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Porosity of SBA-15 after functionalization of the surface with aminosilanes

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ABSTRACT

Functionalization of the mesoporous silica walls by organic species results in formation of porous hybrid materials. Combination of organic and inorganic components leads to the materials whose properties differ considerably from those of their individual, isolated components, especially with respect to their surface chemistry, hydrophilicity/hydrophobicity and/or pore connectivity and size distribution. In this paper a detailed porosity characterization of SBA-15 silica before and after its surface functionalization with $(R_2O)_3$-Si-R_1-NH_2 molecules is reported. The results obtained from nitrogen sorption were compared to those derived from quasi-equilibrated thermodesorption of n-nonane and from water and n-heptane thermoporosimetry. A small decrease of the pores size and pore volume upon the modification was detected for all amine functionalities, the largest in the case of N-(2-aminoethyl)-3-(trimethoxysilyl) propylamine. Water thermoporosimetry was found to be the most sensitive method, allowing to quantify these differences.

1. Introduction

Mesoporous materials are nowadays being extensively investigated due to their increasing use in various fields, such as catalysis [1] adsorption [2], electronics [3], chromatography [4], drug delivery [5,6] or medical diagnostics [7]. Among these materials, SBA-15 mesoporous silica attracts great attention because of the ordered pore system, uniform pore size, the ease of tailoring the mesopores of various diameter and relatively thick silica walls providing high stability and ensuring long storage time [8]. It additionally offers the opportunity of incorporating organic components within its silica framework in order to achieve combination of the properties of both components. Possibility of combining the enormous functional diversity of organic chemistry with the advantages of a thermally stable and robust inorganic substrate is especially attractive for the materials scientists [4].

In order to use mesoporous materials in any fields of science or technology its porosity should be precisely characterized. Low temperature adsorption of gases (mainly N_2 or Ar) is considered as the standard method for porosity characterization. However, due to some limitations of this method (such as time-consuming

measurements, expensive equipment, relatively large samples needed and limited choice of the adsorptives) [12,13], alternative methods for characterization of porous materials are still being investigated and developed.

One of novel experimental methods for studying porous properties of solids is quasi-equilibrated temperature programmed desorption and adsorption (QE-TPDA), employing the standard temperature programmed desorption (TPD) apparatus equipped with a chromatographic thermal conductivity detector (TCD) [14]. The QE-TPDA measurements are performed by slow heating or cooling a small sample of the porous adsorbent, purged with a carrier gas containing small admixture of the adsorptive. In principle, QE-TPDA measures the amount of substance desorbed or adsorbed by a sample as a function of temperature which is changing cyclically. In the case of n-nonane the QE-TPDA measurements cover both the micropores and the mesopores since its concentration in the carrier gas (ca. 0.4%) is close to the saturation value at room temperature (0.52% at 25 °C). The more detailed description of the QE-TPDA of n-nonane was published earlier [14–16]. Mesopore size distributions can be calculated from the obtained profiles according to a modified BJH method [14]. The main advantages of this method are relatively short time of the measurements (about 2 h), simple and inexpensive equipment, very small samples required (2–10 mg) and possibility of

performing cyclic measurements combined with modification of the studied sample. The main drawbacks are hidden in the assumptions of the BJH scheme.

Another promising method for characterizing mesoporous materials is thermoporosimetry (TPM). It is based on the fact that a fluid confined in the pores of a solid material experiences an important shift of its liquid to solid transition temperature (ΔT) and this shift is related to the size of the pores, in which the liquid is trapped [17], according to the Gibbs -Thomson equation. In the standard TPM experiment the sample of a porous material is soaked in the liquid medium, whose melting or crystallization profiles are measured with differential scanning calorimetry (DSC). This method is simple, inexpensive and nondestructive. Additionally, it requires only a small amount of sample (c.a. 2 mg) and short time for experiment (about 30 min). Owing to the possibility of using different liquid compounds TPM offers a wide range of potential applications. Water is the most commonly used liquid probe, especially for examining the hydrated materials which can collapse or change their properties during drying [18–20]. On the other hand n-alkanes, with non-polar molecules exhibiting weaker surface-fluid interactions, can be used for investigation porosity of hydrophobic materials. Despite simplicity and versatility of the DSC porosimetry, so far this method has been rarely used for routine characterization of the porous materials. A serious drawback of the TPM technique lies in the fact that the physical parameters of Gibbs-Thompson equation, such as surface tension, heat of fusion and density, and they temperature dependencies must be known a priori. This is challenging if not impossible to determine them independently. Other complications arise from the presence of an unfrozen adsorbed layer on the pore walls. It is well known that not all the probe takes part in the phase transition, as its significant part adsorbed on the surface of the pore remains liquid. Consequently, the radius determined using the Gibbs-Thomson equation does not reflecting the real pore size. In order to avoid these problems the experimental work often resorts to the use of reference materials with known pore size for calibration procedure [19–24].

The aim of this work was a detailed porosity characterization of a series of SBA-15 silicas as well as their derivatives obtained by grafting with different aminesilanes, with special attention focused on porosity changes resulting from anchoring of bulky amine functional groups onto their internal and/or external surfaces. Typical changes in porosity upon such a modification are quite small [25,26], therefore their precise quantification is rather demanding. By complementary use of three methods for studying porosity deeper insight into the properties of studied materials could be obtained. On the other hand, such an approach gave also opportunity to compare and contrast the methods used for porosity characterization.

2. Experimental

2.1. Materials

The SBA-15 silicas denoted as F1, F2 and F3 were prepared in the same way, according to the method described in our previous papers [21,22]. Briefly, the mixture of Pluronic P123 [(EO)20(PO)70(EO)20, Sigma Aldrich], H_2O, HCl (37%) and TEOS [tetraethylorthosilicate, Sigma Aldrich], corresponding to a molar ratio of 1 SiO_2/0.017 P123/2 HCl/80 H_2O was aged at 55 °C for 24 h and then hydrothermally treated for the next 24 h at 130 °C. The products were dried at 80 °C and calcined at 550 °C for 5 h in air to remove the organic template. Before the functionalization procedure the samples F1, F2 and F3 were exposed for 5 h to water vapour by keeping them at room temperature in desiccator containing saturated solution of $ZnSO_4$, which provides 90% humidity. In the next step the samples were dried for 2 h at 200 °C.

Conditioned in such way SBA-15 support F1 (1 g) reacted with 20 mmol/dm^3 of 3-aminopropyltriethoxysilane (APTES; Sigma-Aldrich) diluted in hexane, F2 with 3-aminopropyltrimethoxysilane (APTMS; Sigma-Aldrich) also diluted in hexane (Sigma-Aldrich) and F3 with N-(2-Aminoethyl)-3-(trimethoxysilyl) propylamine (AEAPTS; Sigma-Aldrich) diluted in toluene. Next, the obtained suspensions were stirred under 40 °C for 20 h. The resultant white solids (named F1A, F2A, F3A, respectively) were filtered off and dried. The parameters of the agents taken for functionalization procedure were collected in Table 1.

Prior to the porosity investigations the studied materials were characterized by small angle X-ray diffraction, electron microscopy (SEM/TEM) and thermogravimetry.

2.2. XRD and SEM/TEM

Small angle X-ray diffraction patterns were recorded with a Philips 1710 powder diffractometer using Ni filtered Cu K_α radiation. Morphology and structural ordering of the investigated materials were studied by means of JEOL JSM − 7500F Field Emission Scanning Electron Microscope, equipped in TED detector.

2.3. Thermogravimetry

Thermogravimetric analyses (TG) were performed using a TGA/SDTA 851^e Mettler Toledo apparatus, with accuracy equal to 10^{-6} g. For the experiments the samples were placed in alumina crucible and the measurements were carried out in both argon (flow 80 cm^3/min) and air (flow 60 cm^3/min atmosphere. The samples were heated from 25 to 1000 °C with a constant heating rate $\beta = 10$ °C/min. Simultaneously, evolved gaseous products were analysed using a ThermoStar GSD300T Balzers quadruple mass spectrometer (QMS). The mass spectrometer was operated in electron impact mode (EI) using channeltron as a detector. Screening analyses were performed in the selected-ion monitoring (SIM) mode. The following ions' characteristics of each molecule, such as 18 and 44, for H_2O and CO_2, respectively, were monitored. Additionally, the QMS line 15 was chosen as good representation of the molecules formed in decomposition of amine used for functionalization because it is quite stable in apparatus and does not undergo further fragmentation.

2.4. Nitrogen adsorption-desorption isotherms

The nitrogen adsorption-desorption isotherms were obtained at −196 °C with a Quantachrome Nova 2000 apparatus. Prior to the measurement the samples were outgassed for 18 h at 200 °C. Specific surface area determination was based on BET formalism. The mesopore size distributions were calculated from the desorption branch using the classical BJH scheme [27] as well as the NLDFT method (DFT Kernel: N_2 at 77 K on silica, cylindrical pore, NLDFT equilibrium model) which is presently the recommended approach to PSD determination [28]. The micropore volume was determined using the *t*-plot method.

2.5. QE-TPDA of nonane

For this study small samples of ca. 2–4 mg were used. In order to avoid any thermal damage of the samples, they were not activated by heating in flow of He, but they were only purged with pure He for 30 min prior to the QE-TPDA measurements. The initial adsorption was carried out at room temperature by replacing pure helium with helium containing a small admixture of nonane (ca.