

Microporous carbon spheres modified with EDA used as carbon dioxide sorbents

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Abstract

Carbon spheres for CO₂ adsorption were prepared using a modified Stöber method in a microwave assisted solvothermal reactor. For comparison purposes, the same preparation procedure was applied in an autoclave. A starting mixture composed of water-ethanol, ammonia water, EDA, resorcinol, potassium oxalate and formaldehyde, was stirred for 24 h at room temperature and then subjected to a pressure treatment in an autoclave (24 h at 100°C) or in a microwave solvothermal reactor (15 min under 2 MPa). The material with EDA prepared in the solvothermal reactor exhibited high CO₂ adsorption capacities, up to 5 mmol/g under ambient conditions and 6.6 mmol/g at 0°C. Copyright © 2018 VBRI Press.

Keywords: Carbon spheres, CO₂ capture, EDA

Introduction

Carbon is one of the most vital elements, both for life and for industry. A perfect carbon cycle occurring in nature has been recently interfered with intense industrial development, associated with an increase of carbon dioxide concentration in atmosphere, which has risen from 280 ppm before the industrial revolution to 390 ppm in 2010. The increase has contributed to the greenhouse effect and resulting climate changes [1]. Then, there is a challenge of a crucial importance to decrease the anthropogenic emissions of carbon dioxide and, if possible, to transform them into useful chemicals. The bottle-neck is the high thermodynamic stability of CO₂ molecule, then new processes are needed to resolve the problem. The processes intensively investigated are catalytic hydrogenation and methane dry reforming.

Polanski et al. [2] successfully performed a low temperature carbon dioxide methanation, using unalloyed nano-Ru/Ni catalyst supported on silica and reached an excellent efficiency at 200°C only with 100% conversion. Methane dry reforming can successfully occurs on nickel oxide nanoparticles supported on mesoporous silica [3]. Both catalytic processes are still at the laboratory scale due to the complexity of the reaction system and coking effect. The initial step before any carbon dioxide transformation or storage is its separation from exhaust gases. The existing processes used for PCCC (post combustion CO₂ capture) and based mainly on absorption in liquids (as amines, potassium carbonate or methanol) are costly, inefficient and may have inherent environmental problems. There is a need to develop new

PCCC technologies, more cost and energy efficient, and friendly for environment. Solid sorbents can be used in such processes, instead of traditional liquids. Carbon spheres can be applied as such a solid sorbent, which was described for the first time by the team of Inagaki [4,5,6], and next by Liu [7] and Jaroniec [8,9,10]. To produce spherical carbon materials Liu et al. applied the method of Stöber, applying a treatment of resorcinol and formalin in an autoclave followed by carbonisation under nitrogen atmosphere. The research group of Jaroniec improved the method involving potassium oxalate as one of reactants and, in some cases, using ethylenediamine as an additional modifier [9].

All the produced materials were obtained in an autoclave using an one-stage process and had a high specific surface area (up to 2900 m²/g), as well as a high adsorption of CO₂ at 0°C (up to 6.6 mmol/g).

We have modified the preparation method of spherical carbon materials for the adsorption of CO₂ using a microwave assisted solvothermal reactor instead of an autoclave, which was patented [11] and described in our previous paper [12]. In the present paper a modification with ethylenediamine (also conducted in the microwave assisted solvothermal reactor) is presented.

Experimental

Materials/ chemicals details

The following reactants were applied to produce carbon spheres: resorcinol, ethanol, ammonium hydroxide, potassium oxalate, formaldehyde, ethylenediamine.

Material synthesis / reactions

Spherical carbon materials were prepared in a following way: 0.60 g of resorcinol was added to the mixture consisting of 60 ml of water, 24 ml of ethanol, and 0.30 ml of ammonium hydroxide under magnetic stirring for 10 min at room temperature. Next, 4.95 g of $K_2C_2O_4 \cdot H_2O$ was added to the synthesis mixture under stirring for 30 min to achieve the potassium-carbon weight ratio equal to 7:1.

Next, ethylenediamine (0.2 ml or 1 ml) was added to the mixture. Afterwards, 0.9 ml of formaldehyde was added and the mixture was stirred for 24 h and then subjected to a treatment in the solvothermal microwave assisted reactor ERTEC MAGNUM II (pressure 1–3 MPa) for 15 min.

Subsequently, the solution was transferred to a Petri dish and dried at 80°C for 2 days. The dried materials were carbonised in argon atmosphere at 350 °C for 2 h (1 °C min⁻¹ heating rate); then, temperature was raised to 700°C, 750°C and 800 °C (with a heating rate of 1 °C min⁻¹) and kept at the highest temperature for 2 h. The carbonised materials were washed with deionised water until pH~7 was reached, to remove salt residues. Finally, the materials were dried at 80 °C for 24 h.

Characterizations / device fabrications /response measurements

The helium density of the prepared samples was measured under helium using a Micro-Ultrahpzc 1200e equipment at the pressure of 17 psi. The samples were purged with helium for 20 min.

The textural properties of the carbon spheres were determined by physical adsorption of N₂ at -196°C using a Quadrasorb apparatus (Quantachrome Instruments).

Specific surface area was assessed using multi-point BET (Brunauer–Emmet–Teller equation) [13] method using the N₂ adsorption isotherm over a relative pressure (P/P₀) in the range of 0.05–0.20. The total pore volume, V_p, including both the micropores and the mesopores, was estimated by converting the amount of N₂ gas adsorbed at a relative pressure of 0.99 to the liquid volume of the adsorbate (N₂). Micropore volume (< 2 nm), V_{mic}, was determined using the Density Functional Theory (DFT).

CO₂ adsorption isotherms were measured up to 1 bar at 0°C and 25°C using Quadrasorb volumetric apparatus. As in the previous case, samples before measurements were degassed under vacuum at 250 °C for 16 h.

Carbon dioxide adsorption isotherms at 0°C and nitrogen adsorption isotherms at 0°C were determined using a Quadrasorb volumetric apparatus (Quantachrome Instruments).

Prior to each measurement all samples were degassed under vacuum at 250 °C for 16 h.

Results and discussion

The low-temperature nitrogen adsorption-desorption isotherms measured on the carbon spheres produced in the autoclave are presented in Fig.1.

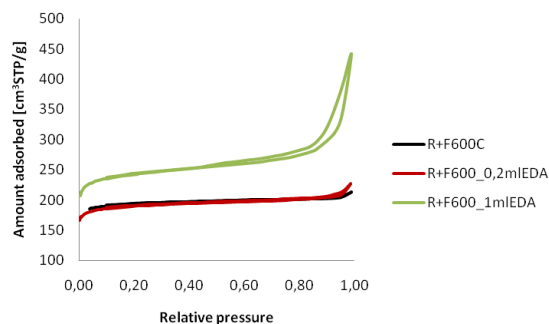


Fig. 1. Nitrogen adsorption-desorption isotherms for the carbon spheres produced in the autoclave.

The two of adsorption isotherms in Fig. 1 (samples R+F600C and R+F600C_0,2mlEDA) are of Type I according to the IUPAC classification, which is characteristic for microporous materials. On the contrary, adsorption isotherm of the sample R+F600C_1ml EDA corresponds to Type IV, which according to the IUPAC classification is characteristic for mesoporous materials. Then, higher volume of EDA applied can block smaller pores.

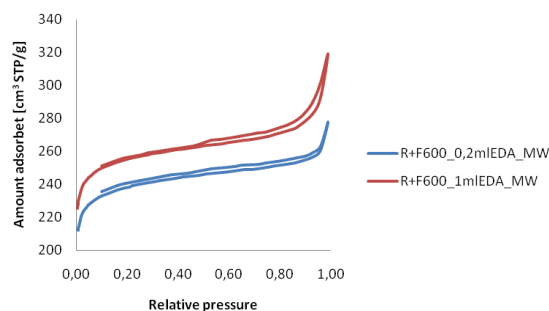


Fig. 2. Nitrogen adsorption-desorption isotherms for the carbon spheres produced in the solvothermal reactor.

Fig. 2. shows low-temperature nitrogen adsorption-desorption isotherms for samples produced in the microwave assisted solvothermal reactor.

Both adsorption isotherms are of Type IV, which is characteristic mainly for mesoporous materials.

The textural parameters of both kinds of samples (produced in the autoclave and in the microwave assisted solvothermal reactor) are presented in Table 1. The first sample in the table corresponds to the material without addition of ethylenediamine.

Table 1. Structural parameters of the spherical carbon materials samples obtained in autoclave and in solvothermal reactor.

Sample		S _{BET} [m ² /g]	Total Pore Vol. [cm ³ /g]	Micro-pore Vol. [cm ³ /g]
Autoclave	R+F600C	594	0,330	0,276
	R+F600C_0,2mlEDA	761	0,352	0,269
	R+F600C_1mlEDA	957	0,684	0,326
Solvothermal reactor	R+F600C_0,2mlEDA_MW	954	0,431	0,339
	R+F600C_1mlEDA_MW	1024	0,495	0,358

According to the results presented in **Table 1**, an addition of ethylenediamine resulted in an increase of the specific surface area and of the micropore volume. In the case of the sample with addition of 1 ml EDA obtained in the autoclave a significant increase of total pore volume can be observed, due to the presence of mesopores.

Spherical carbon materials produced in the solvothermal reactor have higher specific surface area than those produced in the autoclave. The specific surface area S_{BET} of the sample produced with 1 ml of EDA in the solvothermal reactor (R+F600C_1mlEDA_MW) increased to 1024 m²/g, although the total pore volume for the sample decreased (compared with the sample from the autoclave). Nevertheless, an increase of micropore volume can be observed for this sample, and these pores are essential for carbon dioxide adsorption.

The pore distribution determined using DFT method is shown in **Fig.3**.

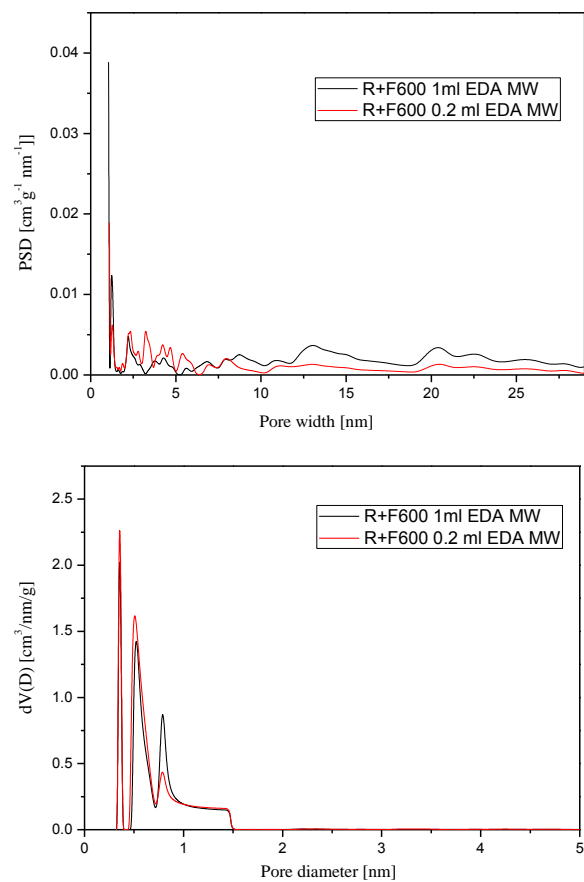


Fig.3. Pore distribution for the samples produced in the solvothermal reactor.

It can be seen that the obtained spherical carbon materials contain both micropores (pores with diameter below 2 nm) and mesopores (pores with diameter in the range between 2 and 50 nm), which is in accordance with measured nitrogen isotherms.

The produced materials demonstrated a high adsorption capacity of carbon dioxide, due to the high specific surface area and high micropore volume.

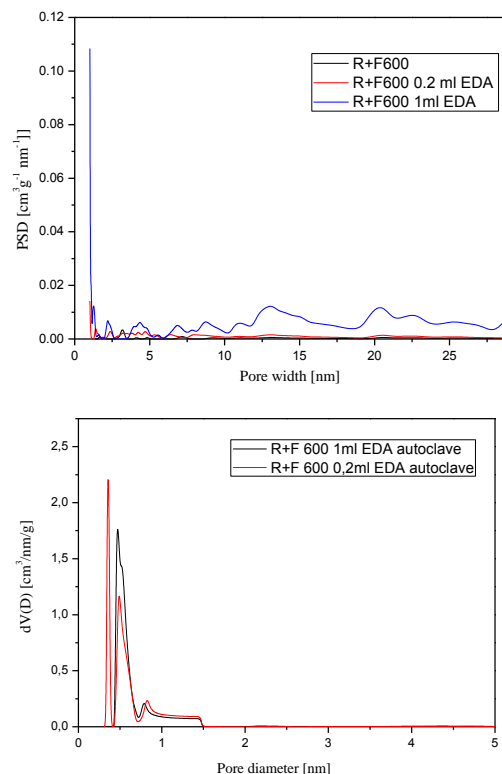


Fig.4. Pore distribution for the samples produced in the autoclave.

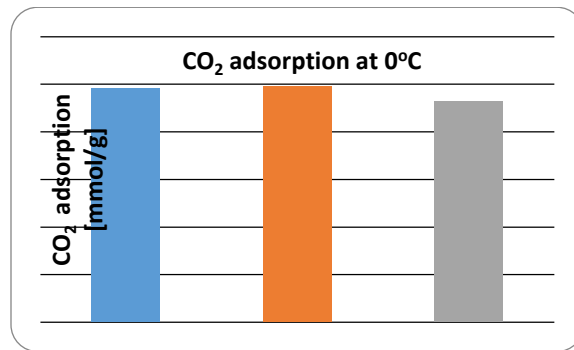


Fig. 5. Carbon dioxide adsorption measured at 0 °C on the samples produced in the autoclave.

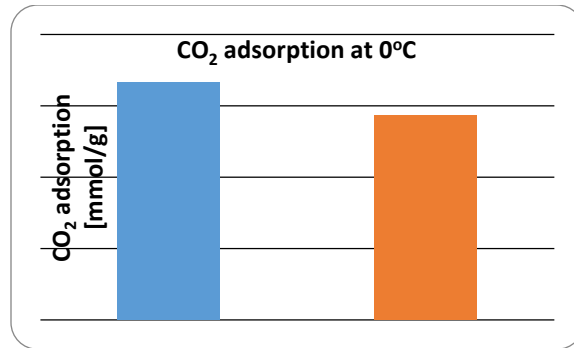


Fig. 6. Carbon dioxide adsorption measured at 0 °C on the samples produced in the solvothermal reactor .

The results of the measurements of carbon dioxide adsorption capacity are presented in **Fig. 5, 6** and **7**.

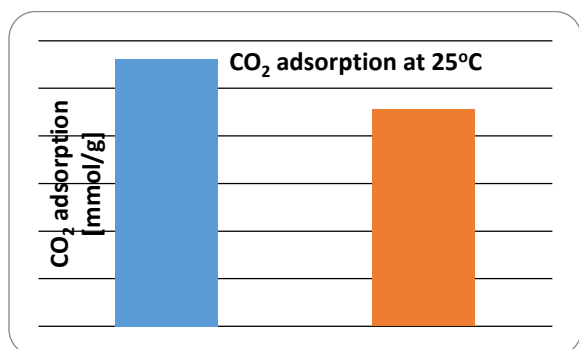


Fig. 7. Carbon dioxide adsorption measured at 25 °C on the samples produced in the solvothermal reactor .

As it can be seen in **Fig. 5**, an addition of EDA does not affect the adsorption capacity on the samples produced in the autoclave, which at the level of 5 mmol/g. A significant increase can be observed for the samples produced in the microwave assisted solvothermal reactor. The best result of 6.6 mmol/g was obtained for the sample containing 0.2 ml of EDA. Although an increase of EDA content to 1 ml resulted in a drop of CO₂ adsorption capacity, it was still very high. Even the increase of adsorption temperature to 25 °C did not result in a significant adsorption capacity, which is very promising for future applications.

Conclusions

Application of the microwave assisted solvothermal reactor for preparation of spherical carbon materials delivered better results than the use of the autoclave. Modification of the material with ethylenediamine resulted in an improvement of CO₂ adsorption properties, up to 5 mmol/g under ambient conditions and 6.6 mmol/g at 0 °C .

Author's contributions

Conceived the plan: AWM, DS, UN; Performed the experiments: DS, JSN, BM, JS, RJW; Data analysis: DS, JSN, UN; Wrote the paper: UN, DS. Authors have no competing financial interests.

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