroxide are expected to be removed from the hydrotalcite structure between 70 and 260 °C. Further removal of H_2O, which was formed by the decomposition of magnesium hydroxide is expected to take place between 260 and 380 °C. As is also mentioned in the previous section, CO_2 removal from the hydrotalcite structure took place between 380 and 550 °C, giving a maximum in the TGA curve at around 457 °C.

Trona is a natural soda material. As a result of its calcination, soda ash is produced [10]. The TGA analysis of trona showed that the removal of H_2O and CO_2 during the calcination process (Reaction 1) was completed between 80 and 180 °C (Fig. 2):

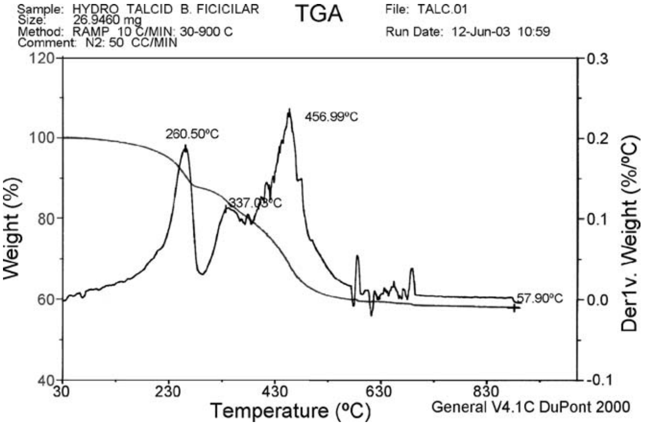

Fig. 1. Thermogravimetric analysis of hydrotalcite.

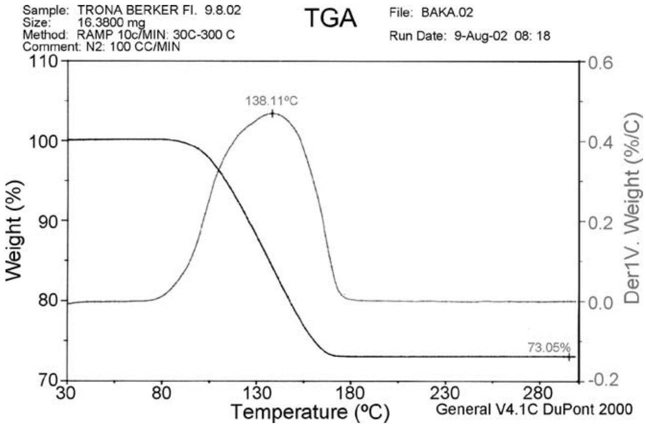

Fig. 2. Thermogravimetric analysis of trona.

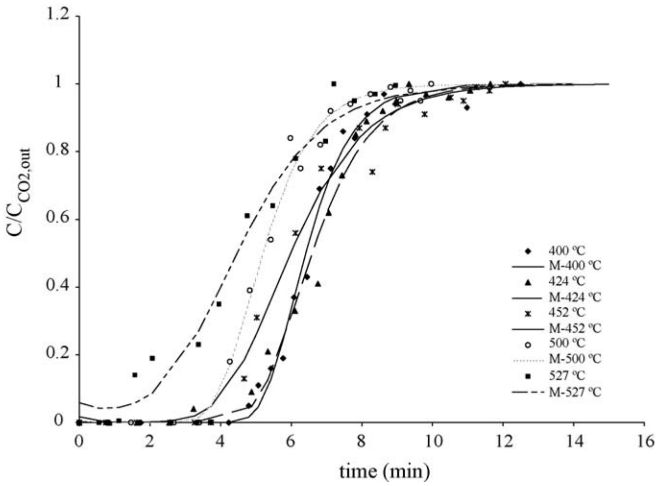

Fig. 3. Typical experimental and predicted (from the deactivation model) CO_2 breakthrough curves obtained with hydrotalcite in the absence of water vapor (the lines correspond to the calculated values from Eq. (3)).

$$2[Na_2CO_3\cdot NaHCO_3\cdot 2H_2O] \rightarrow 3Na_2CO_3 + CO_2 + 5H_2O \qquad \text{(Reaction 1)}$$

3.2. CO_2 sorption results

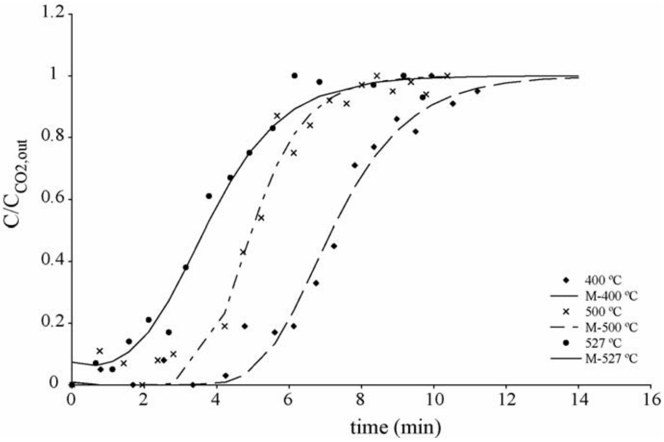

Fig. 4. Typical experimental and predicted (from the deactivation model) CO_2 breakthrough curves obtained with hydrotalcite in the presence of excess water vapor (the lines correspond to the calculated values from Eq. (3)).

Typical experimental CO_2 breakthrough curves obtained at the adsorber outlet with the calcined hydrotalcite are given in Figs. 3 and 4, in the absence and presence of water vapor, respectively. Our results showed that, in the absence of water vapor the breakthrough curves obtained between 400 and 452 °C were quite close to each other (Fig. 3). A shift of the breakthrough curves was observed with an increase in temperature (especially over 500 °C). This shift corresponds to a decrease in the CO_2 sorption capacity. Total sorption capacities of CO_2 (Table 3) obtained in the absence and presence of water vapor are found to be comparable, around 1.10 mmol/g below 452 °C. However, the breakthrough capacities, which correspond to the capacities until the effluent concentration reaches to 5% of the inlet value, are found to be lower in the presence of excess water vapor. In the literature [6], an increase of total sorption capacity of CO_2 was indicated in the presence of small amounts of water vapor. However, in the case of excess water vapor (as in our case), the total sorption capacity was not significantly affected. The decrease of the breakthrough capacity in the presence of excess water vapor is an indication of a decrease in the sorption rate of CO_2, probably due to the increased significance of diffusion resistance. In the presence of excess water vapor, shrinkage of pore mouths due to sorption of $H_2O + CO_2$ on the active hydrotalcite surfaces near the pore mouths may be more significant, causing partial pore mouth closure and an additional diffusion resistance for the transport of CO_2 to the active sites of the sorbent. All these results showed that the best temperature range was between 450 and 500 °C for the sorption of CO_2 on activated hydrotalcite both in the absence and presence of water vapor. The total

Table 3
CO_2 sorption capacity of calcined hydrotalcite in the presence and absence of water vapor

Temperature (°C)	CO_2 mole fraction	In the absence of steam		In the presence of steam	
		Total capacity (mmol/g)	Breakthrough capacity (mmol/g)	Total capacity (mmol/g)	Breakthrough capacity (mmol/g)
400	0.153	1.18	0.72	1.07	0.37
424	0.146	1.06	0.51	1.17	0.41
452	0.167	1.16	0.70	1.10	0.46
500	0.161	0.97	0.67	0.87	0.31
527	0.155	0.80	0.27	0.66	0.18

Amount of sorbent, 2 g; sorbent calcination temperature, 550 °C; column diameter, 1/4 in.; volumetric flow rate of the gas, 50 cm^3/min; atmospheric pressure.

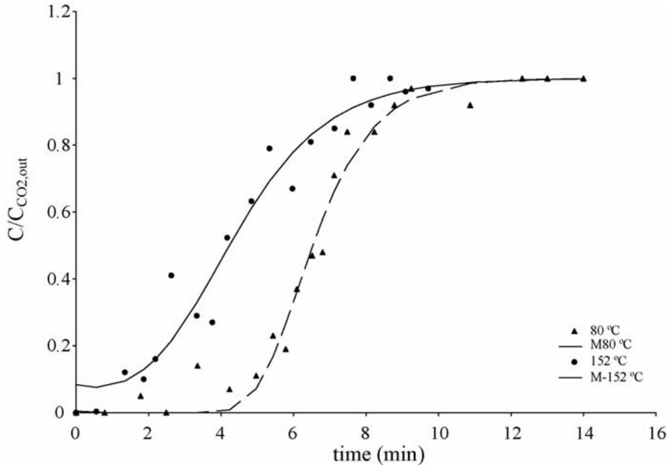

Fig. 5. Typical experimental and predicted (from the deactivation model) CO_2 breakthrough curves obtained with trona in the presence of excess water vapor (the lines correspond to the calculated values from Eq. (3)).

sorption capacities as high as 1.16 mmol/g and breakthrough capacities as high as 0.70 mmol/g are rather attractive for CO_2 recovery from process and fuel gases. In some previous studies, CO_2 sorption capacities of about 0.6 were reported [3,6] on hydrotalcite, in the presence of steam, at 400 °C.

Typical CO_2 breakthrough curves obtained at 80 and 152 °C, with the activated trona, are shown in Fig. 5. In the presence of water vapor, CO_2 fixation is expected to take place through the following reaction step:

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3 \qquad \text{(Reaction 2)}$$

According to this reaction, very high CO_2 sorption capacities are expected assuming complete conversion. However, the chemical equilibrium limitations do not allow such high sorption capacities. Experiments carried out with activated trona in the presence of excess water vapor, showed a decreasing trend in the total CO_2 sorption capacity with an increase of temperature from 80 to 152 °C (Table 4). For this sorbent, CO_2 sorption was favored at temperatures lower than 100 °C. At higher temperatures thermodynamics of this sorption process becomes less favorable. The total and the breakthrough capacities obtained at 80 °C (1.15 and 0.43 mmol/g, respectively) were of comparable magnitude to the corresponding values obtained with the hydrotalcite at 452 °C.

Table 4
Total and breakthrough sorption capacities of CO_2 on activated trona (soda ash) in the presence of excess water vapor

Temperature (°C)	CO_2 mole fraction	Total capacity (mmol/g)	Breakthrough capacity (mmol/g)
80	0.161	1.15	0.43
101	0.158	0.84	0.28
125	0.150	0.79	0.26
152	0.163	0.82	0.25

Amount of sorbent, 2 g; sorbent calcination temperature, 200 °C; column diameter, 1/4 in.; volumetric flow rate of the gas, 50 cm^3/min; mole fraction of water vapor, 0.2; atmospheric pressure.

3.3. Deactivation model predictions

The sorption of CO_2 on both activated trona and activated hydrotalcite are not simple physical adsorption processes. Rather, these sorption processes may be described as chemisorption or as gas–solid non-catalytic reactions. In these processes, changes in the pore structure and in the active surface area are expected with the extent of sorption. In addition to the pore diffusion resistance, formation of a product layer over the pore surfaces creates an additional diffusion resistance for the transport of CO_2 to the active sites of the sorbent. Formation of the product layer may also cause partial closure of mouths of some pores. All these factors are expected to cause a decrease in the activity of the sorbent with an increase in conversion. Number of models, such as grain models and pore models, are proposed in the literature to describe the conversion-time relations in such gas–solid reactions. These models contain large number of adjustable parameters related to the pore structure, to the product layer and pore diffusion resistances as well as the surface sorption rate parameters. Another model, which was successfully used in the literature for the prediction of the breakthrough curves in such gas–solid reaction–sorption processes, is the deactivation model [11,12]. In this model, decrease of the solid reactant concentration and effects of the textural changes of the solid reactant on the observed rate were expressed in terms of an activity term a, introduced into the rate expression. The rate of decrease of the activity of the solid reactant is also expected to be proportional to the activity itself and also to the concentration of the adsorbing gas. Considering the pseudo steady state assumption and neglecting the axial dispersion term, species conservation equation for the concentration of CO_2 in the packed bed adsorber, and the equation for the rate of change of activity of the solid reactant with respect to time may be written as:

$$-Q\frac{\mathrm{d}C_\mathrm{A}}{\mathrm{d}W} - k_0 C_\mathrm{A} a = 0 \qquad (1)$$

$$-\frac{\mathrm{d}a}{\mathrm{d}t} = k_\mathrm{d} C_\mathrm{A}^n a^m \qquad (2)$$

For the concentration independent deactivation, the value of n is equal to zero. However, the deactivation rate was expected to depend upon the concentration of the adsorbing gas. Considering a first order dependence of the deactivation rate on the concentration of the adsorbing gas ($n = 1$) and also on the activity itself ($m = 1$), the solution of this model gave the following approximate equation for the breakthrough curves [11,12]:

$$\frac{C_\mathrm{A}}{C_{\mathrm{A}_0}} = \exp\left\{\frac{\left[1 - \exp\left((k_0 W/Q)(1 - \exp(-k_\mathrm{d}t))\right)\right]}{[1 - \exp(-k_\mathrm{d}t)]}\exp(-k_\mathrm{d}t)\right\} \qquad (3)$$

This is a two parameter model, containing the initial sorption rate constant k_0 and the deactivation rate constant k_d. The experimental breakthrough data obtained for the sorption of

Table 5
The initial sorption rate constant k_0 and the deactivation rate constant k_d of CO_2 on the activated hydrotalcite in the absence and presence of excess water vapor

Temperature (°C)	k_0 (cm^3/min g)		k_d (min^{-1})	
	Dry	Wet	Dry	Wet
400	385.5	261.2	1.12	0.71
424	314.4	212.2	0.90	0.60
500	330.5	311.0	1.05	1.03
527	195.3	171.6	0.68	0.76

Table 6
The initial sorption rate constant k_0 and the deactivation rate constant k_d of CO_2 on the activated trona in the presence of excess water vapor

Temperature (°C)	k_0 (cm^3/min g)	k_d (min^{-1})
80	156.8	0.89
101	73.2	0.54
125	64.7	0.46

CO_2 on the activated hydrotalcite and on the activated trona showed good agreement with the predictions of this model. The initial sorption rate constant and the deactivation rate constant values obtained by the non-linear regression analysis of Eq. (3) are reported in Tables 5 and 6, for hydrotalcite and trona, respectively. The predictions of the breakthrough curves from Eq. (3), using these rate constants, are also shown in Figs. 3–5. For the activated hydrotalcite, both k_0 and k_d values did not change much until about 500 °C. In the temperature range between 400 and 500 °C, the average value of k_0 was 343 cm^3/min g (with a ±10% fluctuation) under dry conditions. Higher fluctuations were observed for the wet system, with a highest k_0 value of 311 cm^3/min g at 500 °C. Above this temperature, a significant decrease was observed in the rate constants for both in the absence and in the presence of excess water vapor (Table 5). Such fluctuations may limit the application of this model, especially at high temperatures. At 527 °C, the breakthrough curve was not as sharp as the breakthrough curves obtained at lower temperatures. Breakthrough curve started at a time close to zero. In fact, the breakthrough capacities obtained at this temperature were also very low (Table 3). At such high temperatures, the activity of the hydrotalcite for CO_2 removal was significantly decreased. In the case of trona (Table 6), a steady decrease was observed in the sorption and in the deactivation rate constants with an increase in temperature. This is simply due to the less favorable thermodynamics of (Reaction 2) at higher temperatures.

4. Concluding remarks

Hydrotalcite was found to be an attractive sorbent for the high temperature CO_2 removal, both in the presence and absence of water vapor. The total CO_2 sorption capacities as high as 1.16 mmol/g and the breakthrough capacities of about 0.70 mmol/g, obtained in the temperature range between 450 and 500 °C, are rather attractive and even higher than many of the CO_2 sorption capacities reported in the literature. The total CO_2 sorption capacities were found to be similar in the absence and presence of excess water vapor. However, the breakthrough capacities were found to be lower in the presence of excess water vapor. Although the presence of small amounts of water was reported to have a positive effect on the total CO_2 sorption capacity in the literature, sorption rate was found to decrease in the presence of excess water vapor. Activated trona was also found to be an effective sorbent for CO_2 removal in the presence of water vapor at temperatures lower than 100 °C. The results of this work also showed that the deactivation model was a good representation of the CO_2 breakthrough curves obtained in a fixed bed adsorber.

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