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Study of the Adsorption Properties of MCM-41 Molecular Sieves Prepared at Different Synthesis Times

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Abstract. The variation of surface properties of SiMCM-41 and AlMCM-41 nanoporous materials as function of synthesis time was examined. The main properties studied were: surface area, pore diameter, pore volume, mesoporous parameter, and wall thickness. Siliceous MCM-41 molecular sieves were synthesized starting from hydrogels with the following molar compositions: $4.58SiO_2$:$0.435Na_2O$:1 CTMABr:200 H_2O for SiMCM-41, and $4.58SiO_2$:0.485 Na_2O:1 CTMABr:0.038 Al_2O_3:200 H_2O, for AlMCM-41. Cetyltrimethylammonium bromide (CTMABr) was used as the structural template. The crystallographic parameters were obtained from XRD data and by nitrogen adsorption using the BET and BJH methods. The results obtained showed a significant variation of the surface properties of the MCM-41 materials as a function of the synthesis time reaching silica wall thickness of ca. 2 nm on the fourth day.

Keywords: MCM-41, synthesis time, wall thickness

Introduction

Since the 1990's a lot of research has been conducted on mesoporous materials (Zhao et al., 1996; Beck et al., 1992). The use of these materials in chemical engineering, chemistry and catalysis has been increasing recently. Among the important characteristics of these mesoporous materials are: high surface area, well-defined mesoporous array, and possibility of generating surface acidity. Silica based MCM-41 is the main material of the M41S family (Fig. 1), which was discovered by Mobil Company. The formation of the MCM-41 phase occurs according to the liquid crystal template (LCT) mechanism, in which tetrahedral SiO_4 species react with the surfactant template under hydrothermal conditions (Beck et al., 1992). A typical preparation of the MCM-41 hexagonal array needs basically a solvent, a template (surfactant molecule) and a silica source. The use of mesoporous molecular sieves type MCM-41 in industrial processes is a goal of several researchers.

In this field four important factors influence directly the quality of these materials: the surface area (S_{BET}), pore volume (V_p), mesoporous parameter (a_o), pore diameter (D_p) and the silica wall thickness (W_t). Some works in the literature were published concerning the study of the surface properties of the MCM-41 materials. Among them we can highlight Blin et al. (2001) that performed a kinetic study of SiMCM-41 synthesis at different times and temperatures. Other works studying those parameters were published by Cheng et al. (1997) and Monnier et al. (1993). Those papers evaluated the adsorption properties of the SiMCM-41 and the variation of those properties with the incorporation of aluminum in the nanoporous structure under the same synthesis conditions.

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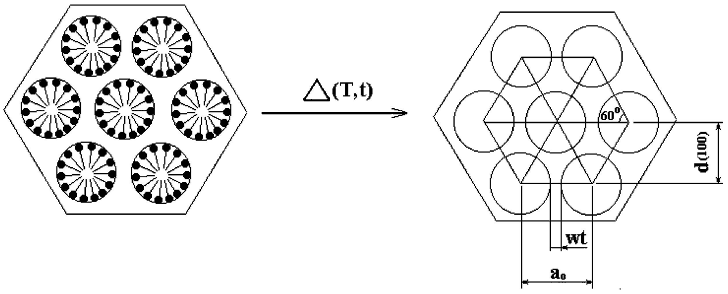

Figure 1. Schematic representation of the mesoporous array of the MCM-41 before and after calcination. Where (•— = surfactant molecule; T = temperature; t = time; w_t = silica wall thickness; $d_{(100)}$ = interplanar distance in the (100) plane and a_o = mesoporous parameter).

Experimental

The SiMCM-41 and AlMCM-41 materials were synthesized starting from silica gel (Merck, 95.5%), sodium silicate (Riedel de Haeh, 63 % SiO_2 and 18 % Na_2O), cetyltrimethylammonium bromide (CTMABr, VETEC, 98%), Pseudoboehmite (Vista, 70% Al_2O_3) and distilled water. The chemicals were mixed in order to obtain gels with the following molar composition: 4.58 SiO_2: 0.435 Na_2O: 1 CTMABr. 200H_2O. The procedure used to obtain 1.3 g of calcined SiMCM-41 was: (i) 0.917 g of silica, 0.712 g of sodium silicate and 8.40 g of water were placed into a 100 mL Teflon beaker and stirred at 60°C for 2 h in order to obtain a clear solution; (ii) a solution prepared from 1.756 g of cetyltrimethylammonium bromide and 8.40 g of distilled water was added to the above mentioned mixture and aged for 1 h at room temperature. The hydrogels were placed into 45 mL Teflon-lined autoclave and heated at 100°C for 1–4 days. Their pH was measured each day and adjusted to 9.5–10.

The synthesis procedure for AlMCM-41, to obtain the same mass of calcinated material, was: (i) 0.861 g of silica, 0.787 g of sodium silicate and 8.362 g of distilled water were placed into a 50 mL Teflon beaker and stirred at 60°C for 2 h; (ii) 0.026 g of pseudoboehmite was placed in 2.0 g of distilled water and stirred at 60°C for 1 h. The solution (ii) was added to the solution (i) and stirred at 60°C for 30 minutes. A solution (iii) prepared from 1.751 g of cetyltrimethylammonium bromide and 6.362 g of distilled water was added to the (i) + (ii) mixture and aged for 1 h at room temperature. The hydrogels were placed into 45 mL Teflon-lined autoclaves and heated at 100°C for 1–4 days. The obtained material was filtered, washed and dried at 100°C in an oven for 2 hours. The molar formula of the hydrogel was 4.58 SiO_2: 0.485 Na_2O: 1 CTMABr. 0.038 Al_2O_3: 200 H_2O.

The obtained materials were calcined at 450°C for 1 h in N_2 atmosphere and then for 1 h in air at the same temperature at a flow rate of 100 mL min^{-1}. The temperature was increased from room temperature to 450°C at a rate of 5°C min^{-1} (Araujo et al., 2004). XRD measurements were carried out in Philips x-ray equipment using CuK_α radiation in 2θ angle of 1 to 10° with step of 0.02°. The specific surface area was determined by nitrogen adsorption according to the Brunauer-Emmett-Teller (BET) method (Brunauer et al., 1938) in the relative pressure range 0.1–0.3. Pore size distributions were calculated according to the Barrett-Joyner-Halenda (BJH) algorithm (Barrett et al., 1951). The final aluminum content was determined by Energy Dispersive X-ray analysis (EDX) analysis in a Philips model XL30-ESEM unit.

Results and Discussion

EDX analysis of the AlMCM-41 material yielded a Si/Al ratio of 65.3 and a Na/Al ratio of 0.78 on the fourth day of synthesis. Figure 2 shows the EDX spectra of the SiMCM-41 and AlMCM-41 nanostructured materials. Both materials were free from impurities in the studied range.

From the XRD analysis of the MCM-41 materials obtained at different synthesis times, it was possible to observe that all materials presented characteristic peaks in the 2θ ranges of 1 to 10°, related to (100), (110), (210) Miller indices, which are characteristic of AlMCM-41 materials (Zhao et al., 1996; Beck et al., 1992). Figure 3 shows the XRD powder patterns of the SiMCM-41 and AlMCM-41 samples. As presented in that figure, on the second day, the most intense XRD peaks were observed. This fact is associated with the production of a highly ordered hexagonal structure (Araujo and Jaroniec, 2000). The XRD analyses also showed

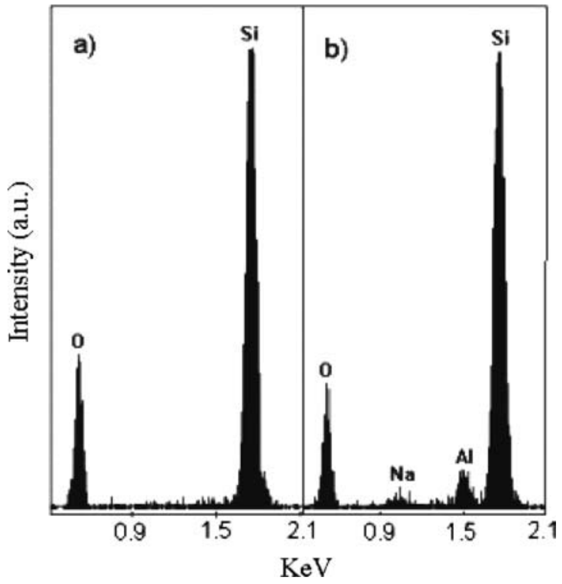

Figure 2. EDX analysis for SiMCM-41 (a) and AlMCM-41 (b) materials obtained on the fourth day.

movement of the main peak (plane (100)) to small angles in proportion to the synthesis time, evidencing the gradual increase the mesoporous parameter (a_o), as foreseen by Corma and collaborators (1997). The value of a_o represents the sum of the pore diameter (D_p) and the silica wall-thickness (W_t). Equation (1) correlates the inter-planar distances with the value of the mesoporous parameter (Beck et al., 1992). In addition, through simplification for reflection (100) the general expression (Eq. (2)) can be obtained that correlates the $d(100)$ value with a_o. The data from pore distributions (Fig. 4) can be related to the XRD data (as shown in Fig. 5) according Eq. (3).

$$\frac{1}{d(hkl)^2} = \frac{4(h^2 + hk + l^2)}{3a_\mathrm{o}^2} + \frac{l^2}{c} \qquad (1)$$

$$a_o = \frac{2d(100)}{\sqrt{3}} \qquad (2)$$

$$Wt = a_\mathrm{o} - D_p \qquad (3)$$

Nitrogen adsorption provides a powerful technique to determine the surface area, pore volume and pore size distribution. The surface area is generally obtained correlating the data of P/Po in the range of 0.05–0.3 by the Brunauer-Emmett-Teller method (BET) (Brunauer et al., 1938).

Figure 4 shows the pore size distributions obtained by the BJH method (Barret et al., 1951) for samples of SiMCM-41 and AlMCM-41. Table 1 provides information about the surface properties of the MCM-41 materials. In the case of SiMCM-41, the pore size varied from 2.40 to 2.65 nm, and for AlMCM-41 the pore size wasin the range of 2.25 to 3.2 nm. In all the cases

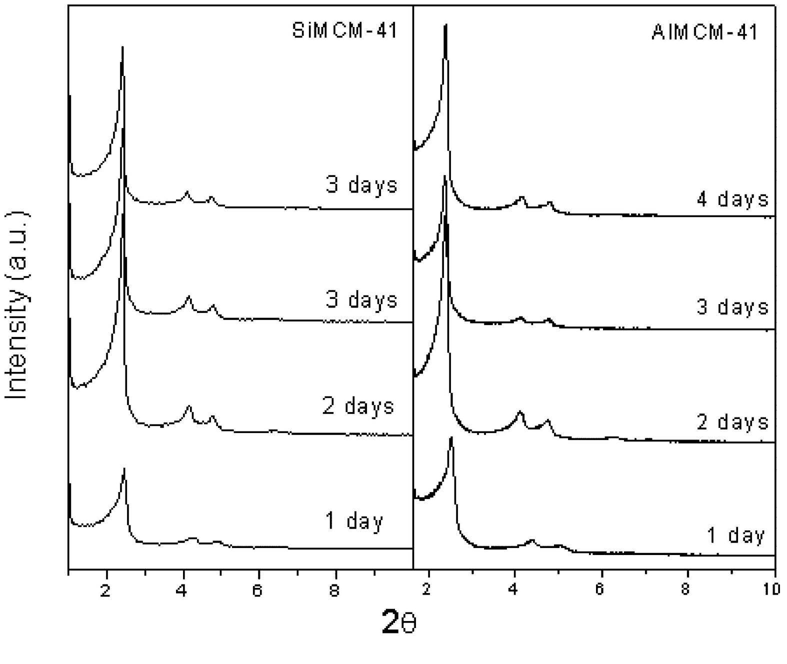

Figure 3. XRD powder patterns of MCM-41 materials as function of synthesis time.

Table 1. Surface properties of the MCM-41 materials

Sample	Time (days)	a_o (nm)	D_p (nm)	W_t (nm)*	V_p (cm^3 g^{-1})	S_{BET} (m^2 g^{-1})	W_t rate (nm/day)
SiMCM-41	1	4.13	2.64	1.49	0.46	738	1.49
SiMCM-41	2	4.23	2.55	1.68	0.78	931	0.19
SiMCM-41	3	4.24	2.43	1.81	0.52	864	0.13
SiMCM-41	4	4.25	2.42	1.83	0.51	840	0.02
AlMCM-41	1	4.06	3.12	0.94	0.41	560	0.94
AlMCM-41	2	4.27	2.56	1.71	0.41	642	0.77
AlMCM-41	3	4.28	2.35	1.93	0.42	710	0.22
AlMCM-41	4	4.29	2.27	2.02	0.40	694	0.09

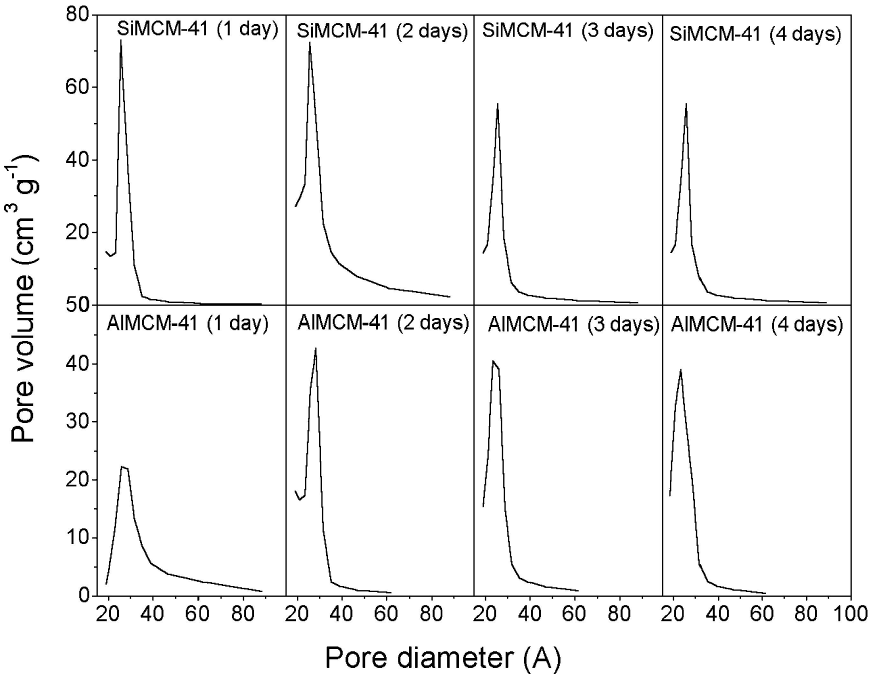

Figure 4. Pore distributions of the MCM-41 materials at several synthesis times.

a decrease was observed in the mean pore diameter as the synthesis time increased. This fact is attributed to gradual increase of the silica wall-thickness, reaching equilibrium on the fourth day.

Materials with significant values of the surface area were obtained and there was a direct correspondence between the value of the surface area and the relative intensity of XRD patterns, shown in Fig. 3. In the case of SiMCM-41 the BET surface areas were: 738, 931, 864 and 840 m^2 g^{-1}, respectively, proceeding from the first day to the last day. In the case of ALMCM-41, the surface areas were a little smaller than for SiMCM-41, viz., 560, 642, 710 and 694 m^2 g^{-1}, respectively, proceeding from the first day à to the last day. None of the materials exhibited a significant variation in the pore volume with synthesis time. SiMCM-41 yielded pore volumes in the range of 0.46 to 0.51 cm^3 g^{-1}. An exception was observed in the sample obtained after two days of synthesis that presented an unusually high pore volume value of 0.78 cm^3 g^{-1}. In contrast, the pore volumes of the AlMCM-41 samples were very constant in the range of 0.40 to 0.41 cm^3 g^{-1}.

Combining the XRD data with the BJH method it was observed that the pore diameters decreased with

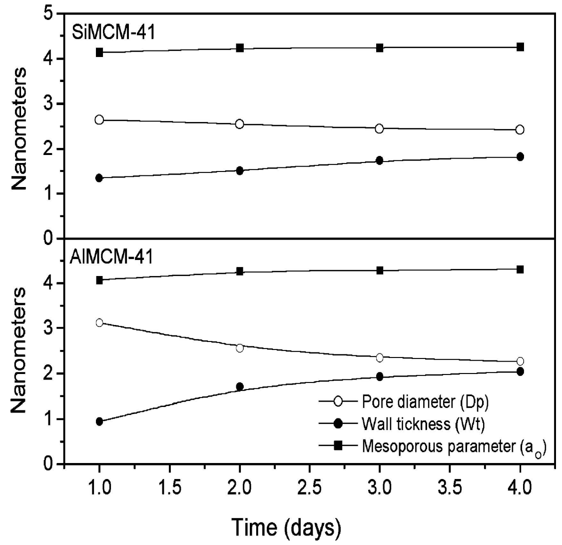

Figure 5. Variation of the pore diameter, wall thickness, and mesoporous parameter with the synthesis time.

the hydrothermal synthesis time (, as shown in Fig. 5). The values of the mesoporous parameter (a_o) are the sum of pore diameter and the silica wall thickness, and in all case the values increase with synthesis time. The increase of a_{o} followed by the progressive decrease of the pore diameter is indicative of the growth of the silica wall thickness (W_t). As also observed in the Table 1, the SiMCM-41 and AlMCM-41 materials exhibited higher rates of wall thickness growth in the first and second days of synthesis. The values decreased quickly in the third and fourth days, and they stabilized indicating the end of the hydrothermal reactions. As we can see in Fig. 5, the silica wall thickness (W_t) increased then stabilized, reaching values of ca. 2 nm on the fourth day. Figure 6 shows the relationship between a_{o} and W_t.

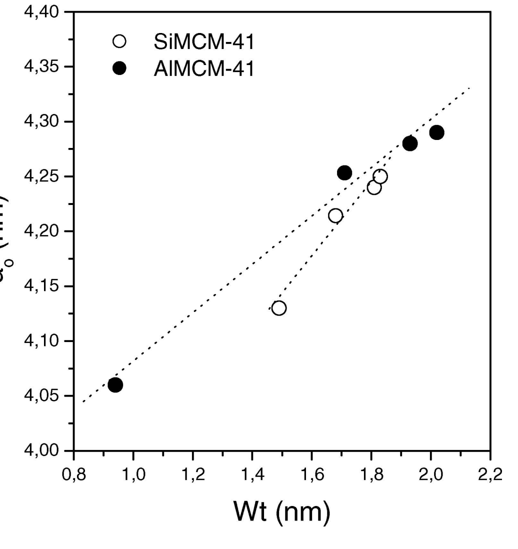

Figure 6.

Conclusions

In this work the surface properties of the SiMCM-41 and AlMCM-41 nanostructured materials obtained at different synthesis times were evaluated. The results showed a significant increase in the wall thickness with the synthesis time reaching ca. 2 nm on the fourth day. A gradual increase in the mesoporous parameter, a_{o}, was also observed, along with a gradual decrease in the pore size. All the materials exhibited similar behavior, indicating that the presence of aluminum does not influence in the gradual hydrothermal self-assembly process. SiMCM-41 presented larger values of surface area than AlMCM-41 at the same experimental conditions, but AlMCM-41 materials yielded large a_{o} values indicating that the aluminum presence influences in the process of wall growth.

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