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Pore size distribution calculation from ^{1}H NMR signal and N_2 adsorption–desorption techniques

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ABSTRACT

The pore size distribution (PSD) of nano-material MCM-41 is determined using two different approaches: N_2 adsorption–desorption and ^{1}H NMR signal of water confined in silica nano-pores of MCM-41. The first approach is based on the recently modified Kelvin equation [J.V. Rocha, D. Barrera, K. Sapag, Top. Catal. 54(2011) 121–134] which deals with the known underestimation in pore size distribution for the mesoporous materials such as MCM-41 by introducing a correction factor to the classical Kelvin equation. The second method employs the Gibbs–Thompson equation, using NMR, for melting point depression of liquid in confined geometries. The result shows that both approaches give similar pore size distribution to some extent, and also the NMR technique can be considered as an alternative direct method to obtain quantitative results especially for mesoporous materials. The pore diameter estimated for the nano-material used in this study was about 35 and 38 Å for the modified Kelvin and NMR methods respectively. A comparison between these methods and the classical Kelvin equation is also presented.

1. Introduction

Nano-materials play an important role in many applications of science and technology. There is an increasing interest in using these materials in different fields ranging from chemistry, medicine, and biochemistry to electrical engineering. The characterization of the pores of these materials is an essential step before any application. Thus it is important to have a very fast, reliable and straightforward method for characterization of these materials. With gases such as nitrogen, nitrogen adsorption–desorption (NAD) or mercury intrusion porosimetry is the conventional way for calculating the pore size distribution (PSD) of porous materials [1]. These methods usually underestimate the real pore sizes especially for mesoporous materials (pore sizes in the range of 20–50 Å) [2,3]. Nuclear Magnetic Resonance (NMR) studies have been carried out previously to characterize different materials (silica gel, controlled pore glass, zeolites, etc.) [4–7]. In addition, a number of NMR techniques have been used: spin–lattice relaxation T_1, spin–spin relaxation T_2 and NMR diffusion measurements [8–10] have been utilized for determining PSD in porous materials. These methods need prior information regarding the interaction between the solid and the liquid used and also the relaxation parameters that often are not available.

On the other hand, NMR has a unique advantage in studying the freezing phenomena of confined water. This is because T_2 of water is much larger ($\sim$a few seconds) than that of solid ice ($\sim 6\ \mu s$). This will ensure that the NMR signal below 273 K, the freezing temperature of bulk water, will arise essentially from the non-frozen confined water in the sample. This idea was used previously for estimating the PSD of materials [11–17]. These studies indicated the importance of using NMR for calculation of large pores; however limited studies are found for small pores ($\sim$30 nm). In this work we assess the usefulness of using NMR measurements for determination of the PSD for small pores ($\sim$30 nm) and to compare the result of this technique with that of NAD measurements. The melting point depression of liquid in confined geometries is utilized to obtain the PSD of a porous material. This is done by using the ^{1}H NMR signal of unfrozen water versus temperature of hydrated sample mesoporous material MCM-41 which is fully saturated with water.

2. Experimental

The method described in refs. [18–20] for the synthesis of MCM-41 is used to prepare the material needed for this work. The final product of the material needs to be hydroxylated. This is done by immersing the product inside deionized water and

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letting it stay for about 1 week in an open glass vial. To prepare fully saturated samples of MCM-41 with water, an amount of MCM-41 powder is immersed in deionized water inside two different small glass vials. The samples are then equilibrated at room temperature for 2 days. In order to force water to enter the pores (air leaving the pores), two different methods are used. In the first method, one of the glass vials containing the sample is placed in a high-speed centrifuge at 15,000 rmp. The centrifugation process is repeated several times. In the second method the other glass vial, containing the sample, is connected to a vacuum system and carefully pumped out till small bubbles are observed leaving the powder through the water. This is an indication that water is replacing the air inside the pores. This process is continued till no further air bubbles are seen leaving the immersed powder. The product, in both batches, is placed into two different filter papers to let them dry under ambient condition (for about 12 h) so that most of the excess water evaporates. The existence of some quantity of bulk water in the sample is also important as it ensures the observation of the bulk melting temperature and provides us with a calibration point for the melting curve of water within the pores.

The samples are packed into 4 mm (ID) Magic Angle Spinning rotors and sealed with Viton O-rings along with Zirconia caps (from Wilmad LabGlass company). A standard 90° pulse sequence of 4 μm with repetition time of 10 s is used. The ^{1}H NMR spectrum is taken, for each of these samples, at different temperatures corresponding to bulk water freezing point, 273, and 20 K below it (253 K). The results show that the sample prepared using centrifugation has larger amount of water as a bulk compared with the other one. The data presented in this study is for the sample prepared with the vacuum system which has some amount of bulk excess water outside the pores. The bulk water has no influence on the freezing depression ΔT of the pore water [21].

The experimental data is taken using a Bruker DMX 500 spectrometer of magnetic field of 11.7 T. The ^{1}H NMR spectra are measured, every 2 K, in the range of temperature between 210 and 275 K. The temperature is controlled using a temperature controller of type BVT3000 provided with the spectrometer. The accuracy of the temperature determination is within 0.5 K and calibrated using pure methanol [22]. The temperature of the sample is lowered from room temperature to 210 K and the NMR spectra are recorded in the heating run. An equilibrium time of about 15 min is allowed at each temperature before collecting data.

NAD measurements were carried out using a volumetric adsorption equipment (AUTOSORB-1MP, from Quantachrome Instruments) at 77 K with an outgas temperature at 473 K. X-ray diffraction patterns for the sample used in this study were recorded on a Rigaku D/M-2200T automated diffractometer (Ultima+) using Cu Kα radiation (λ=1.5406 Å).

3. Theoretical background

3.1. PSD determination and NAD measurements

The pore radius R_p of the material under study is the sum of the Kelvin radius R_k and the thickness of the initially adsorbed layer t_{ads} of nitrogen gas on the pore surface [22]:

$$R_p = R_k + t_{ads} \tag{1}$$

There are different suggested methods to obtain t_{ads} from experimental relative pressure (P/P_o). In this study, the following equation is used which is more suitable for cylindrical pores such as those of MCM-41 [24]. Thus the t_{ads} value in Å is determined by

$$t_{ads} = \left[\frac{60.65}{0.03071 - \log(P/P_o)}\right]^{0.3968} \tag{2}$$

The Kelvin radius R_k is given by the following equation (which from now on will be referred to as the classical Kelvin equation):[25]

$$R_{\mathrm{k}} = \frac{-K_{ab}}{\ln(P/P_o)} \tag{3}$$

K_{ab} is the adsorption constant, which is equal to $2\gamma\ V/RT$, where γ is the surface tension of liquid nitrogen, 8.88×10^{-3} (J/m^2), V_L is the molar volume of the liquid nitrogen, 3.468×10^{25} (Å^3/mole), R is the ideal gas constant, 8.3143×10^{20} (J Å^2/F m^2 mole) and T is the absolute temperature of adsorption, 77 K; thus K_{ab}=9.62 Å[26].

In a recent study on MCM-41 [27] a correction factor f_c is added to the classical Kelvin equation which gives an optimal match between experimental and simulated isotherm curves. Therefore, the modified-Kelvin radii R_k, expressed in Å, for the adsorption and desorption branches, respectively, are given by

$$R_k = \frac{-K_{ab}}{2\ln(P/P_o)} + f_c$$
$$R_k = \frac{-K_{ab}}{\ln(P/P_o)} + f_c \tag{4}$$

Finally, to determine the PSD, an expression for dV/dR_p versus dR_p is needed which can be written as

$$\frac{dV}{dR_p} = \frac{dV}{d(P/P_o)}\frac{d(P/P_o)}{dR_k}\frac{dR_k}{dR_p} \tag{5}$$

where $dV/d(P/P_o)$ is determined by numerical differentiation of the NAD data with respect to $d(P/P_o)$. The last two terms in the product, on the right hand side of Eq. (5), can be expressed in terms of $d(P/P_o)$ using Eq. (3) or (4). Thus the final expression is given as

$$\frac{dV}{dR_p} = \alpha \frac{dV}{d(P/P_o)}\left[\ln^2\left(\frac{P}{P_o}\right)\right]\left(\frac{P}{P_o}\right) \tag{6}$$

where α is a constant (α=0.98 Å^{-1} if Eq. (3) is used, α=2 Å^{-1} if the adsorption part of Eq. (4) is used and α=1 Å^{-1} if the desorption part of Eq. (4) is used).

The PSD of the porous material can be obtained by plotting dV/dR_p (Eq. (6)) versus R_p (Eq. (1) and (3) or (1) and (4) depending on whether classical Kelvin or modified Kelvin pore radii are used, respectively).

3.2. PSD determination from NMR

The melting point depression ΔT_m of a liquid in a confined geometry is given by the Gibbs–Thompson equation[28]

$$\Delta T_m = T_m - T_m(r) = \frac{4\sigma T_m}{r\,\Delta H_f\,\rho} \tag{7}$$

where T_m is the normal melting point of the bulk liquid, $T_m(r)$ is the melting point of the same liquid confined in a confinement r, σ is the surface energy at the liquid–solid interface, ΔH_f is the bulk enthalpy of fusion and ρ is the density of the solid. In the above equation the contact angle between solid, water and the pore wall is assumed to reach π radians. The equation can be written, for a particular liquid, as

$$T_m - T_m(r) = \frac{k}{r} \tag{8}$$

where k is a constant whose value depends on the liquid.