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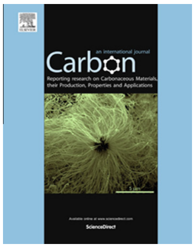

Potassium salt-assisted synthesis of highly microporous carbon spheres for CO_2 adsorption

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A B S T R A C T

Highly microporous carbon spheres for CO_2 adsorption were prepared by using a slightly modified one-pot Stöber synthesis in the presence of potassium oxalate. Formaldehyde and resorcinol were used as carbon precursors, ammonia as a catalyst, and potassium oxalate as an activating agent. The resulting potassium salt-containing phenolic resin spheres were simultaneously carbonized and activated at 800 °C in flowing nitrogen. Carbonization of the aforementioned polymeric spheres was accompanied by their activation, which resulted in almost five-time higher specific surface area and total pore volume, and almost four-time higher micropore volume as compared to analogous properties of the carbon sample prepared without the salt. The proposed synthesis resulted in microporous carbon spheres having the surface area of 2130 $m^2 g^{-1}$, total pore volume of 1.10 $cm^3 g^{-1}$, and the micropore volume of 0.78 $cm^3 g^{-1}$, and led to the substantial enlargement of microporosity in these spheres, especially in relation to fine micropores (pores below 1 nm), which enhance CO_2 adsorption. These carbon spheres showed three-time higher volume of fine micropores, which resulted in the CO_2 adsorption of 6.6 mmol g^{-1} at 0 °C and 1 atm.

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1. Introduction

In the light of the report published by the Intergovernmental Panel on Climate Change (IPCC) [1], carbon dioxide (CO_2) mitigation efforts have become of great importance to the scientific community. IPCC states that CO_2 is the main gas contributing to greenhouse effect. CO_2 is released to the atmosphere from various anthropological sources such as industrial processes, including cement production, and chemical, petrochemical, and refining processes [2,3]; however, the combustion of fossil fuels represents over 70% of the global CO_2 emissions. Thus, the long-term goal is to reduce greenhouse gases emissions, especially CO_2, and expand the low-carbon power generation. IPCC proposes to implement the carbon capture and storage program, which is intended to reduce the carbon concentration and then to stabilize, and recycle it to chemicals such as carbonates, urea, and fuels (e.g. methanol) [4,5]. The CO_2 capture must be efficient but most of all economically rational. The efforts are made to find new technologies and improvements that could potentially aid economical implementation of CO_2 capture. So far, absorption in amine solutions [6] is used in industry but adsorption on solids is proposed to replace it in the future as it is more cost effective and environmentally friendly. Materials investigated toward CO_2 capture include metal–organic frameworks [7], porous polymers [8], zeolites [9], modified silicas [10] and organosilicas [11], and carbons [12,13]. Especially carbons possess high specific surface area, large volume of pores with the proper size, favorable surface chemistry, and exhibit high chemical (water, alkaline, and acidic media) and thermal stability. These sorbents can be produced from widely available inexpensive precursors such as coal, petroleum pitch, wood, and various biomass sources.

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Recently, highly microporous carbons were prepared by carbonization of organic salts. Such carbons [14,15] have been proposed as good CO_2 sorbents because of their well-developed porous structure. Atkinson and Rood [16] carbonized lithium, sodium, and potassium dichloroacteates to obtain highly microporous carbons with specific surface area as high as 740 $m^2\,g^{-1}$. Sevilla and Fuertes [17] showed that pyrolysis of sodium, potassium, and calcium gluconates, citrates, and alginates can produce carbons with surface area up to 1960 $m^2\,g^{-1}$ and micropore volume up to 0.85 $cm^3\,g^{-1}$. Also, Adeniran et al. [18] carbonized potassium hydrogen phthalate to produce highly microporous carbons. The resulting material adsorbed 4.8 mmol g^{-1} of CO_2 at 1 bar and 25 °C.

Post-synthesis activation (chemical or physical) has been widely used to develop extra surface area and porosity and improve sorption properties of carbons. Our previous studies showed that this process can be used to enhance the microporosity in phenolic resin-based carbons; Gorka and Jaroniec [19] used CO_2 and water vapor post-synthesis activation of these carbons, whereas Souza et al. [20] utilized potassium hydroxide (KOH) as an activating agent. Wickramaratne and Jaroniec [21] reported that CO_2 activation of carbon spheres obtained by extended Stöber method can produce materials with CO_2 capacity as high as 8.05 mmol g^{-1} at 0 °C and 1 atm. Therefore, activated phenolic resin-based carbon spheres are attractive for adsorption of CO_2 because they possess intrinsic microporosity with high fraction of small micropores (<1 nm) that according to recent studies [22–25] enhance CO_2 uptake at ambient conditions. Especially potassium compounds such as KOH [26], potassium carbonate (K_2CO_3) [27], and potassium oxalate ($K_2C_2O_4$) [28], have been used for chemical activation of carbons; however, this process involves post-synthesis impregnation of carbons, which can be time consuming and somewhat difficult due to the hydrophobic nature of these materials. Physical mixing can be used instead of impregnation, but it often leads to an uneven distribution of the activating agent, resulting in poor activation. Overall, the post-synthesis activation is an additional step in the preparation of carbons.

This work shows a simple strategy to enhance microporosity in the carbon spheres prepared by Stöber method, which involves the addition of potassium oxalate to the ethanol–water–ammonia solution of resorcinol and formaldehyde. This one-pot modified Stöber synthesis produces the salt-containing polymer spheres, the carbonization of which in the presence of potassium species is accompanied by their activation, resulting in the development of additional microporosity. This is the first report showing the effect of direct addition of potassium organic salt during formation of phenolic resin spheres, which plays the role of an in-situ activating agent and additional carbon precursor. The proposed method affords carbons with spherical morphology, high surface area and high volume of micropores.

2. Experimental

2.1. *Chemicals*

Resorcinol ($C_6H_4(OH)_2$, 98%), formaldehyde (HCHO, 37 wt% solution in water, stabilized with 10–15% methanol) and potassium oxalate monohydrate ($K_2C_2O_4{\cdot}H_2O$, 99%) were purchased from Acros Organics (Geel, New Jersey, USA). Ammonium hydroxide (ACS grade, 29 wt%) was purchased from Fischer Scientific (Fair Lawn, New Jersey, USA). Technical grade ethanol and deionized water were used in all experiments.

2.2. *Synthesis of carbon spheres*

Carbon spheres were prepared by a suitably modified recipe reported by Liu et al. [29]; namely, 0.20 g of resorcinol was added to the mixture consisting of 20 mL of water, 8 mL of ethanol, and 0.10 mL of ammonium hydroxide under magnetic stirring for 10 min at room temperature. Next, 0.75 g, 1.20 g, or 1.65 g of $K_2C_2O_4{\cdot}H_2O$ were added to the synthesis mixture under stirring for 30 min to achieve the potassium-carbon weight ratio equal to 3:1, 5:1, and 7:1, respectively. Afterwards, 0.28 mL of formaldehyde was added and the mixture was stirred for 24 h and then subjected to the hydrothermal treatment in an autoclave at 100 °C for 24 h. Subsequently, the solution was transferred to a Petri dish and dried at room conditions overnight. The dried materials were carbonized in nitrogen atmosphere at 350 °C for 2 h (1 °C min^{-1} heating rate); then, temperature was ramped to 800 °C (1 °C min^{-1} heating rate) and kept at that temperature for 2 h. The carbonized materials were washed with 0.01 M HCl solution and deionized water until pH ~7 to remove salt residue. Finally, the materials were dried at 100 °C for 12 h. The resulting carbon materials were labeled C-K-*r*, where *r* denotes the potassium-carbon weight ratio. For the purpose of comparison, one carbon sample was prepared without salt addition and labeled as C.

2.3. *Measurements*

Nitrogen adsorption–desorption isotherms were measured at −196 °C, carbon dioxide adsorption isotherms were measured at 0, 25, 50 and 120 °C on an ASAP 2020 surface area and porosity analyzer manufactured by Micromeritics (Norcross, GA, USA). All samples were degassed using vacuum at 200 °C for 2 h prior to each measurement.

Scanning electron microscopy (SEM) images were taken on a Hitachi S-2600N scanning electron microscope using 25 or 30 kV accelerating voltage.

2.4. *Calculations*

Specific surface area (S_{BET}) was evaluated by Brunnauer–Emmett–Teller (BET) equation [30] in a relative pressure range of 0.05–0.2 using a nitrogen cross-section area of 0.162 nm^2 [31]. Total pore volume (V_t) was evaluated by converting the amount adsorbed at a relative pressure of 0.99 to the volume of liquid nitrogen at experiment conditions [31]. Pore size distributions (PSD) were calculated from adsorption branches of nitrogen adsorption–desorption isotherms using the 2D-NLDFT Heterogeneous Surface model for carbon materials implemented in SAIEUS program provided by Micromeritics [32,33]. The volume of micropores, pores below 1 nm, and ultramicropores (V_{mi}, $V_{mi<1nm}$ and V_{umi} respectively), were calculated on the basis of the PSD curves obtained by the

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