**CO₂ SELECTIVE CERAMIC MEMBRANE FOR WATER-GAS SHIFT
REACTION WITH CONCOMITANT RECOVERY OF CO₂**

Quarterly Report for the Period October 2001 - December 2001

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Technical Summary

To become a viable CO₂ transport membrane, a reversible interaction between CO₂ and the membrane material at the operating condition is a must. In the past quarter, we have conducted a comprehensive reversibility study using TGA and MS at ~200°C for both adsorption and desorption. This quarterly report summarizes the results. Evidently, CO₂ can be reversibly adsorbed and desorbed on the hydrotalcite surface via a pressure swing operation (i.e., between 1 bar and vacuum). About 2wt% working capacity was obtained. Even in the presence of water, the reversibility still holds. In the next quarter, we will focus on the reversibility under other operating conditions and the kinetic aspect of the reversibility study.

Introduction

Hydrotalcites, also known as anionic clays or layered double hydroxides (LDH's) consist of two different types of metallic cations, which constitute the positively charged brucite-like layers with the aid of a close-packed configuration of OH⁻ groups. The interlayer between the brucite layers contains, in addition, water molecules and exchangeable anions for charge compensation. The general chemical structure formula for hydrotalcites is shown below,

where M^{II} represents a divalent metal cation (Mg, Mn, Fe, Co, Ni, Cu, Zn, Ga), M^{III} represents a trivalent metal cation (Al, Cr, Mn, Fe, Co, Ni, and La), and X^{m-} represents an anion with m- valence, such as inorganic anions (CO₃²⁻, OH⁻, NO₃⁻, SO₄²⁻, ClO₄⁻), heteropolyacid anions (PMo₁₂O₄₀³⁻, PW₁₂O₄₀³⁻), and even organic acid anions. Usually, the optimum value of x is in the range of 0.2 ≤ x ≤ 0.33. The composition of the hydrotalcite used in the experiments reported here is Mg_{0.71}Al_{0.29}(OH)₂(CO₃)_{0.15}·0.46H₂O, as determined by ICP and TGA.

Recently, hydrotalcites are finding use in reactive separation applications for increasing catalytic reaction conversion through product removal. The emphasis in this project is on the preparation of hydrotalcite-based microporous membranes. Since the various hydrotalcite applications take place under different operating conditions, it is important to try to understand the thermal behavior and evolution of the hydrotalcite structure under a broad range of experimental conditions.

TG/MS experiments

For the study of the evolution of the hydrotalcite structure we have carried out *in situ* thermogravimetric and mass spectrometry measurements. The thermogravimetric (TG) instrument is basically composed of a microbalance and a furnace for monitoring *in situ* the weight change of the sample, while its temperature and other environmental conditions are varied in a controlled, predetermined manner. For example, the sample may be heated or cooled (temperature programmed desorption/adsorption), or its temperature may be held constant (isothermal), in order to study adsorption/desorption phenomena and the structure evolution under these conditions.

Fig. 1. TG result with hydrotalcite sample

Some representative results indicating the type of experiments that have been carried out in our ongoing investigations of the hydrotalcite structure are shown in Figure 1. In this experiment the temperature of hydrotalcite has been changed in a predetermined fashion in an Ar atmosphere in order to examine the thermal evolution of hydrotalcite. In Figure 1 the temperature of the hydrotalcite is ramped linearly in some regions, while in regions in between is kept isothermal. There are three distinct regions of weight change (loss) in this figure. The first important weight loss is observed in the temperature range from 100°C to 300°C, and the corresponding evolved component is loosely bonded water. (This is verified by *in situ* mass spectrometry, see Figure 2). The second distinct weight loss region is in the temperature range between 300°C and 400°C, and it is due to the evolution of H₂O and small amounts of the CO₂ species. The third one is in the temperature range between 400°C to 600°C, and this weight loss is attributed to the removal of CO₂ (in the form of CO₃²⁻) in the hydrotalcite.

Fig. 2. TG/MS result with hydrotalcite sample

As noted above, the thermogravimetric measurements are coupled with *in situ* mass spectrometric measurements in order to verify the nature of the component evolved during the corresponding distinct weight loss. The mass spectrometric results from an

experiment, in which the hydrotalcite temperature was linearly ramped between room temperature and 650°C with a heating rate of 5°C/min, are shown in Figure 2. The mass spectrometric data indicate that H₂O with small amount of CO₂ were evolved in the region below 380°C, and almost no H₂O was detected in the region over 400°C. This TG/MS results are also consistent with the results obtained by Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), which is another *in situ* technique we have utilized in order to monitor the thermal evolution of hydrotalcite.

Reversibility experiments

The characteristic reversible adsorption/desorption behavior of hydrotalcite makes it a potentially good candidate material as an adsorbent and membrane. To study the reversibility characteristics of hydrotalcite we have utilized the TG/MS system previously described. Typically the desorption part of the cycle was implemented by heating under inert gas or in vacuum; the adsorption part of the cycle was carried out in the presence of dry or humidified CO₂ for adsorption. During the experiment, in addition to the weight change, the composition of the various components released is typically measured. The results of 3 cycles of pressure swing type TG experiment under isothermal conditions are shown below:

The experimental conditions were:

Temperature: Raise temperature at 5 °C/min from room temperature to 200 °C, then, keep temperature at 200 °C during de/adsorption cycles

Pressure: Apply vacuum for the desorption step (1hr), expose sample to atmospheric CO₂ during the adsorption step (2hr)

Two types of experiments were carried out. In the first series of experiments the sample during the adsorption part of the cycle was exposed to dry CO₂, while in the second type

of experiment the sample is exposed to CO₂, which is humidified by passing it through a bubbler.

(1) Dry CO₂

1st wt. loss: 2.12%

1st wt. gain: 2.06%

2nd wt. loss: 1.96%

2nd wt. gain: 1.82%

3rd wt. loss: 1.69%

3rd wt. gain: 1.51%

(2) Humid CO₂

1st wt. loss: 2.26%

1st wt. gain: 2.12%

2nd wt. loss: 2.01%

2nd wt. gain: 1.87%

3rd wt. loss: 1.73%

3rd wt. gain: 1.58%

In this series of experiments complete reversibility is not observed. This is because the adsorption time is not long enough. In other experiments under both temperature and pressure swing adsorption conditions previously reported in which the adsorption was carried out for longer periods of time, complete reversibility was observed. Currently experiments are under way in which we investigate the effect of changing the adsorption time on reversibility under isothermal pressure swing type conditions. During these

experiments we will be also monitoring the composition of the gases that are desorbed using mass spectrometry in order to verify the nature of gaseous species that are desorbed. Similar experiments were previously reported under nonisothermal pressure swing conditions and CO₂ was the gas that was predominantly desorbed.

Conclusions:

Preliminary adsorption experiments are reported here with hydrotalcite adsorbents under isothermal conditions. The experiments indicate that adsorption under such conditions appears to be reversible, an observation also made (and previously reported) under nonisothermal conditions. Experiments are currently under way to study the effect of time of adsorption on the degree of reversibility, and to also investigate the composition of the gases desorbed.