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# Pith based spherical activated carbon for $CO_2$ removal from flue gases

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ABSTRACT

Serials of pitch based spherical activated carbons (PSACs) were prepared and used as adsorbent for $CO_2$ adsorption from flue gases. The results indicate that the ultrafine micropores ($<1$ nm) are effective pores for $CO_2$ adsorption, and the equilibrium adsorption capacity of $CO_2$ has a linear relationship with the specific surface area of ultrafine micropores ($S_{<1\ \mathrm{nm}}$). The adsorption capacity of $CO_2$ can obtain 1.12 mmol/g at 15 kPa and 30 °C on one of PSAC sample due to its high $S_{<1\ \mathrm{nm}}$ (845 $m^2/g$). Because the molecular $CO_2$ can be polarized into polar molecules and has four kinds of adsorption configuration, the adsorption selectivities of $CO_2$ vs. $N_2$ and $O_2$ are 86.99% and 69.91%, respectively. When the combined Electric Swing Adsorption and Vacuum Swing Adsorption were applied for $CO_2$ desorption, about 100% desorption efficiency can be obtained, the desorption rate is twice of that with Temperature Swing Adsorption (TSA) and the energy consumption is only 69% of that with TSA.

## 1. Introduction

In recent years, climate warming has become a major global environmental issue of common concerns, and the rise of global surface temperature is mainly attributed to the increase in atmospheric levels of $CO_2$ (Rochelle, 2009; An et al., 2010; Hook, 1997). Undoubtedly, fossil fuel energy plays a crucial role on $CO_2$ emission, and the flue gases produced from coal-fired plants are thought to be the major cause of $CO_2$ emission (Alie et al., 2005; Ciferno et al., 2009; Yeh et al., 2001). It is noteworthy that, after $SO_2$ removal, the flue gases consist of 10–15 vol% $CO_2$, the main gases are $N_2$, steam, $O_2$, $SO_3$ and $NO_x$. Therefore, $CO_2$ capture from flue gases is challenging and expected to be a mid-term solution for the use of fossil fuel energy technologies against environmental calamities.

Current large-scale separation equipment used to capture $CO_2$ from fuel combustion is based on liquid amine absorption techniques (Romeo et al., 2008; Yamaguchi et al., 2007; Chaffee et al., 2007), while the absorption process still has drawbacks. The most serious problems are related to the corrosive property of liquid amine, the amine waste during the operation and the high energy consumption in the regeneration process. Therefore, many researchers paid much attention to develop alternative procedure for $CO_2$ capture explored in coal-fired plants, such as cryogenic technologies, adsorption (Ishibashi et al., 1996) and membrane based techniques (Yamaguchi et al., 2007).

Owing to the relatively low energy consumption, adsorption has been considered to be a promising technique for $CO_2$ capture (Chaffee et al., 2007; Ishibashi et al., 1996; Na et al., 2001). Then various $CO_2$ adsorbents have been extensively developed, including porous carbons (Arenillas et al., 2005; Siriwardane et al., 2001; Radosz et al., 2008; Pevida et al., 2008), metal organic framework materials (Yazaydın et al., 2009; Millward and Yaghi, 2005; An et al., 2010), zeolite molecular sieves (Yue et al., 2008; Konduru et al., 2007), lithium zirconate (Fernandez et al., 2006), silicon based mesoporous materials (Kim et al., 2008; Ma et al., 2009; Hu and Liu, 2010) and other metal oxides materials (Yang and Lin, 2006). In the meantime, the Pressure Swing Adsorption (PSA), Temperature Swing Adsorption (TSA) and the PSA–TSA combined process were intensively researched (Ho et al., 2008; Chou and Chen, 2004; Xiao et al., 2008; Merel et al., 2006; Siriwardane and Biegler, 2005).

Above mentioned adsorbents are believed to have their own advantages for $CO_2$ adsorption due to their special pore structures or surface chemistry. If the gases compositions and practical operating conditions of flue gases are concerned, we should give a new consideration to the adsorbents. Generally, the adsorbents by chemisorption (i.e., zeolite molecular sieves) have high adsorption selectivity for $CO_2$ than that of adsorbents by physisorption. However, if the adsorbents by chemisorption were applied for $CO_2$ capture from flue gases, the molecular polarity of $H_2O$ and/or $SO_3$ (or $NO_x$) will have a significant effect on the $CO_2$ adsorption capacity and cycle efficiency. Because the adsorbents have a higher adsorption selectivity for polar molecules than that of $CO_2$. Additionally, the effect of $O_2$ on the chemical stability of the adsorbents by loading polyethyleneimine (PEI) should be taken into account.

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Among the adsorbents by physisorption, porous carbons have their particular advantages for $CO_2$ adsorption due to their high specific surface area, including granular activated carbon, monolithic activated carbon, spherical activated carbon and high surface area activated carbon (Arenillas et al., 2005; Siriwardane et al., 2001; Radosz et al., 2008; Pevida et al., 2008). Owing to the low concentration of $CO_2$ in flue gases, besides the specific surface area, the pore size characters and surface chemistry play crucial roles on the adsorption capacity and adsorption selectivity. Additionally, to satisfy the requirements for engineering applications in flue gases, other physical properties of porous carbons must be considered. For example, a low pressure drop and a large loading density are required for porous carbons in the adsorption process; the porous carbon must have a high density and a high mechanical strength, guaranteeing that it cannot be powdered, blown away or pumped away in the adsorption and/or desorption process. In a word, it is required for porous carbon used as adsorbent for $CO_2$ capture from flue gases, not only a good comprehensive adsorption performance, but also a good comprehensive physical properties.

As a kind of adsorption material for $CO_2$ capture from flue gases, spherical activated carbon shows many charming characters due to the high microporosity, suitable ball size, high mechanical strength, high loading density and high electric conductivity. In our present works, serials of pitch based spherical activated carbons (PSACs) were prepared and the adsorption/desorption performance were investigated for $CO_2$ capture from flue gases.

## 2. Experimental

### 2.1. Preparation of PSACs

Pitch sphere was prepared from coal tar pitch through the emulsion method, followed by air stabilization and carbonization (Liu et al., 1999; Liu et al., 2008a, 2008b; Wang et al., 2009), and then the synthesized pitch sphere was activated with $CO_2$ or $H_2O$ activation agent. When the synthesized pitch sphere was activated with $CO_2$ at 900 °C, the product was labeled as PSAC*x*, in which *x* denotes the activation time. When it was activated with $H_2O$, the product was labeled as PSAC-*x*-*y*, in which *x*, *y* denote the activation temperature and activation time, respectively. For example, PSAC-850-2.5 represents that the synthesized pitch sphere was activated with $H_2O$ at 850 °C for 2.5 h.

### 2.2. Characterization of PSACs

Nitrogen adsorption/desorption isotherms was measured at −196 °C with a Micromeritcs ASAP 2020 analyzer. Before the measurement, the sample was degassed in vacuum at 200 °C for 8 h. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas using adsorption data in a relative pressure $P/P_0$ range from 0.04 to 0.2. The total pore volume was estimated from the adsorbed amount at $P/P_0=0.985$. The pore size distribution was derived from desorption branch of isotherms using the density functional theory (DFT) model. The morphology of PSAC was observed by scanning electron microscopy (SEM) using JEOL JSM-6360LV microscope.

### 2.3. $CO_2$ adsorption/desorption measurements

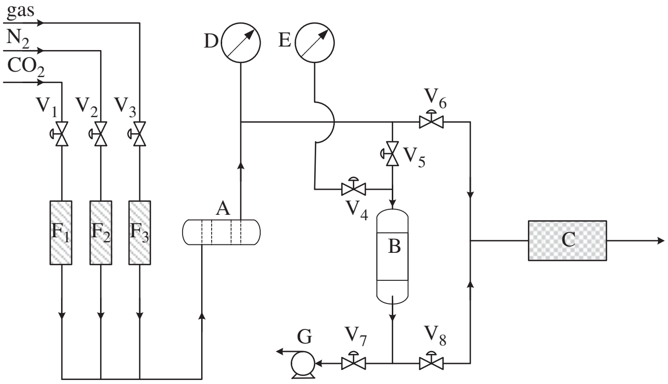

**Fig. 1.** Schematic diagram of the $CO_2$ adsorption/desorption setup.

Fig. 1 shows the schematic diagram of $CO_2$ adsorption/desorption test system. The concentration of $CO_2$ was detected by gas chromatography. The adsorption process was operated according to the following procedure: simulated flow gases ($CO_2+N_2$ (or $O_2$)) were mixed until $CO_2$ reached the expected concentration at the outlet of the column. After that, the flow gases were switched to adsorption reactor, and then the breakthrough curve of $CO_2$ could be obtained. Adsorption isotherms of $CO_2$ were performed in a magnetic suspension microbalance (Rubotherm, Germany) operated in a closed system. The accuracy of the microbalance is about $\pm 2\times10^{-8}$ kg, and Lucas Schaevitz pressure transducers was used with an accuracy $\pm 2.5$ kPa. The electric swing adsorption (ESA) was performed as reported by Carlos (Carlos and Alĺrio, 2008; Carlos et al., 2009).

## 3. Results and discussion

### 3.1. Relationships between equilibrium adsorption capacity of $CO_2$ and the pore structure characteristics of PSACs

When the pitch sphere was activated with $CO_2$ at 850 °C, the specific surface area ($S_{BET}$) and total pore volume ($V_t$) of PSACs increase with the activation time extending, while the specific surface area of micropores ($S_{mic}$) and pore volume of micropores ($V_{mic}$) decrease, particularly, the surface area of micropores with pore size less than 1 nm ($S_{<1\ nm}$). When the activation time extended from 2 to 10 h, although the $S_{BET}$ increases from 527 to 1716 $m^2/g$, the $S_{mic}$, $S_{<1\ nm,}$ $V_{mic}$ decrease from 526 $m^2/g$, 413 $m^2/g$, 0.26 $cm^3/g$ to 124.5 $m^2/g$, 121 $m^2/g$, 0.07 $cm^3/g$, respectively. As seen from Fig. 2a, the pore size of PSAC distributes in a wider range with the activation time extending. When pitch sphere was activated for 2 h, all the pores of PSAC2 sample are less than 2 nm, i.e., micropores, while PSAC10 had a wider pore size distribution in a range of 0.4–4 nm. The results suggest that when the activation time is long enough, $CO_2$ will go on reacting with the active sites ($C_f$) on the wall of micropores to yield CO gas, and then some micropores turn into mesopores or macropores.

Compared with $CO_2$ agent, $H_2O$ is easier to react with active sites ($C_f$) abiding by the vapor activation mechanisms (Liu et al., 1999). When the pitch sphere was activated with $H_2O$ at 900 °C for 1.5 h, the $S_{mic}$ is 871 $m^2/g$. If it was activated at 850 °C for 2.5 h, the $S_{mic}$ gives 921 $m^2/g$. It is noteworthy that the pores of PSAC-850-2.5 sample are all micropores and 70% of them are less than 1 nm as shown in Fig. 2b. Although the activation temperature for preparation of PSAC-850-2.5 sample was lower than that of PSAC-900-1.5 sample, while higher $S_{mic}$ and $S_{<1\ nm}$ were given. It suggests that when $H_2O$ is used as activation agent, the activation temperature with 850 °C is high enough to prepare activated carbon, but a long activation time is required.

Adsorption breakthrough experiment was performed with 5 g PSACs under the conditions of 30 °C atmospheric pressure and 12.5 vol% $CO_2$. It can be deduced from Fig. 3 that the breakthrough