

STUDIES ON ADSORPTION/DESORPTION OF CARBON DIOXIDE WITH RESPECT TO THERMAL REGENERATION OF HYDROTALCITES

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ABSTRACT

This research is focused on evaluation of conditions for thermal regeneration of hydrotalcite. In this study synthesized hydrotalcite prepared under reported optimum conditions namely calcination temperature (600°C) and Mg/Al mol ratio (3.0), and commercial hydrotalcite are compared for adsorption and desorption capacities. Initially synthetic hydrotalcite is prepared using the common co-precipitation method by mixing magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and aluminium nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) for Mg/Al mol ratios varied from 2 to 4.5 and calcinations temperatures varied from 400°C to 800°C. The synthesized and commercial samples of hydrotalcite were characterized for BET surface area. It was re-confirmed that the optimum preparation conditions for synthetic hydrotalcite were 600°C of calcination temperature and 3.0 of Mg/Al mol ratio as reported by previous studies. The optimum synthesized sample and also commercial hydrotalcite samples were then saturated with carbon dioxide. The saturated samples were tested for BET surface area and pore sizes. The saturated samples were thermally regenerated (heat treated) at 200°C, 450°C and 700°C and surface morphology and pore distribution were re-evaluated. TGA studies on these samples were carried out. It was observed that two regions of desorption exist, namely the first region at 185°C and the second region at 385°C with percentage CO_2 reduction of 13% and 25% respectively based on the original sample. This could be attributed to different modes of association of CO_2 in hydrotalcite. The structural changes attributing to the behaviour of carbon dioxide on hydrotalcite under adsorption and re-generation are discussed. A temperature of 700°C is found to be best suited for regeneration.

Keywords : Hydrotalcite; Adsorption; Regeneration; Carbon dioxide

INTRODUCTION

Natural gas is a gaseous fossil fuel consisting primarily of methane (70% - 90%) but including significant quantities of ethane (5% - 15%), butane (<5%), propane (<5%), carbon dioxide (0.7 - 50%) and small amounts of nitrogen, helium and hydrogen sulfide [1], [2]. Because of the existence of carbon dioxide in the natural gas, its calorific value is lowered leading to requirements of handling higher volumes of natural gas in applications. As a result it has been felt that removal of carbon dioxide from the natural gas is important.

Hydrotalcite. Hydrotalcite possesses capabilities to separate carbon dioxide by means of adsorption because of high abrasion resistance, high thermal stability and small micropore diameter which results in higher exposed surface area and hence high capacity of adsorption and stable interdispersion of the active species with high reproducibility [3], [4]. The high affinity of

hydrotalcite materials to carbonate species has mostly led to the use of carbonate containing compounds as precursors of catalysts [3]. Hydrotalcite is a natural layered mineral or anionic clay, constitute a class of lamellar ionic compound where as Layered Double Hydroxides, LDH or Hydrotalcite like compounds is synthetically prepared. It contains a positively charged (cations) hydroxide layer or brucite sheet and charge-balancing anions which is carbonate in the interlamellar space besides water molecules (Figure 1). Hydrotalcite like compounds are represented by the general formula $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x-}[A_{x/n}^{n-}]mH_2O$ where M^{2+} and M^{3+} are bi and tri-valent metal cations, respectively and A is an interlamellar anion with charge n- [5].

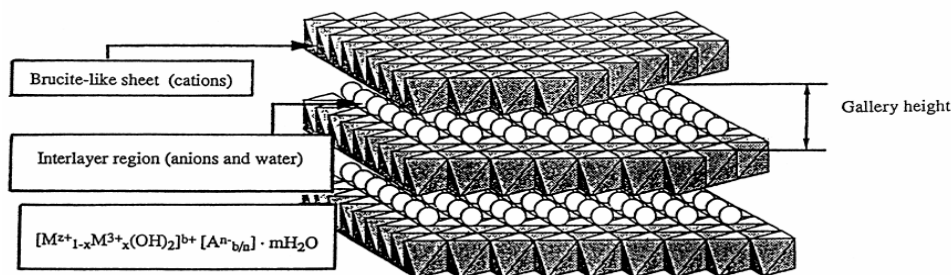


Figure 1: Hydrotalcite type structure [6]

These materials have been used as catalyst or adsorbents for several applications and their use in the carbon dioxide adsorption at temperature range between 400°C to 480°C was reported recently [7], [8]. This application is very important for the purification of natural gas, the possibility of CO₂ emissions controlled in the combustion of fossil fuels and for a new steam reforming process [9].

Co-precipitation method is the most commonly used method to prepare hydrotalcite like compounds. It is applied because other methods like decomposition-recrystallization, urea method and microwave irradiation are time consuming and require high amounts of water [10].

MATERIALS AND METHODS

Preparation of Hydrotalcite. The method used in the preparation of hydrotalcite samples were in conformity with previous studies [9]. Here, magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O), Aluminium nitrate nonahydrate (Al(NO₃)₃·9H₂O) and 32ml deionized water were mixed together to form a solution. Mg/Al ratio used is 2, 3, 4 and 4.5. Then, the mixture is added with 95ml potassium carbonate, K₂CO₃ (1M) dropwise under vigorous stirring over hot plate magnetic stirrer at 60°C for 15 minutes to. An amount of sodium hydroxide, NaOH is added to the solution and the pH is maintained at 10. After that, the precipitation solution was maintained in stirring mode at 60°C for 3 hours. The precipitate was filtered and washed several times with deionized water to remove nitrate, NO₃ and excess sodium ion, Na⁺. The solution was washed until the filtrate achieved pH 7 (neutral) [11]. The precipitate is dried in oven for 1 day at 100°C. Finally, the dried precipitate is calcined in furnace at 400°C, 600°C and 800°C for 15 hours [9].

Experimental setup. Figure 2 shows the schematic diagram of the experimental setup. A continuous flow reactor contained samples connected to a cylinder gas (purified carbon dioxide), pressure gauge and flowmeter are needed. A small amount of sample in powder form is placed inside the reactor to saturate the hydrotalcite samples with CO₂. The reactor was sealed tightly in

order to prevent gas leakages. The gas is fixed at 5 ml/min at ambient temperature. The process is left to run for more than 24 hours when samples could be assumed to be completely saturated with carbon dioxide gas. The saturated samples later tested for BET surface area and pore sizes. Then, the saturated samples were thermally regenerated by heating in the carbolite furnace at 200°C, 450°C and 700°C for 4 hours.

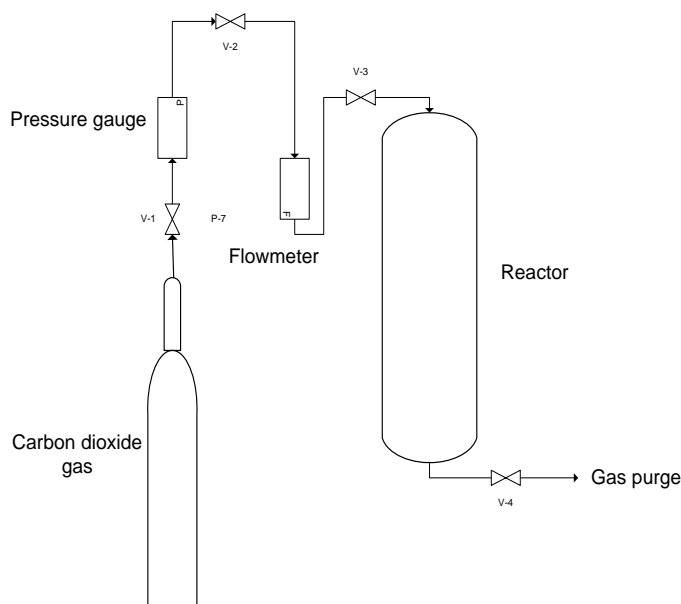


Figure 2: Schematic diagram of experimental setup

Characterization of Sample. The saturated sample with carbon dioxide gas and thermally regenerated sample were characterized to determine the desorption effects towards hydrotalcite. X-ray Diffraction, XRD (Diffraktometer D5000, Siemens) was tested to determine the significant chemical composition inside the samples. Thermogravimetric Analyzer, TGA (Perkin Elmer) was used to measure the weight loss at increasing temperature and time. Quantachrome Autosorb analyzer was used to measure the surface area and pore size inside the sample. Finally, Scanning Electron Microscopy, SEM was tested to monitor the structures of synthesized and commercial Hydrotalcite.

RESULTS AND DISCUSSION

Thermogravimetric analyses at 20°C/min of synthesized hydrotalcite, commercial hydrotalcite and regenerated samples where regeneration was conducted at 200°C, 450°C and 700°C. For the synthesized sample, the sample prepared under optimum reported condition (i.e. sample preparation at calcined temperature of 600°C) was taken. A typical TGA curves for commercial TGA are shown in Figures 3 to 6. The TGA results for the synthetic hydrotalcites were of similar behaviour. Analysis of TGA curves showed that significant reductions of CO₂ occurred at temperatures indicated in table below.

Table 1: Analysis of TGA curves for fresh and regenerated samples of commercial and synthesized hydrotalcite.

Sample	1 st Reduction		2 nd Reduction	
	Temperature (°C)	Percentage Reduction (%)	Temperature (°C)	Percentage Reduction (%)
Fresh Commercial Hydrotalcite	160	15	560	27.5
Regenerated Commercial Hydrotalcite at 200°C	160	15	580	27.5
Regenerated Commercial Hydrotalcite at 450°C	180	11.5	620	24.5
Regenerated Commercial Hydrotalcite at 700°C	200	14	600	23
Average	180.0	13.5	593.3	25.0
Fresh Synthesized Hydrotalcite	360	22.5	450	27.5
Regenerated Synthesized Hydrotalcite at 200°C	300	24	570	23.5
Regenerated Synthesized Hydrotalcite at 450°C	360	10	600	20
Regenerated Synthesized Hydrotalcite at 700°C	230	12.5	750	26.5
Average	316.7	15.0	600.0	24.7

The highest desorption temperature has been reported to be at 457°C [7] which is in conformity with the present findings. The results are also compatible with other previous studies [12], [13], [14]. The findings for synthesized hydrotalcite are slightly different from commercial hydrotalcite as seen from Table 1. In order to investigate the above behaviour around 200°C, 450°C and 700°C, a series of investigations based on BET surface area, SEM and XRD were carried out.

Table 2 and Table 3 show the BET surface areas, micropore areas and the average pore diameters of the fresh hydrotalcite, CO₂ adsorbed hydrotalcite and heat treated hydrotalcite at various regeneration temperatures of synthesized and commercial hydrotalcite as obtained from the Quantachrome Autosorb. Commercial hydrotalcite is seen to have significant micropore areas compared with the synthesized hydrotalcite. Furthermore it can be seen that the available BET area decreased to about 97% and 89% after CO₂ adsorption for synthesized and commercial hydrotalcites respectively showing significant adsorption of CO₂ in adsorption process. Figures 3 to 6 show the TGA studies made for commercial hydrotalcite samples regenerated at 200°C, 450°C and 700°C respectively. Respective reductions of BET and micropore areas seem to be nearly 99.9% for 200°C, nearly 100% for 400°C and it is negligible for 700°C respectively (Table 2). It can be seen that the micropore areas are quite insignificant after regeneration showing either the micropores are destructed beyond 200°C or the CO₂ is still intact with the hydrotalcites beyond 200°C. In order to ascertain the reason for this phenomenon, SEM studies are carried out for the samples. Figures 7, Figure 8, Figure 9(a), Figure 9(b), Figure

9(c), Figure 9(d), Figure 9(e) and Figure 9(f) compare the SEM images obtained for fresh, CO₂ saturated and regenerated at 450°C and 700°C of synthesized and commercial hydrotalcite respectively. The figure shows similarities between structures of fresh and CO₂ adsorbed samples. However after heat treatments the structures differed drastically from fine to agglomerate type for both types of hydrotalcites.

For regenerated samples of both types of hydrotalcite subsequent to adsorption with CO₂, the BET surface area showed a minimum peak around 450°C whereas the micropore area still remained negligible. This effect was investigated using XRD analysis of the respective samples. The XRD patterns showed a reduction of hydrotalcite content to periclase content at 450°C and regaining of the hydrotalcite content at 700°C for both synthetic and commercial hydrotalcites. This shift could have led to an increase in adsorption BET surface areas at 700°C. Also both synthetic and commercial hydrotalcite showed dominance of periclase content at 450°C and a shift of the dominance from periclase content to magnesia content at 700°C. The structural changes observed between SEM images of samples regenerated at 450°C and 700°C could be attributed to this phenomenon.

Table 2: Autosorb properties for fresh synthesized hydrotalcite, CO₂ adsorbed synthesized hydrotalcite and heat treated synthesized hydrotalcite at various temperatures.

Autosorb	Fresh	After CO ₂ adsorbed	After heat treatment (°C)		
			200	450	700
BET surface area (m ² /g)	110.98	2.90	19.24	1.08	6.97
Micropore area (m ² /g)	1.69	-	0.0018	-	negligible
Average pore diameter (nm)	12.14	25.58	23.97	1.92	1.8

Table 3: Autosorb properties for fresh commercial hydrotalcite, CO₂ adsorbed commercial hydrotalcite and heat treated commercial hydrotalcite at various temperatures.

Autosorb	Fresh	After CO ₂ adsorbed	After heat treatment (°C)		
			200	450	700
BET surface area (m ² /g)	552.07	60.63	53.92	33.57	60.45
Micropore area (m ² /g)	292.91	3.50	negligible	negligible	negligible
Average pore diameter (nm)	2.35	19.22	1.8	1.94	1.92

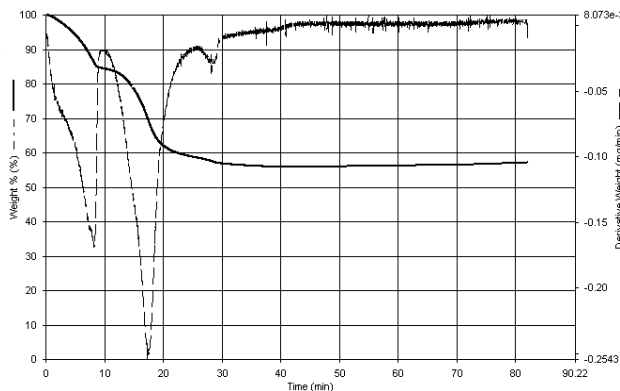


Figure 3: Thermogravimetric analysis (20°C/min) of fresh commercial hydrotalcite

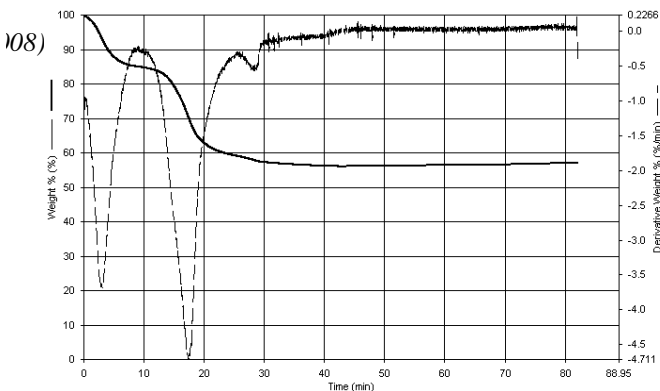


Figure 4: Thermogravimetric analysis (20°C/min) of heat treated commercial hydrotalcite at 200°C.

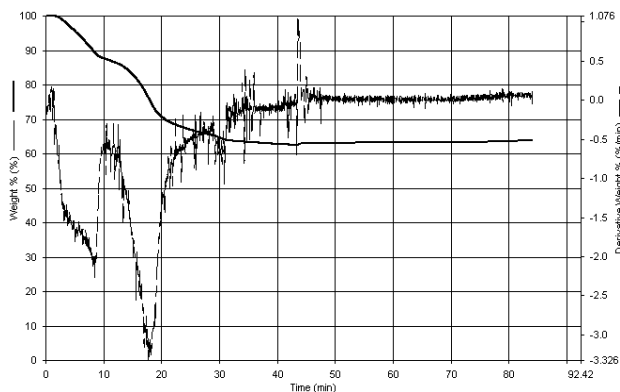


Figure 5: Thermogravimetric analysis (20°C/min) of heat treated commercial hydrotalcite at 450°C.

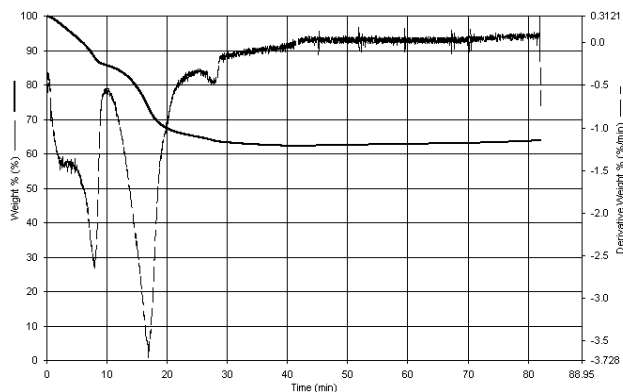


Figure 6: Thermogravimetric analysis (20°C/min) of heat treated commercial hydrotalcite at 700°C.

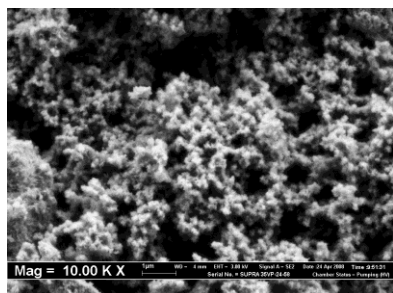


Figure 7: SEM image of fresh synthesized hydrotalcite calcined at 600°C

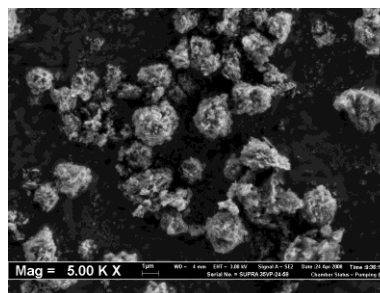
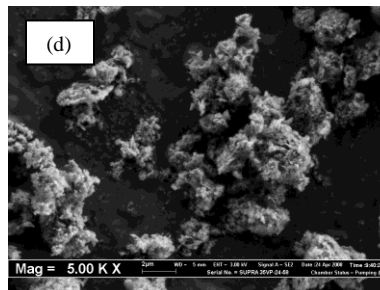
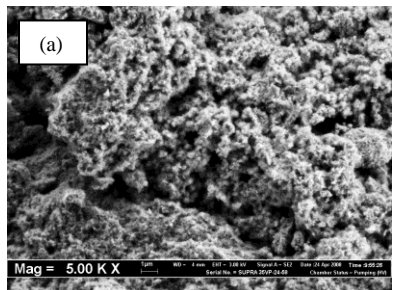


Figure 8: SEM images of fresh commercial hydrotalcite



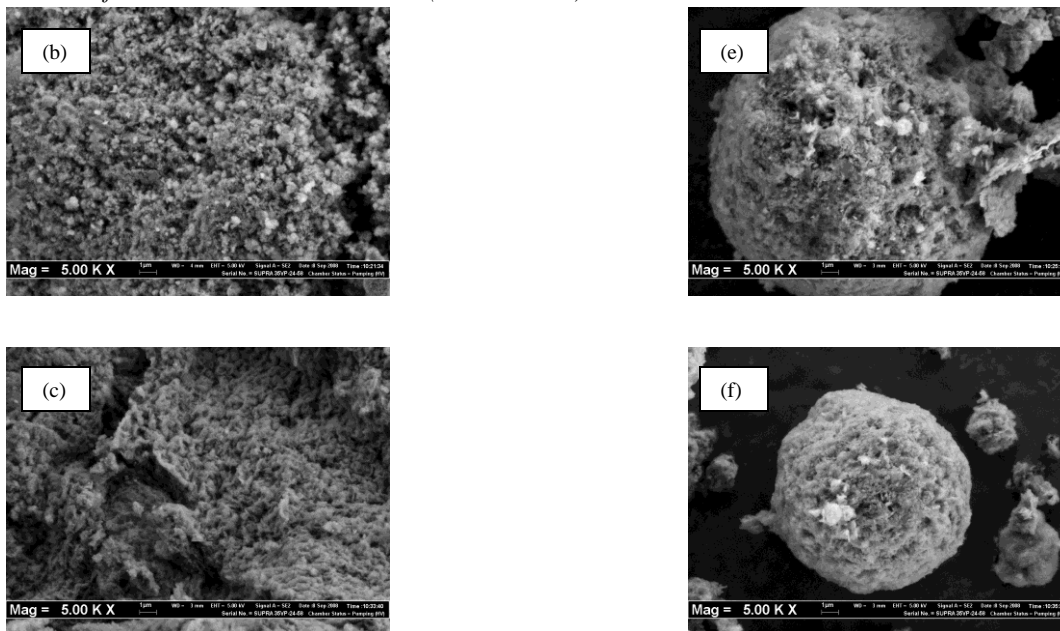


Figure 9: SEM images of (a) CO₂ adsorbed synthesized hydrotalcite, (b) heat treated synthesized hydrotalcite at 450°C, (c) heat treated synthesized hydrotalcite at 700°C, (d) CO₂ adsorbed commercial hydrotalcite, (e) heat treated commercial hydrotalcite at 450°C and (f) heat treated commercial hydrotalcite at 700°C.

CONCLUSIONS

Thermal gravimetric analysis was studied to investigate the thermal desorption properties of CO₂ in synthesized hydrotalcite and commercial hydrotalcite carried out at regeneration temperatures of 200°C, 450°C and 700°C. It was found that there are two regions of CO₂ adsorption/desorption in the hydrotalcite structures. From the above analysis, it could be concluded that:

1. Desorption of CO₂ from adsorbed samples of hydrotalcite reached an optimum at approximately 600°C.
2. The percentage reduction is found to be around 25% of the original weight.
3. At around 180°C the commercial hydrotalcite showed an initial desorption of about 13.5% and at around 316.7°C an initial desorption of approximately 15 % for the synthetic hydrotalcite.
4. At 450°C, both hydrotalcites showed a minimum BET surface area which could be attributed to the formation of periclase.
5. However, increase of temperature further showed a re-formation of hydrotalcite which was confirmed by XRD analysis for samples regenerated at 700°C.
6. After 600°C, desorption rate did not show any significant change.

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