Development of Mesoporous Membrane Materials for CO₂ Separation

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Abstract

The huge emissions of carbon dioxide from fossil fuel fired power plants and industrial plants over the last century have resulted in an increase of the atmospheric carbon dioxide concentration. Climatological modeling work has predicted severe climate disruption as a result of the trapping of heat due to CO_2. As an attempt to address this global warming effect, DOE has initiated the Vision 21 concept for future power plants. We first synthesized mesoporous aluminosilicates that have high surface area and parallel pore channels for membrane support materials. Later we synthesized microporous aluminosilicates as the potential thin membrane materials for selective CO_2 adsorption. The pore size is controlled to be less that 1 nm so that the adsorption of CO_2 on the pore wall will block the passage of N_2.

Mesoporous and precipitated alumina were synthesized as the base material for CO_2 adsorbent. The porous alumina is doped with Ba to enhance its CO_2 affinity due to the basicity of Ba. It is shown by gas chromatograph (GC) that the addition of Ba enhances the separation CO_2 from N_2. 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 may play an important role in selective adsorption of CO_2. It is speculated that mesoporous alumina is more reactive than precipitated alumina creating the $xBaO \cdot Al_2O3$ phase that may be more affinitive to CO_2 than N_2. On the other hand, the barium aluminates phase ($Ba_3Al_2O_6$) in the mesoporous sample does not help the adsorption of CO_2.

Microporous aluminosilicate was chosen as a suitable candidate for CO_2/N_2 separation because the pore size is less than 10 Å. If a CO_2 adsorbent is added to the microporous silica, the adsorption of CO_2 can block the passage of N_2 and an effective CO_2/N_2 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 CO_2 was observed. It was found that alumina must be added to facilitate CO_2 adsorption. However, no microporous aluminosilicates have been shown before. We developed a process that partially coat alumina on microporous silica. It was demonstrated that microporous aluminosilicates can be obtained by the coating process and a candidate material for selective CO_2 separation is available.

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1. Introduction

In the Vision 21 concept, future power plants are expected to eliminate any emission of pollutants. However, over the last century, the huge emissions of carbon dioxide from fossil fuel fired power plants and industrial plants have resulted in an increase of the atmospheric carbon dioxide concentration. Climatological modeling work has predicted severe climate disruption as a result of the trapping of heat due to CO_2. This global warming effect due to CO_2 has become an international issue and the removal of CO_2 becomes an urgent issue.

Over the past three decades, the applications of gas separation membrane technology have gradually been adopted for CO_2 removal.[1] This is mainly due to the development of polymer membrane as sheets or tubes of various cross sections. They are easy to be assembled into high packing density. More recently, hollow fiber membranes were developed and even higher packing densities can be achieved. These membrane absorbers can be made more compact than conventional packed column or tray columns. However, a severe drawback of polymer membranes is their low thermal stability that limits their operation temperatures below 150°C. Improvements in the thermal stability is needed.

For thermal stability, porous ceramic membranes will be a better choice. Microporous ceramics such as zeolites are thermally stable up to at least 500°C. Selectivity between CO_2 and other flue gas such as N_2 is a major challenge for the separator technology because the kinetic diameters of CO_2 and N_2 molecules are relatively close to each other. In order for the separation of CO_2 from N_2 to be successful, selective interaction between the molecules and the membrane materials is required. In addition, the low permeability of zeolites needs to be improved. The crystallinity of zeolites caused cracks to be formed in thin membrane layers and multiple coating is necessary to prevent leakage through cracks. The resulting thick layers lower the permeability of the membranes. The goal of the proposed study is to develop materials that have high permeability and high CO_2/N_2 selectivity.

The main objective of our proposed work is to develop a membrane material that can separate N_2 and CO_2 with high selectivity and permeability. Selection due to size will not work because the kinetic diameters of CO_2 and N_2 molecules are close to each other (0.36 nm and 0.40 nm, respectively). We will synthesize porous inorganic materials that can selectively adsorb CO_2 and are amorphous to avoid crack formation and reduce thickness.

2. Executive Summary

The current approach to separate CO_2 from other gases, especially N_2, 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 small size would be ideal for selective separation since the adsorption of CO_2 can block the passage of N_2. However, zeolite is crystalline and is difficult to be crack-free during processing. Amorphous microporous membranes would be preferred.

The selectivity for CO_2 comes from the dopants that prefer to bond with CO_2. Horiuchi et

al.[2] showed that basic metal oxides in alumina could enhance the selectivity of CO_2. The addition of alkali metal oxides such as Cs_2O and alkaline-earth oxides such as BaO were shown to increase the retention time for CO_2 than pure alumina. On the other hand, higher surface area is expected to improve the adsorption of CO_2 as well. Rossignol and Kappenstein[3] 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 CO_2, we chose Ba as the dopant in the present study.

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.[4] 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.[5]

It is shown that the templating method produced alumina with higher surface area after 500°C heat treatment for 4 hours. Mesoporous alumina has surface area ~380 m^2/g compared to precipitated alumina with 240 m^2/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 CO_2 than precipitated alumina. Ba improves the affinity of mesoporous alumina with CO_2. The results indicate that in addition to surface area, pore size and pore volume are also important characteristics of porous materials.

Recently microporous silica has been shown to have a uniform pore size smaller than 10 Å.[6] The kinetic diameter of CO_2 and N_2 molecules are 3.6 Å and 4.0 Å respectively. At pore size smaller than 10 Å, the adsorption of CO_2 in the pores can block the passage of N_2 thereby facilitating the separation of CO_2 from N_2 by molecular sieving. Microporous silica membrane with thickness less than 30 nm has been demonstrated by Verweij et al.[6] In addition, the permeability for CO_2 is in the order of 2×10^{-7} $mol/m^2s \cdot Pa$ which is similar to the requirement of DOE. Therefore microporous silica can be a good choice for the CO_2 selective membrane material. Microporous silica membranes as gas separators have been studied for CH_4/He and CO_2/He.[7]

We have successfully synthesized the microporous silica and performed BET analysis to confirm that they are microporous. If the microporous silica can adsorb CO_2 selectively, an effective CO_2/N_2 separator would be found. Previously we have shown that Ba addition enhanced the adsorption of CO_2 on alumina. We would like to investigate whether the doping of Ba can enhance the adsorption of CO_2 on microporous silica. We impregnated Ba on the microporous silica and performed gas chromatograph (GC) to study the separation of CO_2 from N_2.

It was found that Ba addition in silica did not enhance the adsorption of CO_2. Therefore, alumina is needed for the CO_2 adsorption. However, as far as we know, no microporous aluminosilicates have been demonstrated in the literature. We developed a process by partially coating alumina on microporous silica. It is shown that the modified process can produce microporous aluminosilicates with a pore size about 12 Å.

3. Experimental Procedure

3.1. Precipitated alumina

5.0 N NH_4OH and 0.5 M $Al(NO_3)_3 \cdot 9H_2O$ 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 $70^{\circ}C$.

3.2. 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 Al_2O_3=1:1). Dry @ R.T. for 3-4 days.

3.3. 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$^{\circ}C$ till all the water evaporates. The powder obtained was heat-treated at 400$^{\circ}C$ for 3 hours at the rate of 0.5 $^{\circ}C$/min.

3.4. Microporous Silica

Microporous silica was synthesized following the procedure by Verweij et al.[6, 8] 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$^{\circ}C$/min. The powders were analyzed by a BET surface-area analyzer (Quantachrom NOVA 2210) using N_2 physical adsorption at 77K after out-gassing at 300$^{\circ}C$ for 24 hours. The micro pore volume, surface area, and approximate pore size were calculated by the t-method using Halsey equation.

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.

3.5. 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 N_2 and CO_2 (50/50) was passed through the column to determine the difference in retention time between the two gases.

3.6. Alumina coating on silica

The procedure used is according to our earlier paper.[9] 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.

Table 1
Composition of standard silica polymeric sol ($StSiO_2$)

	TEOS	H_2O (r_w)	C_2H_5OH ($r_{alcohol}$)	HNO_3 (1M) (r_{H+})
mol:		0.094	0.6	0.36	0.008
mol ratio (X/TEOS):	(1)	(6.4)	(3.8)	(0.085)

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4. Results and Discussions

4.1. Alumina

It is shown that the templating method produced alumina with higher surface area after 500°C heat treatment for 4 hours. Mesoporous alumina has surface area ~380 m^2/g compared to precipitated alumina with 240 m^2/g. However, at 500°C heat treatment, it was 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 results of XRD and the BET surface area analyzer are tabulated in Table 2. 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 $xBaO \cdot Al_2O_3$ phase that is more affinitive to CO_2 than N_2. On the other hand, the barium aluminate phase ($Ba_3Al_2O_6$) 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.

Table 2. Phase and Structural Properties of Precipitated and Mesoporous Alumina after Heat Treatment at Elevated Temperatures.

Aluminum oxide	500°C heat treatment				700°C heat treatment			
	SSA (m^2/g)	Pore Size (nm)	Pore volume (cc/g)	Phases	SSA (m^2/g)	Pore Size (nm)	Pore volume (cc/g)	Phases
As synthesized (pH=6)	240	3.0	0.178	Amorphous	161	3.9	0.159	Al_2O_3
As synthesized +8.9mol% Ba	218	3.5	0.189	?	157	4.7	0.185	Al_2O_3
Cured (pH=6)	224	4.3	0.245	Al_2O_3	14.3	6.9	0.025	Al_2O_3
Cured +8.9mol% Ba	164	4.7	0.194	Al_2O_3	104	7.4	0.192	Al_2O_3
Mesoporous	381	6.1	0.577	Al_2O_3	244	9.0	0.548	Al_2O_3
Mesoporous +8.9mol%Ba	354	5.2	0.464	Al_2O_3+ $Ba_3Al_2O_6$ (?)	216	8.1	0.436	Al_2O_3+ $Ba_3Al_2O_6$ (?)

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.[2] who showed that basic metal oxides in alumina could enhance the selectivity of CO_2.

4.2. Silica

The adsorption isotherm of microporous silica is shown in Fig.2. The Langmuir-type isotherm indicates the existence of micropores. According to the t-plot method, as shown in Fig.3, 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 m^2/g, the slope of the line *b* gives the external area of 2.3 m^2/g. Therefore the micropore surface area is 349.4 m^2/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 CO_2
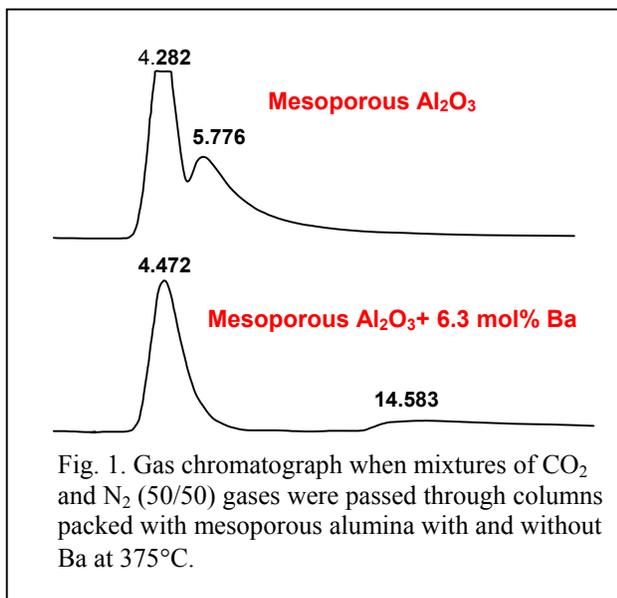
Fig. 1. Gas chromatograph when mixtures of CO_2 and N_2 (50/50) gases were passed through columns packed with mesoporous alumina with and without Ba at 375°C.
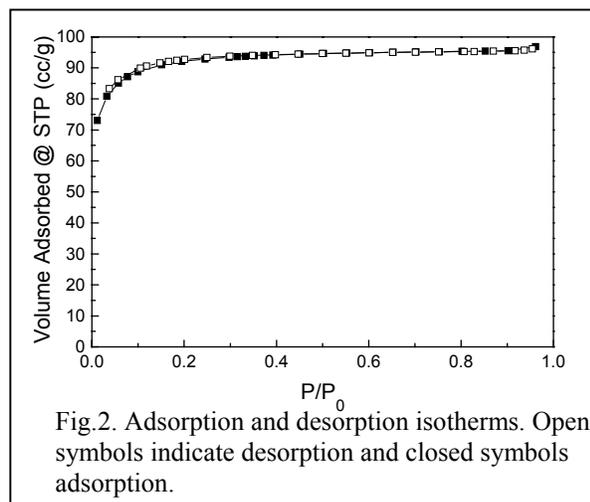
Fig.2. Adsorption and desorption isotherms. Open symbols indicate desorption and closed symbols adsorption.
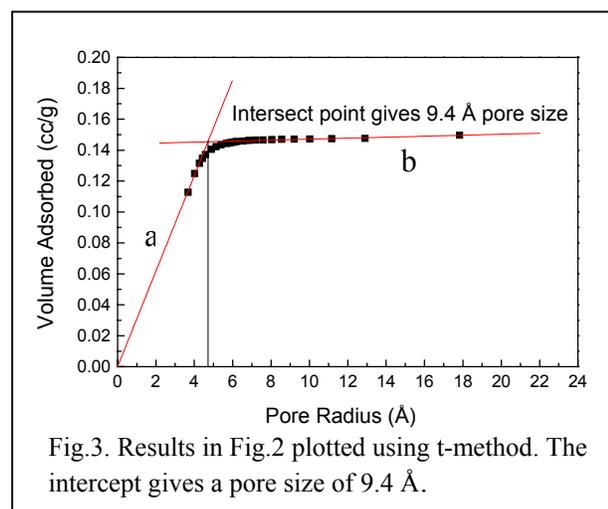
Fig.3. Results in Fig.2 plotted using t-method. The intercept gives a pore size of 9.4 Å.

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 N_2/CO_2 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 CO_2 adsorption in microporous silica. This result is different from that of alumina. Even though Ba is basic and would attract CO_2 molecules, it was speculated that the acidic silica prevented the CO_2 from approaching Ba. We attempted to add alumina to microporous silica since Ba helps the CO_2 adsorption in alumina. However no separation of CO_2 and N_2 in the GC measurement was found, even for alumina amount as high as 50 mol%.

More recently Bal et al.[10] showed that silica doped with alkaline metals can adsorb CO_2 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 CO_2 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 CO_2 and N_2 by the Ba-doped microporous silica. The results are shown in Fig.4. The separation of retention time between CO_2 and N_2 increases with decreasing temperature. The results in Fig.4 are very exciting and indicate that a microporous membrane for separating CO_2 and N_2 is possible.

Fig.4. Gas chromatograph of 50/50 silica/alumina powders doped with 6.3% Ba obtained when mixtures of CO_2 and N_2 (50/50) gases were passed through the column packed with the powders at three temperatures. The numbers mark the retention time (minutes).

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 Fig.5. 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.
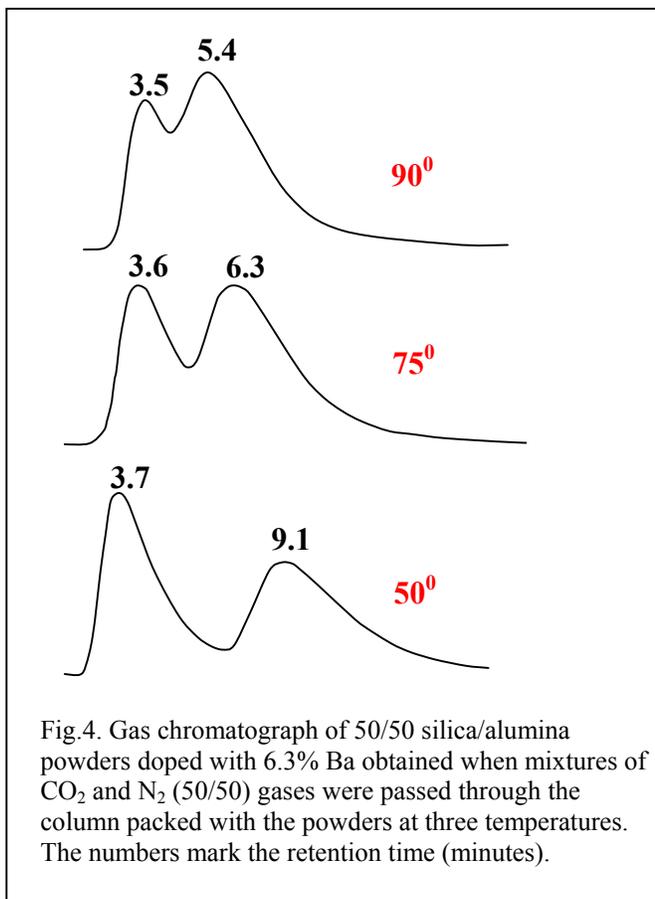
4.3. Alumina-Coated Silica

BET surface analysis of the powder prepared by the coating method is shown in Fig. 6. The curve resembles the isotherm of type I characteristic of microporous solids. However 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 m^2/g. The microporous nature was confirmed by analysis of a different batch of the same powders which yielded a specific surface area of about 350 m^2/g (also shown in Fig.2). Also the presence of the hysteresis confirms that pores larger than micron size are present.
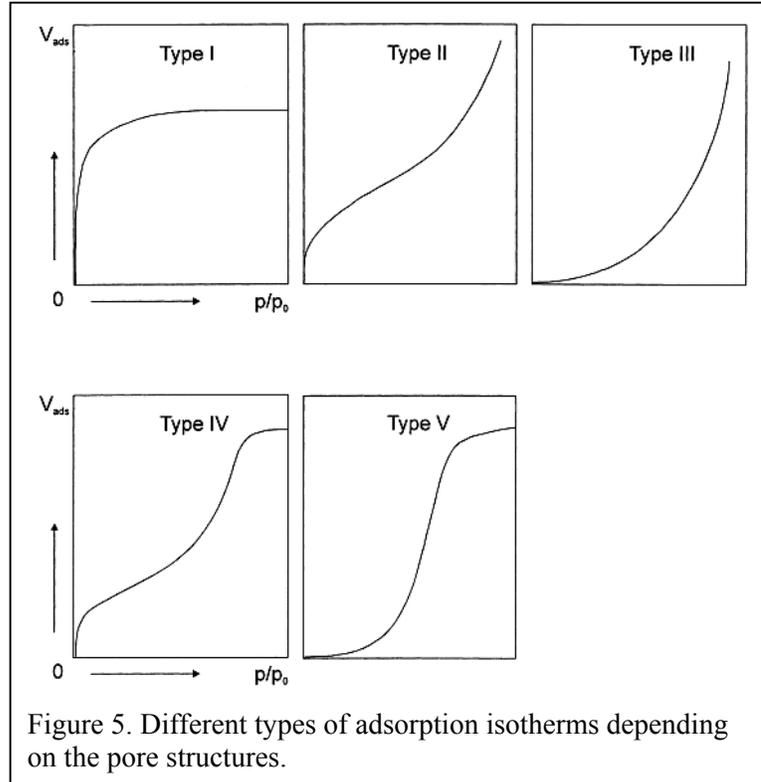
Figure 5. Different types of adsorption isotherms depending on the pore structures.

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 7 for two samples. The two linear regions of the t-plot indicate the presence of micropores about 12 Å. The slope of the line *a* (steep line) gives the total surface area 467 m^2/g, the slope of the line *b* (near horizontal line) gives the external area of 3.1 m^2/g. Therefore the micropore surface area is 463.9 m^2/g. From the second plot, the slope of the line *a*
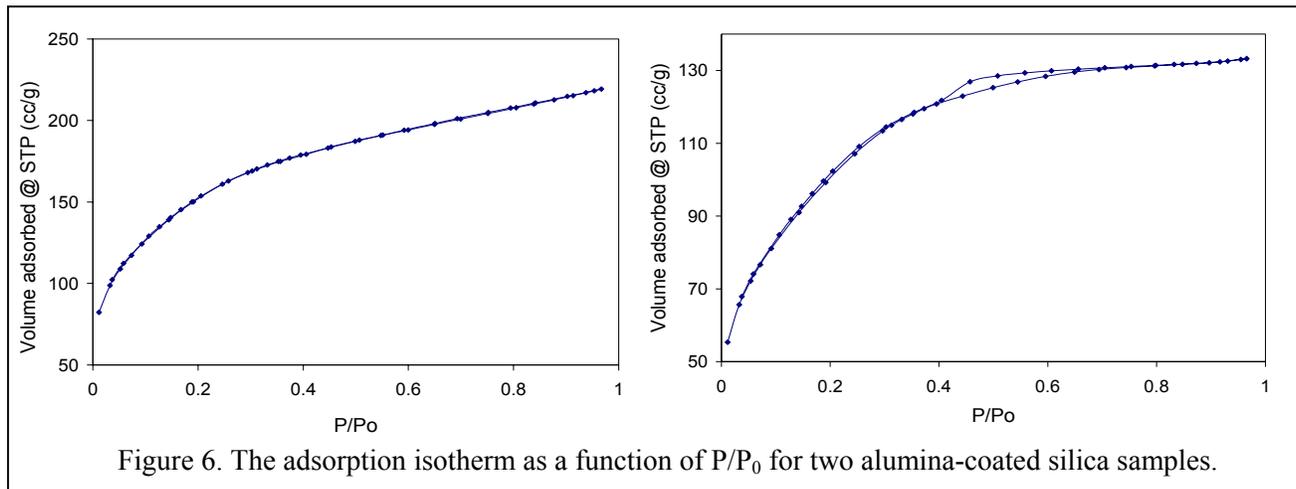
Figure 6. The adsorption isotherm as a function of P/P_0 for two alumina-coated silica samples.

(steep line) gives the total surface area 750 m^2/g, the slope of the line b (near horizontal line) gives the external area of 16 m^2/g. Therefore the micropore surface area is 734 m^2/g.

The intercept of the line b with the volume axis give the micropore volume of 0.2 cc/g and 0.35 cc/g respectively, and the intersect point of lines a and b give the approximate pore size of 12 Å for both plots.

4.4. Zeta Potential

Zeta potential is an important surface property and can be used to predict and control the stability of colloidal suspensions. The pH value at which the zeta potential is zero is defined as the isoelectric point (IEP). The zeta potential and the IEP can be used to check whether the surface of the particles resembles silica or alumina, hence determining the extent of alumina coating over silica.

Zeta-meter 3.0 by Zeta-Meter System was used to measure the zeta potential of the powder prepared by the coating method. It was found that the IEP of the powder was between 3 and 4 which is higher than the IEP of 2-3 for pure silica. This suggests that the silica is coated but not fully coated with alumina. The plot of zeta potential as a function of pH for the alumina-coated silica is compared with that of pure silica in Figure 8.

Fig.7. Average pore size obtained from the t-plots.

5. 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 $xBaO \cdot Al_2O_3$ phase that may be more affinitive to CO_2 than N_2. On the other hand, the barium aluminates phase ($Ba_3Al_2O_6$) in the mesoporous sample does not help the adsorption of CO_2.

Even though mesoporous alumina has a high surface area, the pore size of mesoporous alumina is large, 50-60 Å, and Knudsen diffusion would dominate. It is known that the separation of N_2 and CO_2 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 suitable for CO_2/N_2 separation. They could be a good support material in a membrane design.

Microporous silica would be a better choice than mesoporous alumina because of their small pore size as well as their ease to be processed as crack-free thin films. Furthermore, if a CO_2 adsorbent is added to the microporous silica, the adsorption of CO_2 will block the passage of

Fig.8. Zeta potential of silica and alumina-coated silica as a function of pH.

N_2 and an effective CO_2/N_2 separator will be found. We succeeded in synthesizing microporous silica with pores less than 1 nm. However, microporous silica does not adsorb CO_2, We further showed that by coating alumina on the microporous silica, a microporous aluminosilicate can be produced. The silica-alumina (1:1) powder impregnated with 6.3% BaO showed separation of CO_2 and N_2. The impregnated powder was found to exhibit an adsorption isotherm characteristic of microporous solids. We conclude that there exists a microporous material that can separate CO_2 from N_2 and the idea of a microporous membrane for CO_2/N_2 separation will work.

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