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Journal of Molecular Catalysis A: Chemical 238 (2005) 135–137
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
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A note on micro- and mesopores in the walls of SBA-15 and hysteresis of adsorption isotherms

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Received 20 March 2005; received in revised form 18 May 2005; accepted 19 May 2005
Available online 5 July 2005

Abstract

The hysteresis of adsorption/desorption of condensable vapors in porous materials is a highly debated area of research. The adsorption isotherms is useful for getting important structural parameters such as pore size distribution and surface area. Earlier, hysteresis was attributed to the networking of the pores. Since the discovery of cylindrical pore MCM-41 materials, it has been attributed mainly to the adsorption temperature, pore diameter and heterogeneity of surface. Recently, Esparza et al. [J.M. Esparza, M.L. Ojeda, A. Campero, G. Hernandez, C. Felipe, M. Asomoza, S. Cordero, I. Kornhauser, F. Rosa, J. Mol. Catal. A: Chem. 228 (2005) 97] presented extremely valuable experimental data related to characterization of SBA-15 and other micro- and mesoporous materials. They found that adsorption on a 7.6 nm pore diameter SBA-15 sample shows hysteresis and attributed it to the presence of bulges and necks along the pore channel due to the U-shaped pores or sinuosity. In our opinion, the results open up a debate regarding the accurate structure of SBA-15 as well as the reasons behind hysteresis. The *t*-plot analysis of the nitrogen isotherm of their SBA-15 found that it consists of micropores (8% of total volume). These micropores are absent in MCM-41 and although not related to hysteresis, it is an important characteristics of SBA-15 not addressed during the discussion. The experimental as well as theoretical investigations of adsorption hysteresis of MCM-41/SBA-15 or cylindrical nanotubes leads us to conclude that these ordered porous materials (MCM-41, SBA-15) will always show hysteresis for nitrogen adsorption at 77 K if the pore diameter is above ∼4 nm. The hysteresis criticality (i.e. absence of hysteresis beyond a certain diameter or temperature) is a fundamental property of adsorbed fluids inside cylindrical pores and it may depend upon the temperature, pore diameter, shape of meniscus or surface heterogeneity. However, the presence of a bulge/neck (U-shaped pores/sinuosity) may not be responsible for hysteresis in SBA-15. The present note represents our arguments in an ongoing debate in the area of hysteresis of adsorption and the structure of SBA-15.

Keywords: Microporous; Mesoporous; Adsorption; Isotherm; MCM-41; SBA-15; Hysteresis; Nanoporous; Nitrogen

1. Micro- and mesopores in the walls of SBA-15

Stucky and co-workers [1] developed SBA-15 using tri-block co-polymer templates. These materials consist of parallel cylindrical pores with axes arranged in a hexagonal unit cell. Several characterization techniques such as small angle X-ray scattering (SAXS), gas adsorption as well as high resolution transmission electron microscopy (HRTEM) have revealed that the walls of SBA-15 in between the main mesopores channels contain micropores 0.5–1.5 nm in diameter [2–4]. Using HRTEM, Liu et al. [2] suggested that walls of SBA-15 consist of spherical cages of ∼0.5 nm in diameter in the walls. Goltner and co-workers [3] used SAXS and gas adsorption and found that up to 63% of the specific surface area of SBA-15 is due to microporosity. Miyazawa and Inagaki [4] studied the systematic variation of microporosity in the walls of SBA-15 by varying the synthesis conditions. Jaroniec and co-workers [5] with the help of gas adsorption suggested that in addition to the main mesopore channels, SBA-15 consists of micropores as well as mesopores of size smaller than 3.4 nm in the walls. Galarneau et al. [6] in a systematic investigation prepared SBA-15 with no micropores. They suggested that the micropores in the walls are replaced by mesopores because of high-temperature synthesis

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1381-1169/$ – see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.molcata.2005.05.013

condition. We believe that SBA-15 structures synthesized at low temperature may consist of both micropores and mesopores in the walls consistent with earlier findings of Jaroniec and co-workers [5].

2. Information about SBA-15 from CMK-3 and CMK-5

Information about the structure of SBA-15 can also be obtained from the structure of carbon based CMK-3 and CMK-5 materials [7,8]. These are synthesized using SBA-15 as a template and considered to be a negative image of SBA-15. The only difference between CMK-3 and CMK-5 is that the latter consists of carbon tubes instead of rods. Ryoo and co-workers [7] prepared CMK-3 by carbonizing sucrose or furfuryl alcohol in the pores of SBA-15 and then dissloving the silica in NaOH. The HRTEM, X-ray diffraction (XRD) and gas adsorption results have led researchers to believe that CMK-3 consists of carbon rods running parallel to each other (in a hexagonal unit cell) with a spacer to keep the rods separate. Although, there is no concrete evidence about the exact shape and size of these carbon spacers, they are believed to be random, 0.5–3 nm in size with the shape, which may not be perfectly cylindrical rods [7,8]. These spacers are believed to be formed due to the casting of micropores as well as lower size mesopores present in the walls of SBA-15.

3. Estimates of microporosity from nitrogen adsorption

In the present work, we have estimated the total amount of micropores present in the SBA-15 sample using the nitrogen adsorption data presented by Esparza et al. [9] with the help of *t*-plot analysis [10]. As discussed earlier, the SBA-15 consists of micropores, a key fact in characterization of these materials, which remained to be discussed by Esparza et al. [9]. As seen from Fig. 1, the *y*-intercept is about 40 cm^3/g (at STP) corresponding to the ~7–8% of the micropores in the total pore volume.

Based on the above discussion, we believe that the schematic of the pore structure of SBA-15 is as shown in Fig. 2. The structure consists of main mesopore channels and extra pores (which could be micropores and mesopores) in the pore wall. The main parallel mesopore channels of SBA-15 are connected to each other through some of these micropores in the walls. The exact amount of these mesopores and micropores in the walls depends upon the synthesis conditions. Although there is no direct evidence, the SBA-15 may also contain blocked pores that are not accessible from the main mesopores channels. It has been suggested [6] that during synthesis of SBA-15, the micropores are formed due to the interaction between the micelles of pluronic surfactant through ethylene oxide head groups. If this hypothesis is true then the SBA-15 walls may contain a negligible amount of these inaccessible micropores and mesopores.

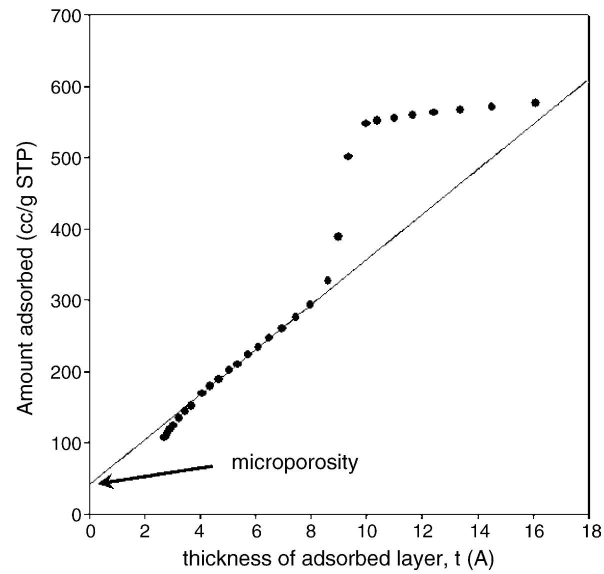

Fig. 1. The *t*-plot for the isotherm of SBA-15 reported by Esparza et al. [1] showing micropores.

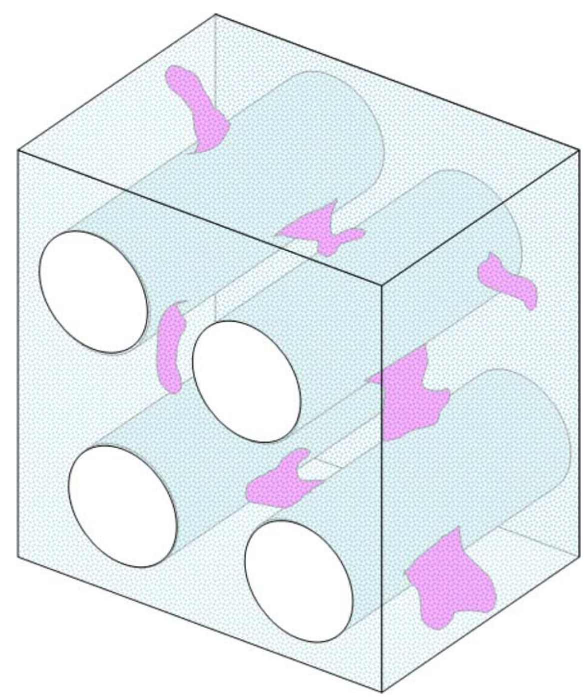

Fig. 2. Schematic of a three dimensional pore structure of SBA-15.

4. Hysteresis of nitrogen isotherms

A summary of theories proposed by several researchers for absence of hysteresis for nitrogen adsorption at 77.4 K in MCM-41 below ~4 nm is provided here. Critical pore diameter refers to the diameter of cylindrical pores of size below which the hysteresis is absent.

- Shape of meniscus (spherical during desorption and cylindrical during adsorption) [10].

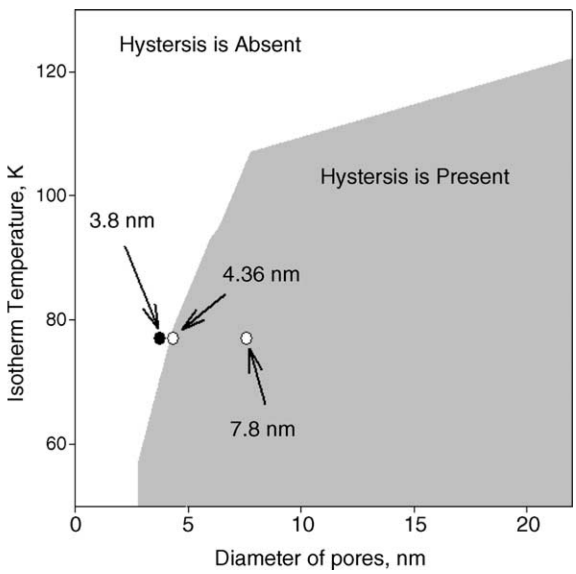

Fig. 3. The phase diagram of adsorption hysteresis criticality for nanoporous materials. The gray area represents the region where hysteresis will be present. The samples of pore diameter 7.6 nm (SBA-15), 4.3 nm (MCM-41) show hysteresis but samples with 3.7 nm (MCM-41) does not show hysteresis.

- Surface heterogeneity of MCM-41 walls in GCMS simulations of nitrogen adsorption gave a critical pore diameter of 2.8–3.2 nm[11].
- Mechanical stability of the meniscus provides a critical diameter of 3.4 nm [12–16].
- Intrinsic pore size distribution with Saam–Cole theory indicated a critical diameter of 3.6–3.8 nm [17].
- Nucleation at the vapor like spinodal pressure using the non-local density function theory [18] gave a pore critical diameter of 1.9 nm.

Morishige and co-workers [19,20], presented an experimental study of nitrogen adsorption isotherms at different temperature on SBA-15 and MCM-41 of different pore diameter. They concluded that for a given temperature, there exists a critical diameter below which no hysteresis is present. A plot of criticality is shown in Fig. 3. The experimental data for the Fig. 3 is taken from literature [19,20]. The darker region (gray) shows the area where hysteresis will be observed. The boundary line between the white and gray area represents the criticality curve. The open circles on this line have been obtained using the adsorption–desorption curves reported in the literature. The SBA-15 sample studied by Esparza et al. [9], as seen from Fig. 3, lies in the gray area, and therefore, it is expected to show hysteresis. This is confirmed by the isotherm shown in their paper. The borderline between gray area and white area is obtained from the experimental data on series of MCM-41 and SBA-15 taken from the literature [19,20].

Esparza et al. [9] found the hysteresis in SBA-15 samples with pore diameter ∼7.6 nm. They attributed the hysteresis to the sinuosity (bulges and throats) present in the main pore channel of SBA-15. However, based on the above discussion and Fig. 3, the hysteresis is likely a fundamental property of the condensable fluid inside a cylindrical pore and the sinuosity (the bulge and throat) observed in the SBA-15 may not have anything to do with the hysteresis observed in their situation. In addition, the presence of micropores in the walls of SBA-15 also do not have any effect on hysteresis. All the cylindrical pores above ∼4 nm will always show hysteresis for nitrogen adsorption at 77 K.

Acknowledgments

The US DOE Office of Basic Energy Sciences is acknowledged for financial support through Catalysis Science Contract No. DE-FG02-03ER15459. CGS acknowledges Jacqueline Mohalley Snedeker for help with the manuscript, Professor Christopher Jones and John Richardson for useful discussions.

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