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Krypton adsorption technique for assessment of structural properties of mesoporous silica and titania thin films

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Gas adsorption-based methods are the most convenient ones for the study of the texture of porous solids. Nitrogen is commonly used as an adsorbate for samples providing several tens square meters of total surface area. In the case of thin mesoporous films deposited on a substrate, the samples for nitrogen adsorption measurements are obtained by detaching the films from the substrates [1] or a relatively great number of substrates with films is introduced into the sample cell [2]. The use of special apparatuses such as surface acoustic wave device [3] or quartz crystal microbalance [4] for the measurement of nitrogen adsorption isotherms on thin films is restricted to samples enabling to be coated onto the device.

The volumetric adsorption technique using gasses with low saturated vapor pressure has been found to be an effective method to assess structural properties of small amount of porous materials. According to this strategy, several reports using krypton as an adsorbate can be found in the recent literature [5–8]. Since the measurements of krypton isotherms are carried out at the boiling point of liquid nitrogen, 77 K, the saturated vapor pressure of Kr is only 212 Pa. When the volumetric technique is applied, a constant volume of the sample tube must be kept at this temperature regardless of the difference in liquid nitrogen level. To meet this requirement, the Micromeritics Instruments Corp. (USA) has developed a liquid nitrogen wicking sleeve from porous polymer, which slides over the stem of the sample tube and by capillary action draws liquid nitrogen from the Dewar flask into contact with the sample tube. This maintains a constant temperature within the stem of the sample tube as long as the sleeve is in contact with liquid nitrogen. Thus, the volume of the cold part of the sample tube remains constant during the adsorption measurement without liquid nitrogen level control.

If the krypton isotherm exhibits a hysteresis loop, the adsorption/desorption branch of this loop is obtained by progressive addition/withdrawal of the gas to the adsorbent, respectively. The amount of gas entering or releasing the sample tube is calculated from the change $\Delta p = p_\mathrm{d} - p_\mathrm{e}$ in pressure of the dosing volume of the adsorption apparatus. (p_d is the pressure of Kr in the dosing volume and p_e is equilibrium pressure after this gas is allowed to enter or release the sample tube.) When the dosing volume was evacuated, $p_\mathrm{d} = 0$ and the maximum size of the desorbed dose corresponded to the $\Delta p = -p_\mathrm{e}$. As this pressure is always lower than 212 Pa, a relatively large dosing volume is needed to achieve reasonably large desorbed dose.

The aim of this work is to characterize the texture of mesoporous silica and titania thin films by means of Kr adsorption and desorption isotherms measured at 77 K directly on films deposited on glass slides. The films were synthesized in accordance with procedures reported in the literature; Pluronic poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymers were used as structure directing agents.

The stock solution for the synthesis of mesoporous silica films [1] was prepared as follows: 10.4 g of tetraethyl orthosilicate (Aldrich) was prehydrolyzed in a solution containing 26.3 g of ethanol, 2.2 g of H_2O and 5 g of HCl (0.1 mole l^{-1}) for 1 hr at 80 °C under reflux. After cooling to room temperature, a solution containing 6.3 g of Pluronic F127 ($EO_{106}PO_{70}EO_{106}$, BASF) in 19.7 g of ethanol was added under vigorous stirring and the mixture was allowed to age at room temperature for 2 hr. The stock solution for the synthesis of mesoporous titania films [9] was prepared by the slow addition of 13.8 g of $TiCl_4$ (Aldrich) under vigorous stirring to a solution containing 7.3 g of Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, BASF) in 72.5 g of ethanol. The mixture was maintained in an open beaker at 40 °C for 5 days, evaporated ethanol being filled up every 12 hr.

The films were prepared by dip-coating on 7.5 cm × 2.5 cm sized slides of soda-lime-silica glass; the applied withdrawal rates are listed in Table I. The silica films were dried at room temperature for 1 hr and calcined in air at 350 °C for 6 hr (heating rate: 1 °C min^{-1}). The titania films were aged at 40 °C for 2 days and calcined in air at 400 °C for 5 hr (heating rate: 1 °C min^{-1}).

The film thickness, h was determined using a Veeco DEKTAK 3030ST profilometer. The data in Table I reveal the film thickness increase with increasing withdrawal rate due to viscous drag upward on the stock solution by the moving substrate.

Measurements of krypton isotherms were performed on an Accusorb 2100E (Micromeritics) volumetric apparatus, equipped with two dosing volumes of 30.16 and 162.06 cm^3. The latter relatively large dosing

TABLE I Withdrawal rate U, thickness h and porosity characterization of silica (S) and titania (T) films

Sample	U (mm/min)	h (nm)	S_{BET} (cm^2/cm^2)	V_{ME} (cm^3/cm^2)	D_{ME} (nm)	S_{BET}/h (1/nm)	V_{ME}/h (nm/nm)
S1	20	111	42	4.0×10^{-6}	3.8	0.38	0.36
S2	30	159	64	8.8×10^{-6}	5.5	0.40	0.55
S3	40	218	91	1.3×10^{-5}	5.7	0.42	0.60
T1	30	245	113	1.3×10^{-5}	4.6	0.46	0.53
T2	50	278	140	1.6×10^{-5}	4.6	0.50	0.57

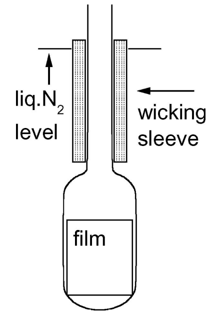

Figure 1 Cross section of the sample tube. The substrate with the film is located in the sealed bulb.

volume has enabled us to measure the desorption branches of Kr isotherms up to 40 Pa. The sample tube (Fig. 1) contained one 4 cm × 2.5 cm sized slide, which was cut off from the slide with deposited film. Liquid nitrogen wicking sleeve over the neck of the sample tube was purchased from Micromeritics as spare part for ASAP 2010 volumetric adsorption instrument. Before the measurements, all films were degassed at 200 °C until the vacuum of 10^{-4} Pa was achieved.

The krypton isotherms on silica and titania films are shown in Figs 2 and 3. The adsorption is expressed in nanomoles of Kr adsorbed on the film coating 1 cm^2 of the substrate. The krypton isotherms are characterized by a significant hysteresis loop, which evidences the volume filling of mesopores. As desorption branches of all isotherms begin with almost horizontal plateaus, the mesopore volume can be supposed being completely filled and the desorption from outer surface takes place here. Although the relationship between the krypton isotherm at 77 K and parameters of porous structure is not fully understood in the literature, some conclusions on the mesopore structure of films can be deduced. The isotherms on silica films S2 and S3 exhibit steep increase/decrease of mesopore filling/emptying, the desorption branches being almost vertical. This indicates their narrower pore size distributions in comparison with the film S1. The hysteresis loops of the isotherms on titania films T1 and T2 show that mesopore filling and emptying occur over relatively wide range of equilibrium pressures. This fact indicates that titania films have lower structural uniformity than silica films S2 and S3.

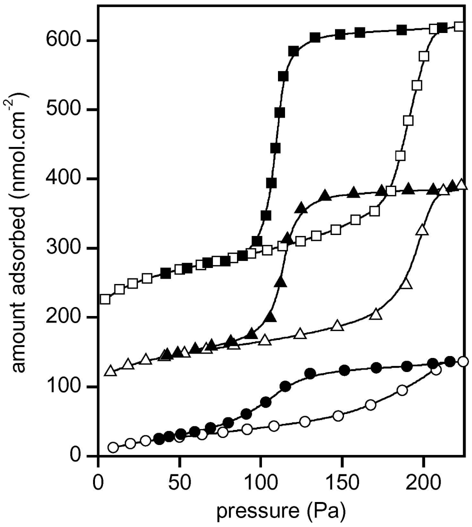

Figure 2 Nitrogen adsorption isotherms for films S1 (–), S2 (8) and S3 (□). Except for that on film S1, isotherms are shifted by 100 nmol cm^{-2} each. Solid symbols denote desorption.

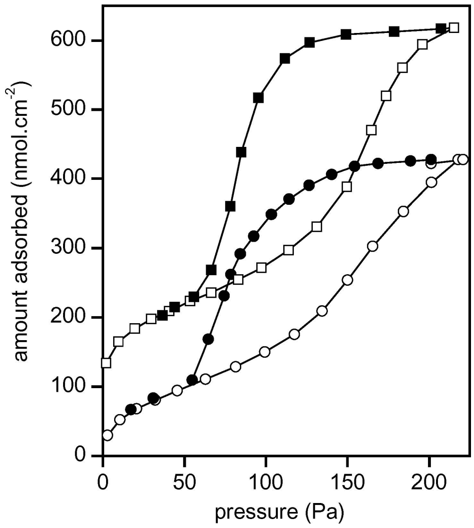

Figure 3 Nitrogen adsorption isotherms for films T1 (–) and T2 (□). The isotherm on film T2 is shifted by 100 nmol cm^{-2}. Solid symbols denote desorption.

The surface area S_{BET} of the film coating 1 cm^2 of the substrate (i.e. the surface area of the film is expressed in cm^2 per cm^2 of the substrate) was calculated using data in a pressure range from 30 to 100 Pa. In accordance with the usual practice, the saturation vapor pressure of the supercooled liquid (321 Pa at 77.2 K) and the molecular cross-sectional area of 0.21 nm^2 were used. The mesopore volume, V_{ME} expressed analogously in cm^3 per cm^{2}of the substrate, was determined from the amount adsorbed at equilibrium pressure of 175 Pa using the krypton molar volume of 31.04 cm^3/mol [5]. The mesopore diameter was assessed according to the geometrical formula $D_{\mathrm{ME}} = 4\ V_{\mathrm{ME}}/S_{\mathrm{BET}}$. The obtained parameters S_{BET}, V_{ME} and D_{ME} are listed in Table I.

The ratios S_{BET}/h and V_{ME}/h (Table I) show, that except the film S1, the surface area and the mesopore volume are proportional to the film thickness. The film S1 reveals the influence of the substrate surface on the

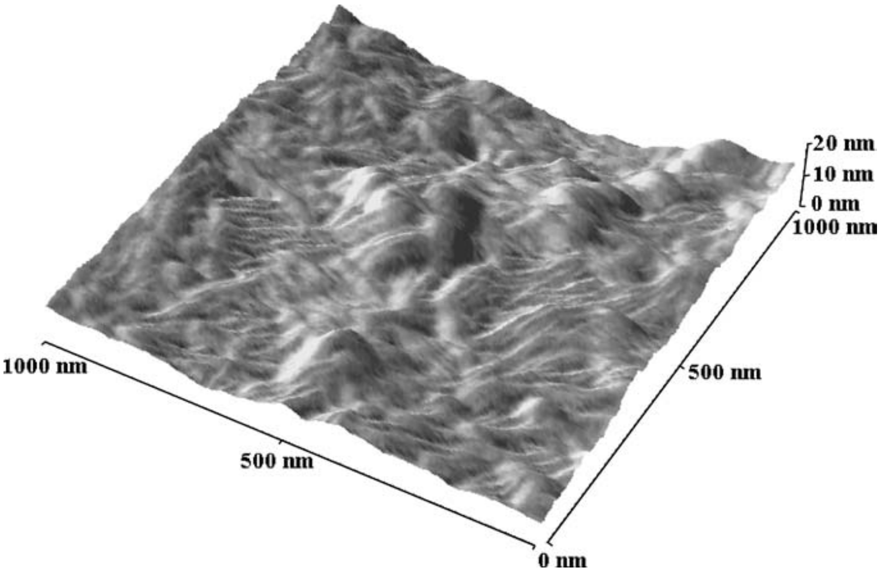

Figure 4 AFM image of the glass slide surface.

uniformity of thin mesoporous films. The surface relief of the glass slide was obtained by atomic force microscopy using a Digital Instruments NanoScope apparatus. Fig. 4 presents this relief with height variations in range of ca 10 nm, which represents ca 10% of the thickness of the film S1. Therefore, the pore structure of the film S1 can be expected to be partially disorganized due to the surface roughness of the supporting slide.

The presented results clearly show that the krypton adsorption at 77 K represents the efficient method for the characterization of thin mesoporous films. Keeping essential experimental precautions, krypton adsorption isotherms can be measured on films coating both sides of 2.5 × 4.0 cm sized substrate. Thus obtained data provide useful information describing the mesoporous structure of thin solid films in contact with the substrate.

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