



The acid–base properties of nitrogen-containing mesoporous carbon materials



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ABSTRACT

Three kinds of mesoporous carbon materials (MC and N-containing nitrogen-containing MC: N-MC and C₃N₄-MC) were prepared from cost-effective raw materials and their textural and structural properties were investigated by XRD, XPS, N₂ adsorption isotherm, TG, TEM, and Raman spectroscopy. The surface acid–base properties of the samples were studied at different temperatures using probe molecule adsorption calorimetry both in gas phase (NH₃, SO₂) and liquid phase (phenylethylamine (PEA), benzoic acid (BA)) and also by TPD (PEA). Consequently the numbers of active acid–base sites have been determined and related to the BET surface area, porosity and surface functional groups. Depending whether the samples are probed on the static vacuum or in liquid media (water or n-decane) the interactions between the sites and the probes give rise to very different heats of adsorption. Moreover, the adsorption behavior of these mesoporous carbons towards aromatic compounds has shown their potential to be used as adsorbents.

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1. Introduction

Porous carbon materials are widely used for energy storage, separation, catalysis and electrodes [1–6]. The pore structure is the key feature related to their different applications. In comparison to the classical activated carbon materials with micropores (<2 nm), mesoporous carbon materials (pore size from 2 to 50 nm) have advantages in the transportation of molecules [7], especially when there are big molecules. In last decade, synthesis of mesoporous carbons has been intensively investigated [8–13]. The common methods of mesoporous carbon preparation suffer from some drawbacks such as the complicated procedures and high cost [1]. In a former work, we have used metal chloride as a template and succeeded in preparing mesoporous carbons and N-containing mesoporous carbons displaying high surface area and mesoporous structure [14,15]. The method has the advantages that the template is cheap and could be recycled and the mesoporous carbons thus prepared are of high quality.

When N as a heteroatom is introduced into a carbon support, it will change the surface composition, thus leading to different behaviors in applications. For example, it can favor the catalytic

activity toward oxygen reduction, which greatly increases the energy efficiency, specific power and energy density of fuel cell, or act as catalyst for SO₂ oxidation [16–20]. It also enhances the stability of the precious metal catalysts due to enhanced bonding of precious metals to the support and to the basic properties of N atoms that donate electrons [19,20]. In addition, the incorporation of N can enhance the H₂ adsorption ability of porous carbon materials [21–24].

Graphitic C₃N₄ (g-C₃N₄) is regarded as the most stable allotrope of carbon nitride. It is a potentially useful substitute for amorphous and graphitic carbons in different applications, for example, as a catalyst or an active catalytic support. It is reported that g-C₃N₄ can be used as a metal-free catalyst for visible-light catalysis [25,26] or as an electrocatalyst for oxygen reduction [27], and transition metal-modified g-C₃N₄ can be used for selective hydrocarbon oxidation [28]. However, g-C₃N₄ has a low surface area which is not suitable for catalysis. A method to solve this problem is to fix it on a mesoporous support thus leading to a high surface area and an enhancement of the catalytic activity [28]. The preparation of g-C₃N₄ has been intensively investigated and the two main reported methods are physical and chemical vapor deposition methods and polycondensation of the liquid precursors [29].

Surface acid–base properties are the key factor to influence the adsorption ability of solid materials which can decide the performance of materials in different applications such as separation and

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catalysis. Mesoporous carbon materials are used in industry both in gas phase and liquid phase, so it is important to know about their acid–base properties in both media. Calorimetric and thermal techniques based on adsorption or desorption of probe molecules are common methods to determine the number, the strength and the distribution of acid–base sites [30–33]. In liquid phase, solids are surrounded by a solvent which can influence greatly the surface properties of the solids due to their different features [33]. So it is important to distinguish between the “effective” acid–base properties strongly influenced by the solvent and the “intrinsic” acid–base properties determined in gas phase. Effective acid–base properties have a prominent importance to study the activity in a liquid phase while the “intrinsic” acid–base properties are more related to the activity in gas phase [31–33].

In this work, three kinds of mesoporous carbon materials called MC (mesoporous carbon), N-MC (N-containing mesoporous carbon materials) and C₃N₄-MC (mesoporous carbon with g-C₃N₄ supported on it) were prepared using cost-effective raw materials such as fructose and melamine with a metal chloride as the template. Their textural, structural and thermal properties were studied by XRD, Raman spectroscopy, N₂ adsorption isotherm at 77 K, TG, TEM, XPS and chemical analysis. In addition, particular attention has been paid to the acid–base properties of these materials. Microcalorimetric measurements of probe molecule adsorption were performed both in gas phase and liquid phase (water and n-decane) and TPD measurements of probe molecule desorption were also used to detect the surface acid–base properties.

2. Experimental

2.1. Preparation of materials

Mesoporous carbon (MC) was prepared from fructose (99%, ADM) using ZnCl₂ (>98%, Nanjing Chemical Reagent Co., Ltd) as catalyst and template according to a previous work [14].

N-containing mesoporous carbon (NMC) was prepared from melamine (99%, Aldrich) and formaldehyde (37wt. in water, Sigma–Aldrich) carbonization using CaCl₂ (≥95%, Fluka) as template according to a previous work [15].

C₃N₄-MC was prepared starting from MC used as support. In a typical procedure, 3 g melamine (99%, Aldrich) and 2 g MC were used. The raw materials were put separately in a container with a cover. They were heated firstly at 773 K for 2 h and then at 873 K for 2 h in N₂ flow. Melamine converted to g-C₃N₄ and g-C₃N₄ precipitates on the surface of MC.

2.2. Characterization

Chemical composition of prepared materials was determined by inductively coupled plasma–optical emission spectroscopy (ICP–OES) with an ACTIVA spectrometer from Horiba JOBIN YVON.

Surface areas were determined by low temperature nitrogen adsorption performed at 77 K, on a Micromeritics 2020 apparatus, after pretreatment performed for 2 h at 623 K under vacuum. The BET (Brunauer–Emmett–Teller) and BJH (Barrett–Joyner–Halenda) methods were used to derive surface areas and porosity from the resulting isotherms.

The structural characteristics of samples were examined by XRD and Raman spectroscopy techniques. XRD patterns were recorded on a Bruker (Siemens) D5005 diffractometer at room temperature using Cu K_α radiation (0.154 nm) from 1° to 10°, for low angle X-ray diffraction (LAXRD) measurements, and from 4° to 80°, for wide angle XRD (WAXRD), in 0.02° steps with 1 s per step. Raman spectra were collected under the ambient conditions on a LabRAMHR (Jobin Yvon) spectrometer. The excitation was provided by the

514.5 nm line of an Ar⁺ Kr⁺ ion laser (Spectra Physics), keeping the sample under microscope. The power of the incident beam on the sample was 100 μW. Because the laser beam can be precisely focused, it was possible to perform quantitative evaluation of band intensities between the samples studied. The laser beam was focused through microscope objective lenses (100×) down to a 1 μm spot on the sample. The acquisition time was adjusted according to the intensity of the Raman scattering. The wavenumber values reported from the spectra are accurate to within 2 cm^{−1}. For each solid, the spectra were recorded at several points of the sample to ascertain the homogeneity of the sample; the averages of these spectra are plotted and presented in this paper.

The recording of transmission electron micrographs (TEM) was carried out using a JEOL 2010 LaB₆ equipment operating at 200 kV. The samples were dispersed in ethanol using a sonicator and a drop of the suspension was dripped onto a carbon film supported on a copper grid and then ethanol was evaporated.

Thermogravimetry (TG–dTG, performed on a “Labsys-TG” instrument from Setaram) was used in order to determine the thermal stability of the samples. The samples (~50 mg) were heated from 300 K to 1073 K with a heating rate of 5 K min^{−1} in a flow of N₂.

Surface concentrations of N, C and O were determined by means of XPS technique, which was done using KRATOS AXIS Ultra DLD spectrometer equipped with a hemispherical electron analyzer and an Al anode (Al K_α = 1486.6 eV) powered at 150 W, a pass energy of 20 eV, and a hybrid lens mode. The detection area analyzed was 700–300 μm. Charge neutralization was required for all samples. The peaks were referenced to the C–(C, H) components of the C1s band at 284.6 eV. Shirley background subtraction and peak fitting to theoretical Gaussian–Lorentzian functions were performed using an XPS processing program (vision 2.2.6 KRATOS). The residual pressure in the spectrometer chamber was 5 × 10^{−9} mbar during data acquisition.

2.3. Surface acid–base properties

2.3.1. Gas phase adsorption calorimetry

The acid–base properties in gas phase were studied by adsorption microcalorimetry of NH₃ (PA (Proton Affinity in gas phase) = 853.6 kJ/mol) and SO₂ (PA = 672.3 kJ/mol) respectively. Experiments were performed at 423 K in a heat flow calorimeter (C80 from Setaram) linked to a conventional volumetric apparatus equipped with a Barocel capacitance manometer for pressure measurements [34]. The samples were pretreated in a quartz cell by heating overnight under vacuum at 623 K; this temperature was reached using a heating rate of 1 K min^{−1}. The differential heats of adsorption were measured as a function of coverage by repeatedly sending small doses of respective gas onto the sample until an equilibrium pressure of around 67 Pa was reached. The sample was then outgassed for 30 min at the same temperature, and a second adsorption run was performed at 423 K on each sample, until an equilibrium pressure of about 27 Pa was attained. The difference between the amounts adsorbed in the first and second adsorptions at 27 Pa represents the irreversibly adsorbed amount (V_{irr}) of the respective gas, which provides an estimation of the number of strong acidic/basic sites. A 1:1 stoichiometry for the adsorption on the active site was assumed.

2.3.2. PEA-TPD

The temperature programmed desorption measurements of 2-phenylethylamine (PEA, ACROS, purity ≥ 99.5%) from the saturated powders have been performed in a thermogravimetric analyzer (Labsys-TG, from Setaram). Prior to the desorption analysis, the samples were dried in an oven at 393 K overnight and then saturated by pure PEA at 303 K in N₂ flow [30,33]. The saturated

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