

Development of Mesoporous Membrane Materials for CO₂ Separation

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Abstract

We propose to use microporous aluminosilicate 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. No adsorption of CO₂ was observed. Alumina must be added to facilitate CO₂ adsorption. However, no microporous aluminosilicates have been shown before. In this six-month study, we developed a process that partially coat alumina on microporous silica. Microporous aluminosilicates were synthesized by the coating process.

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 2×10^{-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.

Previously 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. On the other hand, Ba addition in silica did not enhance the adsorption of CO₂. Therefore, alumina is needed for the CO₂ adsorption. However, as far as we know, no microporous aluminosilicates have been demonstrated in the literature. In the last six months, we developed a process by partially coating alumina on microporous silica. It is shown that the modified process can produce microporous aluminosilicates.

Experimental Procedure

The experimental procedures for the synthesis of microporous silica and the impregnation of Ba(OH)s have been described in the last report. Here we will only describe the synthesis of the alumina coating. The procedure used is according to our earlier paper.⁴ The procedure is described below.

1. Prepare a suspension by adding 5 grams of silica powder to 225 ml distilled water.
2. Stir and ultrasonicate the suspension for about 15 minutes.
3. Heat the suspension to 90°C.
4. Add 21.58 g of 95% aluminum secondary butoxide (which will give 5 g of boehmite) with vigorous stirring.
5. Keep the solution heated at 90°C for about 30 minutes.
6. Adjust the pH of the solution to 3 by adding hydrochloric acid.
7. Dry the solution on a hot plate.
8. After drying, wash the powder with distilled water till the chloride is removed. (Chloride removal is checked by using silver nitrate solution to see if black precipitate of silver chloride is formed.)
9. Dry the powder in oven at about 90°C.

Results and Discussion

Analysis of isotherms of physical adsorption of gases represents a standard method for obtaining information about the pore structure of materials. Brunauer has defined five different types of adsorption isotherms as shown in Figure 1. Type I isotherms are characteristic for microporous adsorbents, such as zeolites, carbons etc. Type IV isotherms are typical for mesoporous solids in which capillary condensation takes place at higher pressures of adsorbate in addition to multilayer adsorption at lower pressures. Important features are the increase in mesopores as well as a hysteresis loop. A distinct increase in adsorbate volume in the low p/p_0 region in type IV isotherms indicates the presence of micropores associated with mesopores.

BET surface analysis of the powder prepared by the coating method are shown in Figure 2.

The curve resembles the isotherm of type I characteristic of microporous solids. But if observed closely, at higher pressures, the curve for microporous solids is horizontal, while our curve continues to increase gradually. This is indicative that the powder is not totally microporous and has larger pores. The specific surface area of the powder was calculated to be about $560 \text{ m}^2/\text{g}$. The microporous nature was confirmed by analysis of a different batch

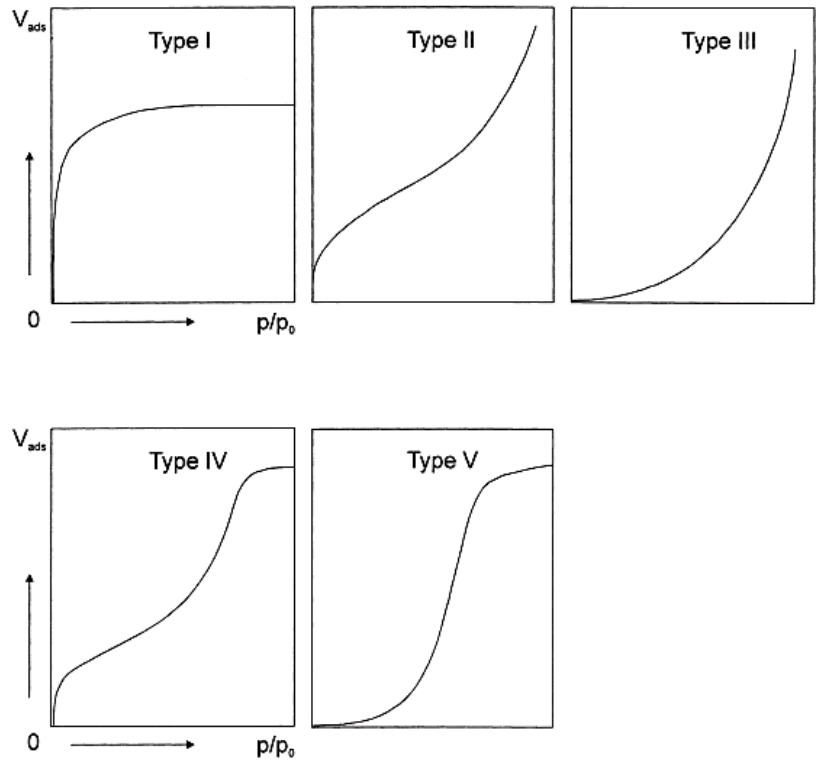


Figure 1. Different types of adsorption isotherms depending on the pore structures.

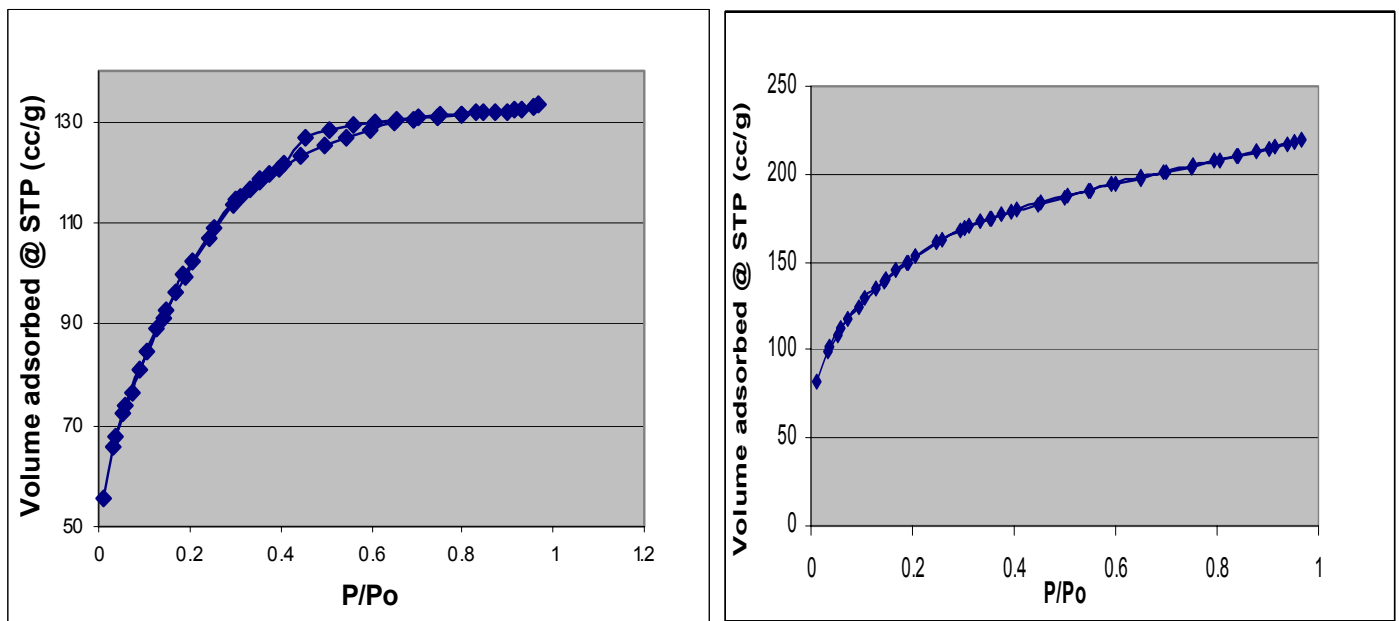


Figure 2. The adsorption amount as a function of P/P_0 for two samples.

of the same powders which yielded a specific surface area of about 350 m²/g (also shown in Fig.2). Also the presence of the hysteresis confirms that pores larger than micron size are present.

The average pore size can be estimated using the t-plot which uses the Halsey equation. The intersection of the two lines gives the approximate pore radius which is around 6-7 Å. The curve is shown in Figure 3 for two samples.

In comparison, in the last report on the microporous silica, 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.

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. However, microporous silica does not adsorb CO₂, We propose to use microporous aluminosilicate 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 aluminosilicates. 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.

References

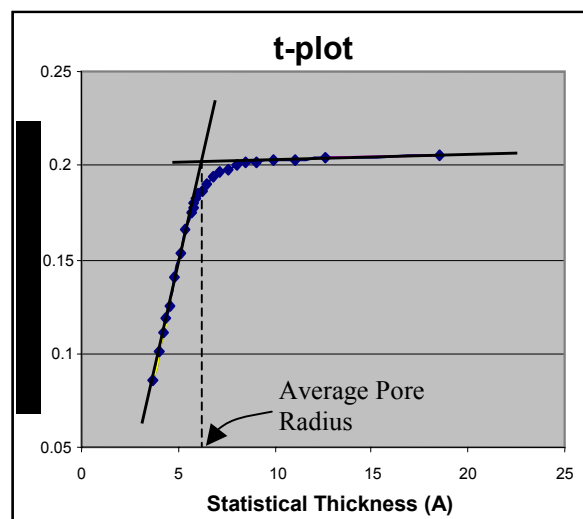
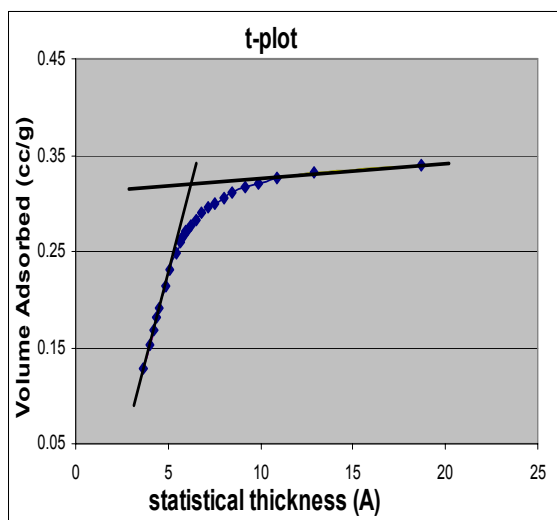


Fig.3. t-plot gives the approximate pore size. The microporosity was confirmed by two samples.

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⁴ C. Y. Yang, W. Y. Shih, and W.-H. Shih, “Gelation, Consolidation, and Rheological Properties of Boehmite-Coated Silicon Carbide Suspensions,” *J. Am. Ceram. Soc.*, **83**[8] 1879-84 (2000).