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Combined influence of pore size distribution and surface hydrophilicity on the water adsorption characteristics of micro- and mesoporous silica

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ABSTRACT

Adsorption processes are ubiquitous in nature as well as of great technological importance for gas separation, purification, storage and thermally driven heat pumps. This has led to a strong interest in the fundamental mechanisms governing adsorption phenomena and their exploitation to tailor adsorption systems for specific applications. In particular, the adsorption of water on porous silica exhibits remarkable properties due to the strong polarity of the adsorbate and moderate hydrophilicity of the adsorbent. It is generally accepted that the adsorption of water vapor on porous silica depends upon the concentration of surface silanols and the pore size. In fact, materials with ordered mesopores and a well-defined pore size have been used as model systems to demonstrate that water adsorption occurs predominantly through capillary condensation. While the pore surface chemistry is modified to become more hydrophilic after filling of the pores in these materials, the overall shape of the water adsorption isotherm (Type V) is not significantly affected in subsequent adsorption measurements. The present contribution shows that conservation of the isotherm shape is a unique phenomenon related to ordered mesopores but doesn't apply to materials with a more complex pore structure. For materials with wider pore size distributions including micropores, a synergistic effect of surface hydroxylation and pore size leads to a dramatic change in the water adsorption isotherm after the first adsorption/desorption cycle. In fact, we demonstrate that the water cycling capacity at relative pressures below the onset of capillary condensation increases significantly in these systems. These results contribute to a fundamental understanding of water adsorption in complex systems and have important implications in applications such as adsorption heat pumps where a large water cycling capacity in a specific relative pressure window is required.

1. Introduction

During the past two decades adsorption-based heating and cooling technologies have regained significant attention in the scientific community. Indeed, adsorption heat pumps are believed to be energy efficient alternatives to conventional vapor compression systems. This is especially true where low-grade heat (below 100 °C) is widely available, for instance in industrial processes, combined heat and power plants, solar thermal installations or datacenters. Mechanistically, an adsorption heat pump is based on the adsorption/desorption of a working fluid onto a porous solid sorbent (the working pair) using thermal energy to drive the desorption process [1,2]. In terms of cost, safety and latent heat of vaporization, water is the most attractive and environmentally benign working fluid. With regards to the porous adsorbent, a wide range of materials have been reported for heat pump applications, such as silica, aluminophosphates, salt composites, porous carbons and more recently metal-organic frameworks [2–5]. Among these, porous silica is one of the most well known water adsorbents and frequently used materials in heat pump technology to date [6]. This is mainly due to its low cost of production and water cycling at moderate temperature lifts suitable for low-grade heat utilization. However, an important drawback of silica gel adsorbents is their limited water cycling capacity for specific applications [7]. As a result, a large amount of silica gel and heat exchanger area are

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needed for a given thermal power of the adsorption heat pump, which increases system cost.

In order to address the limited water cycling capacity of silica, a fundamental understanding of the adsorption of water on silica is required. While it is generally accepted that the adsorption characteristics depend upon the porous volume, the pore surface chemistry and the pore size distribution of the adsorbent, a clear understanding of the synergistic effects between these parameters has yet to be established. Previous investigations on silica materials with highly ordered porosity reported Type V water adsorption isotherms with a clear capillary condensation regime in the first adsorption cycle, while the second and subsequent adsorption isotherms are steeper in the regime of partial monolayer coverage and the capillary condensation regime is shifted to lower relative pressure due to enhanced hydrophilicity of the adsorbent [8–12]. In contrast, industrial-grade silica gels such as types A or RD exhibit high surface areas, wide pore size distributions including micropores and disordered pore networks. These materials have been found to exhibit nearly linear water adsorption isotherms over a wide range of relative pressures [13,14] which is fundamentally different from the Type V water adsorption isotherms exhibited by the highly ordered porous silicates with narrow pore size distributions. Attributing the different shape of the adsorption isotherm to the broader pore size distribution alone neglects the importance of surface chemistry in the adsorption of water vapor on porous silica and the fact that the hydrophilicity may readily change following the first water adsorption cycle. This change has been attributed to irreversibly adsorbed water or hydroxylation of the silica surface which occurs spontaneously during the adsorption isotherm measurement even at room temperature [11,12,15].

The present study provides insight into the different mechanisms of water adsorption on silica materials with ordered and disordered porosity in the micro- and mesoporous regimes. The pore size distributions as well as the silanol content of the as-calcined, dry materials were characterized. The measurement of two successive water adsorption isotherms provided the adsorption characteristics of the hydrophobic samples (1st adsorption isotherm) as well as the hydrophilic samples (2nd adsorption isotherm). Finally, the pore size distributions and silanol content were determined for the hydrophilic samples in order to correlate the water adsorption characteristics with changes in pore size or surface chemistry. For hydrophobic surfaces, it is shown that the adsorption isotherms are of Type V and pore filling occurs over a limited range of p/p_{sat} regardless of the pore organization. After the first adsorption cycle, the water adsorption characteristics change dramatically for the porous silicates with disordered pore networks and broad pore size distributions comprising a significant fraction of micropores, whereas the Type V isotherm shape is maintained in the case of ordered mesopores with narrow pore size distribution. These observations are explained in terms of the combined effects of different adsorption mechanisms for micropores and mesopores as well as a change in surface hydrophilicity due to water exposure. These findings contribute to the fundamental understanding of water adsorption on porous silica with synergistic effects between pore size distribution and surface chemistry and will help to qualify existing porous silica and design novel silica adsorbents for applications involving water adsorption, such as desiccants or adsorption heat pumps.

2. Experimental section

2.1. Materials

MCM-41 (ACS Material) and RD-type silica (Fuji Silysia Chemical) were obtained from the suppliers and calcined at 600 °C for 3 h in air prior to use. Further, two silica adsorbents with narrow pore size distributions including both micro- and mesopores were synthesized using established liquid crystal templating techniques [16–22]. The templated porous silica materials were synthesized by first mixing aqueous hydrochloric acid (0.01 M) and cetyltrimethylammonium bromide (CTAB) (50/50 wt%) using a vortex mixer. Tetraethylorthosilicate (TEOS) was then added to this mixture and stirred. A TEOS:H_2O:CTAB molar ratio of 0.5:1:0.05 was used for the final product labeled PSM1, while a TEOS:H_2O:CTAB molar ratio of 0.1:1:0.05 was used for the final product labeled PSM2. As the reaction proceeded, ethanol was formed which was then removed *in vacuo* on a rotary evaporator. The viscous mixture was left to stand for 72 h at room temperature. The resulting precipitate was recovered by filtration on a Buchner funnel, washed with water and ethanol and dried in an oven at 100 °C overnight. The dried powder was then calcined at 600 °C for 3 h in air in order to remove the organic template. All chemicals were used as provided by the supplier (Sigma–Aldrich) without any further modifications.

2.2. Characterization

Water sorption isotherms were recorded on a dynamic vapor sorption apparatus (DVS Vacuum 1 from Surface Measurement Systems, UK). Measurement pressures in the chamber were controlled by introducing water vapor from a water reservoir at 50 °C *via* a mass flow controller. Adsorption/desorption cycles were performed at a constant temperature of 50 °C. In a typical experiment, a few milligrams of the sample material were placed in the experiment chamber. In a first step, the sample was heated to 90 °C for 1 h at a vacuum better than 10^{-4} mbar for complete degassing and desorption. The resulting mass was taken to be the dry reference mass. The sample was then cooled to 50 °C *in vacuo* prior to the measurement. To obtain the adsorption isotherm, the sample mass was recorded every 10 s for vapor pressure (p) increments from $p/p_{sat} = 0–0.9$, where p_{sat} is the saturation pressure of water at 50 °C (124 mbar). For each pressure step, the pressure was maintained until the change in mass (Δm) over time (Δt) became negligible ($\Delta m/\Delta t < 0.05\%/\text{min}$) and the corresponding values for pressure and mass were taken as the equilibrium values for the adsorption and desorption isotherms. For all samples, a second water adsorption isotherm was recorded directly after the first water adsorption isotherm without any sample treatment in between the two isotherm measurements.

The silica materials were characterized in two physical states, referred to as dry (-D) and wet (-W). The dry state refers to the material obtained after the 600 °C calcination process with minimal exposure to moisture. The wet state of the materials was obtained by exposing the silica samples to saturated water vapor at 50 °C for 12 h. The 1st water adsorption isotherms of the wet samples were found to be equivalent to the 2nd water adsorption isotherms of the corresponding dry samples (Fig. S1), indicating that the rehydration of the surface occurs mostly within the timescale of a few hours for the adsorption isotherm measurement, with little changes observed upon further exposure to saturated water vapor. Also, the degassing procedure described above does not restore the 1st adsorption isotherm of the samples once the samples have been rehydrated (Fig. S1).

Nitrogen adsorption–desorption experiments were performed on degassed (90 °C *in vacuo* for 2 h) powdered samples (approximately 100 mg) at 77 K on a Micromeritics ASAP2020 analyzer equipped with 1, 10 and 100 Torr transducers and employing a 65-point pressure table in adsorption/desorption ranging from 0.01–940 mbar of N_2. The pressure range used to calculate the BET specific surface area was selected according to the rules by