

Development of Mesoporous Membrane Materials for CO₂ Separation

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Abstract

We propose to use microporous silica as a suitable candidate for CO₂/N₂ separation because the pore size is less than 10 Å. If a CO₂ adsorbent is added to the microporous silica, the adsorption of CO₂ can block the passage of N₂ and an effective CO₂/N₂ separator will be found. It was first demonstrated that microporous silica could be synthesized. The microporous silica was then impregnated with Ba(OH)₂. The results of GC study showed that at temperatures between 50°C and 90°C, Ba-doped microporous silica can separate CO₂ from N₂ and the idea of a microporous membrane for CO₂/N₂ separation is feasible. The new result gives strong support to the proposed research that was outlined in the Phase II proposal. We hope to be able to continue the research and build an effective CO₂/N₂ membrane separator in the Phase II of this project.

Executive Summary

Recently microporous silica has been shown to have a uniform pore size smaller than 10 Å.¹ The kinetic diameter of CO₂ and N₂ molecules are 3.6 Å and 4.0 Å respectively. At pore size smaller than 10 Å, the adsorption of CO₂ in the pores can block the passage of N₂ thereby facilitating the separation of CO₂ from N₂ by molecular sieving. Microporous silica membrane with thickness less than 30 nm has been demonstrated by Verweij et al.¹ In addition, the permeability for CO₂ is in the order of 2x10⁻⁷ mol/m²s·Pa which is similar to the requirement of DOE. Therefore microporous silica can be a good choice for the CO₂ selective membrane material. Microporous silica membranes as gas separators have been studied for CH₄/He and CO₂/He.²

The selectivity for CO₂ comes from the dopants that prefer to bond with CO₂. Horiuchi et al.³ 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. In the last report, we have shown that the addition of Ba in mesoporous Al₂O₃ can separate CO₂ from N₂ by enhancing the adsorption of CO₂. It is quite plausible that the results by Horiuchi et al. on alumina and our results on

mesoporous alumina can be extended to silica and dopants that enhance adsorption of CO₂ to alumina are suitable for silica as well.

In the last six months we have successfully synthesized the microporous silica and performed BET analysis to confirm that they are indeed microporous. If the microporous silica can adsorb CO₂ selectively, an effective CO₂/N₂ separator would be found. A dopant is needed for the CO₂ selectivity. Previously we have shown that Ba addition enhanced the adsorption of CO₂ on alumina. We would like to investigate whether the doping of Ba can enhance the adsorption of CO₂ on microporous silica. We impregnated Ba on the microporous silica and performed gas chromatograph (GC) to study the separation of CO₂ from N₂.

Experimental Procedure

Microporous silica was synthesized following the procedure by de Vos and Verweij.^{1,4} Nitric Acid in water was added dropwise to TEOS in ethanol solution in an ice bath. The mole ratio of TEOS/ethanol/Nitric Acid/water in the final mixture is 1/3.8/0.085/6.4. The mixture was refluxed at 60°C for 3 hr and cool down to room temperature then dilute 19 times by ethanol. And the sol was dried in Petri dish at room temperature. The sol first became a gel. Powders obtained from continuous drying were heat treated to 400°C and held for 3 hr. Both the heating and cooling rate are 0.5°C/min. The powders were analyzed by a BET surface-area analyzer (Quantachrom NOVA 2210) using N₂ physical adsorption at 77K after out-gasing at 300°C for 24 hours. The micro pore volume, surface area, and approximate pore size were calculated by the t-method using Halsey equation.

1. Microporous Silica

The procedure for silica synthesis is shown below.

- A. Measured amount of acid was added to a flask containing measured amount of distilled water.
- B. Measured amount of TEOS was added to a flask containing ethanol and kept in ice.
- C. Acid mixture was then added dropwise using a dropping funnel to the flask containing TEOS and ethanol with vigorous stirring.
- D. The whole reaction mixture was then refluxed for 3 hours at 80°C under stirring. (Molar ratios are given in table 1)
- E. The mixture was allowed to remain at room temperature till we obtained the dried powders which were then ground.
- F. The powder thus obtained was heat-treated at 400°C for 3 hours at a rate of 0.5 °C/min.

Table I
Composition of standard silica polymeric sol (SiSiO₂)

	TEOS	H ₂ O (r _w)	C ₂ H ₅ OH (r _{alcohol})	HNO ₃ (IM) (r _{H+})
mol:	0.094	0.6	0.36	0.008
mol ratio (X/TEOS):	(1)	(6.4)	(3.8)	(0.085)

2. Impregnation with Barium Hydroxide (Ba(OH)₂)

- 6.3 % mole Barium hydroxide was dissolved in water forming a solution.
- The heat-treated silica powder was impregnated with the above solution of barium hydroxide in water.
- 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.

3. Gas Chromatography (GC)

- A GC column of approximate length 32 cm was filled with the silica powders impregnated with Ba.
- 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.
- 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.
- 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 Discussion

The adsorption isotherm is shown in Fig.1. The Langmuir-type isotherm indicates the existence of micropores. According to the t-plot method, as shown in Fig.2, the two linear regions of the t-plot indicate the presence of micropores larger than 7Å. The slope of the line *a* gives the total surface area 351.7 m²/g, the slope of the line *b* gives the external area of 2.3 m²/g. Therefore the micropore surface area is 349.4 m²/g. The intercept of the line *b* with the volume axis give the micropore volume of 0.145 cc/g, and the intersect point of lines *a* and *b* give the approximate pore size of 9.4 Å.

Doping of Ba in microporous silica was studied to investigate the CO₂ adsorption using GC similar to our study with alumina. First, it was checked with BET that the Ba-impregnated silica was still microporous. A 50/50 N₂/CO₂ gas mixture was passed through a GC column of microporous silica doped with Ba, and the column was held at 375°C. Only a single peak was observed indicating that Ba has no enhancement on the CO₂ adsorption in

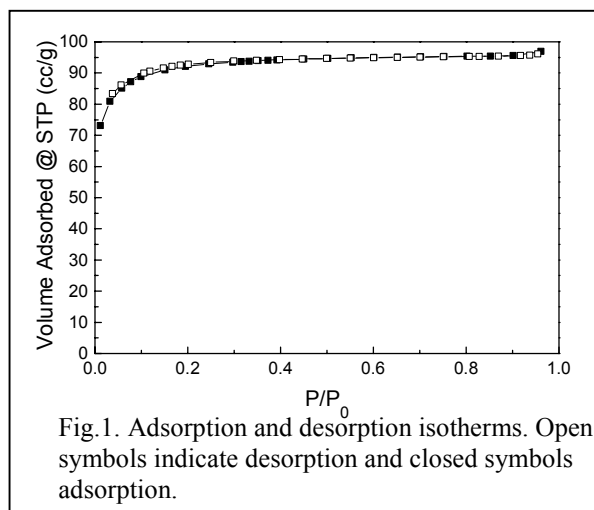


Fig.1. Adsorption and desorption isotherms. Open symbols indicate desorption and closed symbols adsorption.

microporous silica. This result is different from that of alumina. Even though Ba is basic and would attract CO₂ molecules, it was speculated that the acidic silica prevented the CO₂ from approaching Ba. We attempted to add alumina to microporous silica since Ba helps the CO₂ adsorption in alumina. So far, our preliminary study on Ba doping has shown no separation of CO₂ and N₂ in the GC measurement, even for alumina amount as high as 50 mol%.

In February of 2002, we discovered the paper by Bal et al.⁵ that shows that silica doped with alkaline metals can adsorb CO₂ in the temperature range of 100 to 200°C. We realized that our experiments on microporous silica were done at a temperature that was too high for silica. The temperature of 375°C is too high for CO₂ adsorption on silica. As a result, we repeated our GC experiments at lower temperatures, in the range of 50°C to 200°C. Sure enough we saw the separation of CO₂ and N₂ by the Ba-doped microporous silica. The results are shown in Fig.3. The separation of retention time between CO₂ and N₂ increases with decreasing temperature. The results in Fig.3 are very exciting and indicate that a microporous membrane for separating CO₂ and N₂ is possible.

Conclusion

Previously we have investigated the use of mesoporous alumina as the candidate for CO₂/N₂ separator. However, the pore size of the mesoporous alumina is large and Knudsen diffusion would dominate. It is known that CO₂ and N₂ cannot be separated by the Knudsen diffusion mechanism because of their similar kinetic size. We propose to use microporous silica as a suitable candidate for CO₂/N₂ separation because the pore size is less than 10 Å. In this report, we reported the success of the synthesis of microporous silica. If a CO₂ adsorbent is added to the microporous silica, the adsorption of CO₂ will block the passage of N₂ and an effective CO₂/N₂ separator will be found. It is shown in Fig.3 that there exists a microporous material that can separate CO₂ from N₂ and the idea of a microporous membrane for CO₂/N₂ separation will work. The new result gives strong support to the proposed research that was outlined in the Phase II proposal. We hope to be able to continue the research and build an effective CO₂/N₂ membrane separator in the Phase II of this project.

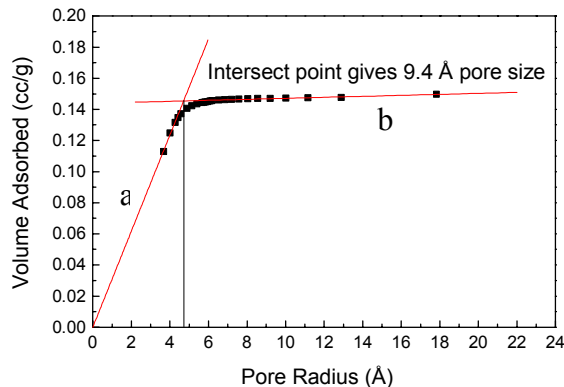


Fig.2. Results in Fig.4 plotted using t-method. The intercept gives a pore size of 9.4 Å.

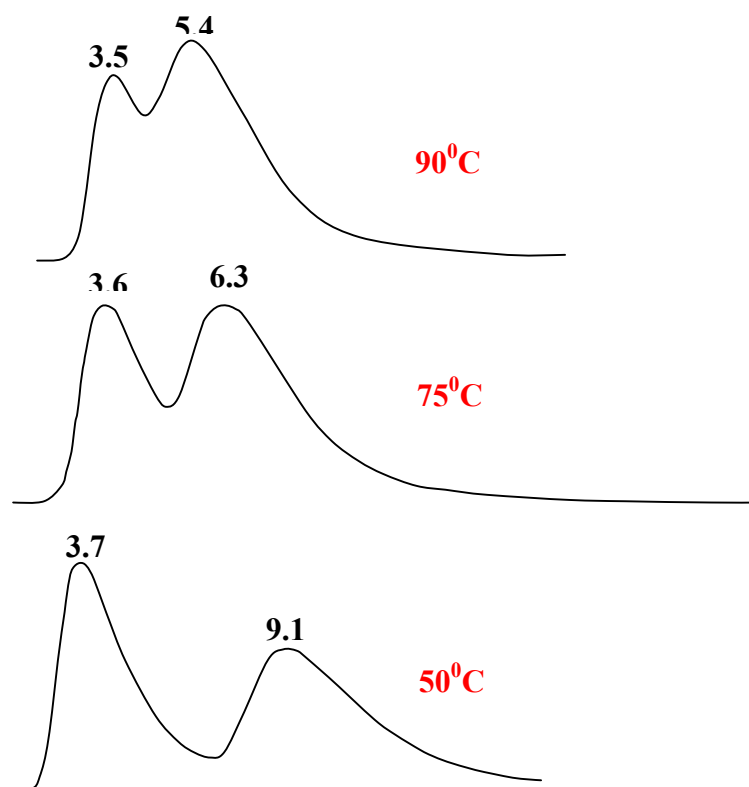


Fig.3. Gas chromatograph of microporous silica doped with 6.3% Ba obtained when mixtures of CO₂ and N₂ (50/50) gases were passed through the column packed with the silica powders. The numbers mark the retention time (minutes).

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