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CARBON DIOXIDE SORPTION STUDIES ON MAGNESIUM OXIDE

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ABSTRACT

The sorption of carbon dioxide on magnesium oxide obtained by decomposing hydromagnesite is evaluated as a possible means for collecting atmospheric carbon dioxide. Both carbon dioxide adsorption and desorption were investigated in the presence of air and water vapor. In a 24 h period, 2–3 g of carbon dioxide were adsorbed per 100 g of magnesium oxide. Desorption data shows that the carbon dioxide was largely physically adsorbed on the surface of the magnesium oxide and only a small fraction, if any, formed a carbonate. In view of this result, other high specific surface area sorbents may be more suitable for carbon dioxide collection from the atmosphere at room temperature.

INTRODUCTION

The concentration of CO_2 in the atmosphere has increased by about 15% in the last hundred years and continues to rise [1]. If this rate of addition continues, it may be necessary to remove some of the CO_2 because of its potential impact on the climate [2,3]. A possible method to remove the CO_2 is by sorption on sorbents which have a high affinity for CO_2 relative to the other constituents in air. The sorbent can be regenerated by desorbing the CO_2 and this concentrated CO_2 can be collected for various industrial uses. The sorbent should have a low desorption temperature to minimize energy costs. Magnesium compounds have these advantages.

A number of papers have discussed the decomposition of magnesium compounds [4–9]. Sawada and co-workers [5–7] and Holand and Heide [9] have reported the important effect of CO_2 concentration in the gas phase and the heating rate on the thermal decomposition of these compounds. The adsorption of CO_2 on magnesium compounds, however, has not been as completely evaluated. Evans and Whateley [10] report on the effect of moisture on the formation of bidentate carbonate ions and on the adsorption of CO_2 on MgO at room temperature and at 300–500°C. In this paper, we report the initial results of a study of room temperature CO_2 adsorption on thermally decomposed hydromagnesite and the effect of excess H_2O vapor during the adsorption. This study attempts to quantify the effect of CO_2

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adsorption–desorption cycling on sorbent surface area, the rates of adsorption at room temperature, temperatures required for desorption and the species formed during adsorption.

EXPERIMENTAL

Material

The magnesium compounds investigated were magnesium hydroxide supplied by Martin Marietta Chemicals and hydromagnesite (4 $MgCO_3 \cdot Mg(OH)_2 \cdot n\ H_2O$) supplied by Baker Chemical Company. Both the magnesium hydroxide and the hydromagnesite were pretreated by heating in a flowing nitrogen atmosphere. The adsorption gases used were CO_2 at 330 and 660 ppm in air, supplied by AGA-Burdox as certified standard gas mixtures, 5% CO_2 in air and 100% CO_2.

Procedure

The carbon dioxide adsorption–desorption studies were carried out on a Cahn 1000 electrobalance using both powder and pressed-pellet samples which were pretreated by heating in an electric tube furnace until the weight was constant. Different concentrations of carbon dioxide gas were passsed through the balance apparatus at room temperature while the rate of weight gain was monitored. The samples were then heated in a flowing nitrogen atmosphere to the desired final desorption temperatures, while the rate of weight loss was recorded and the amount of carbon dioxide desorbed was

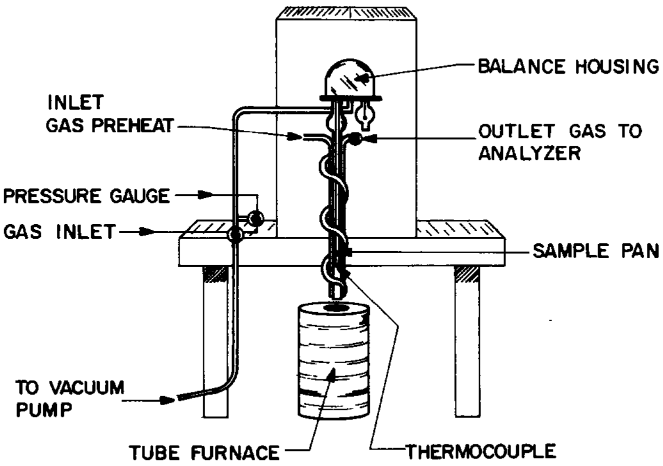

Fig. 1. Schematic diagram of balance apparatus and analysis system.

monitored using a Beckman 865 non-dispersive infrared analyzer. A schematic of the system is shown in Fig. 1. The surface area was then measured after evacuating the system using the single point analytical modification of the BET method [11] described by Katz [12].

Additional adsorption–desorption experiments were done with the adsorption gas first flowing through a water bubbler to produce a water-saturated stream before admission to the sample tube in the electrobalance.

RESULTS

The hydromagnesite and magnesium hydroxide were pretreated to maximize the initial surface area, and hence to increase the sorption rates. Table 1 lists the temperature and surface area ranges for these compounds. The highest surface area was obtained by heating to 500°C for powdered and pressed pellet hydromagnesite, and 300°C for magnesium hydroxide. However, the hydromagnesite had the higher surface area so it was used in the adsorption–desorption experiments after pretreatment at 500°C.

After pretreatment, the hydromagnesite samples, both powder and pressed pellets, were exposed to several CO_2 adsorption–desorption cycles. The change in the amount of gas adsorbed on the powder was negligible; however, the amount adsorbed on the pellet decreased after each cycle. For example, adsorption on a 229 mg pellet from 100% CO_2 for $5\frac{1}{4}$ h followed by desorption at 500°C for 1 h resulted in a weight gain of 6.28% in cycle 1, 6.10% in cycle 2, and 5.63% in cycle 3. The carbon dioxide adsorbed was entirely desorbed between cycles.

Figure 2 shows a plot of the change in surface area as a function of the number of adsorption–desorption cycles. The three samples were all pretreated by heating to 500°C. The powder sample weighed 4.2 mg, the pellet desorbed at 400–450°C weighed 140 mg and the pellet desorbed at 500°C weighed 214 mg. The adsorption gases were 330 ppm CO_2 for the powder

TABLE 1

Surface areas of sample compounds

Sample	Pretreatment temperature range (°C)	Surface area range (m^2 g^{-1})
Magnesium hydroxide	300–550	117.2– 14.8
Hydromagnesite (powder) [a]	500–575	183.2– 39.4
Hydromagnesite (pellet)	500–575	266.1–194.6

[a] Surface area as received, 35 m^2 g^{-1}.

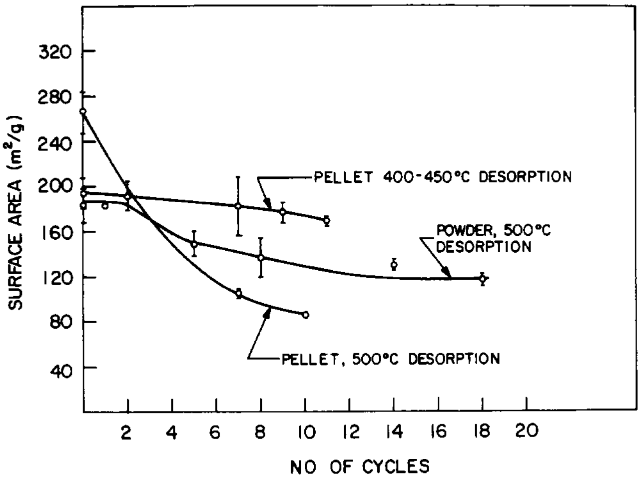

Fig. 2. Effect of adsorption–desorption cycles on the sorbent surface area; surface area vs. number of cycles.

and 660 ppm and 100% CO_2 for the pellets, respectively. The surface area decreases for both the powder and the pellet samples when the final desorption temperature is 500°C. The surface area of the powder sample decreases approximately 4% per cycle initially and tapers to 1% per cycle

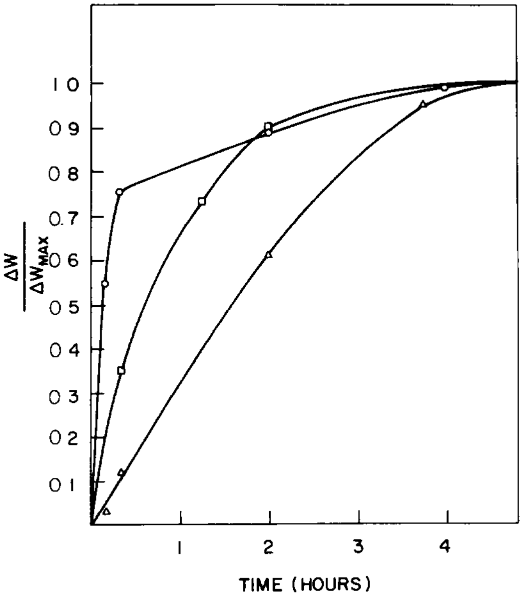

Fig. 3. Weight gain as a fraction of the final weight gain, $\Delta W/\Delta W_{max}$ vs. time, for the three concentrations of adsorption gas shown on pretreated hydromagnesite pellets. ○, 100% CO_2; □, 5% CO_2; △, 330 ppm CO_2.

TABLE 2

Total weight loss vs. carbon dioxide desorbed for sample run

Temperature range (°C)	Weight loss (% of total weight)	Carbon dioxide (% of total weight)
RT–50	0.29	0.09
50–100	0.24	0.23
100–200	1.02	1.00
200–300	0.57	0.28
300–400	0.57	0.11
Total	2.69	1.71

Weight of pellet before adsorption 137.60 mg; adsorption gas, 660 ppm CO_2 in air; amount adsorbed, 3.51 mg; adsorption time, 22.75 h.

after 10 cycles. The surface area of the pellets decreases approximately 10% per cycle at 500°C and only 1% per cycle at 400–450°C.

As seen in Fig. 3, the weight gain curves show an initial rapid adsorption rate that slows down as the weight gain approaches a saturation point. At 330 ppm and 5% CO_2, the maximum weight gain is about 3% and at 100% CO_2 it is 6% by weight of the pellet for most experiments, an amount that is much lower than anticipated if the CO_2 were stoichiometrically reacting with MgO to produce the carbonate.

TABLE 3

Total weight loss vs. carbon dioxide desorbed for sample run with excess water present in adsorption gas

Temperature range (°C)	Weight loss (% of total weight)	Carbon dioxide desorbed (% of total weight)
RT–50	19.10	0.33
50–100	2.15	
100–200	2.09	0.01
200–300	24.89	1.69
300–400	2.61	0.01
Total	50.84	2.04

Weight of pellet before adsorption, 139.88 mg; adsorption gas, 533 ppm CO_2 in N_2 passed through H_2O bubbler; amount of gas adsorbed, 68.64 mg; adsorption time, 24 h

The desorption studies indicate that air and water are desorbed below 50°C and then essentially all of the carbon dioxide is desorbed between 50 and 300°C. Table 2 lists the weight loss and amount of carbon dioxide desorbed at various temperatures for a typical run and Table 3 lists the same for a run when the adsorption gas was passed through a water bubbler at 20°C before entering the sample tube.

DISCUSSION

The maximum weight gains observed in our experiments could be explained by the assumption that CO_2 is adsorbed as a monolayer on the MgO surface. In this case, the rate of CO_2 adsorption would be proportional to the uncovered surface area. If surface area coverage is proportional to the CO_2 loading of the sorbent, then

$$\frac{dW}{dt} = k'(W_{max} - W)$$

where k' is the CO_2 adsorption rate constant, h^{-1}, W is the weight of CO_2 per unit weight of MgO, and W_{max} is the weight of CO_2 per unit weight of MgO in equilibrium with the CO_2 partial pressure.

Integrating and rearranging this expression yields

$$\ln\left(1 - \frac{W}{W_{max}}\right) = -k't$$

Thus, if surface area availability controls the adsorption rate, a plot of

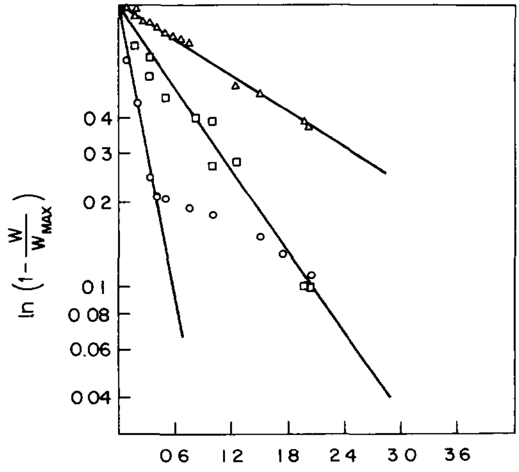

Fig. 4. Effect of surface availability on carbon dioxide adsorption rate, $\ln(1 - W/W_{max})$ vs. time for the experiments presented in Fig. 3. ○, 100% CO_2; □, 5% CO_2; △, 330 ppm CO_2.

TABLE 4

CO_2 Adsorption rate constants on calcined hydromagnesite

CO_2 Pressure (mm Hg)	Adsorption rate constant, k (h^{-1})
0.250	0.206
38	0.483
760	1.72

$\ln(1 - W/W_{max})$ against time should be linear. Figure 4 shows such a plot. The data fall in straight lines for surface coverage of up to 60% or more of saturation. Values of the adsorption rate constant, k', obtained from Fig. 4 are given in Table 4.

A plot of weight loss vs. temperature during the decomposition of hydromagnesite shows two stages of decomposition, one commencing at 120°C and the other at 350°C. This is consistent with reports in the literature that hydromagnesite decomposes to magnesia after heating to 500°C, via dehydration below 300°C and decarbonation above 350°C [6]. However, in the adsorption–desorption experiments, all of the carbon dioxide was desorbed at temperatures well below 350°C, indicating that little, if any, magnesite (magnesium carbonate) was formed. The fast initial adsorption rate and the low desorption temperature support the assumption that physical adsorption predominantly occurs with little or no chemisorption. Gregg and Ramsay [13] have found that at room temperature two types of CO_2 chemisorption occur: in the first, a bidentate carbonate ion forms on the surface; then at a slower rate, a second type of carbonate ion similar to bulk magnesium carbonate forms.

It has been reported [14] that magnesium oxide adsorbs water and carbon dioxide to form the hydroxide and carbonate

$$MgO + H_2O \rightarrow Mg(OH)_2$$

$$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O$$

To determine the effect of moisture on carbonate formation in this system, adsorption–desorption experiments were carried out with water-saturated gases. In these experiments, weight increases were much greater than when dry gas was used. Our experiments show, however, that these large weight gains were largely due to water sorbed in two forms: the first as physisorbed water which desorbed at temperatures below 100°C; the second as a hydroxide which desorbed between 200–300°C. The amount of carbon dioxide adsorbed was comparable to that adsorbed without water present. A true carbonate did not appear to form as all of the CO_2 desorbed under 300°C. However, the CO_2 desorbed at a higher temperature in comparison to the experiments without water present.

The CO_2 adsorption on MgO appears to be a surface-limited phenomenon, as the quantity of CO_2 adsorbed per unit weight of MgO is very small. Our experiments indicate that in a 24 h period only 2–3 g of CO_2 are adsorbed per 100 g of MgO with a BET surface area of about 220 $m^2\ g^{-1}$. This amount of CO_2 is consistent with monolayer surface coverage of the sorbent species and is far from the theoretical 109 g of CO_2 per 100 g of MgO that would be absorbed if $MgCO_3$ were formed.

CONCLUSION

Room temperature adsorption of atmospheric CO_2 on magnesium oxide derived from calcined hydromagnesite appears to be largely a physical phenomenon. Only 2–3% by weight CO_2 is adsorbed by MgO with a surface area of about 220 $m^2\ g^{-1}$. This CO_2 desorbs at temperatures below 300°C. Little or no $MgCO_3$ forms in adsorption experiments of less than 24 h duration, which indicates that carbonate formation is a very slow process. The presence of moisture in the adsorption gases did not appear to change the CO_2 capacity of the MgO sorbent or to promote carbonate formation. In view of these results, it appears desirable to investigate the atmospheric CO_2 adsorption on other sorbents with high surface areas such as activated carbon, zeolites, and silica gel.

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