Development of Mesoporous Membrane Materials for CO₂ Separation

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Abstract

Mesoporous and precipitated alumina were synthesized as the base material for CO₂ adsorbent. The porous alumina is doped with Ba to enhance its CO₂ affinity due to the basicity of Ba. It is shown by gas chromatograph (GC) that the addition of Ba enhances the separation CO₂ from N₂. It was found that mesoporous alumina has larger specific surface area and better selectivity of CO₂ than precipitated alumina. Ba improves the affinity of mesoporous alumina with CO₂. Phase may play an important role in selective adsorption of CO₂. It is speculated that mesoporous alumina is more reactive than precipitated alumina creating the xBaO·Al₂O₃ phase that may be more affinitive to CO₂ than N₂. On the other hand, the barium alumnate phase (Ba₃Al₂O₆) in the mesoporous sample does not help the adsorption of CO₂.

Introduction

CO₂ is a greenhouse gas that contributes to global warming. The major source of CO₂ comes from emissions of power plants, industrial production plants, automobiles, etc. The emitted flue gas also contains significant amount of N₂ at temperature of hundreds of Centigrade. The main objective of our proposed work is to develop a cost-effective membrane that can separate N₂ and CO₂ with high selectivity. Selection due to size will not work because the kinetic diameters of CO₂ and N₂ molecules are close to each other (0.36 nm and 0.40 nm, respectively). We proposed to synthesize porous inorganic materials that can selectively adsorb CO₂. We will synthesize high surface-area mesoporous alumina which is doped with a basic element, Ba, to enhance the CO₂ adsorption.

Executive Summary

The current approach to separate CO₂ from other gases, especially N₂, in the hot gas effluent of power plants has been the use of zeolite membranes. Zeolites are microcrystalline aluminosilicates that have pores in the order of < 1 nm. The gas permeability of zeolites is limited due to the tortuous pore structures. In addition, the selectivity between CO₂ and N₂ by zeolites is low because the kinetic diameters of CO₂ and N₂ are similar in size. Recently, there were several studies indicated that the selective adsorption of CO₂ could be an effective way of
enhancing the permeation of CO₂. The idea is to have adsorption sites on the pore wall for the CO₂ to facilitate its surface diffusion along the pore wall. Higher specific surface area would increase the adsorption of CO₂ and enhance the selectivity. The new mesoporous molecular sieves developed by researchers at Mobil in the early 90s offer an opportunity for improvement. The mesoporous molecular sieves have larger pore size than zeolites and the pore size can be varied by the size of the organic template.

The selectivity for CO₂ comes from the dopants that prefer to bond with CO₂. Horiuchi et al.¹ showed that basic metal oxides in alumina could enhance the selectivity of CO₂. The addition of alkali metal oxides such as Cs₂O and alkaline-earth oxides such as BaO were shown to increase the retention time for CO₂ than pure alumina. On the other hand, higher surface area is expected to improve the adsorption of CO₂ as well. Rossignol and Kappenstein² have recently shown that the addition of Ba to alumina can increase the surface area at elevated temperatures. Combining the requirements of high surface area and selective adsorption of CO₂, we chose Ba as the dopant in the present study.

Our preliminary objective is to synthesize high surface-area alumina powders which can selectively adsorb CO₂ over N₂. Alumina was synthesized by two methods. One is the precipitation method using Al(NO₃)₃. It has been shown recently by Chuah et al.³ that holding the precipitated alumina in the mother liquids at higher temperatures (digestion) can increase the surface area. Another method is the templating approach using tartaric acid.⁴

Preliminary results show that the templating method produced alumina with higher surface area after 500°C heat treatment for 4 hours. Mesoporous alumina has surface area ~380 m²/g compared to precipitated alumina with 240 m²/g. At 500°C heat treatment, it is found that the addition of Ba lowers the surface area of alumina. This is reasonable since the effect of Ba on the surface area is expected to occur near the γ-α phase transition temperature (~1100°C) rather than at 500°C. It is generally believed that stabilizing dopants can delay the γ-α phase transition temperature thereby avoiding the destruction of the high surface-area structure of the γ phase. However, there is an interesting difference between the Ba-doped mesoporous alumina and Ba-doped precipitated alumina. For the precipitated alumina, Ba doping results in larger pore size and pore volume. On the other hand, the addition of Ba to mesoporous alumina results in smaller pore size and pore volume.

It was found that mesoporous alumina has larger specific surface area and better selectivity of CO₂ than precipitated alumina. Ba improves the affinity of mesoporous alumina with CO₂ Phase plays an important role in selective adsorption of CO₂. It is speculated that mesoporous alumina is more reactive creating the xBaO·Al₂O₃ phase that may be more affinitive to CO₂ than N₂. On the other hand, the barium alumnate phase (Ba₃Al₂O₆) in the mesoporous sample does not help the adsorption of CO₂. The preliminary results indicate that in addition to surface area, pore size and pore volume are also important characteristics of porous materials.
Experimental Procedure

Precipitated alumina

5.0 N NH₄OH and 0.5 M Al(NO₃)₃⋅9H₂O were mixed to form a solution. The solution was added to distilled water in a dropwise fashion while the pH of the distilled water was kept at 6. The precipitated powders were centrifuged and dried at 70°C.

Mesoporous alumina

Al-sec-butoxide was dissolved in distilled water (mole ratio=1:100). Mix and stir @ 80°C for 0.5h. Cool down to R.T., adjust pH~3, and add DBTA (weight ratio with Al₂O₃=1:1). Dry @ R.T. for 3-4 days.

Impregnation of Ba

A. 6.3 % mole barium nitrate was dissolved in water forming a solution.
B. The heat-treated alumina powder was impregnated with the above solution of barium nitrate in water.
C. The marshy mixture was kept in oven at around 60-80°C till all the water evaporates. The powder obtained was heat-treated at 400°C for 3 hours at the rate of 0.5 °C/min.

Gas Chromatography (GC)

A. A GC column of approximate length 32 cm was filled with the silica powders impregnated with Ba.
B. The column was kept at a temperature of 380°C with the injector and detector at a slightly higher temperature of 395°C. This does the job of flushing away the gases that may be present in the column.
C. The actual measurement was taken at a column temperature of 375°C. The flow rate of carrier gas (helium) was maintained at 10 ml per 36-38 sec.
D. A mixture of N₂ and CO₂ (50/50) was passed through the column to determine the difference in retention time between the two gases.

Results and Discussions

Preliminary results show that the templating method produced alumina with higher surface area after 500°C heat treatment for 4 hours. Mesoporous alumina has surface area ~380 m²/g compared to precipitated alumina with 240 m²/g. At 500°C heat treatment, it is found that the addition of Ba lowers the surface area of alumina. This is reasonable since the effect of Ba on the surface area is expected to occur near the γ-α phase transition temperature (~1100°C) rather than at 500°C. It is generally believed that stabilizing dopants can delay the γ-α phase transition temperature thereby avoiding the destruction of the high surface-area structure of the γ phase. However, there is an interesting difference between the Ba-doped mesoporous alumina and Ba-doped precipitated alumina. For the precipitated alumina, Ba doping results in larger pore size.
and pore volume. On the other hand, the addition of Ba to mesoporous alumina results in smaller pore size and pore volume. The preliminary results indicate that in addition to surface area, pore size and pore volume are also important characteristics of porous materials. The results of XRD and the BET surface area analyzer are tabulated in Table 1.

We attended the review meeting on June 5, 2001, at Pittsburgh. Our objective in this period is to synthesize high surface-area alumina powders which can selectively adsorb CO$_2$ over N$_2$. Alumina was synthesized by two methods. One is the precipitation method using Al(NO$_3$)$_3$. It has been shown recently by Chuah et al.\textsuperscript{5} that holding the precipitated alumina in the mother liquids at higher temperatures (digestion) can increase the surface area. Another method is the templating approach using tartaric acid.\textsuperscript{6} We adopted the templating approach that we developed earlier. It was shown that mesoporous alumina has surface area $\sim$380 m$^2$/g compared to precipitated alumina with 240 m$^2$/g. The incorporation of Ba in mesoporous alumina improves the affinity of mesoporous alumina with CO$_2$. In collaboration with Prof. R. Mutharasan and Mr. D. Luu at Department of Chemical Engineering, we set up the gas chromatograph (GC) with a thermal conductivity detector to measure the effect of Ba doping on the retention time of CO$_2$ and N$_2$ as they pass through a column of the alumina powders. We investigated how the Ba doping and the surface area affect the CO$_2$ and N$_2$ adsorption of alumina. The gas chromatography (GC) of CO$_2$/N$_2$ 50/50 mixture gas passing through columns of mesoporous alumina with and without Ba are shown in Fig. 1. Clearly with Ba, the separation between the retention time for CO$_2$ and N$_2$ is increased. Similar results as Fig.1 for precipitated alumina were found. Our results are consistent with that found by Horiuchi et al.\textsuperscript{7} who showed that basic metal oxides in alumina could enhance the selectivity of CO$_2$. Rossignol and Kappenstein\textsuperscript{8} have recently shown that the addition of Ba to alumina can increase the surface area at elevated temperatures. However, we found that the addition of Ba lowers the surface area of alumina. This is reasonable since the effect of Ba on the surface area is expected to occur near the $\gamma$$-\alpha$ phase transition temperature ($\sim$1100°C) rather than at 500°C that was studied here. It is generally believed that stabilizing dopants can delay the $\gamma$$-\alpha$ phase transition temperature thereby avoiding the destruction of the high surface-area structure of the $\gamma$ phase.

Phase plays an important role in selective adsorption of CO$_2$. It is speculated that mesoporous alumina is more reactive than the precipitated alumina thereby creating the xBaO$\cdot$Al$_2$O$_3$ phase that is more affinitive to CO$_2$ than N$_2$. On the other hand, the barium aluminate phase (Ba$_3$Al$_2$O$_6$) found in several samples does not help the adsorption of CO$_2$ because the GC results do not show any increase in the separation of retention times.

**Conclusion**

It was found that mesoporous alumina has larger specific surface area and better selectivity of CO$_2$ than precipitated alumina. Ba improves the affinity of mesoporous alumina with CO$_2$. Phase plays an important role in selective adsorption of CO$_2$. It is speculated that mesoporous alumina is more reactive creating the xBaO$\cdot$Al$_2$O$_3$ phase that may be more affinitive to CO$_2$ than N$_2$. On the other hand, the barium aluminate phase (Ba$_3$Al$_2$O$_6$) in the mesoporous sample does not help the adsorption of CO$_2$. 

There were several comments about our presentation at the review meeting. The major comment was that the pore size of mesoporous alumina is large, 50-60 Å, and Knudsen diffusion would dominate. It is known that the separation of N₂ and CO₂ cannot be achieved when Knudsen diffusion operates because the kinetic diameters of the two gases are similar. As a result, mesoporous alumina may not be the best material to study. We plan to synthesize microporous silica as an alternative to mesoporous alumina for the membrane material. Microporous silica has been shown to have pore size smaller than 10 Å. At this small size, the adsorption of CO₂ in the pores can block the passage of N₂ thereby facilitating the separation. We will be working on the synthesis of microporous silica with Ba for the next few months.

Table 1. Phase and Structural Properties of Precipitated and Mesoporous Alumina after Heat Treatment at Elevated Temperatures.

<table>
<thead>
<tr>
<th>Aluminum oxide</th>
<th>SSA (m²/g)</th>
<th>Pore Size (nm)</th>
<th>Pore volume (cc/g)</th>
<th>Phases</th>
<th>SSA (m²/g)</th>
<th>Pore Size (nm)</th>
<th>Pore volume (cc/g)</th>
<th>Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>As syn. (pH=6)</td>
<td>240</td>
<td>3.0</td>
<td>0.178</td>
<td>Amorphous</td>
<td>161</td>
<td>3.9</td>
<td>0.159</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>As syn. +8.9mol% Ba</td>
<td>218</td>
<td>3.5</td>
<td>0.189</td>
<td>?</td>
<td>157</td>
<td>4.7</td>
<td>0.185</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Cured (pH=6)</td>
<td>224</td>
<td>4.3</td>
<td>0.245</td>
<td>Al₂O₃</td>
<td>14.3</td>
<td>6.9</td>
<td>0.025</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Cured +8.9mol% Ba</td>
<td>164</td>
<td>4.7</td>
<td>0.194</td>
<td>Al₂O₃</td>
<td>104</td>
<td>7.4</td>
<td>0.192</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Mesoporous</td>
<td>381</td>
<td>6.1</td>
<td>0.577</td>
<td>Al₂O₃</td>
<td>244</td>
<td>9.0</td>
<td>0.548</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Mesoporous +8.9mol% Ba</td>
<td>354</td>
<td>5.2</td>
<td>0.464</td>
<td>Al₂O₃⁺Ba₃Al₂O₆ (?</td>
<td>216</td>
<td>8.1</td>
<td>0.436</td>
<td>Al₂O₃ + Ba₃Al₂O₆ (?)</td>
</tr>
</tbody>
</table>
Mesoporous Al$_2$O$_3$

Mesoporous Al$_2$O$_3$ + 6.3 mol\% Ba

Fig. 1. Gas chromatograph when mixtures of CO$_2$ and N$_2$ (50/50) gases were passed through columns packed with mesoporous alumina with and without Ba.
References


