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Systematic investigation of the pore structure and surface properties of SBA-15 by water vapor physisorption

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ABSTRACT

In order to establish a structure-property correlation in water vapor sorption, various sets of the ordered mesoporous silica SBA-15 with systematically varying properties were synthesized and characterized. General trends concerning the surface polarity, aging temperature during synthesis and micropore volume were observed. Calcining the materials with increasing temperatures of 300–800 °C decreases the performance in water vapor sorption which correlates mainly with the amount and type of silanol groups on the silica surface. Furthermore, the aging temperature during synthesis influences the water vapor sorption capacity of SBA-15 at low relative pressure. The best results in terms of an increased uptake of water over a broad range of relative pressure can be obtained for materials with high micropore volume and high surface polarity. They can be tailor-made by using a routine to remove the template, i.e., a combination of extraction with ethanol and subsequent calcination at 300 °C.

1. Introduction

Increasing energy costs and concerns about the environment have led to a new interest in adsorption heating and cooling systems. Heating and cooling of buildings is an energy-consuming technology and makes up a large part of the final energy consumption all over the world providing a big potential to save energy [1]. Since adsorption heat transformers (AHT) can use heat as a main energy source instead of electricity, they are able to make use of low temperature heat sources like industrial waste heat, geothermal energy or even ambient temperature [2]. The big drawback is that AHT are not yet able to compete with conventional air-conditioning systems due to their low efficiency [3]. So far, mostly industrially available materials such as zeolites and silica gels are used in combination with water. They have, however, never been systematically optimized for applications in this field [4].

In recent years, many new promising adsorbent materials have been synthesized and tested in water vapor sorption [5]. Nonetheless, systematic studies focusing on structure-performance correlations are limited. However, in order to tailor adsorbents for different AHT processes, it is necessary to know about the influence of different material properties on the water vapor sorption performance. The important material properties at this point are the physical properties, e.g., surface area, pore volume and pore diameter, and the chemical properties such as the surface polarity [5]. For a systematic investigation of the material properties influence ideally the properties can be varied independently from each other. This approach will allow to assign the reason for changes in water sorption behavior to either physical or chemical properties. In the end, it will give insights into the influence of specific material characteristics which may be useful in the preparation of new adsorbent materials for water sorption and AHT.

Herein, SBA-15 is depicted as a perfectly suited model material for water vapor sorption even though it is not an efficient adsorbent for use in AHT. The synthesis of SBA-15 is well-known and different synthetic and post-synthetic routes can be used for the adjustment of the material properties [6–8]. The typical SBA-15 material is synthesized in a template-assisted approach. The template is removed by calcination at 550 °C. It is well-known that calcination at high temperatures leads to condensation of silanol groups on the surface of the material [9,10]. Thus, SBA-15 is reported to be rather hydrophobic and only adsorbs high amounts of water at high relative pressure [11–13]. Since for applications in AHT a steep uptake of water at rather low relative pressure is essential, SBA-15 is not suitable for the list of potential candidates for AHT [5,14]. Nevertheless, the different synthetic approaches allow to purposefully

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modify specific material properties rendering SBA-15 an interesting model material to explore structure-property correlations. It offers the unique opportunity to control various structural and chemical parameters and thus, bridges a materials gap between typically applied amorphous silica and structurally well-defined zeolites.

There are different possibilities to affect the structural properties in the scope of well-known synthetic procedures. The mesopore size and micropore volume can be controlled by the aging temperature during synthesis [6]. Moreover, there are other methods besides calcination to remove the template from the pores. The template can be extracted with an acidic ethanol solution which does not involve any high temperature treatment and thus, results in less shrinkage and less condensation of silanol groups [15,16]. Another possibility is to cleave the ether bonds in the template with sulfuric acid, followed by calcination at 300 °C. This rather gentle procedure yields materials with large mesopores that are also more stable than the typical SBA-15 [8].

In this work, different aging temperatures and combinations of template removal methods were used to create a variety of SBA-15 materials with either similar structural parameters and differing surface polarity or vice versa. Using different aging temperatures, materials with an increasing mesopore diameter are synthesized. Then, the materials are calcined at 550 °C in order to remove the template. For SBA-15 materials prepared in the same manner, Palkovits et al. found that the silanol number is higher for SBA-15 aged at 100 °C than for SBA-15 aged at 60 °C [17]. Thus, an increase in water uptake would be expected with increasing aging temperature.

In order to vary the surface polarity by calcination while maintaining the pore structure, the starting material has to be thermally stable. Therefore, SBA-15 is synthesized using the sulfuric acid route and calcined at 300 °C which produces a very stable intermediate. It may then be calcined again at temperatures between 300 and 800 °C for variation of the surface polarity without loss of structure. In addition, the micropore volume can be modified. Using a combination of extraction and calcination, materials with an extraordinarily high micropore volume for an SBA-15 are available and show a very good water uptake.

The insights gained in this first systematic study on structure property relations for water vapor sorption provide a basis to tailor suitable adsorbents for applications such as AHT and enable an improvement of efficiency.

2. Experimental

2.1. Materials

All reagents and solvents used were analytical grade and used as received. Triblock copolymer Pluronic P123 $(EO)_{20}(PO)_{70}(EO)_{20}$ and tetraethyl orthosilicate (TEOS, >99%) were purchased from Aldrich. Concentrated hydrochloric acid (HCl, 35–38%) and sulfuric acid (H_2SO_4, 95%) were purchased from Chemsolute. Ethanol and distilled water were technical grade.

2.2. Syntheses

2.2.1. Preparation of SBA-15 samples

SBA-15 was synthesized according to literature [6]. In a typical synthesis, 6 g of Pluronic P123 $[(EO)_{20}(PO)_{70}(EO)_{20}]$ were dissolved in 90 g of water and 180 g of 2 M aqueous HCl solution with stirring (400 rpm) at 35 °C. When P123 was completely dissolved, 2.1 g of TEOS were added to the solution and stirring was continued for 24 h. This mixture was hydrothermally treated under static conditions for 24 h at either 60, 80, 100 or 120 °C. Afterwards, the product was separated by filtration while the solution was still hot. Then, the solids were washed with acetone, except for materials synthesized at 60 °C which proceeded without washing since better material properties were observed when the materials aged at 60 °C were not washed. The obtained materials were then dried at 80 °C for 48 h.

2.2.2. Template removal

In order to remove the template, one part of the as-made material was calcined at 550 °C for 6 h (heating rate 1 K min^{-1}) [6]. Another part was treated with sulfuric acid and calcined at a lower temperature as described elsewhere [8]. 3.5 g of as-made SBA-15 were stirred (500 rpm) in a solution of 150 ml of ethanol and 5 drops of conc. HCl for 30 min at room temperature. The solid was recovered by filtration and dried without washing at 80 °C over night. 1 g of the extracted SBA-15 material was then stirred (400 rpm) in 60 ml of 48% H_2SO_4 solution at 90 °C for 24 h. The mixture was cooled down, decanted twice and filtered. The solid was washed with water until the eluent was neutral, then washed again with acetone and dried at 80 °C over night. To remove the remaining template, the solid was calcined at 300 °C for 3 h (heating rate 2 K min^{-1}). In order to obtain different concentrations of silanol groups in these materials, 0.2 g of the material were then calcined a second time at temperatures between 300 and 800 °C for 6 h (heating rate 2 K min^{-1}).

Moreover, the template can be removed by extraction and calcination. 1 g of as-made SBA-15 was stirred (400 rpm) in a solution of 150 ml ethanol and 15 drops of conc. HCl under reflux for 24 h. The solid was recovered by centrifugation and dried at 80 °C over night. In order to remove the remaining template, the material was calcined at 300 °C for 3 h (heating rate 2 K min^{-1}).

The samples are labeled as follows: calcined materials (C) and extracted materials (E) with aging temperature of 60–120 °C, e.g. C-60 or E-120, acid-treated materials (A) with temperature of the second calcination step 300 up to 800 °C, e.g. A-500. A comprehensive overview on all prepared samples with the respective synthesis conditions is given in Table S1.

2.3. Characterization

Powder XRD patterns were measured on a Siemens D5000 instrument using Cu-Kα radiation (λ = 0.154 nm). The nitrogen adsorption/desorption isotherms were measured on a Quadrasorb SI (Quantachrome Instruments). Prior to the measurement, the samples were degassed at 120 °C for at least 12 h. In order to calculate the specific surface area, the BET model was applied in the range of $0.05 \leq p/p_0 \leq 0.2$. The total pore volume was calculated from the amount of nitrogen adsorbed according to Gurvich at a relative pressure of 0.98. The pore size distribution and the average pore sizes were determined using the NLDFT-model for nitrogen at −196 °C on cylindrical silica pores. For analysis of the micropores, the t-plot model by Harkin and Jura was used. Water vapor adsorption/desorption isotherms were measured at 20 °C on an Autosorb iQ (Quantachrome Instruments). Before the measurement, the samples were degassed at 120 °C until they passed the degassing test (21 millitorr min^{-1}). The pore volume was calculated at relative pressures of 0.1 and 0.9. In order to relate the pore volume occupied by adsorbed water at high relative pressure to the total pore volume in the sample, the pore filling degree (PFD) was calculated as quotient of the pore volume from water adsorption at $p/p_0 = 0.9$ and the total pore volume determined from nitrogen physisorption.

3. Results and discussion

3.1. Adsorbent synthesis and general characterization

In order to obtain materials with varying structural properties, SBA-15 was synthesized at four different aging temperatures,