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The effect of surfactants on carbon xerogel structure and CO_2 capture

Shasha Wang[a,b,c], Yuelong Xu[b,c], Meifang Yan[b,c], Lihui Zhang[b,c], Zhenfa Liu[b,c,*]

[a] School of Chemical Engineering, Hebei University of Technology, Tianjin 300130, People's Republic of China
[b] Institute of Energy Resources, Hebei Academy of Sciences, Shijiazhuang 050081, Hebei Province, People's Republic of China
[c] Hebei Engineer Research Center for Water Saving in Industry, Shijiazhuang 050081, Hebei Province, People's Republic of China

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ABSTRACT

Porous carbon xerogels were successfully fabricated by carbonization of resorcinol-formaldehyde-phloroglucinol gels in the presence of surfactants. The effect of non-ionic, cationic, anionic and zwitterionic surfactants on the porous structure of carbon xerogels was investigated. Micropore structural carbon xerogels were obtained when a cationic surfactant was used. The result of surface tension test showed the non-ionic surfactant Tween 60 gave the lowest surface tension. Thermal conductivity experiments revealed the carbon xerogels in this work possessed low thermal conductivity and are suitable as thermal insulation materials. The pore size directly determined the thermal conductivity of carbon xerogels, and the thermal conductivity decreased with pore size. Among the obtained samples, the one using hexamethylenetetramine (HTM) exhibited the highest CO_2 adsorption capacity (2.89 mmol g^{-1}) and adsorption selectivity as a result of the high microporosity (88.0%). Therefore, HTM-CA was identified as a promising material for CO_2 adsorption.

1. Introduction

Carbon xerogels (CA), with extremely high porosity and highly cross-linked three-dimensional networks, are relatively new materials. CAs have unique features, including low density, continuous porosity, high specific surface area, good thermal conductivity and good electrical conductivity. Their desirable properties originate from their characteristic pore structure, allowing them to be applied in a variety of fields, such as hydrogen fuel storage [1], catalyst support [2], capacitive deionization [3], and capacitors [4–6].

The structure of CAs, i.e. surface area and pore size distribution, can be modified using different synthesis parameters, including the type of the precursor (reactants, solvent, and catalyst), the selection of the synthesis route, the curing and drying methods as well as the pyrolysis conditions [7]. The properties of CAs can be enhanced by post-processing techniques, such as activation processes; however, the composition of the organic precursors significantly influences the carbon material structure [8–9]. The use of additives, such as surfactants, can effectively improve the composition of the organic precursor and the final structure of CAs. Matos et al. studied the effect of the type and concentration of surfactants on pore structure of CAs [10]. The authors found that cationic surfactants can increase the pore size. However, there was no obvious change in the pore size distribution when low concentrations of non-ionic surfactants (0.5–3 wt%) were used. He and co-workers used non-ionic surfactant F127 (PEO 106–PPO 70–PEO 106) to enhance the mesoporosity of CAs, and the ratio of the mesopore volume to the total pore volume (mesoporosity) reached 86% when CAs were prepared with 0.6 wt% F127 [11].

CAs are advantageous materials for the adsorption of CO_2. The large adsorption capacity, high chemical stability, ease of surface decoration, and low cost of CAs make them attractive materials for this application [12–15]. Sevilla et al. used polysaccharides and biomass as raw materials to prepare a series of porous carbon materials by hydrothermal reaction and KOH activation [16]. Under different activation conditions, the specific surface area can reach 2850 $m^2\,g^{-1}$, and the static adsorption capacity of CO_2 can reach 4.8 mmol g^{-1} at conditions of 25 °C and 1 bar. They found that the high adsorption capacity was mainly related to the rich microporous structure (pore size < 1 nm), and the specific surface area is a secondary factor. Fan et al. used chitosan as a raw material and K_2CO_3 as an activator to prepare a series of carbonaceous adsorbents [17]. The structural parameters and surface functional groups of these activated carbon adsorbents could be controlled by changing the ratio of K_2CO_3 to chitosan and the activation temperature. There is a direct relationship between degree of micropore development and CO_2 adsorption performance. In addition, the amount of adsorption did not decrease after 5 cycles of adsorption and desorption, indicating that the activated carbon had excellent cycle stability.

In this work, a series of porous CAs were prepared by sol-gel process

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[*] Corresponding author at: Institute of Energy Resources, Hebei Academy of Sciences, Shijiazhuang 050081, Hebei Province, People's Republic of China.
E-mail address: lzf63@sohu.com (Z. Liu).

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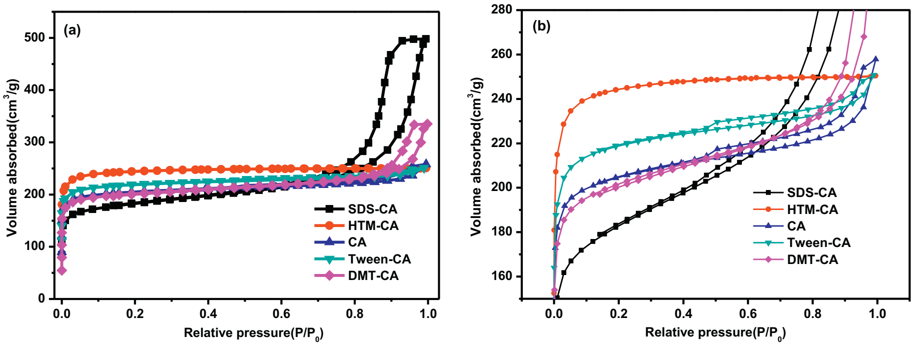

Fig. 1. (a) Nitrogen adsorption-desorption isotherms of carbon xerogels, and (b) a partial enlargement of 150–280 g/cm^3 volume absorbed.

of resorcinol, formaldehyde, and phloroglucinol in the presence of cationic (HTM), neutral (Tween), SDS (anionic) or DMT (zwitterionic) surfactants, followed by drying and pyrolysis. Further, the effect of surfactant on the structure and capture performance of CO_2 was investigated.

2. Experimental

2.1. Synthesis of carbon xerogels

Carbon xerogels (CA) were prepared by a one-pot synthesis method. Resorcinol (R, Aladdin, Shanghai), formaldehyde (F, 36.5% in water, Aladdin, Shanghai), phloroglucinol (P, Aladdin, Shanghai), deionized water (W, Shanghai) and surfactants (S, Aladdin, Shanghai) were dissolved in distilled water without any catalyst. The molar ratio of P/R/F/S/ DI water was 5:35:80:1:150, and the overall concentration of the initial solution was 45% (*w*/w). To ensure a homogeneous mixture, Resorcinol (R), formaldehyde (F), phloroglucinol (P), deionized water (W) and surfactants (S) were treated by ultrasonication for 30 min at room temperature and then transferred to a glass vial (40 mL). The vial was sealed and placed in a water bath at 50 °C for 72 h, followed by 80 °C for 24 h to cure and obtain the wet gels. Next, the wet gels underwent a water-acetone exchange every 24 h for 3 consecutive days. Then, the gels were dried at atmospheric pressure for 24 h. The resulting organic xerogels were carbonized under N_2 flow (100 cm^3/min) in a tube furnace, using a heating rate of 2 °C/min up to 900 °C for 3 h. The anionic, zwitterionic, cationic, and non-ionic surfactants used are as follows: sodium dodecyl sulfate (SDS, Aladdin, Shanghai), dimethylthetin (DMT, Aladdin, Shanghai), hexamethylenetetramine (HTM, Aladdin, Shanghai), and Tween 60 (Tween, Aladdin, Shanghai), respectively. The obtained carbon xerogels were named SDS-CA, DMT-CA, HTM-CA, and Tween-CA, respectively. Pure carbon xerogel without any surfactant is referred to as CA.

2.2. Characterization

Textural characterization was performed by N_2 adsorption–desorption using a Micromeritics ASAP 2420 device. Samples were degassed at 90 °C for 1 h and at 250 °C for 6 h. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the surface area (S_{BET}). The mesopore size distribution was analyzed from the desorption branches of the isotherms via Barrett–Johner–Halendar (BJH) theory. The average pore diameter (D) was measured for all pores. The total pore volume (V_{total}) was estimated from the amount adsorbed at a relative pressure of 0.988 bar. The DFT method [18] was used to determine the micropore volume (V_{micro}). This method based on density functional theory (DFT) represent the more recent approach to the calculation of pore volume and pore size distribution (particularly for micropores) from adsorption isotherm. The approach consists of the construction of a grand potential functional of the average local density and of a minimization of this with respect to local density to obtain equilibrium density profile and thermodynamic properties. The proposed approaches differ according to the smoothed density approximation term used [19, 20]. The mesopore volume (V_{meso}) was calculated by the difference of V_{total} and V_{micro}, and micropores porosity (%) was the ratio of V_{micro} to V_{total}. The surface morphology of the carbon xerogel samples was examined by scanning electron microscopy (SEM; Tescan Maia3 MHL). During the gelation process, the change in surface tension of the solution over time was measured by a surface tensometer (Biolin Sigma 701). The gelation time was defined as the time at which the solution no longer flowed in a tube held at a 45° angle at given gelation temperature [21]. Differential scanning calorimeter (DSC) and thermogravimetric (TGA) analyses were conducted at a heating rate of 10 °C/min in N_2 on a SDT Q600 (TA). The CO_2 and N_2 adsorption isotherms were measured using a Micromeritics ASAP 2420 device at 25 °C. Prior to each adsorption experiment, the sample was degassed for 3 h at 300 °C to remove the guest molecules from the pores.

3. Results and discussion

The pore structure of the CAs was investigated by low-temperature N_2 adsorption measurements. The N_2 adsorption isotherms and BJH pore size distribution curves are shown in Fig. 1 and Fig. 2, respectively. The porosity data obtained from the isotherms are listed in Table 1. The adsorption capacity of HTM-CA increased rapidly at lower relative pressure and saturated at a certain relative pressure (Fig.1), the pore size distributions (Fig.2) over a broader range including wider micropores and narrow mesopores ($<$ ~2.5 nm). The isotherm of HTM-CA belongs to the I(b)-type [22]. This suggests the existence of a large number of micropores, and the micropores porosity of HTM-CA was the highest (88.0%, Table 1). Each of the other carbon xerogels synthesized show type IV(a) isotherms [22]. The hysteresis loops of SDS-CA and DMT-CA belong to H1-type, indicating that the pore size distribution was narrow and mainly classified as mesoporous in size Thus, the microporosity was low for these materials, as shown in Table 1. The hysteresis loops of CA and Tween-CA are H4-type, and there was no obvious saturation adsorption plateau, indicating CA and Tween-CA consisted of complex structures of micropores and mesopores.

CAs fabricated with different surfactants show different pore sizes, as shown in the size distributions curves (Fig. 2). When SDS was used, hierarchical porous CAs were obtained, with pore sizes around 1.6 nm and 17 nm (Fig. 2 (a)) and average pore size (D) of 10.60 nm. Anionic surfactant SDS tends to form micelles in water [23]. After micelle formation, a cluster with bigger core was obtained due to a strong electrostatic repulsion between the SDS anion and the resorcinol/phloroglucinol anion. These large cores become mesopores after carbonized. In contrast, due to electrostatic attraction of the cations from HTM and the anions from resorcinol/phloroglucinol, smaller cores were obtained. After carbonization, these small cores become micropores. Moreover, the surfactants decomposed during carbonization, leaving