Original Article

Effect of pore size and surface chemistry of porous silica on CO_2 adsorption

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Abstract

In the present study, porous silica synthesized using sodium silicate as a low-cost raw material was selected as a CO_2 sorbent. The effects of pore size and amount of silanol content on CO_2 adsorption capacity were investigated. The physical properties and surface chemistry (silanol content) of the porous silica products were characterized by means of N_2-physisorption, Fourier transform infrared spectroscopy and thermogravimetric analysis technique. The pore size of the porous silica materials did not affect the equilibrium CO_2 capacity; however the porous silica with large pore size could enhance the diffusion of CO_2. The amount of silanol content was found to be a key factor for the CO_2 adsorption capacity. A greater CO_2 adsorption capacity would be obtained with an increase of the silanol concentration on the surface of the porous silica materials.

Keywords: porous silica, sodium silicate, pore size, silanol content, CO_2 adsorption

1. Introduction

The problem of global warming caused by CO_2 emission, which is the main part of greenhouse gases, has raised serious concerns. The combustion of fossil fuels is one of the major sources of CO_2 emission to the atmosphere. However, due to the fact that these fossil fuels are essential as they supply more than 70% of the world's energy consumption. It is therefore important to find novel technologies that can allow us to utilize fossil fuels with less CO_2 emission. Generally, there are three steps for CO_2 management involving separation, transportation, and sequestration (Olajire, 2010). The key point of the CO_2 management is the separation of CO_2 from the flue gas because it contributes 75% to the overall costs.

Various technologies for CO_2 capture, such as absorption, adsorption, cryogenic and membrane technologies, have been proposed and investigated (MacDowell *et al.*, 2010). Among these techniques, adsorption is one of the most promising approaches as it can reduce the cost associated with the capture step. Several porous materials such as zeolite, alumina, activated carbon, and porous silica, have been considered for low temperature CO_2 separation. As the use of low-cost porous material can significantly reduce the cost of CO_2 management, porous silica is then becoming very competitive because of its economical potential and availability as it can be produced from the renewable resource such as rice husk ash.

Recent research work has been devoted for the development of the synthesis of porous silica materials of varying sizes in a controllable manner (Witoon *et al.*, 2011), among the different routes are sol-gel process, precipitation, plasma, flame spray pyrolysis, and others. Sol-gel process, which is consisted of hydrolysis and polycondensation reactions of a metal salt, is an effective method that is preferred

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to control the pore structure and surface properties of porous silica. The pore size and surface chemistry of porous silica can be controlled by adjusting the pH of the mixture, aging temperature, precursor concentration, catalysts and calcination temperature (Brinker and Scherer, 1990).

Due to the fact that the pore size and surface chemistry (silanol groups) of porous silica mainly affect the mass transfer and surface reactivity, it is of great interest to investigate the effect of these parameters on the CO_2 adsorption capacity. In this study, the porous silica materials were synthesized using sodium silicate as a low-cost silica source. The pore size of the porous silica materials was varied between 2 and 10 nm by varying the pH values of the gel mixture. The amount of silanol content was controlled by varying the calcination temperature. The pore size and the amount of silanol content of porous silica materials were characterized by using N_2-physisorption, Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA) technique. The CO_2 adsorption capacity of each sample was measured by gravimetric method at different adsorption temperatures.

2. Experimental

2.1 Synthesis of porous silica materials

Porous silica materials were prepared by the sol-gel method based on the hydrolysis and condensation reaction. In a typical synthesis process, 4.5 g of sodium silicate ($Na_2Si_3O_7$: 27 wt.% SiO_2, 4 wt.% NaOH) was introduced into 70 mL of deionized water under stirring for 5 min. The pH of the solution was adjusted to 2, 3, and 4 by using 2 M hydrochloric acid. The solution was stirred continuously at 40°C for 24 h, and then the obtained solution was aged in the Teflon-lined autoclave at 100°C for 24 h. The obtained solid product was consecutively filtered, washed several times with distilled water, dried at 105°C for 12 h, and calcined in air at either 200 or 500°C for 4 h at a heating rate of 1°C/min to adjust the amount of silanol content on the surface of porous silica materials.

2.2 Characterization of porous silica

Pore size, BET surface area and pore volume were determined by using N_2-sorption technique at –196°C (Quantachrome Autosorb 1C instrument). Prior to N_2-sorption measurements, the samples were degassed at 200°C for 12 h. The BET surface area was estimated using relative pressure in the range of 0.05 to 0.30. The pore size distribution was calculated from the adsorption branch by using Barrett–Joyner–Halenda (BJH) method. The total pore volume was obtained from the adsorption data at P/P_0 of 0.99. The functional groups on the surface of porous silica were examined by using Fourier transform infrared spectroscopy (Perkin Elmer System 2000 using KBr pellet). The amount of silanol groups on the surface of porous silica was investigated by

using simultaneous DTA-TGA analyzer (TA instrument, SDT2960 simultaneous DTA-TGA Universal 2000) in nitrogen at a heating rate of 10°C/min.

2.3 CO_2 adsorption/desorption measurements

The CO_2 adsorption/desorption measurements were performed for all silica xerogel products by using a SDT2960 simultaneous DTA-TGA Universal 2000. A 20 mg sample was loaded into an alumina sample pan. Prior to the CO_2 adsorption/desorption experiment, the sample was first activated by heating from room temperature to 110°C in Ar atmosphere (99.99%) at a heating rate of 10°C/min in order to remove preadsorbed CO_2 and H_2O; then the sample was cooled down to a given temperature. Subsequently, pure CO_2 (99.999%) was introduced into the system at a flow rate of 40 mL/min; during this process the change in the sample weight was recorded. The CO_2 adsorption runs were conducted at three different temperatures including 40, 60, and 80°C. When the sample weight was constant, CO_2 was then desorbed by heating to the temperature of 110°C in a flow of Ar (99.99%) at a heating rate of 10°C/min.

3. Results and Discussion

The N_2-sorption isotherm of porous silica products is shown in Figure 1. At pH 2, the isotherm is Type I, indicating that the silica product is mainly composed of microporous structures. The characteristics of microporous–mesoporous materials confirmed by the Type I–IV composite isotherms are found for the product prepared at pH 3. With further increasing the pH value (pH 4), Type IV isotherm is obtained. The pore size distribution of all silica products is depicted in Figure 2. It can be clearly seen that the pore size distribution of silica products displayed multi–peaks at two different length scales: one in the range of micropores (<2 nm) and
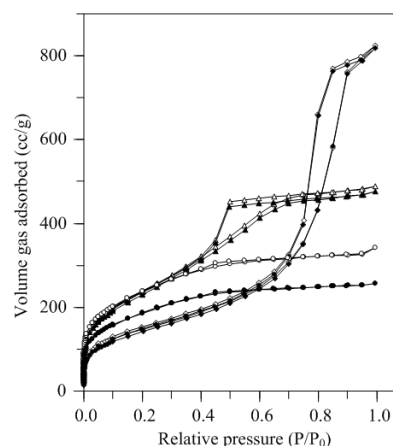

Figure 1. N_2-sorption isotherms of porous silica products synthesized at pH values of 2 (circle), 3 (triangle) and 4 (diamond), and calcined at 200°C (open symbol) and 500°C (filled symbol).
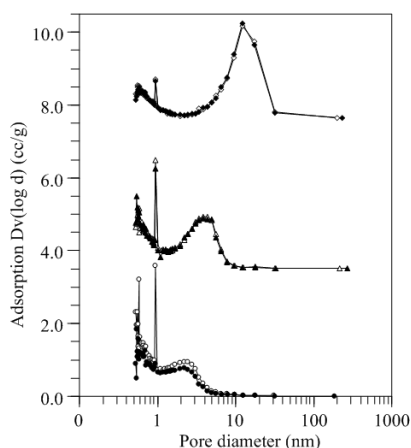
Figure 2. Pore size distribution of porous silica products synthesized at pH values of 2 (circle), 3 (triangle) and 4 (diamond), and calcined at 200 °C (open symbol) and 500 °C (filled symbol).

one in the range of mesopores (2–50 nm). With increasing pH values, the amount of pores smaller than 1 nm is significantly decreased while the pore larger than 1 nm is shifted towards larger pore sizes. Comparing the results for a same pH value of the mixture, the amount of pores smaller than 3 nm of silica product prepared at pH 2 is dramatically decreased when the calcination temperature increased from 200 to 500°C. However, the calcination temperature did not significantly affect the pore structure of silica products prepared at the higher pH values.

The physical properties including, average pore size, BET surface area and pore volume of all porous silica products are given in Table 1. At a low calcination temperature (200°C), the average pore size of porous silica products was increased from 2.6, 3.6 to 10.0 nm when the pH of the gel mixture increased from 2, 3 to 4, respectively. The results can be explained as follows. At pH 2, the hydrolysis rate is fast while the condensation rate of silanol species is low, resulting in the formation of weakly branched silica oligomers, which tend to be interwoven at the gel point (Brinker and

Scherer, 1990). The compliant structure can rather freely shrink in response to solvent removal because a pressure gradient from liquid–vapor meniscus is created. With a further increase of the pH values, a structure of highly branched silica oligomers caused by an increase of the condensation rate of silanol species is obtained. This structure can stop the gel shrinkage due to the stiffness of the impinging clusters. As a result, porous silica products with larger pore size are obtained at higher pH values.

The surface chemistry of the porous silica products was investigated using FTIR technique and the results are shown in Figure 3. The strong band around 1,100 cm^{-1} and small bands around 780 and 460 cm^{-1} represent the characteristics of the Si-O-Si groups. Regarding the presence of OH groups, their vibration bands can be located at different frequencies, depending on the bonding configuration. Accordingly, the shoulder at 950 cm^{-1} indicates the existence of Si-OH asymmetric stretching band (Karbowiak et al., 2010), whereas the broad band between 3,800 and 3,050 cm^{-1} is attributed to the stretching of silanol associated with surface silanols including isolated silanol, vicinal, and geminol groups (Aguiar et al., 2009). It can be seen that intensity of
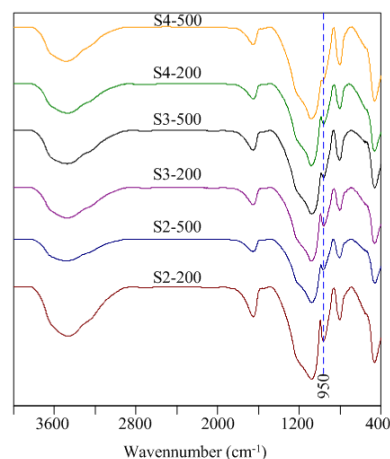

Figure 3. FTIR spectra of all porous silica products.

Table 1. Physical properties of porous silica products synthesized at different conditions and silanol group content determined by TGA techniques.

Samples[a] (m^2/g)	BET surface area diameter (nm)	Average pore (cm^3/g)	Pore volume (%)	Second mass loss (mmol/g)	OH group content
S2-200	830	2.6	0.53	5.22	5.80
S2-500	654	2.3	0.40	2.87	3.19
S3-200	863	3.6	0.75	4.69	5.21
S3-500	843	3.5	0.74	3.89	4.32
S4-200	510	10.0	1.27	2.86	3.18
S4-500	509	9.9	1.26	2.08	2.31

[a] Silica xerogel products were designated as SX-Y where X is the pH of mixture and Y is the calcination temperature.
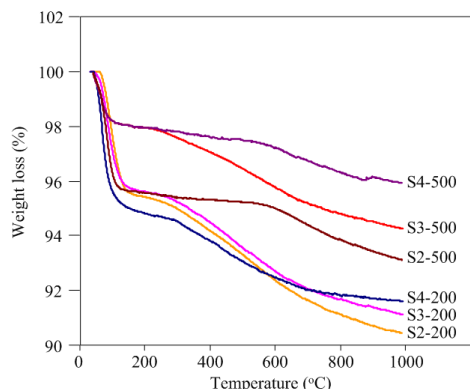
Figure 4. TGA patterns of all porous silica products.

those bands related to the existence of surface silanol is decreased with increasing pH value and calcination temperature.

The TG analysis is performed to determine the quantitative information of the silanol contents on the surface of the porous silica products. TGA patterns of the porous silica products are depicted in Figure 4. It is found that there are two distinct mass loss steps in the TGA curves of all samples. The abrupt change of the first step at temperatures below 120°C is most probably due to the removal of physical adsorbed water from the silica surface. The gradual change of the second step is corresponding to slow condensation of germinals, vicinals, and isolated silanols (Ek *et al.*, 2001). The total silanol group content in the silica surface is determined as the hydroxyl group content and is calculated by using the entire second weight loss (ranging from 200°C to the end point of the measurement at 1,000°C).

The hydroxyl group content (Table 1), estimated by assuming that the condensation occurred based on the reaction of two hydroxyl groups on the silica surface, can be calculated as follows (Kim *et al.*, 2009):

$$n_{OH}(SiO_2) = \frac{2(WL(T_0) - WL(T_{final}))}{100 M_{H_2O}} \qquad (1)$$

where $WL(T_0)$ and $WL(T_{final})$ are the weights of the silica (wt%) at temperature of 200 C and 1,000 °C, respectively, is the molecular weight of water. At a low calcination temperature (200°C), the amount of silanol content significantly decreases when the pH value increases from 2 to 4 due to the increase of silanol-silanol condensation rate. A significant reduction in the silanol surface is also found when the calcination temperature increases from 200 to 500°C, especially that of Sample S2-500. This can be explained by the fact that the pore structure of silica products prepared at pH 2 mainly composed of micropores, which can easily collapse at higher calcination temperatures (Iler, 1979; Brinker and Scherer, 1990). Based on the results of N_2-sorption and TGA analysis, the amount of silanol content of Sample S2-500 and S4-200 is almost the same but their average pore size is different (2.3 and 10.0 nm). Therefore these samples are employed to in-

vestigate the effect of pore size on CO_2 adsorption capacity while the effect of silanol content on CO_2 adsorption capacity is studied by using the porous silica products having the equivalent pore size, but the amount of silanol content is different.

As shown in Figure 5a, the CO_2 adsorption capacities of Sample S2-500 and S4-200 are almost the same at all adsorption temperatures, indicating that the CO_2 adsorption capacities are not affected by the pore size. However, as seen in Figure 5b, the CO_2 adsorption over Sample S4-200 is much faster than over Sample S2-500. The CO_2 adsorption capacity of Sample S4-200 reaches ca. 90% of its equilibrium capacity within 55 min of CO_2 exposure, while it takes 75 min for Sample S2-500. It is demonstrated that the porous silica with large pore sizes can enhance the diffusion of CO_2.

Figure 6 shows the effect of silanol content on CO_2 adsorption at different adsorption temperatures. It can be clearly seen that the CO_2 adsorption capacity is increased with increasing silanol content, indicating that the key factor of CO_2 adsorption on porous silica materials is the number of silanol groups. The porous silica products with the highest silanol group content (S2-200) give the highest CO_2 adsorption capacity (48.9 mg CO_2/g adsorbent). However, differences between the CO_2 adsorption capacities of the silica products at high adsorption temperature are found to be insignificant because the interaction between CO_2 and silanol groups is van der Waals' force, which does not favor the adsorption at higher temperatures.
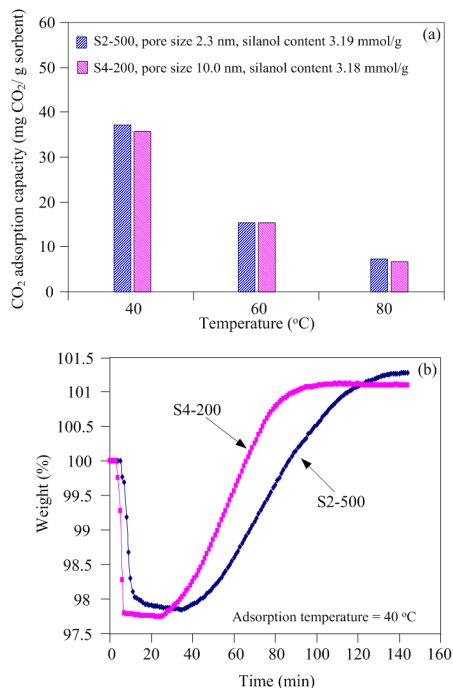

Figure 5. CO_2 adsorption capacity at different adsorption temperature of Sample S2-500 and S4-200 (a), and comparison of dynamic CO_2 adsorption at 40°C of Sample S2-500 and S4-200 (b).
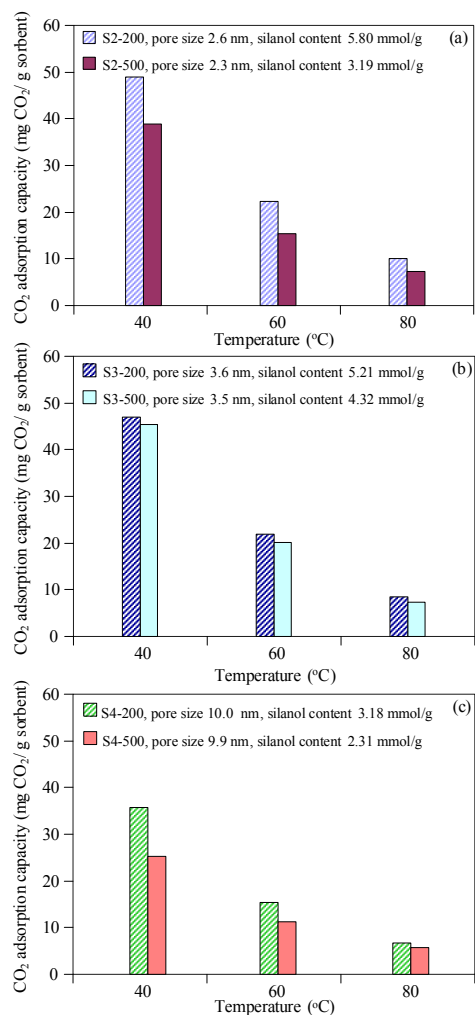
Figure 6. Comparison of CO_2 adsorption capacity at different adsorption temperature of Sample S2-200 and S2-500 (a), S3-200 and S3-500 (b), and S4-200 and S4-500 (c).

4. Conclusion

The pore size and silanol content of porous silica products could be tuned in the range of 2.3-10 nm and 2.31-5.80 mmol/g, respectively, by varying the pH of the mixture and the calcination temperature. The pore size of the porous silica materials did not affect the CO_2 adsorption capacity, however the porous silica with large pore sizes could enhance the diffusion rate of CO_2. The CO_2 adsorption capacity increased with increasing silanol content. It was demonstrated that the silanol concentration on the surface of the porous silica materials was a key factor for the CO_2 adsorption.

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