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The structural comparison between Al-MCM-41 and B-MCM-41

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Abstract

A series of mesoporous aluminosilicate and borosilicate molecular sieves with the MCM-41 structure have been synthesized with different SiO₂/Al₂O₃ or SiO₂/B₂O₃ mass ratios of 5, 10, 25, 50, 70 and 150. The samples were synthesized using the direct method with a duration of 48 h. As silica source colloidal silica (ludox 40%, Prolabo), as aluminium source sodium aluminates and boric acid as the boron source were used in these syntheses. All samples were characterized by X-ray diffraction (XRD), ATR-FT-IR, N₂ gassorption and elemental analysis by electron microscopy.

XRD revealed that the characteristic MCM-41 structure is obtained for both mass ratios greater than 10. B-MCM-41 gives a better organization of the structure than Al-MCM-41. The B substitution in MCM-41 gives a tetrahedral configuration as proven by ATR-FT-IR. The pore diameter is very similar in both samples. *To cite this article: M. Adjdir et al., C. R. Chimie 12 (2009).* © 2008 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

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1. Introduction

Since the synthesis of the crystalline mesoporous M41S materials by Mobil's researchers [1,2], the following study has focused on the MCM-41 material, which shows a hexagonal array of uniform mesopores with uniform sieves ranging from 2 to 10 nm. Their extraordinary high surface and distinct adsorption properties open up many potential applications in catalysis, separation and nanostructured materials [3–5]. Many researches on MCM-41 have been focused on the incorporation of different elements like aluminium and boron in order to modify the framework of MCM-41 and to

generate catalytic sites needed for different type of reactions. The aluminosilicate mesoporous molecular sieves have received much attention for their strong Brønsted acidity. Many efforts have been made to optimize the silicate sources such as cab-o-sil M5 fumed silica, sodium silicate and tetramethylammonium silicate [6], cab-o-sil M5 fumed silica and sodium silicate [7]. The aluminium source has been studied by Borade and Clearfiled [8], Occeili et al. [9] and Badamali et al. [10] who have reported that the sodium aluminate source incorporates aluminium to a maximum amount in the framework sites. In addition, density and the strength of acid sites are found to be significantly higher when sodium aluminate is applied. The syntheses of Al-MCM-41 by a direct method exhibits considerable hydrothermal stability especially at relatively low Al-contents. The Al-MCM-41 mesoporous

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materials prepared via grafting routes are extremely stable in boiling water. Regarding the borosilicate mesoporous molecular sieves, Oberhagemann et al. [11] used a single silica source, tetramethoxy silane whereas Trong et al. [12] took Ludox and sodium silicate to synthesize B-MCM-4. It is found [13] that in borosilicate molecular sieves boron occupies the site of the framework aluminium and the protonic form of borosilicate molecular sieves, are less acidic than their aluminosilicate counterparts due to lack of strong Brønsted acidity. In literature no report is available on comparison between B-MCM-41 and Al-MCM-41 with different contents of aluminium and boron. Here we report the synthesis and characterization of MCM-41 materials with different contents of aluminium and boron. We have studied the effect of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ or $\text{SiO}_2/\text{B}_2\text{O}_3$ ratios from 5 to 150 on the final structure and compared their physical properties.

2. Experimental

2.1. Starting materials

Sodium aluminate (54% Al_2O_3 ; 41% Na_2O ; 5% H_2O ; Aldrich) was used as the aluminium sources, boric acid (H_3BO_3 Aldrich) for the provision of boron. Colloidal silica (Ludox 40%, Prolabo) served as a silicon source and as surfactant cetyltrimethylammonium bromide ($\text{C}_{19}\text{H}_{42}\text{NBr}$; CTAB, Aldrich; 99%). Tetramethylammonium hydroxide ($\text{TMAOH} \cdot 5\text{H}_2\text{O}$, 25 wt.%, Aldrich) was utilized as a base.

2.2. Direct synthesis of Si-MCM-41

The synthesis procedure of Si-MCM-41 was reported in a previous paper [14] according to the following molar composition $1\text{SiO}_2:0.25\text{CTAB}:0.2\text{TMAOH}:40\text{H}_2\text{O}$. Tetramethylammonium hydroxide was dissolved in distilled water, and then 2 g of bromide of cetyltrimethylammonium (CTAB) was added into the suspension under stirring. After 30 min, Ludox was slowly added, giving rise to white slurry. The reaction mixture was continuously stirred for 2 h. Afterwards the obtained hydrogel was transferred into a Teflon autoclave vessel for the crystallization, which lasted 48 h at 373 K. Thereafter, the product was washed several times with demineralised water, filtered and dried at 373 K overnight, afterwards calcined under air at 823 K for 12 h.

2.3. Synthesis of B-MCM-41

The hydrothermal synthesis of B-MCM-41 samples was carried out at 373 K using gel with molar

composition of: $1\text{SiO}_2:0.25\text{MCTAB}:0.2\text{TMAOH}:y\text{H}_3\text{BO}_3:40\text{H}_2\text{O}$. The experimental procedure adopted to prepare B-MCM-41 with $y = 5; 10; 25; 50; 70$ and 150 as a typical case is described as follows. A solution was prepared which contains the hydroxide of tetramethylammonium (TMAOH) in demineralised water, then under stirring 2 g of bromide of cetyltrimethylammonium (CTAB) was added. After 30 min silica and finally 0.0193 g of boric acid (H_3BO_3) was added to the solution. The reaction mixture was stirred for 2 h. The hydrogel obtained is heated at 373 K during 48 h. The solid obtained was washed several times with demineralised water, filtered and dried at 373 K overnight, then calcined under air at 823 K for 12 h.

2.4. Synthesis of Al-MCM-41

For this method three solutions were prepared which contain a source of aluminium mixed with an organic hydroxide of quaternary ammonium type (S1), a source of silica (S2) and a surfactant agent (S3). The solvent used in the three solutions is demineralised water. The molar composition was $1\text{SiO}_2:0.25\text{CTAB}:0.2\text{TMAOH}:x\text{Al}_2\text{O}_3:40\text{H}_2\text{O}$, with $x = 5, 10, 25, 50, 70, 150$. The gel was kept in a Teflon-lined stainless steel autoclave and heated at 373 K for two days for crystallization. The solid product obtained was washed, filtered and dried overnight at 373 K. The as-synthesized samples were calcined at 823 K in air for 12 h.

2.5. Characterization

XRD patterns were recorded for all the samples in order to check the formation and structure of Al-MCM-41. The diffraction patterns were recorded in the 2θ range of $1\text{--}12^\circ$ with a step size of 0.02° 2θ and a step time of 5 s on a Bruker D8 diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation equipped with PSD counter. A $\text{Cu K}\alpha$ anode was powered with 40 kV and 40 mA. A Talc/Vermiculite mixture was applied as internal standard for peak position correction. Single line fitting was performed with the Bruker software Topas 3.0 (polynom 3rd degree as background, pseudo-voigt function as profile function).

N_2 -sorption measurements were performed at 77 K using a Quantachrome Autosorb1 MP. The samples were degassed at 383 K in vacuum for 24 h before measurements. Specific surface areas were calculated by using the Brunauer–Emmett–Teller (BET) method [15]. Pore size distribution curves were calculated using two methods. One is the NLDFT equilibrium

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