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Porous carbon material containing CaO for acidic gas capture: Preparation and properties

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HIGHLIGHTS

- Poly(ethylene terephthalate) heated with calcite gives porous carbon loaded with CaO.
- CaO-loaded carbon efficiently removes CO₂ and SO₂ from air.
- Washing out CaO from the hybrid sorbent gives highly porous carbon material.

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ABSTRACT

A one-step process for the preparation of CaO-containing porous carbons is described. Mixtures of poly(ethylene terephthalate) with natural limestone were pyrolyzed and thus hybrid sorbents could be easily obtained. The polymeric material and the mineral served as a carbon precursor and CaO delivering agent, respectively. We discuss effects of the preparation conditions and the relative amounts of the raw materials used for the preparations on the porosity of the hybrid products. The micropore areas and volumes of the obtained products tended to decrease with increasing CaO contents. Increase in the preparation temperature entailed a decrease in the micropore volume, whereas the mesopore volume increased. The pore creation mechanism is proposed on the basis of thermogravimetric and temperature-programmed desorption measurements. The prepared CaO-containing porous carbons efficiently captured SO₂ and CO₂ from air. Washing out of CaO from the hybrid materials was confirmed as a suitable method to obtain highly porous carbon materials.

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1. Introduction

While many modern biotechnological processes and fabrication methods are used in the production of advanced semiconductor components, maintaining good air quality in the manufacturing environment is also very important. This requires appropriate methods to purify air to achieve an acceptable level of harmful contaminants. Effective purification of air is often performed in large air-conditioning systems to maintain satisfactory quality of indoor air [1,2]. In addition, personal gas masks used for respiratory protection can be considered as small air purification systems for individuals [3,4]. There is an increasing demand for purification systems that are capable of removing both solid and gaseous contaminants from air prior to directing it to clean rooms [5]. Removal

of fine particulates from an air stream is not a difficult task [6]. However, removing contaminant gases from large volumes of air is usually much more challenging because it requires specific treatments. One of the most common methods used for removal of low-concentration gaseous contaminants from air is adsorption onto activated carbon [7,8]. Chemical reactions between undesirable gaseous contaminants and suitable chemicals are also an efficient way to purify air streams [9,10]. Air purification systems employing hybrid sorbents, i.e., porous solids loaded with chemicals that react with the target gas, are available commercially and are continuously being developed [11]. For example, activated carbon impregnated with chemicals of a strong basic character such as hydroxides or carbonates, is a highly efficient material for removing acidic gases from air [12,13]. Because removal of harmful contaminants is accompanied by chemical reactions, such hybrid sorbent materials are used for the production of so-called chemical filters. Activated carbon loaded with chemicals is usually produced through impregnation of commercially available activated carbons

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with a solution of suitable agents, followed by removal of a solvent [14]. An alternative scheme is direct pyrolysis of a mixture of a suitable carbon precursor and a chemical. Appropriate selection of raw materials is crucial because the mixture should be converted to porous carbon containing a chemical that will react with a particular contaminant gas. Hence, if the preparation procedure is planned prudently, a solid material combining features of both physical adsorbents and active chemicals can be easily obtained [15]. SO₂ [16–19] and CO₂ [20,21] are typical target contaminants that need to be removed from air, and CaO [22] and Ca(OH)₂ [23] are well-known agents that react with these gases. For that reason, these chemicals are extensively used in industrial flue gas desulfurization systems. SO₂ from flue gases is also removed according to the industrial Bergbau-Forschung process [24] employing activated coke. Porous carbon materials are also known to be capable of adsorbing CO₂ [25–28].

The aim of our study was to develop a new sorbent material for efficient eliminating acidic gases from air. Pyrolysis of poly(ethylene terephthalate) (PET) combined with natural limestone resulted in a series of CaO-loaded porous carbon materials. The mineral used for preparations mainly consisted of CaCO₃, which is a salt that decomposes thermally at ca. 800 °C to CaO and CO₂. On the other hand, in an inert atmosphere, PET undergoes thermal degradation to yield a carbonaceous residue (char) [29,30]. Therefore, in our experiments, we expected to see an effect similar to that observed for other systems that employed decomposable magnesium compounds for producing highly porous carbon materials revealing significant microporosity and mesoporosity [31]. Hence, we expected the creation of pores due to the in situ reaction between CO₂ released from CaCO₃ and the char formed from PET. Because CaO was deliberately retained in the obtained pyrolyzate, we could produce a hybrid sorbent material with the potential to eliminate acidic gases from air. Although CaO-containing porous carbons prepared by the conventional impregnation method [32,33] or pyrolysis of a triblock copolymer mixed with calcium nitrate [34] are known, the preparation procedure and combination of raw materials described in this work have not been reported previously. It should be emphasized that compared to the commonly used impregnation of commercial activated carbons with suitable chemicals, the proposed method utilizes a completely different approach. Therefore, we believe that the one-step pyrolysis of PET/limestone mixtures comprising readily available and relatively cheap raw materials, aimed at obtaining a hybrid CaO-loaded porous carbon material, is worthy of investigation.

2. Experimental

2.1. Materials

The carbon source used in this work was commercial grade poly(ethylene terephthalate) (PET) purchased from Elana S.A., Poland. The CaO precursor chosen for the preparations was limestone (hereinafter CAL) mined from deposits located near Czatkowice, Poland and supplied by “Czatkowice” Limestone Mine, Ltd. CaCO₃ was the dominant chemical in the mineral whereas the total content of all other components was ca. 4 wt.% (Table 1).

The reference material used in this study was commercially available activated carbon (Airpel 10–KI/KOH) impregnated with KOH and KI. According to the supplier, this sorbent is especially recommended for the efficient capture of acidic gases, including SO₂, CO₂, and H₂S.

Table 1

Chemical composition of the limestone (according to supplier's data).

| Component | Content, wt.% |
|--------------------------------|---------------|
| CaCO ₃ | 96.03 |
| MgCO ₃ | 1.48 |
| SiO ₂ | 2.13 |
| Fe ₂ O ₃ | 0.11 |
| Al ₂ O ₃ | 0.08 |
| K ₂ O | 0.04 |
| Na ₂ O | 0.02 |

2.2. Preparations

The sorbent materials were obtained through simple pyrolysis of the mixtures of PET and limestone. Prior to preparations the mineral was dried in air at 120 °C for 24 h. The raw materials were then ground and mixed in three PET/CAL weight ratios: ca. 83:17 (10 g/2 g), 50:50 (10 g/10 g), and 30:70 (10 g/23.3 g). The fraction of limestone grains used for the preparations was below 0.6 mm. A 30 g portion of each raw mixture was pretreated by means of heating in an argon flow (100 cm³/min) from 25 to 265 °C (10 °C/min), and then, the final temperature was maintained for 1 h. The temperature of 265 °C was chosen to allow melting of the PET material included in the mixtures, thus providing favorable conditions for obtaining blends with CAL grains uniformly dispersed over the PET matrix. After cooling to room temperature, the obtained agglomerates were ground to a powder and subjected to another heating/milling cycle. Next, portions of the finely ground powder were pyrolyzed in an argon flow (100 cm³/min). For that purpose, 5 g sample of a powder was heated (10 °C/min) from room temperature to either 850 °C or 1000 °C and was maintained at the final temperature for 1 h. All above thermal treatments were carried out using flow tube furnace equipped with a quartz pipe (i.d. 75 mm, length 1500 mm). Samples subjected to heating were contained in a quartz boat placed in the central part of the pipe. The lower temperature used for preparations, 850 °C, was determined on the basis of thermogravimetric (TG) studies and X-ray diffraction (XRD) measurements, and was high enough to ensure complete decomposition of the limestone included in the treated PET/CAL mixtures. Because exposure to high temperatures may entail some changes in the pore structure of the treated porous carbon materials [35], heating at 1000 °C was used to determine whether the preparation temperature had a significant impact on the characteristics of the products. The pyrolyzates obtained in several lots were combined and finally pulverized using a laboratory mortar. All the gases used for the preparations were of high purity (99.999%).

In addition, CaO-free porous carbons were obtained from the hybrid products. For that purpose small amounts of the obtained materials containing the oxide were washed with an excess of 3.2 M aqueous HCl. In this way, CaO could be converted to water-soluble CaCl₂ and thus easily removed from the hybrid materials. After agitating for 24 h in the HCl solution, the remaining solids were filtered out, rinsed with distilled water to a constant reaction, (pH 6.0), and finally dried overnight at 120 °C in air.

2.3. Methods

To examine the phase composition of both the limestone and the obtained products, XRD patterns were recorded. A Philips X'Pert PRO diffractometer operating with Cu K_α radiation (λ = 1.54056 Å) was used for that purpose. The diffractograms were recorded within 2θ range of 10–80°, using scan step size of 0.005° and dwell time of 3 s.

The pore structure parameters for the obtained materials were calculated from the nitrogen adsorption/desorption (at 77 K) isotherms measured using a Quadrasorb SI apparatus

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