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Adsorption and Desorption Isotherms at Ambient Temperature Obtained by Ellipsometric Porosimetry to Probe Micropores in Ordered Mesoporous Silica Films

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Abstract. Ellipsometric Porosimetry is a non destructive technique well adapted to the measurement of isotherms of porous thin films. We present results obtained on ordered mesoporous silica films prepared by surfactant templating methods. Although the applications of such films require knowledge of mesoporous network, the micropores, which remain uncontrolled during the film elaboration, could play a main role in the film properties and then need to be characterized. We take advantage of the ability of our experiment to perform isotherms with different organic adsorptives of different sizes (branched or linear molecules) in order to probe micropores in these ordered mesoporous silica films.

Keywords: adsorption, microporous, mesoporous, silica, ellipsometry

1. Introduction

Materials with periodic mesoscale spaces, synthesized through the reactions of inorganic species in the presence of surfactant assemblies via sol-gel technique, have attracted attention in the last ten years. In particular, mesoporous silica films with various structures (2D, 3D hexagonal or cubic) have been subject to growing interest because of their possible applications in the fields of optics, catalysis, sensing and separation. Thin films with good homogeneity and optical quality can be obtained through liquid deposition techniques such as spin and dip-coating (Beck et al., 1992; Zhao et al.,1998; Grosso et al., 2000; Besson et al., 2000).

Owing to the small quantity of matter in thin films, classical methods to obtain sorption isotherms are no more suitable. A recent method involving spectroscopic ellipsometry (Baklanov et al., 2000) has been suggested to measure isotherms on thin films at ambient temperature. Ellipsometry is a non destructive optical technique allowing the measurement of the variation of the film refractive index during sorption process. In a previous paper (Bourgeois et al., 2004), we have already shown that Ellipsometric Porosimetry (EP) gives good results for the characterization of the mesopores in ordered mesoporous silica films. In this report, we focus our attention on their micropores. Indeed, applications of such films require knowledge of the mesoporous network; however the micropores, which remains uncontrolled during the film elaboration, could play an important role in the film properties (mechanical properties, sieving) and then needs to be characterized.

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Usually composite isotherms are obtained with N_2 as adsorptive on micro/mesoporous silica materials, from which the microporosity can be evaluated with different methods (Albouy and Ayral, 2002; Klotz et al., 2000; Colomer and Anderson, 2001; Poladi and Landry, 2002). In the case of microporous materials as those used in gas separation and methane storage, Lozano-Castello et al. (2002) have suggested that the most important parameter is the micropore size distribution They have estimated it in microporous carbon materials from high-pressure CO_2 and CH_4 adsorption isotherms around ambient temperature by application of the General Adsorption Isotherm model (McEnaney et al., 1987).

Recently the use of molecules of different sizes has been suggested by Rouquerol et al. (1999) as a good method for the characterization of microporous adsorbents. We have applied this method to probe micropores in 3D hexagonal mesoporous silica films. We will present in this report a study of isotherms taken at ambient temperature with organic adsorptives of different sizes (ethanol, tertio-butanol, norbornadiene, trimethyl-benzene, heptane), and we will discuss the results in terms of micro/mesoporosity.

2. Experimental Details

Mesoporous silica films were synthesized using a previously described procedure (Besson et al., 2000). The polymeric silica sol was prepared under acidic conditions by mixing TEOS (Si $(OC_2H_5)_4$), water (pH = 1.25) and ethanol in the 1:5:3.8 molar ratio, and aged 1h at 60°C. The CTAB (Cetyl Trimethyl Ammonium Bromide) surfactant was then dissolved into the sol with a CTAB /TEOS molar ratio equal to 0.1. The final solution was diluted with ethanol (1:2) and the films were deposited on silicon wafers by the spin-coating technique. The CTAB surfactant molecules were removed by calcination in air at 400°C for 10 hours. Under these experimental conditions, films about 300 nm thick were obtained, with 3D hexagonal structure, oriented with the c-axis perpendicular to the substrate. After deposition, the films were immediately stocked in dry environment to prevent the pore contamination before the first optical measurement (Brunet-Bruneau et al., 2004).

Ellipsometric measurements were performed in the visible range (0.25 to 0.75 μm) on a rotating polarizer spectroscopic ellipsometer, and in the infrared range (600 to 5000 cm^{-1}) on a Fourier Transform Infra Red (FTIR) ellipsometer. All ellipsometric measurements were performed at an incidence angle of 75°. Ellipsometry measures changes of the light polarization by reflection at an interface; it gives the two quantities $\tan\Psi$ and $\cos\Delta$ defined by the following relation:

$$r_p/r_s = \tan\Psi e^{i\Delta} \tag{1}$$

where r_p and r_s are the reflection coefficients of the electric field on the film surface with polarization parallel and perpendicular to the plan of incidence respectively. The thickness d and the optical properties of films are usually calculated from the ellipsometric parameters $\tan\Psi$ and $\cos\Delta$. The optical properties are expressed either in terms of complex refractive index N ($N = n + ik$) or of complex dielectric function ε ($\varepsilon = \varepsilon_1 + i\varepsilon_2$), which is the square of the complex refractive index :

$$\varepsilon = N^2 \tag{2}$$

In the visible range where the silica films are transparent, the extinction coefficient k (imaginary part of N) is equal to zero. Then the refractive index n (real part of N) and the thickness d of the silica films were deduced from the analysis of the ellipsometric parameters $\tan\Psi$ and $\cos\Delta$ using the Sellmeier approximation. Although the refractive index n was calculated on the whole visible spectral range, only its value at 600 nm is reported in this paper. The thickness d being known, the real ε_1 and imaginary ε_2 parts of the complex dielectric function ε were calculated in the infrared range (where the silica films are not transparent) from the $\tan\Psi$ and $\cos\Delta$ values at each wave number by an iterative procedure. In the range 1400 to 5000 cm^{-1}, the presence of contamination can be checked (H—OH, C—H_2, C—H_3, C=O). At lower wave number, the position of the maximum of ε_2 corresponds to the TO (Transverse Optical) frequency associated with the stretching vibrational mode of Si—O—Si, from which the density of the silica skeleton can be evaluated (Brunet-Bruneau et al., 2004).

After preliminary ellipsometric measurements in air in the visible and infrared ranges, the samples were introduced in a home built vacuum cell (Fig. 1), in which the temperature was controlled. The cell was fitted on the visible ellipsometer for in situ measurements at an incidence angle of 75°. Before introducing vapor, the cell was pumped down to 10^{-7} Torr (pressure measured by a Penning gauge near the sample)

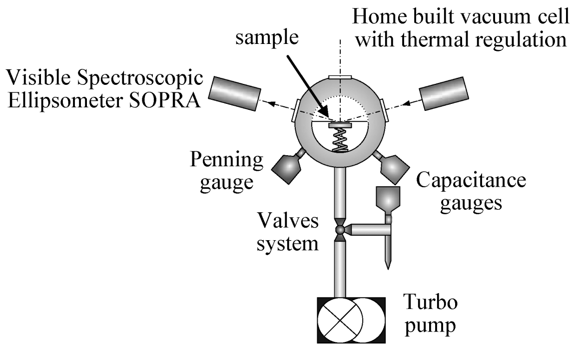

Figure 1. Schematic of the EP tool used in this report.

Table 1. Refractive index n_{liq} (at 600 nm) of organic adsorptives in liquid phase, size of adsorptives (defined as the length between the most distant atoms), final refractive index n_{end} (measured at the end of adsorption process), the pore filling ratio x_{end} calculated at end of adsorption branch. Before adsorption, $n_0 = 1.221$.

	Organic adsorptive n_{liq}	size (nm)	n_{end}	x_{end} (%)
Ethanol	1.360	0.40	1.420	100
Tertiobutanol	1.386	0.40	1.432	99
Norbornadiene	1.470	0.47	1.481	101
Trimethyl-benzene	1.497	0.60	1.487	98
Heptane	1.497	0.93	1.406	69

and a first ellipsometric measurement was performed to confirm that the samples were still non contaminated. Then the vapor pressure P, measured by a capacitance gauge, was progressively increased until saturation P_0 to measure the adsorption branch and finally decreased to obtain the desorption one. At each step of the sorption process, in situ visible ellipsometric measurements were performed to evaluate the thickness d and the refractive index n of films. Experiments were realized at ambient temperature with five different adsorptives: ethanol, tertio-butanol, norbornadiene, trimethyl-benzene, heptane.

3. Results and Discussion

The ellipsometric measurement in the visible range performed before adsorption gives a thickness of 317 nm and a refractive index n_0 of 1.221 for the studied samples. The refractive index n as a function of the relative pressure P/P_0 is plotted on Fig. 2(a) and (b) for ethanol and heptane as adsorptives respectively. The increase of the refractive index of silica thin films, observed in Fig. 2, is induced by the condensation of vapor in the pores. Isotherms, measured with the three other adsorptives (tertio-butanol, norbornadiene and trimethyl-benzene), had the same shape as the one of ethanol and were thus not represented. Film refractive indices n_{end} measured at the end of adsorption branch for each adsorptive are reported in Table 1. For each sorption experiments, no swelling occurs (no significant change of the film thickness).

From the film refractive index n measured at each step of sorption process, the pore filling ratio x (defined as the ratio between the volume fraction of pores filled by the adsorbate and the total porosity) can be calculated by modeling the porous silica films as a mixture of three components (silica skeleton, pores filled by vapor and pores filled by liquid). We use the Bruggeman Effective Medium Approximation (BEMA) (Bruggeman, 1935) as following:

$$(1-f)\frac{\varepsilon_{\text{sk}}-\varepsilon}{\varepsilon_{\text{sk}}+2\varepsilon}+f(1-x)\frac{\varepsilon_v-\varepsilon}{\varepsilon_v+2\varepsilon} + fx\frac{\varepsilon_{\text{liq}}-\varepsilon}{\varepsilon_{\text{liq}}+2\varepsilon}=0 \qquad (3)$$

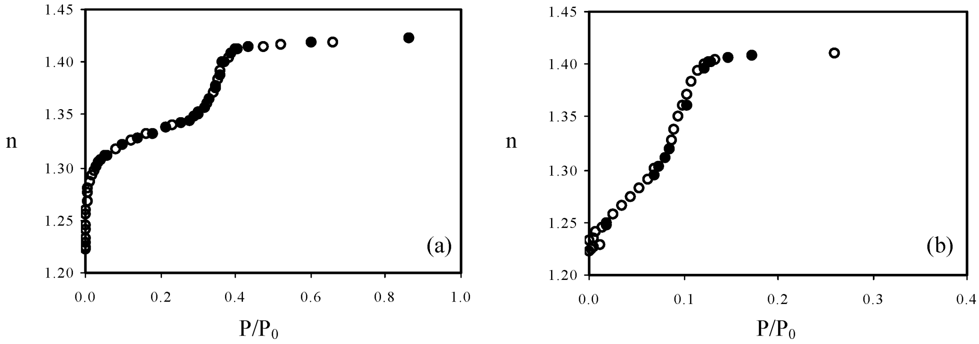

Figure 2. Film refractive index n (at 600 nm) as a function of the relative pressure P/P_0 for ethanol (a) and heptane (b) as adsorptives (empty circle for adsorption, filled circle for desorption).

where $\varepsilon = n^2$ is the dielectric function of the film, $\varepsilon_{\text{sk}} = n_{sk}^2$ is the one of the silica skeleton, $\varepsilon_v = n_v^2$ is the one of the pores filled by adsorptive in vapor phase, $\varepsilon_{\text{liq}} = n_{\text{liq}}^2$ is the one of the pores filled by the adsorbate, and f is the total porosity. When a pore is filled by air or adsorptive in vapor phase, its refractive index n_v is very close to 1 ; on the contrary, when the condensation occurs, the refractive index n_{liq} of the adsorbate is assumed to be the same as the adsorptive in the bulky liquid phase (Table 1).

Prior for calculating the pore filling ratio x, the porosity f and the silica skeleton refractive index n_{sk} must be determined. Following the usual assumption which considers the silica skeleton as a dense amorphous silica (density of 2.2 g·cm^{-3}), the skeleton refractive index n_{sk} would be equal to 1.458. The porosity f can be calculated from the film refractive index measured before at $P/P_0 = 0$ ($n_0 = 1.221$), by modeling the porous silica films as a mixture of two components (silica skeleton and empty pores) and using Eq. (3) with $x = 0$. So the porosity f would be found equal to 50%. With this value of skeleton refractive index ($n_{\text{sk}} = 1.458$) and a porosity of 50%, the ethanol pore filling ratio at the end of the adsorption branch (x_{end}), calculated from Eq. (3), would be over 100% (107%).

Then a correct evaluation of f and x necessitates a determination of the silica skeleton refractive index for each film. It has been done owning to ellipsometric measurements in infrared range. The TO (Transverse Optical) frequency associated with the stretching vibrational mode of Si—O—Si, is found to be 1066 cm^{-1}. Because the film has a high porosity, this TO frequency is only an effective value; the true TO frequency of the silica skeleton is 9 cm^{-1} below the effective value (Brunet-Bruneau et al., 2004), i.e. at around 1057 cm^{-1}. This last value characterizes a slightly constrained silica skeleton with a refractive index $n_{\text{sk}} = 1.488$ and a density $\rho_{\text{sk}} = 2.32$ g·cm^{-3} (Brunet-Bruneau et al., 1997). From this value ($n_{\text{sk}} = 1.488$), a porosity f of 53 % was calculated from the Eq. (3) with $x = 0$.

The variation of the pore filling ratio x during the sorption process, calculated with Eq. (3) with $n_{\text{sk}} = 1.488$ and $f = 0.53$, is reported on Fig. 3(a) for ethanol and on Fig. 3(b) for heptane. Comparison between Figs. 2 and 3 highlights the similarity of the two representations. The absence of hysteresis loop on Figs. 2 and 3 can be explained by a mesopore size less than 3.6–3.8 nm (Inoue et al., 1998). The heptane isotherm (see Fig. 3(b)) is designated as a Type IVc (mesopores) in the IUPAC classification (Sing et al., 1985), the four others are composite isotherms of Type I (micropores) and Type IVc (mesopores). Similar composite isotherms have been already obtained on ordered hexagonal silica powders (Albouy and Ayral, 2002) and layers (Klotz et al., 2000) in the case of nitrogen adsorption at 77.4 K.

The pore filling ratio x_{end} at the end of the adsorption branch, reported in Table 1, is an important parameter because it brings information about the accessible porosity for a given adsorptive. At the end of the ethanol adsorption, the pore filling ratio is equal to 100% (see Table 1). This result proves that the condensation can occur in all pores and thus leads to conclude that the total porosity of 53% is open. On the contrary, heptane condenses only in 69% of the total porosity (see Table 1) and its isotherm shows only the capillary condensation in the mesopores. This result allows to underline that heptane condenses only in the mesopores. So the fraction of mesopores (69%) and micropores (31%) in the total porosity can be evaluated accurately.

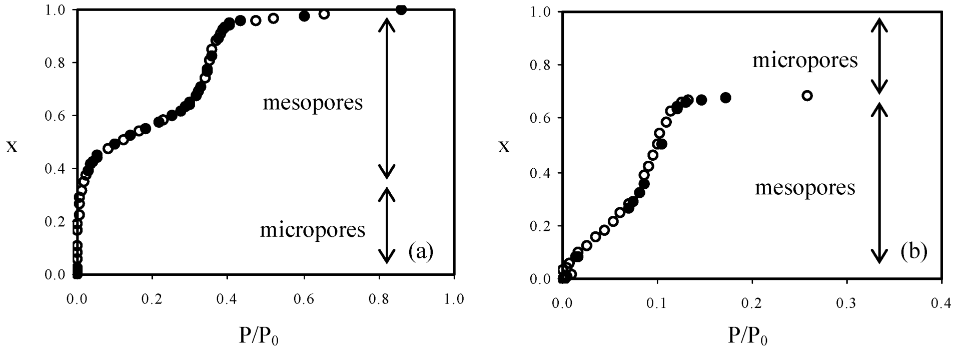

Figure 3. Pore filling ratio x (defined as the ratio between the volume fraction of pores filled by the adsorbate and the total porosity) as a function of the relative pressure P/P_0 for ethanol (a) et heptane (b) as adsorptives (empty circle for adsorption, filled circle for desorption).

This fraction of micropores is reported on the composite isotherm of Fig. 3(a) and is consistent with the shape of ethanol isotherm.

The three other adsorptives have been chosen because they are more bulky than heptane. Nevertheless, their isotherms are similar to this of ethanol, the pore filling ratio x_{end} at the end of their adsorption branch is around 100% too (Table 1). It means that the micropores are also accessible to these three other adsorptives. Thus, we underline that the more bulky branched molecules (norbornadiene, trimethyl-benzene) can be adsorbed in the micropores, whereas the linear one (heptane) is not, probably through entropic effects. The size of each adsorptive, defined as the length between the most distant atoms, is given as an indicative parameter in Table 1. The micropore filling being complete with trimethyl-benzene (the bulkiest branched molecule), no sieve effect has been observed. So the use of this molecule as adsorptive gives us a lower limit of the micropore size (0.60 nm). On the contrary, we do not indicate an upper limit of the micropore size because entropic and steric effects can be combined in heptane isotherm.

4. Conclusion

In this work, Ellipsometric Porosimetry has been applied on ordered mesoporous silica films to obtain isotherms with organic adsorptives of different sizes (ethanol, tertio-butanol, norbornadiene, trimethyl-benzene, heptane). The study of isotherms has allowed to probe micropores, which are present but uncontrolled in these silica films. A total Porosity of 53% has been calculated, provided that the silica skeleton refractive index (i.e. skeleton density) has been previously determined. The total porosity is open; it is accessible to all adsorptives except heptane, which condenses only in mesopores. The volume fractions of mesopores (69%) and micropores (31%) have been evaluated. No sieve effect has been observed with all studied adsorptives except heptane, so a lower limit of micropore size of 0.6 nm has been evaluated. No upper limit of micropore size have been determined because entropic and steric effects can be combined in heptane isotherm.

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