



A comparative study of direct versus post-synthesis alumination of mesoporous FSM-16 silica



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ABSTRACT

Al-FSM-16 mesoporous silicas were synthesized either by direct method, from Al-kanemite (Al-FSM-16/D), or by post-synthesis impregnation of purely siliceous FSM-16 with $\text{Al}(\text{NO}_3)_3$ (Al-FSM-16/P) and characterized with XRD, XRF, SEM, TEM, nitrogen sorption isotherms, ^{27}Al and ^{29}Si MAS NMR, FTIR, XPS, NH_3 -TPD, FTIR of pyridine adsorption and catalytic decomposition of ethanol. Only substitutional Al sites exist in Al-FSM-16/D, while in Al-FSM-16/P some Al remains in extra-lattice positions. Upon transformation of Al-FSM-16/D into hydrogen form a certain amount of extra-framework Al is formed. Direct alumination introduces a higher degree of structural disorder. In Al-FSM-16/D, Al is preferentially accumulated at inner pore walls, while in Al-FSM-16/P external surface is Al-rich. Post-synthesis alumination is more efficient in introducing acid sites into FSM-16. The generated acidity is of Brønsted and Lewis nature, the latter being stronger than the former.

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1. Introduction

Ordered mesoporous silicas represent an important class of porous structures with well defined pores of controlled dimensions, shape and connectivity. The materials find many applications, particularly in the field of catalysis, separation processes, and host-guest chemistry. Alumination of the mesoporous silicas is one of the most popular method of their modification. Isomorphous substitution of Al for Si aims at development of cation exchange/acid properties, and extends further potential of these materials as hosts, adsorbents or catalysts. Formation of Al-containing ordered mesoporous silica frameworks had already been described in the 1992 reports on the syntheses of MCM-41 [1], and the material referred to later as FSM-16 [2]. FSM-16 silicas, derived from kanemite, a layered sodium silicate of the formula $\text{NaHSi}_2\text{O}_5 \times 3 \text{H}_2\text{O}$, are structurally analogous to the extensively studied MCM-41 materials, as they are highly ordered mesoporous solids with a

hexagonal array of uniform channels, high specific surface area and pore volume [3].

Insertion of aluminum into mesoporous silicas is usually carried out by one of the two well established synthesis routes: direct method, consisting in addition of Al source to the synthesis gel, or post-synthesis treatment, in which Al source is incorporated into purely siliceous mesoporous framework by such means as grafting or impregnation. The literature on MCM-41 alumination by either of the procedures is plentiful [1,2,4–32], and includes many studies comparing the effects of direct versus post-synthesis alumination [20–32]. It has been shown that the method of Al insertion determines the material structure, stability, Al distribution, acidity and catalytic properties.

In contrast to copious findings related to MCM-41 aluminosilicates, the reports investigating the effect of alumination on FSM-16 structure and properties are much fewer [2,33–39]. It should be noted, that despite close structural similarities between MCM-41 and FSM-16, the materials are formed via essentially different mechanisms [40–42]. The cooperative self-assembly of surfactant and a dissolved silica source, operating during the synthesis of MCM-41, leads to a direct build up of the hexagonal mesophase

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without formation of any transient ordered silicate-surfactant phases. In contrast, transformation of kanemite, exchanged with surfactant cations, to FSM-16, involves ordering of fragmented anionic silicate sheets into an intermediate layered silica-surfactant mesophase, followed by subsequent evolution of the actual hexagonal structure. Comparative studies of purely siliceous forms of MCM-41 and FSM-16 revealed that some properties of these structurally related materials show considerable differences. Thus, it has been observed that FSM-16 solids have higher thermal and hydrothermal stability than MCM-41 ones [43,44], the effect attributed to a higher degree of condensation within the pore walls of the former. Also, comparison of photocatalytic activity of FSM-16 and MCM-41 in several organic transformations demonstrated superiority of the kanemite-derived mesoporous silica catalyst [45].

In view of the above, and considering the uniqueness of the self assembly process leading to the FSM-16 structure, we decided to investigate in more detail the process of Al insertion into the structure of FSM-16, focusing on the role of the employed alumination route and the effect it has on the structure, texture, Al localization and evolution of the acid function of the resulting solids.

2. Experimental

2.1. Materials

Kanemite was synthesized from water glass (Aldrich, reagent grade, molecular formula $\text{Na}_2\text{Si}_3\text{O}_7$), following the procedure optimized in our laboratory [46,47]. Briefly, the Na/Si ratio was adjusted to 1 by addition of appropriate amount of 2 M NaOH solution. The liquid was dried in air at 100 °C for 24 h and the remaining solid calcined at 700 °C for 1 h, ground, and stirred in water for 10 min, to yield kanemite. The FSM-16 solids were obtained according to the method originally proposed by Inagaki et al. [2], by mixing the kanemite powder with the 0.1 M aqueous solution of hexadecyltrimethylammonium bromide and adjusting pH to 11.5 by addition of NaOH. The mixture was heated to 70 °C

and stirred for 3 h. Afterwards the pH was lowered to 8.5 by dropwise addition of 1 M HCl and the mixture stirred for further 3 h. The FSM-16 product was filtered, washed and dried in air. The template was removed by calcination at 550 °C for 6 h. Directly aluminated materials were obtained by addition of required amount of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to the mixture of NaOH and SiO_2 , at the stage of kanemite preparation, and continuing the synthesis as described above. Post-synthesis alumination consisted in impregnation of purely siliceous FSM-16 with a required amount of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dissolved in a small quantity of water, followed by drying at 80 °C and calcination for 1.5 h at 550 °C. The directly and the post-synthesis aluminated samples are referred to as Al-FSM-16(x)/D and Al-FSM-16(x)/P, respectively, where x is the Si/Al ratio ($x = 20, 40$ or 60). The purely siliceous FSM-16 sample is denoted FSM-16. Transformation of the as received Al-FSM-16(x)/D into hydrogen form was carried out by subjecting the solids to exchange with ammonium cations (from NH_4NO_3 solution), followed by washing, drying and thermal decomposition of NH_4^+ species at 400 °C for 6 h. The hydrogen-forms are denoted H-Al-FSM-16(x)/D.

2.2. Methods

X-ray diffraction (XRD) patterns were recorded with a Philips 1710 powder diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation. Transmission electron microscopic (TEM) studies were performed with FEI Tecnai G² transmission electron microscope at 200 kV. Chemical analysis was carried out with an Orbis Micro-EDXRF analyzer with a Rh anode as X-ray source (operating at 30 kV and 500 mA) and Si(Li) detector, using Orbis Vision software. BET specific surface area and pore size distribution based on non-local density functional theory were determined from the nitrogen adsorption-desorption isotherms obtained at -196 °C with a Quantachrome Nova 2000 apparatus. Prior to the measurement the samples were outgassed for 18 h at 200 °C. Solid state MAS-NMR spectra were measured on a home-made pulse NMR spectrometer at the magnetic field of 7.05 T. A Bruker HP-WB high-speed MAS probe equipped with the 4 mm zirconia rotor and KEL-F cap was used to record the MAS spectra at 8 kHz spinning

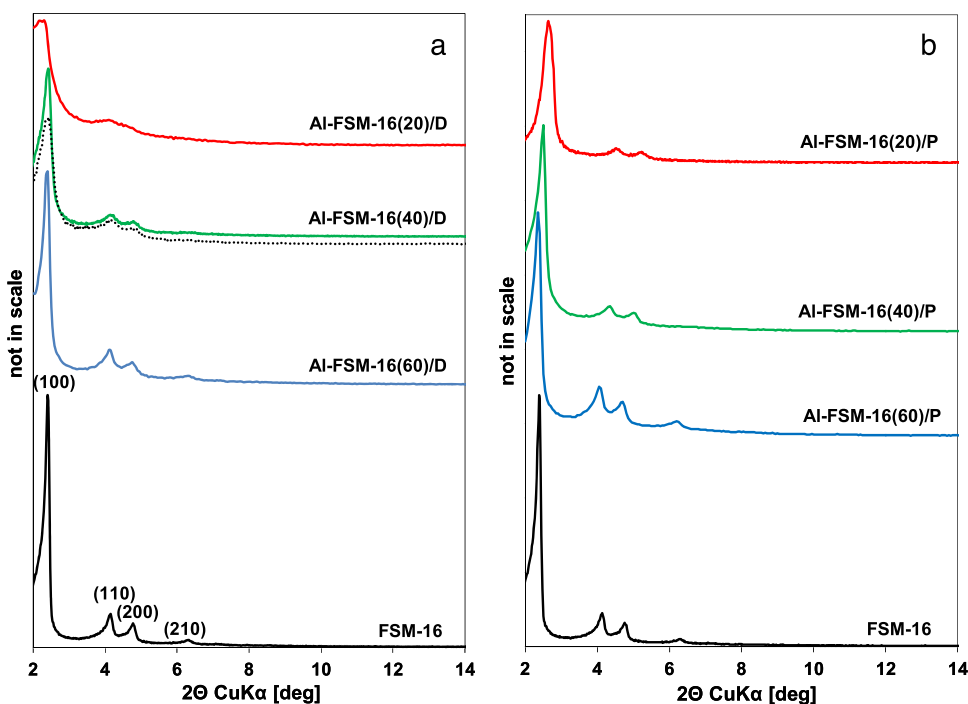


Fig. 1. XRD patterns of aluminated FSM-16 solids: a) direct method (dotted line: H-Al-FSM-16(40)/D sample), b) post-synthesis treatment.

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