CO_2 SELECTIVE CERAMIC MEMBRANE FOR WATER-GAS SHIFT REACTION WITH CONCOMITANT FOR THE RECOVERY OF CO_2

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1. Hydrotalcite (Bulk Material) Synthesis and Characterization

Rationale/Justification

The first step of this project was to identify the conditions for the formation of hydrotalcite material. A commonly discussed Al/Mg hydrotalcite as chosen for this project study. In addition, the crystal growth kinetics, such as size and rate vs time, are essential background information for us to develop a hydrotalcite membrane synthesis technique. The conditions we chose for the formation of hydrotalcite were well documented in the literature [2]. However, no literature data known to us deals with the crystal size and growth rate. Our objective here is to establish the crystal growth kinetics from a simple empirical study, while leaving the comprehensive study for this project. Crystal formation and its characterization are presented in this section. The crystal growth rate and size are discussed in the next section.

Experimental

1. Hydrotalcite crystals were formed by adding the equal volumes of $AlCl_3$ (0.073 mole/l) and $MgCl_2$ (0.28 mole/l) to a Na_2CO_3 solution (0.25 mole/l) at room temperature and a pH of ca. 11.5 under a well mixed condition. To increase the crystal size, we also allowed the mixture to age under a well-mixed condition for up to 72 hours. The crystals thus formed were isolated via filtration and then rinsed thoroughly with water to remove residual sodium, carbonate, and chloride.

2. The composition of the precipitate was analyzed by Direct Current Plasma (DCP) spectrophotometer to determine the relative ratio of Mg to Al. In addition, the precipitate after drying was characterized by XRD and TGA/DTG for comparison with the literature.

Results

1. Al and Mg contents of the precipitates are summarized in Table 1. The Al/(Al + Mg) ratio reported here is within the range reported in the literature of up to 0.45 [4]. The difference between the two samples is most likely attributed to the completeness of the crystal formation as a function of the aging time.

2. The XRD of a representative precipitate is shown in Figure 1. Characteristic peaks of hydrotalcite obtained in the literature [1] is inserted in this figure for comparison. These peaks are all present in our precipitate.

3. The weight loss vs temperature of the precipitate is obtained from a TGA/DTG study as shown in Figure 2. According to the literature, three major weight loss peaks are observed represented by (i) inter layer water loss, (ii) intracrystal water loss, and/or (iii) carbonate ion loss. The weight loss of our material shown in Figure 2 is consistent with the literature data [1,3,4].

Implication

1. Based upon the composition analysis, XRD pattern, and TGA/DTG curve, it is believed that the protocol we adopted here produces typical hydrotalcite crystals. This protocol can be incorporated into the hydrotalcite membrane synthesis.

Table 1. Summary of the aluminum and magnesium contents of the precipitate after ten minutes and six hours of mixing.

Sample ID	#1	#2
Comments [-]	Sample collected after 10 minutes of mixing.	Sample collected after 6 hours of mixing.
Al [ppm]	1.82	1.03
Mg [ppm]	3.07	2.28

Al/(Al + Mg)[mole fraction, experimental]	0.40	0.29
Al/(Al + Mg) [stochiometric]	0.21	0.21

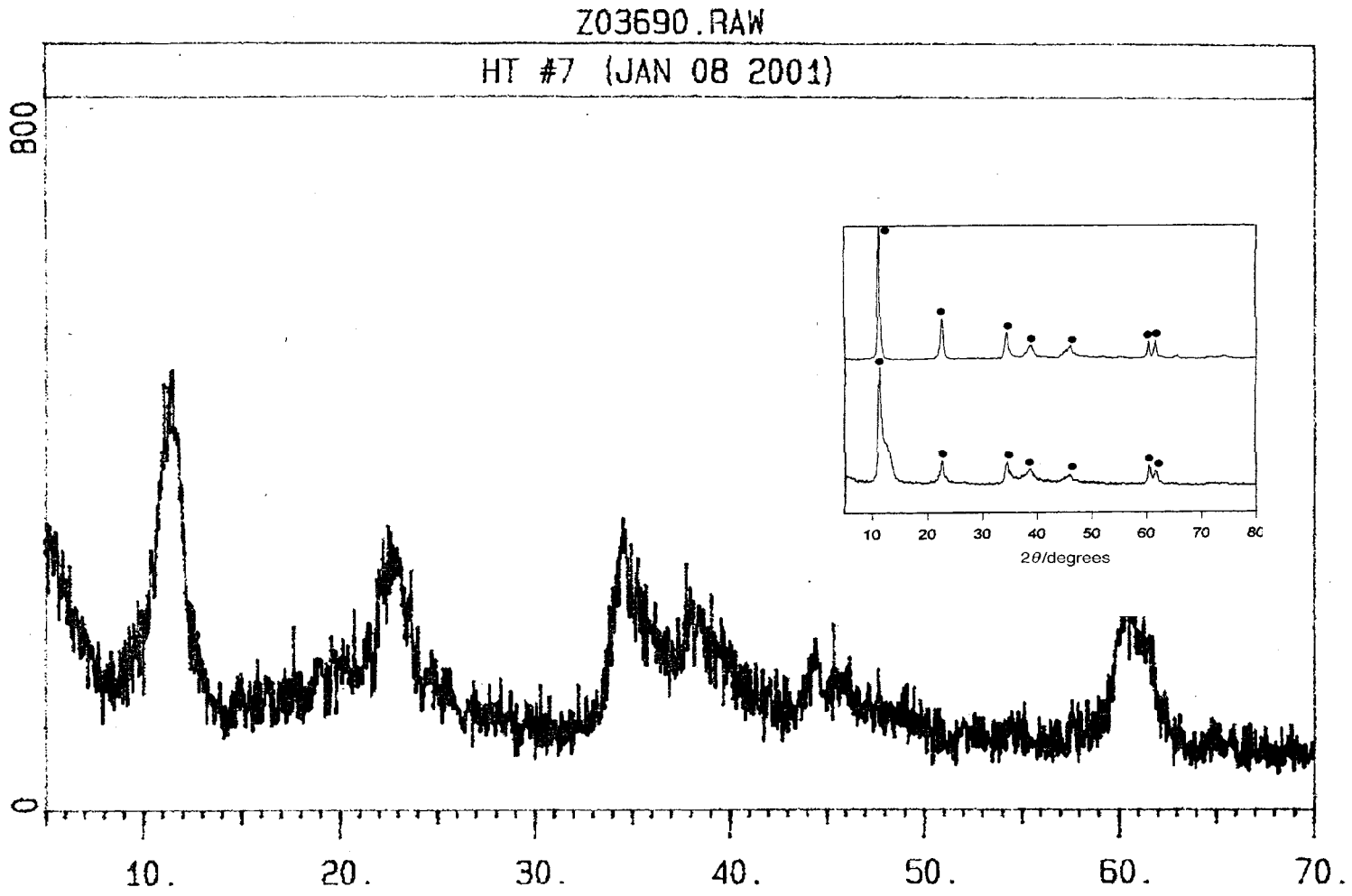

Figure 1. XRD pattern for hydrotalcite prepared under this project. Inset shows the XRD pattern for a hydrotalcite sample from the literature for comparison.

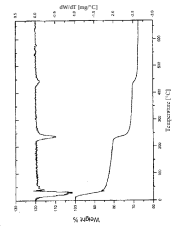

Figure 2. TGA/DTG thermogram hydrotalcite prepared under this project.

2. Crystal Size and Growth Rate

Rationale/Justification

1. As stated in the preceding section, information on the crystal growth rate and size are essential for us to develop a hydrotalcite membrane. Once this is accomplished, an appropriate substrate pore size and crystal growth time and conditions for membrane synthesis can be selected. Since no literature data is available in this specific topic, we have taken an empirical approach to generate the required information, which is discussed below.

Experimental

1. An empirical approach has been designed by us, specifically, to characterize the crystal size formation vs time during the hydrotalcite crystal growth. Our commercial ceramic membranes with well defined pore sizes were used as filters to gauge the crystal size while the crystal population density was determined by turbidity and Al and Mg concentration measurements. Both 0.2μm and 500Å pore size membranes were selected as first candidates for this study.

Results

1. It was found that the hydrotalcite formed immediately following addition of the $AlCl_3/MgCl_2$ solution to the Na_2CO_3 solution. The turbidity of the solution increases almost instantaneously while very little turbidity is detected in the filtrate from the membrane (see Table 2 at time $\geq$198min). Furthermore, the magnesium concentration in the membrane filtrate is extremely low in comparison with the feed. This indicates that little Mg has permeated the membrane either as hydrotalcite crystals or as Mg ions. Hence, all of the magnesium is incorporated very rapidly into hydrotalcite crystal formation. The fact that the aluminum concentration in the permeate is relatively constant (but the permeate turbidity is low) indicates that not all of the aluminum ions have been incorporated in the hydrotalcite crystals. Finally, the hydrotalcite crystal size formed is evidently $\geq 0.2\mu$m, since the crystals formed were nearly completely rejected by the 0.2μm membrane. These results indicate that hydrotalcite crystal formation and growth is very rapid, occurring in the initial mixing (see Table 2) for the experimental conditions we selected.

Implications

1. Our study suggests that the hydrotalcite crystals nucleate and grow very rapidly to a size $\geq 0.2\mu$m, if they can be forced to nucleate in the membrane pores, it is possible that single crystals can be embedded in each of the pores at the surface of the 0.2μm membrane. The in-situ crystallization (ISC) technique discussed in the next section offers one method to achieve this goal. Single crystals embedded in the pores is the ideal morphology for the hydrotalcite membrane. This morphology would yield continuous CO_2 transport channels (within a single crystal) and deliver a high quality membrane capable of achieving very high CO_2 permselectivities.

Table 2: Permeation Rate and Feed and Permeate Characteristics of 0.2μm Membrane Before and After Addition of the Al/Mg Stock Solution to Form Hydrotalcite. Feed Recirculation Rate is ca. 1 liter/min. Feed Volume is 500cc.

Time [min]	Permeation Rate [cc/min]	Feed Turbidity [NTU]	Permeate Turbidity [NTU]	Feed Aluminum [ppm]	Permeate Aluminum [ppm]	Feed Magnesium [ppm]	Permeate Magnesium [ppm]
0	19.67						
193	18.46						
198	Add 5 cc of stock Mg/Al solution						
200	15.16	9.8	0.05	26.2	4.74	5.20	0.4
211	15.33						
290	17.60	6.3	0.36	23.9	4.80		
399	15.60						
430	16.90			14.8	3.3	1.69	0

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