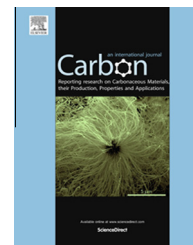


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Complexity of CO₂ adsorption on nanoporous sulfur-doped carbons – Is surface chemistry an important factor?

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ABSTRACT

Nanoporous S-doped carbon and its composites with graphite oxide were tested as adsorbents of CO₂ (1 MPa at 0 °C) after degassing either at 120 °C or 350 °C. The adsorption capacities were over 4 mmol/g at ambient pressure and 8 mmol/g at 0.9 MPa in spite of a low volume of micropores. The nitrogen adsorption experiments showed an increase in porosity upon an increase in the degassing temperature. The extent of this effect depends on the stability of surface groups. Interestingly, the CO₂ adsorption, especially at low pressure, was not affected. The good performance is due to the presence of ultramicropores similar in sizes to CO₂ molecule and to sulfur in various functionalities. Sulfur incorporated to aromatic rings enhances CO₂ adsorption via acid–base interactions in micropores. Moreover, sulfonic acids, sulfoxides and sulfones attract CO₂ via polar interactions. Hydrogen bonding of CO₂ with acidic groups on the surface can also play an important role in the CO₂ retention. These carbons have high potential for application as CO₂ removal media owing to their high degree of pore space utilization. The results obtained also show that high degassing temperatures might result in the decomposition of surface groups and thus in changes in surface interactions.

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1. Introduction

Owing to an increase in the energy consumption, contemporary society faces the problems of global warming related to a release to the atmosphere such gases as CH₄ or CO₂ [1,2]. The atmospheric concentration of the latter increased from 315 ppm in 1958 to 377 ppm in 2004 [3] and to ~390 ppm currently [4]. To slow down the global warming and related to it climate changes the researches focus on the development of alternative sources of energy (solar, wind, geothermal). Another important research focus is related to a CO₂ capture. One of the methods applied for this purpose is based on

adsorption processes. So far various adsorbents have been tested including zeolites [5,6], functionalized mesoporous silica [7,8], carbon nanotubes [9,10], metal oxides [11,12], Metal Organic Frameworks (MOFs) [13–15] or aminated graphite oxides and their composites with Cu-based MOF [16], and activated carbons [17–31]. Often the adsorbents are further modified to introduce basic groups to the surface (as amines) [7,8,32,33], or heteroatoms providing basicity, as in the case of activated carbons [24–26].

Even though the capacities reported on MOFs are extremely high [13–16], the drawbacks in application of these materials is their low stability in the presence of moisture

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and high costs associated with their production. These aspects direct the attention of the researchers to activated carbons, classical well-known adsorbents exhibiting a high surface area and well-developed porosity [34]. Another important feature of these materials is a relative easiness of their surface modifications via an incorporation of heteroatoms [35].

The most important asset of activated carbons for their application as adsorbents is their high volume of micropores. It has been shown that the volume of pores smaller than 1 nm is crucial for a high CO₂ adsorption capacity, especially at ambient conditions, owing to an enhanced adsorption potential in pores similar in their sizes to an adsorbate molecule (kinetic diameter of the CO₂ molecule is 0.33 nm) [2,17–20,29]. To achieve as high as possible volume of small pores a well-known activation with KOH [36] is often used for various carbonaceous precursors. Thus this kind of activation was applied to phenolic resin [21], polysaccharides and biomass [17], soft-templated produced carbons [20], hard templated carbons [30] and petroleum residue [23]. As a result of these treatments, carbons with surface areas close to 3000 m²/g were obtained [17,20–22] with the CO₂ adsorption capacity at 1 bar and 25 °C reaching 4.55 mmol/g [22], 3.5 mmol/g [17], 4.8 mmol/g [17,23], and 4.4 mmol/g [20]. 8.9 mmol/g was reported by Wickramaratne and Jaroniec at 0 °C and ambient pressure [21]. The researchers mentioned the importance of the volume in pores with sizes less than 0.7 nm [17–19,20,23].

To further increase the CO₂ adsorption capacity the surface of activated carbons was modified with nitrogen. The purpose was to introduce some basicity [24,32,33] and thus to increase specific acid–base interactions owing to the slightly acidic nature of CO₂ [24]. Thus Zhou and coworkers obtained N-doped nanoporous carbons in Y zeolite [24]. The CO₂ adsorption capacity at ambient conditions reached 2.3 mmol/g. On the other hand, Chandra and coworkers reported 4.3 mmol/g on N-doped carbon produced by chemical activation of polypyrrole functionalized graphene sheets [37]. The adsorption capacity measured by Fuertes and coworkers on polypyrrole derived carbons obtained by KOH activation was 6.2 mmol/g at 0 °C [25]. Contrary to other findings, Xing and coworkers proposed that on N-doped carbon CO₂ adsorption is enhanced rather by hydrogen bonding interactions than by acid–base interactions [26]. The adsorption capacity measured on their materials reached 4.24 mmol/g at ambient conditions on carbon with the surface area of about 3000 m²/g.

Recently sulfur doped carbons are of increasing interest [38]. Their very good performance was reported in the field of catalysis/oxygen reduction [39,40], reactive adsorption [41], photoactivity [42,43], and energy storage [44–46]. They were also addressed as CO₂ capture media [27,28]. Xia and coworkers reported relatively high CO₂ adsorption on sulfur doped carbon obtained within the structure of zeolite EMC-2 (about 2.4 mmol/g at 25 °C) [27]. The heat of adsorption at low coverage reached 59 kJ/mol and was indicated as highest reported on porous carbons. Seema and coworkers used chemically activated reduced-graphene oxide/poly-thiophene as a CO₂ adsorbent and they reported 4.5 mmol/g at 25 °C and at ambient pressure [28]. The high capacity was linked to the

“oxidized S-content” and the presence of pores similar in size to CO₂ molecule. The surface area of these materials reached ~1600 m²/g.

Based on the analysis of recent findings in the field of CO₂ capture on the nanoporous carbons, the objective of this paper is the analysis of the combined effect of porosity and surface chemistry of sulfur-doped carbons on CO₂ adsorption. The nanoporous polymer-derived carbon and their composites with a graphene phase [45,46] are used as capture media. These materials possess small micropores, important for CO₂ adsorption and a high sulfur content in various configurations. Their relatively small surface area should lead to a high accessibility of sulfur functional groups for CO₂ molecules. Chemical nature of the species detected on the surface in combination with their possible location in the pore system will be linked to the performance of these materials as the CO₂ capture media. Adsorption of CO₂ is also used here for detailed evaluation of the materials' porosity. The effects of surface functional groups on the measured adsorption capacity are discussed. Moreover, by measuring adsorption of nitrogen and CO₂ after degassing at 120 °C and 350 °C we not only show how functional groups affect the amount of carbon dioxide adsorbed but also indicate the importance of degassing temperature for representing the real surface of carbons.

2. Experimental

2.1. Materials

Poly(sodium 4-styrene sulfonate) was used as a nanoporous carbon precursor. The powdered polymer was carbonized at 800 °C for 40 min under nitrogen, in a horizontal furnace. The details on the initial sample preparation are described in Ref. [47]. This material is referred to as CS. The synthesis of the graphite oxide/carbon composites used in this research was described in details elsewhere [45]. Briefly, the composites were prepared by mixing the amount of polymer corresponding to 95% or 90% of resulting composite with 5% or 10% of highly oxidized GO (Hummers method [48]), respectively. Then the mixtures were carbonized under nitrogen in the same conditions as for the initial polymer. The obtained composites are referred to as CS5 and CS10 (5 and 10 corresponds to the percentage of GO in the composite). The subsamples of the composites were oxidized at 350 °C for 3 h in air [46]. The suffix “O” was added to air oxidized graphene/carbon materials.

2.2. Methods

2.2.1. Surface characterization

Obtained samples were extensively characterized using potentiometric titration, thermal analysis-mass spectroscopy, scanning electron microscopy and electron-dispersive X-ray spectroscopy. The details on experiments procedures are addressed in Refs. [45,46].

2.2.2. Adsorption measurements

Standard nitrogen adsorption isotherms were measured at –196 °C using a volumetric Micromeritics ASAP 2020

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