Textural features of highly ordered Al-MCM-41 molecular sieve studied by X-ray diffraction, nitrogen adsorption and transmission electron microscopy

Marcelo J.B. Souza,*, Antonio S. Araujo, Anne M.G. Pedrosa, Bojan A. Marinkovic, Paula M. Jardim, Edisson Morgado Jr.

a Universidade Federal de Sergipe, Departamento de Engenharia Química, 49100-000, São Cristovão, SE, Brazil
b Universidade Federal do Rio Grande do Norte, Departamento de Química, 59078-970, Natal, RN, Brazil
c Pontifícia Universidade Católica do Rio de Janeiro, Departamento de Ciência dos Materiais e Metalurgia, Rua Marquês São Vicente 225, Gávea, 22453-900, Rio de Janeiro, RJ, Brazil
d Petrobras/CENPES, Pesquisa e Desenvolvimento do Abastecimento, Tecnologia em FCC, Ilha do Fundão, Quadra 7, Rio de Janeiro, RJ, Brazil

Received 26 September 2005; accepted 23 January 2006
Available online 10 February 2006

Abstract

The preparation of an Al-MCM-41 mesoporous materials has been carried out using silica-gel and pseudoboehmite as silica and aluminum sources, respectively, and surfactant cetyltrimethylammonium bromide as structure template. The textural properties of the calcined Al-MCM-41 were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM) and N₂ isothermal adsorption measurements. The hexagonal structure parameter \( a_o \) was calculated based on \( d_{(100)} \) XRD reflection as 4.75 nm. TEM images revealed the formation of a well-ordered Al-MCM-41. Accordingly, nitrogen adsorption measurements (BJH) showed a material with very narrow distribution and medium pore diameter of 3.14 nm. Mesopore volume based on adsorbed nitrogen was 0.51 cm\(^3\) g\(^{-1}\). Through a combination of XRD and N₂ adsorption data, the thickness of the channel walls of 1.61 nm could be calculated.

Keywords: Al-MCM-41; Wall thickness; Pore diameter

1. Introduction

Since 90s, mesoporous materials have attracted a great deal of attention from scientists and industrials because of its increasing use in chemical engineering, chemistry and catalysis fields [1,2]. High surface area, well-defined mesoporous array and possibility to generate surface acidity are important characteristics of the mesoporous materials with possibility of application in catalytic cracking, esterification reactions and other process that requests acid catalysis. The silica based MCM-41 is the main mesoporous material of the M41S family (Fig. 1), discovered by researchers in Mobil Oil Corporation [1]. The formation of the MCM-41 phase occurs according to the liquid crystal template (LCT) mechanism, in which SiO₄ tetrahedra react with the surfactant template under hydrothermal conditions [1]. A typical preparation of the MCM-41 hexagonal array needs basically a solvent, a template (surfactant molecule) and a silica source, whose nature and relative composition in the synthesis gel may influence several properties of these materials such as: superficial area \( S_{BET} \), pore volume \( V_p \), unit cell parameter \( a_o \), pore diameter \( D_p \) and the silica wall thickness \( W_t \). For instance, Jaroniec [3] investigated MCM-41 materials with tailored pore diameter by means of surfactants with different chain lengths. An important variation of MCM-41 is its aluminum derivative—Al-MCM-41—which has been investigated in a less extent than MCM-41 but is especially attractive in catalysis field due to its potential generation of Bronsted acid sites as tetrahedral coordinated Al is incorporated to the framework. However, achieving a well-organized mesoporous texture is generally more difficult with Al-MCM-41 than with MCM-41, due to the presence of another element in the synthesis. Some papers have been published providing textural characterization of Al-MCM-41 materials obtained by a variety

In the present work, the synthesis of Al-MCM-41 with Si/Al ratio of 40 was carried out with pseudoboehmite as alumina source and an extensive characterization of the mesoporous material has been made using XRD (X-ray diffraction), nitrogen adsorption (BJH method) and TEM (Transmission Electron Microscopy), focused on revealing its textural properties.

2. Experimental

The Al-MCM-41 material was synthesized starting from silica gel (Merck, 95.5%), sodium silicate (Riedel de Haeh, 63% SiO₂ and 18% Na₂O), cetyltrimethylammonium bromide (CTMABr, Vetec, 98%), Pseudoboehmite (Vista, 70% Al₂O₃) and distilled water. The chemicals were mixed in order to obtain a synthesis gel with the following molar composition: 4.58 SiO₂: 0.485 Na₂O: 1 CTMABr: 0.057 Al₂O₃: 200 H₂O. Typically, the synthesis procedure to obtain 1.3 g of dry-basis 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 Becker 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. Solution (ii) was added to solution (i) and stirred at 60 °C for 30 min. 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 stirred 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 with water and dried at 100 °C in a stove for 2 h. The as-prepared material was calcined at 450 °C for 1 h in N₂ atmosphere and then for 1 h in air at the same temperature using dynamic flow of 100 mL min⁻¹. The temperature was increased from room temperature to 450 °C at a heating rate of 5 °C min⁻¹ [8]. XRD measurements were carried out, using CuKα radiation in 2θ angle range of 1 to 10° with step of 0.02°, on a Shimadzu XRD 6000 X-ray equipment. Energy dispersive analyses were carried out on an EDX-800 instrument. The specific surface area was determined by nitrogen adsorption, according to the Brunauer–Emmett–Teller (BET) method [9] in the relative pressure range 0.1–0.3. Pore size distributions were calculated according to Barrett–Joyner–Halenda (BJH) algorithm [10]. TEM measurements were performed using a Jeol 2010 instrument with an electron beam accelerating voltage of 200 kV; the sample was dispersed ultrasonically in 2-propanol, and a drop of the suspension was deposited on a holey carbon copper grid.

3. Results and discussion

XRD analysis of the Al-MCM-41 sample, as presented in Fig. 2, revealed characteristic diffraction peaks for this material, namely (100), (110), (200), (210) and (300) [12]. From the main interplanar distance (d₁₀₀), it was possible to obtain the hexagonal structure parameter a₀. The value of a₀ represents the sum of the pore diameter (Dp) and the silica wall-thickness (Wt), as illustrated in Fig. 1. Eq. (1) correlates the interplanar distances with the value of the hexagonal structure parameter [2]. Assuming reflection (100), a simplified expression is

![Fig. 1. Schematic representation of the mesoporous array of the MCM-41 before and after the calcination. Where (●— surfactant molecule; T= temperature; t= time; wt= silica wall thickness; d₁₀₀= interplanar distance in the (100) plane and a₀= mesoporous parameter).](image-url)

![Fig. 2. XRD powder patterns of the calcined Al-MCM-41 material.](image-url)
derived (Eq. (2)) that correlates the $d_{(100)}$ value with $a_o$. Eq. (3) is used to obtain the value of the medium wall-thickness ($W_t$), combining the XRD with BJH data [11]. The $a_o$ value obtained through (100) XRD reflection to Al-MCM-41 sample was 4.75 nm. According to EDX analysis Al-MCM-41 with the following atomic ratio: Si/Al=42.6 and Na/Al=1.5 was obtained.

Nitrogen adsorption–desorption phenomenon provides a technique to determine surface area, pore volume and pore size distribution. The surface area has been obtained correlating the data of $P/P_o$ in the range of 0.05–0.3 by the Brunauer–Emmett–Teller method (BET) [9]. The N$_2$ adsorption–desorption isotherms for the calcined Al-MCM-41 sample are shown in Fig. 3a. It can be seen that the sample exhibits a type IV nitrogen adsorption–desorption isotherm, typical of a uniform mesoporous material according to the IUPAC nomenclature [12]. The isotherms exhibited three stages as follows: adsorption at low pressure ($P/P_o<0.28$) accounts for a monolayer adsorption of nitrogen on the walls of the mesopores. As the relative pressure increases, the isotherms rise steeply (at about $P/P_o$ ca. 0.28), which is characteristic of capillary condensation within mesopores, having a narrow hysteresis loop. At higher relative pressures ($P/P_o>0.4$), the plateau region is due to multilayer adsorption on the outer surface of the particles. The total surface area of the synthesized Al-MCM-41, calculated according to the BET method, was 870 m$^2$ g$^{-1}$.

The pore size distribution determined from the adsorption isotherm by the BJH method [10] covered the pore diameter range of 20–600 Å. As shown in Fig. 3b, a very narrow distribution was obtained for the Al-MCM-41 material, with a medium pore diameter of 3.14 nm and a mesopore volume of 0.51 cm$^3$ g$^{-1}$. The channel wall thickness calculated by applying Eq. (3), based on XRD and BJH data, was 1.61 nm.

Figs. 4 and 5 show transmission electron microscopy images of the calcined Al-MCM-41 sample. It can be noticed that the mesopores possess a highly ordered hexagonal array, that is apparently long-ranged. On one hand, this observation corroborates with the high crystallinity feature of the XRD pattern, where all diffraction peaks appeared and not only the main (100) reflexion (as observed when Al-MCM-41 is disordered). On the other hand, the uniform porosity revealed by TEM analysis is in line with the quite narrow pore size distribution determined by N$_2$ adsorption (BJH).

4. Conclusions

A successful synthesis of a pure and highly ordered Al-MCM-41 could be obtained via hydrothermal process. The textural properties of the obtained nanostructured material were evaluated. By means of XRD and nitrogen adsorption analyses, it was possible to obtain the values of mean pore diameter ($D_p$)
and hexagonal structure parameter ($a_0$). Based on these parameters, silica wall thickness ($W_t$) was calculated to be 1.65 nm. TEM observations confirmed that the synthesized Al-MCM-41 possesses highly ordered, long-ranged hexagonal array of mesopores.

Acknowledgements

The authors acknowledge the support from the Financiadora de Estudos e Projetos (FINEP/CTPetro) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

References