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Nitrogen Adsorption Study of MCM-41 Molecular Sieves Synthesized Using Hydrothermal Restructuring

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Abstract. Nitrogen desorption scanning hysteresis loops (DSHLs) for large-pore MCM-41 silicas (pore diameter from 4.0 to 6.5 nm) are reported for the first time. DSHLs for MCM-41 were compared with those of conventional mesoporous silicas and no appreciable differences were found, although hysteresis loops and DSHLs for the latter were usually broader. Since desorption behavior of conventional porous silicas is appreciably influenced by pore connectivity, the observed similarity in hysteresis behavior suggests single-pore “blocking effects” for MCM-41 due to variation of pore diameter along its nonintersecting channels. It was also shown that the steepness of nitrogen desorption branches at relative pressures close to 0.4 often results from proximity of the lower pressure limit of adsorption-desorption irreversibility and consequently it is not justified to consider it as an indication of narrow pore size distribution. Thus, application of desorption data in calculations of pore size distributions may be grossly misleading.

Keywords: adsorption-desorption hysteresis, scanning hysteresis loops, model adsorbent, gas adsorption, ordered mesoporous silica, MCM-41

Introduction

MCM-41 silicas (Beck et al., 1992) are currently considered as the most promising model mesoporous adsorbents with well-defined porous structures (Franke et al., 1993; Branton et al., 1993; Llewellyn et al., 1994; Schmidt et al., 1995; Kruk et al., 1997). MCM-41 exhibits a honeycomb structure of long, approximately cylindrical and nonintersecting pores with diameters in the range from ca. 2 to 10 nm, which can be tailored using different strategies. In the conventional synthesis of MCM-41 materials, surfactants of different chain lengths are used and the pore size rarely exceeds 4.5 nm (Beck et al., 1992; Huo et al., 1996). Materials with larger pores were initially obtained using expanders, such as mesitylene, during the synthesis (Beck et al., 1992). However, it was shown that such procedures are usually not suitable for preparation of good-quality MCM-41 samples (Huo et al., 1996), that is, materials with three or more distinct X-ray diffraction (XRD) reflections characteristic of hexagonal structure and with narrow pore size distributions. Later, it was demonstrated that high-temperature (usually about 423 K) hydrothermal restructuring or direct synthesis approaches can successfully be used to provide MCM-41 materials with pore diameters up to 7 nm (Khushalani et al., 1995; Huo et al., 1996; Cheng et al., 1997; Corma et al., 1997; Sayari et al., 1997). These methods appear to be very convenient, since common surfactants can be used as templates (Khushalani et al., 1995; Cheng et al., 1997;

Corma et al., 1997; Sayari et al., 1997) and the preparation procedures are well-established.

There have been only a few reports of gas adsorption data on good-quality large-pore MCM-41 materials, especially those with pore sizes above ca. 5.5 nm (Huo et al., 1996; Corma et al., 1997; Kruk et al., 1997; Sayari et al., 1997). Since it was demonstrated that typical MCM-41 samples (pore diameter below 4 nm) do not exhibit hysteresis loops on their nitrogen adsorption isotherms (Franke et al., 1993; Branton et al., 1993), it is interesting to study nitrogen adsorption properties of large-pore materials, which exhibit adsorption-desorption irreversibility (Llewellyn et al., 1994; Schmidt et al., 1995; Huo et al., 1996; Kruk et al., 1997; Sayari et al., 1997). A detailed study of nitrogen adsorption properties of MCM-41 samples with pore sizes in the range from 2 to 6.5 nm was recently carried out and resulted in the development of empirical equations, which can be used to accurately assess pore diameters of MCM-41 and other materials on the basis of nitrogen adsorption isotherms (Kruk et al., 1997). In the current study, desorption scanning hysteresis loops (DSHLs) (Ball and Evans, 1989; Liu et al., 1993) were acquired for several large-pore MCM-41 materials with different degrees of structural ordering. To the best of our knowledge, DSHLs for such model samples have not been reported before. These data were compared with DSHLs for conventional mesoporous silicas. It was concluded that from the point of view of the hysteresis behavior, MCM-41 samples did not differ appreciably from conventional silicas, which confirms the applicability of MCM-41 as model materials to study general features of adsorption behavior in porous media.

Experimental Section

Large-pore MCM-41 silicas were synthesized via the hydrothermal restructuring method (Khushalani et al., 1995; Sayari et al., 1997) and their properties, such as nitrogen adsorption isotherms in a wide range of pressures and structural parameters derived from them as well as XRD spectra, were described in detail elsewhere (Kruk et al., 1997; Sayari et al., 1997). Mesoporous silicas LiChrospher Si-40 and Nova-Pak were acquired from EM Separations (Gibbstown, NJ, USA) and Millipore Co., Waters Chromatography Division (Milford, MA, USA). Nitrogen adsorption measurements were performed at 77 K on an ASAP 2010 volumetric adsorption analyzer (Micromeritics, Norcross, GA, USA). Prior to the measurements, the samples were outgassed at 473 K for 2 h in the degas port of the adsorption apparatus.

Results and Discussion

Nitrogen adsorption isotherms for large-pore MCM-41 silicas and selected conventional mesoporous silicas are shown in Fig. 1. It can be seen that the MCM-41 materials exhibit much steeper steps of capillary condensation, which indicates their narrower pore size distributions. In contrast to MCM-41 samples with smaller pore sizes (below ca. 4 nm) (Franke et al.,

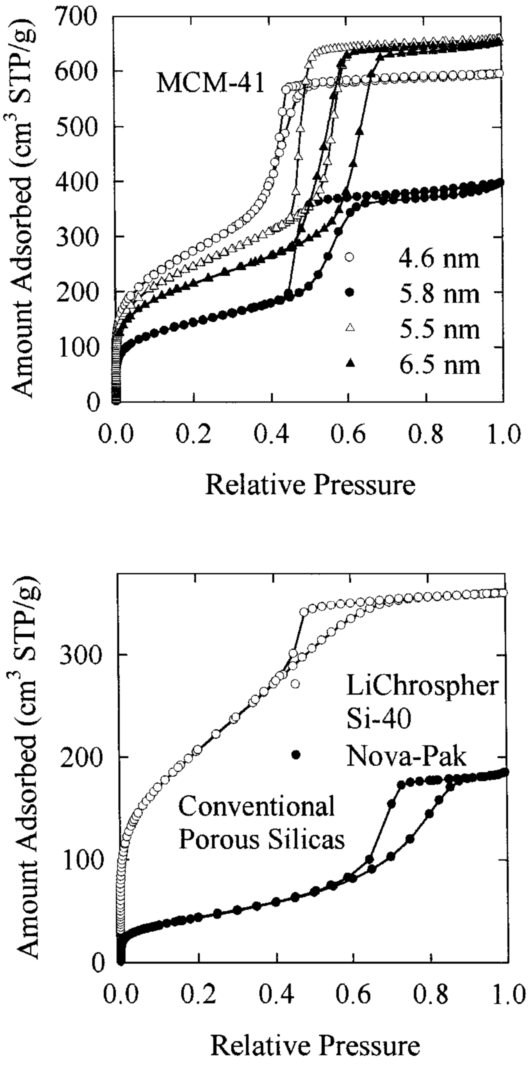

Figure 1. Nitrogen adsorption isotherms for large-pore MCM-41 silicas and conventional porous silicas.

1993; Branton et al., 1993), large-pore materials exhibit pronounced hysteresis loops (Llewellyn et al., 1994; Schmidt et al., 1995; Huo et al., 1996; Kruk et al., 1997; Sayari et al., 1997), similar to those commonly observed for conventional mesoporous silicas. Moreover, in the case of both MCM-41 and conventional mesoporous silicas under study, the hysteresis loops were not observed at relative pressures below ca. 0.4 (Kruk et al., 1997; Sayari et al., 1997), which has been commonly observed in nitrogen adsorption studies carried out at 77 K (Gregg and Sing, 1982).

In order to gain more insight into adsorption-desorption behavior of the materials under study, desorption scanning hysteresis loops (DSHLs) (Ball and Evans, 1989; Liu et al., 1993) were acquired. As can be seen in Fig. 1, MCM-41 with pore size of 4.6 nm exhibited a narrow triangular hysteresis loop with a steep desorption branch at relative pressures close to 0.4. The DSHLs gradually declined and then followed the desorption branch of the isotherm (Fig. 2). Essentially the same behavior was observed in the case of the LiChrospher Si-40 conventional silica, which has a much wider triangular hysteresis loop with the desorption branch at relative pressures ca. 0.45 (Fig. 3). It can be seen that the relative pressure of ca. 0.4–0.45 is a limiting pressure value at which adsorption-desorption hysteresis loops close (Gregg and Sing, 1982; Sing et al., 1985; Kruk et al., 1997). This may result in development of H2 (triangular) hysteresis loops (Sing et al., 1985), which were often associated with pore connectivity problems (Ball and Evans, 1989; Liu et al., 1993; Sing et al., 1985), even for materials with facile pore connectivity, such as good-quality MCM-41 samples. However, in such cases, the hysteresis loops are likely to be narrow (see isotherm for MCM-41 4.6 nm).

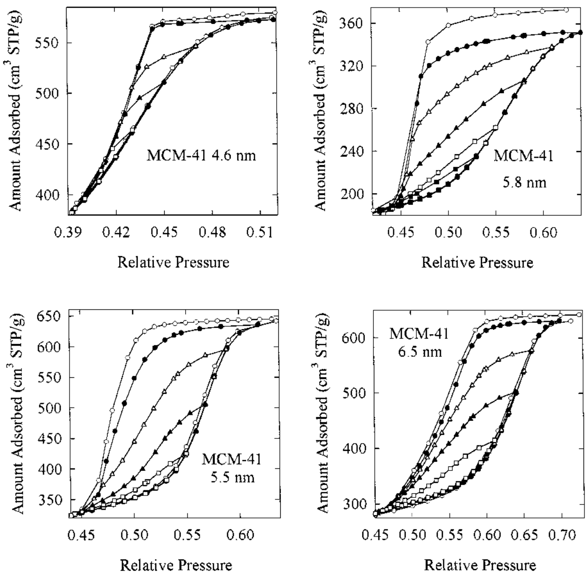

Figure 2. Scanning hysteresis loops for large-pore MCM-41 materials.

In the case of MCM-41 materials, which exhibit hysteresis loops with approximately parallel branches (pore size of 5.5 and 6.5 nm), DSHLs did not follow desorption branches of the isotherms. Instead, the scanning hysteresis loops gradually narrowed as the upper limit of the relative pressure range of adsorption-desorption scans was decreased. Such a behavior is quite similar to that for the mesoporous silica Nova-Pak, which has a hysteresis loop intermediate between type H1 and H2 (Fig. 3). However, desorption scanning curves for the Nova-Pak sample decline somewhat more steeply than the DSHLs for the MCM-41 samples considered (5.5 and 6.5 nm). The shapes of the hysteresis loop and DSHLs for the Nova-Pak silica indicate the presence of pore blocking effects (Ball and Evans, 1989; Liu et al., 1993). Therefore, it can be expected that the scanning hysteresis behavior observed for the good-quality large-pore MCM-41 materials is indicative of single-pore “blocking effects”, which are likely to result from variation of pore diameter along the mesoporous channels of these materials. The hypothetical existence of such modulated pore structures was already discussed in the literature (Stucky et al., 1997). It should be noted that it is not easy to study variations in pore diameter along MCM-41 channels using some more direct experimental techniques, such as transmission electron microscopy (TEM). Indeed, even estimation of the pore wall thickness and pore shape requires proper analysis of TEM data in order to get accurate results and avoid artifacts (see references in Kruk et al., 1999b).

An interesting behavior can be observed for MCM-41 5.8 nm material, which has lower structural uniformity than the other MCM-41 samples considered above (Sayari et al., 1997). Despite its pore size exceeding 5.5 nm, this material exhibited a triangular hysteresis loop (desorption branch at 0.45–0.48 p/p_0). Moreover, the hysteresis loop was excessively broad in comparison to those for other large-pore MCM-41 materials. The DSHL acquired at relative pressures below 0.64 gradually declined before it reached the desorption branch of the isotherm, similarly to MCM-41 4.6 nm of significantly smaller pore size. However, the scanning

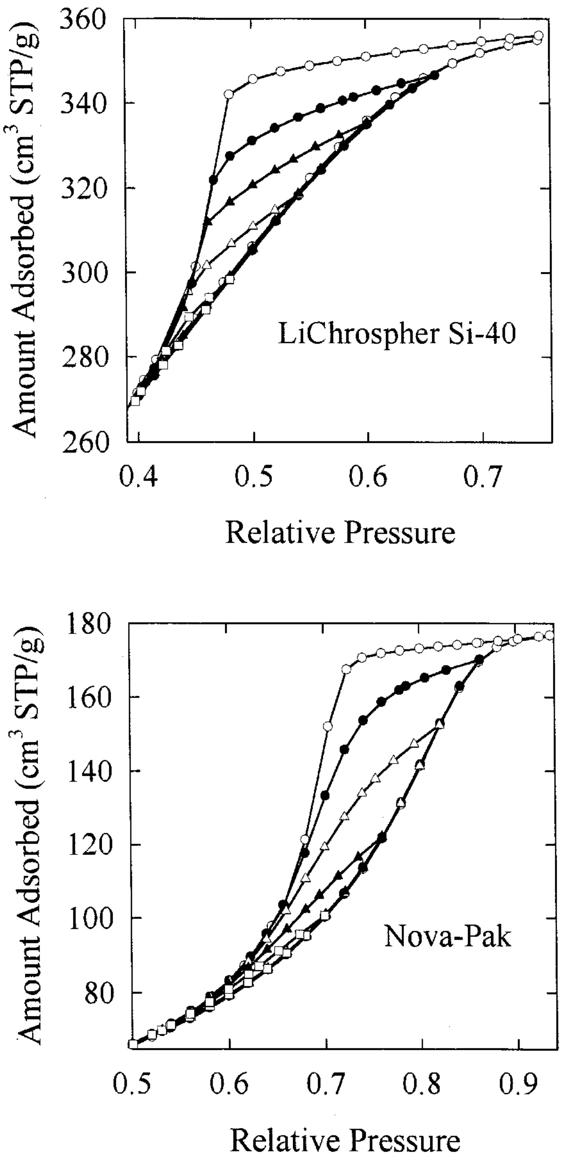

Figure 3. Scanning hysteresis loops for selected conventional porous silicas.

curves measured at lower pressures decreased much more steeply and resembled more closely the behavior of large-pore materials with parallel adsorption-desorption branches. It can be expected that MCM-41 5.8 nm exhibited pronounced pore blocking effects, most likely due to significant variation of the pore diameter along its mesoporous channels, which delayed capillary evaporation for completely filled mesopores down to the pressure limit at which hysteresis loops close. When the mesopores are only partially filled with the condensed adsorbate, the capillary evaporation takes place more readily and the desorption scanning curves are more similar to those for good-quality MCM-41 of similar pore size. It should be noted here that there was evidence for the presence of a small amount of micropores in the structure of MCM-41 6.5 nm and 5.8 nm, whereas MCM-41 5.5 nm was shown to be nonmicroporous. So, one might expect that the observed hysteresis behavior might be to some extent influenced by the presence of micropores, which are likely to be located in the pore walls (Sayari et al., 1997) and may provide some degree of connectivity between adjacent pores. However, the similarity of the hysteresis behavior between MCM-41 6.5 nm and 5.5 nm allows one to draw a conclusion that the presence of micropores does not have any noticeable influence on the DSHLs for these samples.

It is also interesting to discuss the hysteresis behavior of the MCM-41 material which underwent an excessively long hydrothermal treatment (Sayari et al., 1997). The sample exhibited a very broad hysteresis loop (Fig. 4), which did not close even at relative pressures significantly below 0.4, which indicated an extensive structural degradation of the honeycomb pore arrays. Moreover, the presence of a small amount of micropores was detected (Sayari et al., 1997). The adsorption isotherms exhibited a steep increase at pressures close to the saturation vapor pressure with no limiting adsorbed amount, similarly to H3 hysteresis

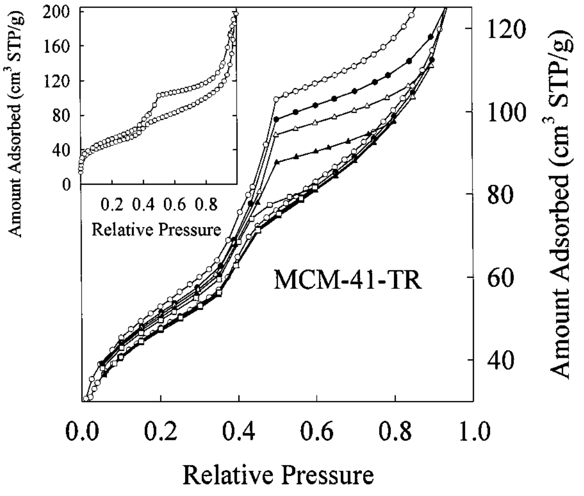

Figure 4. The nitrogen adsorption isotherm and scanning hysteresis loops for the MCM-41 material, which underwent an excessively long postsynthesis hydrothermal treatment.

loops (Sing et al., 1985). The shape of the observed hysteresis loop may be attributed to either i) the presence of both constrictions and much wider parts in the internal structure of the particles of the material (Sayari et al., 1997) or ii) the presence of interparticle pores connected with the surrounding via the nonuniform internal structure of the particles (Kruk et al., 1999a). The desorption scans carried out with a wide range of limiting relative pressures (0.6–0.95) were quite flat in the higher pressure region, i.e., the capillary evaporation from appreciable fraction of pores was delayed until the relative pressure of 0.4–0.5 was reached. Such a behavior is likely to indicate the presence of two separate systems of pores: large pores (probably interparticle pores) and narrow connecting pores (probably inside the particles of the material). Due to the large size of the former, there is no limiting adsorbed amount at high pressures. The presence of much narrower connecting pores with constrictions accounts for delayed capillary evaporation from the larger pores and for the observed low-pressure hysteresis.

Conclusions

The desorption scanning hysteresis loops presented in the current study provided an evidence of single-pore "blocking effect" during desorption even for high-quality ordered mesoporous materials. It was also shown that the steepness of nitrogen desorption branches of isotherms may arise from proximity of lower pressure limit of adsorption-desorption hysteresis rather than from pore size uniformity of materials. These findings for model mesoporous materials provide additional indication that application of desorption data to calculate mesopore size distributions may lead to highly inaccurate results.

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