Pore size distribution of MCM-41-type silica materials from pseudomorphic transformation - A minimal input data approach based on excess surface work

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ABSTRACT

A collection of porous silica based materials have been synthesized by pseudomorphic transformation of silica-gel, commonly used in chromatography, to an ordered MCM-41 type material. The modified materials exhibit a bimodal pore size distribution (4 nm of MCM-41 and 20 nm for silica gel) with slit type geometry of the unmodified silica material and a cylindrical pore geometry of the MCM-41 type structure of the fully transformed material. Based on the Derjaguin-Broekhoff-de Boer (DBdB) theory and the previously published Excess Surface Work (ESW) approach we propose a method to derive the pore size distribution directly from the experimental isotherm without the need for a reference isotherm. Combining the ESW and the disjoining pressure approach an expression for a critical width is derived. This in turn relates the critical width to the relative pressure in a range where capillary condensation occurs. The method is simple, yet it provides information comparable to the standard NLDFT (non-local density functional theory) approach. Due to the absence of an interaction model the method is applicable to cases where interaction parameters are not available. We demonstrate the utility of the method comparing the results of characterization of the bimodal biphasic silica materials with the commonly used NLDFT and the BJH (Barrett-Joyner-Halenda) approach.

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1. Introduction

In the past years a large number of novel functionalized materials has been reported striving to enhance the functional properties of the unmodified porous materials [1,2,3]. The modifications include surface functionalization or incorporation of heteroatoms into the original material. The modifications apart from altering the chemical composition also change the pore size distribution (PSD) of the porous material and in turn affect the adsorption properties of the material. Therefore the distribution of pore sizes and its change upon modification is of main interest in synthesis of tailor made porous materials. The pore size distribution for mesoporous

materials can be obtained from experimental methods like small angle x-ray or neutron scattering (SAXS and SANS), mercury porosimetry, electron microscopy and for meso- and microporous materials from gas adsorption techniques. The last method enjoys a wide popularity since it allows to cover a wide range of pore sizes and is relatively simple and cost-effective to use. Gas adsorption is nowadays routinely used to characterize microporous and mesoporous solids with applications in separation technology, gas capture and storage as well as heterogeneous catalysis. Interpretation of the adsorption isotherms relying on a particular theoretical model provides rich information on the internal surface and pore volume as well as on the energetic characteristics of porous materials. The wide range of pore sizes present in porous materials and the different adsorption mechanisms involved complicate a unified theoretical description and gave rise to a variety of theoretical

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approaches ranging from thermodynamics based effective approaches to atomistic level detail representation of the gas-surface interactions [4]. Several methods have been proposed to determine the PSD employing effective thermodynamics based theories like the BJH method based on the Kelvin equation, the IDBdB (Improved Derjaguin-Broekhoff-de Boer) method [5] based on the Derjaguin-Broekhoff-de Boer [6] theory and the NLDFT and GCMC (Grand Canonical Monte Carlo) methods based on atomistic level of detail descriptions of the molecule-surface interactions. Thermodynamics based methods due to the effective treatment of the adsorption fail to account for molecular size effects that become important for small pores [4]. Corrections introduced to remedy the adsorption in small pores employ empiric corrections at the expense that additional experimental data for a reference isotherms are required to use these methods [7,8,9].

Atomistic representation based methods like DFT (density functional theory) and its variants NLDFT, QSDFT (quenched solid density functional theory) and GCMC provide molecular level information in a concise manner and describe the adsorption also in small pores, provided a parametrized force-field describing the adsorbent-adsorbate interaction is available and the pore geometry is known. For functionalized porous materials lacking either detailed force-field information or reference isotherms of a functionalized nonporous sample the BJH method still remains the method of choice, despite its long-known shortcomings. Given the above described limitations of the methods we propose an approach with minimal experimental input data enjoying improved accuracy, comparable to the NLDFT method. The method starts from the Derjaguin-Broekhoff-de Boer theory [6] and extracts the relevant isotherm parameters from the excess surface work (ESW) representation [10] of the experimental isotherm. The ESW method has been previously used to determine surface energies and specific surface areas from the adsorption isotherm [10]. The DBdB theory has been successfully applied to the characterization of mesoporous materials (pore width larger than 2.5—3 nm) [11—13] and has served as a starting point for further developments, taking into account the dependence of the surface tension on the pore radius [5,14], describing the adsorption induced stress of the porous network [15] and has been extended by Monte Carlo methods describing toluene adsorption on silica materials [16]. The parameters for the DBdB equation were extracted from an experimental isotherm of the reference material using the theoretical disjoining pressure isotherm [8].

To demonstrate the method we have chosen a sequence of modified siliceous materials exhibiting a bimodal pore size distribution for which N_2 adsorption isotherms have been recorded at 77 K. The choice of the porous material is motivated by two considerations: first to provide a comparison with the standard method the material should be amenable to characterization by the NLDFT method and second the material should constitute a demanding test case with a complex bimodal PSD.

In this work, we introduce the procedure combining the ESW with the DBdB method and the disjoining pressure approach. A more general interpretation of the ESW plot will be given below. Finally, we discuss of the applicability of the method and compare our method to the NLDFT and BJH methods using experimental data for a series of bimodal mesoporous siliceous materials.

2. Experimental section

2.1. Materials

Silica gel material for preparative liquid chromatography (MILLIPORE PREPPAKB®-500/SILICA) with a pore size of around 15 nm and a specific pore volume of 1.1 cm^3 g^{-1} was used as starting material for the pseudomorphic transformation [17]. Cetyltrimethylammonium hydroxide (CTAOH) was prepared by ion exchange of cetyltrimethylammonium bromide (CTAB (Fluka, 96%)) using the anion exchanger Ambersep® 900(OH) (Alfa Aesar) for 24 h at room temperature. After ion exchange, the concentration of CTAOH has been determined by back titration of a solution from CTAOH and hydrochloric acid with sodium hydroxide as titrant. After that the solution was diluted to 0.07 M. The transformation reaction into MCM-41 took place in 50 ml PTFE autoclaves at 393 K for 72 h. The amount of CTAOH solution was varied between 0 and 42 ml g^{-1} in the transformation solution. After the synthesis the products were filtered, washed three times with distilled water and dried at 323 K for 24 h. After drying, the products were calcined in air using the following temperature program: heating rate 10 K min^{-1} to 823 K with isothermal steps at 423 K for 1 h, 673 K for 1 h, 823 K for 4 h [17]. Five different materials were used for the nitrogen sorption measurements. First material was the pristine silica-gel from MILLIPORE with a monomodal pore system. Then three materials with a bimodal pore system were synthesized from MILLIPORE silica-gel as a starting material by varying the amount of CTAOH solution from 10 (25%) over 20 (50%) to 30 (75%) ml/g. We will use the following designations: original silica gel - MCM-41-0%; samples with certain amount of modification - MCM-41-25%, MCM-41-50%, MCM-41-75%; fully transformed material - MCM-41-100%. The obtained granules are characterized by a bimodal pore system consisting of the MCM-41 generated by the pseudomorphic transformation and the pore system of the silica-gel. By complete transformation of the silica-gel with 42 (100%) ml g^{-1} of CTAOH a MCM-41 material with monomodal pore structure was synthesized. All textural data are presented in Table 1.

2.2. N2 sorption

Nitrogen physisorption isotherms were recorded at 77 K with static-volumetric/manometric sorption analyzer SURFER from Porotec GmbH/Hofheim/Ts. (Germany) after sample pretreatment in vacuum (less than 10^{-2} Pa) for 10 h at 523 K. Specific surface areas were calculated using the BET method, the total pore volume was obtained at $p/p_0 = 0.995$. The mesopore volume of the MCM-41 phase was determined by the t-plot method in the range of $p/p_0 = 0.6—0.8$.

3. Theory

3.1. The excess surface work - disjoining pressure model

The excess surface work (ESW) has been introduced by Adolphs and Setzer as the product of the adsorbed amount and the change of the chemical potential [19,20]:

$$\Phi = n_{ads}\Delta\mu, \qquad (1)$$

with $\Delta\mu = RT \ln(p/p_0)$ and R = 8.314 J mol^{-1}K^{-1}, absolute temperature T, pressure p and saturation pressure p_0, where $\Delta\mu$ is the

Table 1
Basic characteristics of the samples: pore volume of MCM-41, pore volume of silica gel and BET surface area of the whole sample.

Sample name	V_{MCM-41}/cm^3g^{-1}	$V_{silicagel}/cm^3g^{-1}$	S_{BET}/m^2g^{-1}
MCM-41-0%	0	1.10	290
MCM-41-25%	0.17	0.94	378
MCM-41-50%	0.42	0.62	595
MCM-41-75%	0.67	0.29	822
MCM-41-100%	0.94	0.06	1122