# Hydration of hexagonally ordered mesoporous silica


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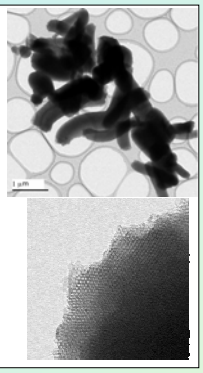
## Introduction

Sorption of gases, especially nitrogen is a standard method of characterization of porous materials. Using sorption of gases one can determine the surface area of a porous material, the volume of pores and estimate the size of the pores. On the other hand, sorption of gases provides only geometrical information about studied systems and is not able to characterize the intermolecular interactions of the material with the molecules typical for the environment at the conditions at which the materials are normally used.

Practically in all applications, nanomaterials are in contact with water vapor, which determines the need for water sorption studies. Moreover, the physical state of water in nanopores is of fundamental interest.

Here we report a study of hydration of MCM-41 (Figure) and present a comparison with data for SBA-15.

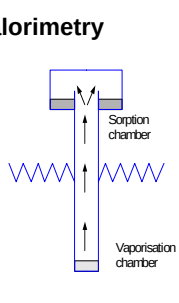


## Sorption calorimetry

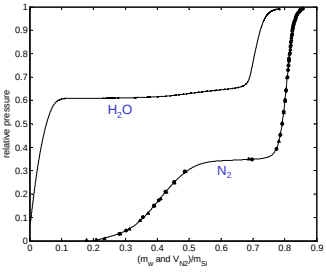
$$H_w^{mix} = H_w^{vap} + P^{sorp}\frac{H_w^{vap}}{P^{vap}}$$

$$a_w = 1 - \frac{P^{vap}}{P^{vap}_{\max}}$$

$$m_w = \frac{\int P^{vap} dt}{H_w^{vap}}$$




## Apparent density of water in MCM-41




The capillary condensation regimes in water and nitrogen sorption isotherms of MCM-41end at different values of volumes of liquids. The same volume of pores is filled by different amounts of liquids. This means that the formal density of water in pores is lower than in the bulk.

| Material | Pore diameter, nm | Method | Temperature, K | Density, g/cm³ | ref |
|---|---|---|---|---|---|
| **Vycor glass** | ~4 | Neutron scattering | - | 0.89 | Benham et al |
| **MCM-41** | 3.3 | $H_2O$ and $N_2$ sorption | 303 | 0.89 | Calculated from Data of Branton et al |
| **MCM-41** | 3.9 | $H_2O$ and $N_2$ sorption | 298 | 0.88 | This work |

## Surface density of OH – groups in calcined MCM-41

Nitrogen sorption: the surface area *A* of MCM-41 from data is 994 m²/g (BET).
Water sorption: the amount of water needed for the monolayer coverage $h_w$ =0.048 g/g.
*This would correspond to 170 m²/g.* Conclusion: the "monolayer" of water does not cover the whole surface, water adsorbs only on OH groups.

Combining $H_2O$ and $N_2$ data we calculated the surface density of OH groups as 1.6 nm$^{-2}$

$$n_{OH} = \frac{h_w N_a}{M_w A \cdot 10^{18}}$$

## Calculations of pore size

X-ray + capillary condensation

$$r = \sqrt{\frac{A_w \phi_p}{\pi}} = d\sqrt{\frac{2\phi_p}{\pi\sqrt{3}}} = 0.6063 \cdot d\sqrt{\phi_p}$$

$$\phi_p = \frac{1}{1 + d_w/(h_w d_s)}$$

The pore radius

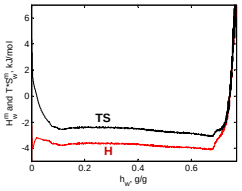
| Density of water | X-ray + capillary cond-n | Kelvin-Cohan equation |
|---|---|---|
| Bulk density | 18.9 Å | 18.4 Å |
| Pore density | 19.4 Å | 20.9 Å |

Capillary condensation (Kelvin-Cohan equation)

$$r - t = -\frac{2\gamma\cos\theta \cdot V_m}{RT\ln a_w}$$

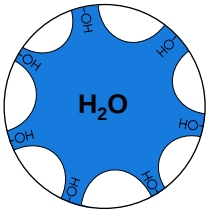
$$r = -\sqrt{\frac{V_{tot}}{V_{tot} - V_{ads}}} \cdot \frac{2\gamma\cos\theta \cdot V_m}{RT\ln a_w}$$

## Enthalpy and entropy of sorption

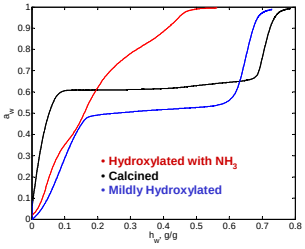



The partial molar enthalpy of mixing of water with MCM-41is exothermic. This indicates that the hydrogen bonds are preserved. The entropic contribution is negative. This indicates an increase of order during capillary condensation.

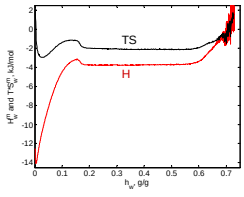
We propose a model to explain these data. Small cavities adjacent to silica walls remain unfilled during capillary condensation (see figure to the left). Hydration of small cavities occurs without breaking the hydrogen bonds.




## Hydroxylated MCM-41

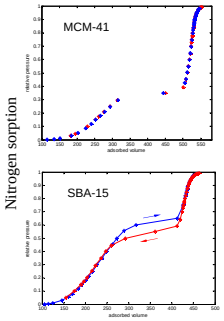



MCM-41 hydroxylated at mild conditions preserves ordered porous structure



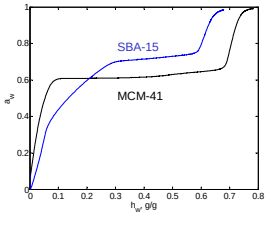

The enthalpy of hydration of hydroxylated MCM-41 is strongly exothermic at low water contents

## MCM-41 and SBA-15




The nitrogen sorption isotherms of MCM-41 and SBA -15 have similar shapes in the adsorption (pre - capillary condensation) regime.

The shapes of water sorption isotherms are different due to adsorption of water in micropores of SBA-15.




Water sorption

## Conclusions

We have studied hydration of MCM-41 silica using sorption calorimetry. The calorimetric results were compared with the results on sorption of nitrogen on the same material. The main conclusions are:

- The **silanol number** calculated from comparison of water and nitrogen adsorption isotherms of the studied material is **1.6 nm$^{-2}$**
- The apparent **density of water** in the pores at RH of capillary condensation is **0.88 g/cm$^3$**
- The data on water sorption can be used for accurate calculations of pore sizes of mesoporous materials
- The **capillary condensation** of water in the pores of MCM-41 **is driven by enthalpy**, the entropy effect is negative
- The observed heat effect and the apparent density of pore water are in agreement with the mechanism of capillary condensation that involves formation of **small unfilled cavities adjacent to the silica walls**
- The uptake of liquid water by MCM-41 leads to **entrapment of air** in the pores while the uptake of water vapor does not
- Sorption of water in micropores of SBA-15 leads to a different type of sorption isotherm compared to MCM-41