Adsorption of L-phenylalanine on ordered mesoporous carbons prepared by hard template method

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A B S T R A C T

Mesoporous carbons, CMK-3 and CMK-8 were synthesised by hard template method with the use of ordered silicas SBA-15, KIT-6 as solid state matrices and sucrose as carbon precursor. The physicochemical properties of materials obtained were characterised by X-ray diffraction, electron transmission microscopy and low-temperature nitrogen adsorption. The results proved the presence of ordered mesoporous structure both in CMK-3 and in CMK-8. Adsorption of L-phenylalanine by mesoporous adsorbents was studied from solutions of different pH 5.6–9.4. Electrostatic, hydrophobic and steric interactions are all likely to be important effects in amino acid adsorption. The maximum sorption capacity was observed at pH 5.6, close to the isoelectric point of L-phenylalanine (pI = 5.48). Above this pH value, the amount of adsorbed amino acid decreases. Mesoporous carbons CMK-8 and CMK-3 show much higher sorption capacities than silica. The adsorption capacities of different mesoporous adsorbents decrease in the following order: CMK-8 (2446 μmol/g) > CMK-3 (1654 μmol/g) > KIT-6 (420 μmol/g) > SBA-15 (389 μmol/g).

1. Introduction

Mesoporous carbons have recently received enormous attention by a number of researchers around the world. The widespread interest in these materials results from their unusual properties such as electric conductivity, chemical inertness and thermal stability. Due to the high surface area and ordered pore structure, the mesoporous carbons have found application in catalysis, adsorption, nanotechnology, energy storage, gas separation, water and air purification [1–3].

By modifications of synthesis method it is possible to control the pore size, pore volume and surface area of mesoporous carbon materials. Nowadays mesoporous carbons with extremely high surface areas and ordered structures have been mostly obtained by hard and soft template methods. The first one involves the use of presynthesised organic or inorganic templates which serve as moulds for replication of mesoporous carbons, and no significant chemical interactions take place between templates and carbon precursors [3–5]. The corresponding porous structures are predetermined by the templates, which have well-defined nanostructures. The mesoporous silica templates offered a considerable benefit from the viewpoint of structural order and diversity in achieving novel carbon structures. The sorption ability

of mesoporous materials obtained by this method is influenced not only by silica matrix used in the synthesis but also by the type of carbon precursor. In the soft template methods the nanostructures are generated through self-assembly of organic compounds [6–8]. The structure of the material obtained is strongly determined by synthetic conditions – temperature, solvents and mixing ratios.

The presence of mesopores (2–50 nm) plays a significant role in the adsorption processes of various molecules such as vitamins, dyes, drugs and amino acids. The adsorption efficiency of organic compounds on mesoporous carbons is influenced by the molecular mass of the adsorbed substance, its size, geometry, solubility, polarity and functional groups.

The ordered pore systems and well-defined pore size distributions of mesoporous materials influence the adsorption processes of active compounds and their controlled release. Recently, porous carbons have been used in adsorption processes of ibuprofen [9], β-carotene [10], tetracycline chloride [11], vitamin B12 [12,13], albumin [12], lysozyme [14] and amino acid such as L-histidine [15,16].

Earlier amino acids have been mainly adsorbed on the surface of hydroxyapatite, zirconium phosphate, modified silica, silica-gels, zeolites [17–20]. However, it was found that because of a low pore volume and hidden pores of these materials the adsorption of amino acids was limited. The promising adsorbents of amino acids were ordered mesoporous silica materials such as MCM-41, SBA-1 and SBA-15 [21]. To our knowledge, the ordered mesoporous carbons (CMK-3) have been used for the first time as adsorbents for

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amino acids by Vinu *et al.* [15]. In this study the adsorption of L-histidine was carried out on various porous materials such as CMK-3, SBA-15 and activated carbon, from solutions of different pH. It has been found that the amount of L-histidine adsorption on CMK-3 was higher than that on SBA-15 and activated carbon [15].

Up to date, there has been relatively few articles regarding the potential application of ordered mesoporous carbons for amino acids adsorption. We have chosen L-phenylalanine as a model adsorbent because it has both aromatic hydrophobic region as well as hydrophilic functional groups. We investigated its adsorption on the surface of ordered mesoporous carbon materials such as CMK-3 and CMK-8 prepared by hard template method with the use of ordered mesoporous silica (SBA-15, KIT-6) as templates and sucrose as carbon precursor.

2. Materials and methods

2.1. Preparation of SBA-15 and KIT-6 templates

2.1.1. SBA-15

A highly ordered SBA-15 sample was prepared using the triblock copolymer, $EO_{20}PO_{70}EO_{20}$ (Pluronic P123, BASF) as template and tetraethyl orthosilicate (TEOS, Aldrich, 98%) as the silica source, following the synthesis procedure reported by Zhao *et al.* [22]. The starting composition was 10 g of P123:0.10 mol TEOS:0.60 mol HCl: 20 mol H_2O. In a typical synthesis, 1.1 g TEOS was added dropwise to 19.0 ml of 1.6 M HCl (Chempur, 37%) containing 0.5 g of P123 at 35 °C. The mixture was stirred with a magnetic stirrer until TEOS was completely dissolved. Then, the mixture was placed in an oven for 24 h at 35 °C and subsequently for 6 h at 100 °C. The white solid product was filtered without washing and dried at 100 °C for 24 h in air oven. Finally, the product was calcined at 550 °C in air to remove the template.

2.1.2. KIT-6

KIT-6 sample was prepared as follows: 4.0 g of Pluronic P123 (BASF) was dissolved in 144 g of distilled water and 7.9 g of hydrochloric acid (Chempur, 37%) solution upon stirring at 35 °C [23]. After complete dissolution, 4.0 g of 1-butanol was added immediately. After 1 h stirring, 8.6 g of TEOS was added to the homogeneous clear solution. The mixture was kept under vigorous and continuous stirring at 35 °C for 24 h. Subsequently, the reaction mixture was aged at 100 °C for 24 h under static condition. The product was filtered without washing and dried at 100 °C for 24 h in air oven. Finally, the sample was calcined at 550 °C in air to remove the template.

2.2. Synthesis of mesoporous carbons

Mesoporous carbons were prepared by hard template method using ordered silicas as templates and sucrose as carbon precursors.

In typical synthesis of CMK-3, 1 g of SBA-15 was added to a solution obtained by dissolving 1.25 g of sucrose (Aldrich) and 0.14 g of H_2SO_4 (Chempur) in 5 g of H_2O [24]. The mixture was placed in a drying oven for 6 h at 100 °C, and subsequently the oven temperature was raised to 160 °C and maintained there for 6 h. The sample turned dark brown or black during the treatment in the oven. The silica sample, containing partially polymerised and carbonised sucrose at the present step, was treated again at 100 °C and 160 °C using the same drying oven after the addition of 0.8 g of sucrose, 0.09 g of H_2SO_4 and 5 g of H_2O. The carbonisation was completed by pyrolysis with heating to typically 900 °C for 6 h in argon atmosphere. The carbon-silica composite obtained after pyrolysis was washed with 5 wt% hydrofluoric acid at room temperature, to remove the silica template. In the next step,

mesoporous carbon was filtered, washed with ethanol, and dried at 105 °C.

CMK-8 material was prepared by the same method using KIT-6 instead of SBA-15 and the amount of water was adjusted to the pore volume of KIT-6.

2.3. Sample characterisation

2.3.1. Powder X-ray diffraction (XRD)

The materials prepared were characterised by X-ray diffraction (XRD) using a D8 Advance diffractometer (Bruker) (Cu Kα radiation, λ = 0.154 nm), with a step size 0.02° in the low-angle range.

2.3.2. Nitrogen sorption

Characterisation of the pore structure of samples obtained was performed on the basis of low-temperature nitrogen adsorption–desorption isotherms measured on a sorptometer Quantachrome Autosorb iQ. Prior to adsorption measurements, the samples were degassed in vacuum at 300 °C for 2 h. Surface area and pore size distribution were calculated by BET (the relative pressure p/p_0 range taken into account in the BET calculations was 0.006–0.2) and BJH methods, respectively. Total pore volume and average pore diameter were determined as well [25].

2.3.3. Transmission electron microscopy (TEM)

For TEM measurements, powdered samples were deposited on a grid with a perforated carbon film and transferred to a JEOL 2000 electron microscope operating at 80 kV.

2.4. L-phenylalanine adsorption

A series of L-phenylalanine amino acid solutions with concentrations ranging from 0.5 to 70 mmol/l were prepared by dissolving different amounts of amino acids in potassium phosphate buffer solutions (pH 5.6–9.4). In each adsorption experiment, 25 mg of adsorbents was suspended in 5 ml of the L-phenylalanine solution. At first the time dependence of L-phenylalanine adsorption onto all mesoporous materials was investigated to determine the time required for equilibrium to be reached between the solid and solution. After a chosen contact time (typically 24 h) the resulting mixture was continuously shaken in a shaking bath at 20 °C. The amount of amino acid adsorbed was calculated by subtracting the amount found in the supernatant liquid after adsorption from the amount of amino acid present before addition of the adsorbent by UV absorption at the λ_{max} of L-phenylalanine, 257 nm.

2.5. Desorption study

The desorption studies were performed with an USP Dissolution Apparatus 2 (Agilent Technologies DS 708). The analyses were carried out in phosphate buffer solution pH 5.6 which is close to the isoelectric point of L-Phe. The medium (200 ml) was maintained at RT and stirred at 100 rpm. The samples were filtered through high-density polyethylene (HDPE) Full-Flow filters and the concentration of desorbed L-Phe was spectrophotometrically monitored at 257 nm. The absorbance of the sample aliquots was used to assess the amount of L-Phe desorbed at each time point.

3. Results and discussion

The low-angle XRD patterns of ordered mesoporous silica and carbons synthesised are shown in Fig. 1. The profiles of SBA-15 and CMK-3 show three well-developed reflexes corresponding to the planes (1 0 0), (1 1 0) and (2 0 0), evidencing the highly ordered