

## **ULTRAFAST SONOCHEMICAL SYNTHESIS OF HIGHLY ALUMINATED MESOPOROUS SILICA MCM-41**

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### **ABSTRACT:**

A rapid synthesis route used in this study to prepare high quality of mesoporous aluminium-rich MCM-41 silica in short time as low as five minutes using cetyltrimethylammonium bromide (CTMABr) as template under basic conditions with the aid of ultrasonic irradiation. The advantages of present synthesis route is to substitute high level of aluminium (Si/Al = 2) in the framework, effectively reduces the total synthesis time from day to five minutes, which is much shorter than the conventional hydrothermal synthesis of Al-MCM-41. The physico-chemical characterisation studies reveals that the much shorted self-assembly time of five minutes does not affect the quality of resultant Al-MCM-41 materials. The presence of aluminium in both as-synthesized and calcined material was confirmed by elemental analysis and  $^{27}\text{Al}$  NMR study, respectively, which exhibits most of the aluminium atoms were incorporated tetrahedrally in the MCM-41 structure.

**KEYWORDS:** *Mesoporous, MCM-41, Silica, Characterization*

### **INTRODUCTION:**

Mesoporous silica MCM-41 has attracted extensive interest because of their high surface areas, uniform pore channels, specific pore volume and good thermal stabilities.<sup>1</sup> However, the framework of pure MCM-41 is chemically inert this material prospect for limited applications such as adsorbents and catalysts supports. The isomorphous substitution of silica framework by heteroatom creates moderately acidic or basic sites make this materials can be used for various applications. For example,

aluminium substituted MCM-41 materials have already proven to be effective catalysts for cracking, hydrocracking, hydrogenation, isomerization and alkylation reactions.<sup>2</sup> However, achieving a well-organized mesoporous texture is generally more difficult with Al-MCM-41 than with pure silica MCM-41, due to the presence of another element in the synthesis.

Extensive efforts have been made to prepare Al-MCM-41 materials with higher amount of aluminium content. Up to now, many reports are available on hydrothermal synthesis of Al-MCM-41 materials with different Si/Al ratios and various aluminium sources.<sup>3</sup> A special care must to be taken when increase the too much aluminium content which lead to disrupt the framework and to the subsequent collapse of pores and channels. Kloetstra et al. found that the Al-MCM-41 samples prepared with Si/Al ratios below 10, most of the aluminum was part of a separate dense phase.<sup>3a</sup> Although huge reports are available on various ratios of silica to alumina, Schmidt et al reports the lowest ratio of the incorporation of aluminium into the framework had been limited to a Si/Al = 8.5.<sup>3b</sup> They also attempted to the synthesis of MCM-41 with Si/Al ratio of 4 using sodium silicate and sodium aluminate as sources of Si and Al, respectively.<sup>4</sup> Borade and Clearfield reported the synthesis of aluminium rich MCM-41 with Si/Al ratios as low as 2 by hydrothermal method. However, their resultant material shows fully amorphous.<sup>5</sup> The formation of Al-MCM-41 containing higher substitution levels of aluminium (Si/Al=1.5) was achieved at room temperature and minimum time of synthesis.<sup>6</sup> The attempt has been made to prepare Al-MCM-41 with Si/Al = 3 by modify the conventional synthesis procedure.<sup>7</sup> Recently Al-MCM-41 with Si/Al ratio of 5 was synthesized by *in-situ* method under hydrothermal condition using metakaolin aluminum sources.<sup>8</sup> But the above results yield poorly crystalline nature with lower surface area and pore volumes while increase the aluminium content. Although many reports are available on synthesis of Al-MCM-41 higher aluminium content, obtaining a good long-range order with high surface area is still a challenging objective.

The existing conventional hydrothermal procedure obviously lies within long and complicated processing strategies that usually takes about three to seven days as well as the careful control of the reaction temperature and pH,<sup>9,10</sup> which severely hampers its practical applications. For many catalytic applications, it is more desirable to have an economically feasible method to prepare Al-MCM-41 in a short synthesis time. To reduce the synthesis time for economical benefits, the use of ultrasonic irradiation is now a subject of growing interests on the preparation of mesostructured materials. Although ultrasound does not cause chemical reactions directly, it has acoustic cavitation effects, which creates high local temperature, pressure and cooling rates to give sonicated solutions unique properties. These effects may enhance the rates of chemical reactions. Surprisingly, only few reports are described on the ultrasonic synthesis of mesoporous silica materials. For example, Tang et al.<sup>11</sup> used this techniques for the preparation of pure mesoporous

silica MCM-41. Attempt has been made to prepare mesoporous silica that is analogous to MCM-41 by using ultrasonic irradiation.<sup>12</sup> However, longer sonication time was applied for the formation of gel and followed by aging its solution. We successfully synthesized the MCM-41 in very short time about five minutes by using ultrasonic irradiation.<sup>13</sup> Lee et al. reported the synthesis of SBA-15 and Ti-SBA-15 silicas with ultrasonic irradiation for 1 h, followed by gellation for 1-3 h.<sup>14</sup> Recently, our group achieved the synthesis of SBA-15 in short period time by temperature-assisted sonochemical method.<sup>15</sup> Ultrafast sonochemical synthesis of periodic mesoporous organosilicas (PMOs) with methane and ethane bridging groups using cationic and triblock copolymer Pluronic P123 as templates, respectively, were reported.<sup>16</sup> To best of our knowledge no reports are available short time synthesis of Al-MCM-41 by using sonication method. By considering the advantages associated with the sonochemical method, we report herein, a successful synthesis of highly ordered Al-MCM-41 under basic conditions via ultrasonic irradiation for only five minutes, which represents a significant time reduction in comparison to the conventional synthesis.

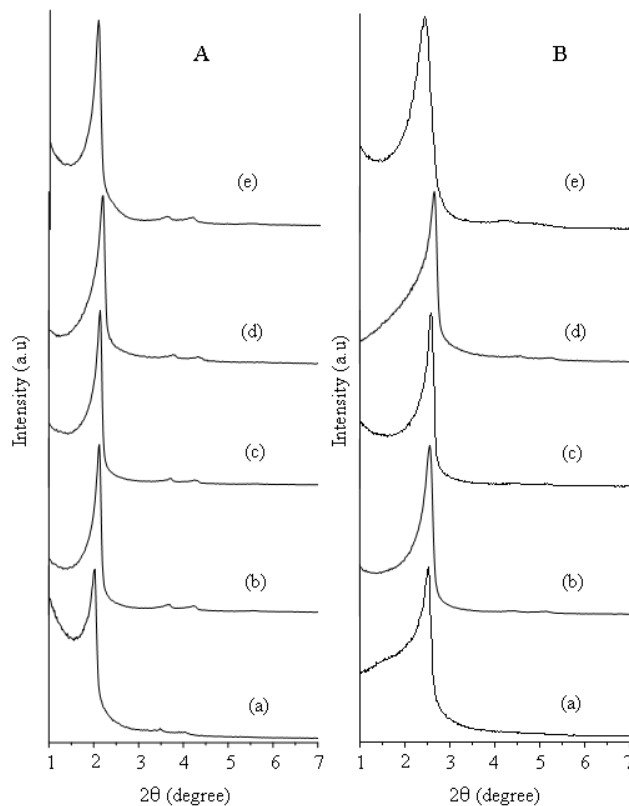
### **EXPERIMENTAL METHODS:**

The Al-MCM-41 samples were synthesized under basic conditions using cetailtrimethylammonium bromide (CTMABr) as the structure direct agent and tetraethylorthosilicate (TEOS) as a silicate source. In a typical synthesis, CTMABr was dissolved in a mixture of  $\text{NH}_4\text{OH}$  (35 wt.%) and water under sonication for 1 min. After a homogeneous solution was obtained, aluminum nitrate was added. After dissolution, TEOS was added dropwise to the above solution, which was then subjected to sonication using an ultrasonic generator, type D200H, with frequency of 43 kHz and power of 200 W for different time periods ranging from 5 to 30 mins. The molar composition of the reaction mixture was 1 TEOS: 2-10  $\text{Al NO}_3 \cdot 9\text{H}_2\text{O}$ : 0.125 CTMABr: 24  $\text{NH}_3$ : 612  $\text{H}_2\text{O}$ . The resultant precipitate were then filtered, washed with deionized water, and dried in oven at ambient temperature, and followed by calcinations in air at 550 °C for 6 h. The samples are denoted as Al-MCM-41-x, where x-represents the Si/Al ratios.

### **RESULTS AND DISCUSSIONS**

The elemental analysis results, determined by ICP-AES, are listed in Table 1. The actual Si/Al ratios of Al-MCM-41 were slightly higher than those in the initial synthesis mixture. Thus, most of the aluminium was, but not completely, incorporated into the MCM-41 silica framework. The structural quality of obtained Al-MCM-41 with higher amount of aluminium content was determined by XRD method. The X-ray diffraction patterns of both as-synthesized and calcined Al-MCM-41-x samples are depicted in Figure 1. All the samples exhibited four diffraction peaks, which can be indexed as (100), (110), (200), and (210) characteristic of the hexagonally ordered MCM-41 mesostructure.<sup>13</sup> It is

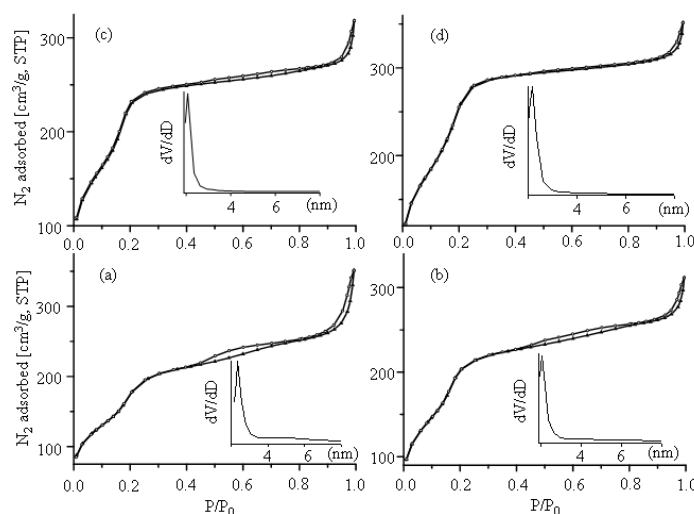
suggested that the long-range order structure was achieved and the regular mesoporous structure was retained after the introduction of aluminum. As seen in Figure 1, the intensity decreased with increase the aluminium content, indicating that the change of T-O-T bond angle due to aluminium incorporation into the silica framework structure results in distortion of long-range order of hexagonal mesostructure. However, the existing of all peaks are evident that the Al-MCM-41 can be prepared with extremely higher amount of aluminium ( $\text{Si}/\text{Al} = 2$ ) content using ultrafast irradiation, which does not collapse the mesostructure during sonication. As excess of aluminium leads to collapse the mesostructure, the conventional synthesis of Al-MCM-41 yields the disorder structure when the ratio of  $\text{Si}/\text{Al}$  below 5.<sup>6-8</sup> After calcinations, the peaks shifted to higher  $2\theta$  values due to pore size contraction. The XRD results reveals that the formation of highly ordered mesoporous silica that is analogous to hexagonal Al-MCM-41 can be achieved in as little time as 5 min under basic conditions with the aid of ultrasound irradiation, which helps to faster the condensation of silica.



**Figure 1.** XRD pattern of (A) As-synthesized and (B) calcined Al-MCM-41-x, where x = (a) 2, (b) 3, (c) 5, (d) 7 and (e) 10

**Figure 2** shows the nitrogen adsorption-desorption isotherms of Al-MCM-41-x and the corresponding structural properties are listed in Table 1. The isotherms of all Al-MCM-41 samples can be classified as type IV isotherms with well-expressed hysteresis loop, indicating that

the samples retain their hexagonal mesophases with narrow pore size distribution after template removal. The BET surface areas and pore volumes of Al-MCM-41 are in the range of 674-1080 m<sup>2</sup>/g and 0.48-0.62 cm<sup>3</sup>/g, respectively. The observed phenomena are significantly higher than those of the conventional Al-MCM-41. It was reported that the NH<sub>4</sub>OH-containing medium favors the formation of longer micelle.<sup>17</sup> This might be the reason for higher surface areas in the present Al-MCM-41 samples. As seen in Table 1, the specific surface area, pore diameter and pore volume decreases for the samples prepared with higher amount of aluminium content, suggesting that the increase of wall thickness and/or by forming more amount of dealumination from framework during calcination.<sup>18</sup> With increase the aluminium content the pronounced hysteresis appeared between P/P<sub>0</sub> 0.4 and 0.6 region associated with formation of secondary mesopores formed during calcination as the extra framework aluminium would have made a wall in the outer pores. All samples show sharp and narrow pore size distribution suggesting that the Al-MCM-41 samples prepared in the sonochemical method have well-uniformed mesoporous channels irrespective of the to aluminium content.

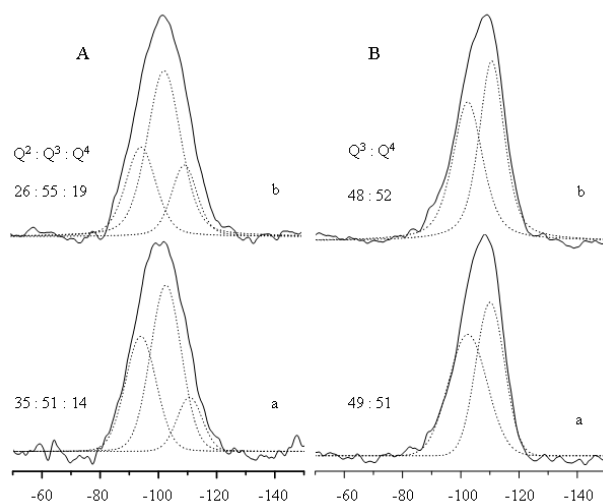


**Figure 2.** N<sub>2</sub>-adsorption-desorption isotherms of Al-MCM-41-x, where R= (a) 2, (b) 3, (c) 5 and (d) 7

**Table 1** Textural properties of Al-MCM-41-x where x represents Si/Al ratios.

Lattice parameters  $a_0$  were calculated based on the formula  $a_0=2d\sqrt{3}$ .  
<sup>b</sup>A<sub>BET</sub>: BET surface area. <sup>c</sup>V<sub>p</sub>: total pore volume

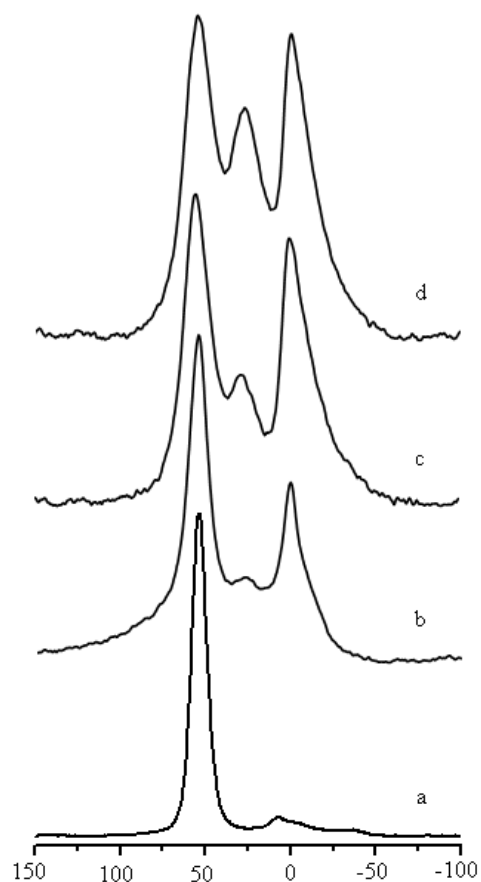
The cross-linking degree of the silica framework was investigated by <sup>29</sup>Si MAS NMR spectroscopy for the as-synthesized samples. Figure 3 displays the <sup>29</sup>Si MAS NMR spectra of Al-MCM-41-x exhibited only a broad unresolved signal that could be ascribed to the overlap of Si(OSi)<sub>2</sub>(OH)<sub>2</sub> (Q<sup>2</sup>) at -96 ppm, Si(OSi)<sub>3</sub>OH (Q<sup>3</sup>) at -101 ppm and Si(OSi)<sub>4</sub> (Q<sup>4</sup>) at -110 ppm, respectively. However, the predominant Q<sup>3</sup> species, instead of Q<sup>4</sup>, regardless of aluminium content indicating a rather incomplete condensation of silica in such a short synthesis time. But such short synthesis time does not seem to harm for structure formation, as confirmed by XRD and nitrogen adsorption-desorption measurements. Where as the Q<sup>4</sup> species is dominant after calcination and higher Q<sup>4</sup>/Q<sup>3</sup> ratio was observed than those of the as-synthesized samples, indicating that further condensation of the silica via the loss of water and more regular wall structure was built up during calcination.<sup>19</sup> The percentages of Q<sup>n</sup> species were calculated by deconvolution of the spectra.



**Figure 3.** <sup>29</sup>Si MAS NMR spectra of (A) as-synthesized and (B) Calcined Al-MCM-41-x, where R = (a) 2 and (b) 5.

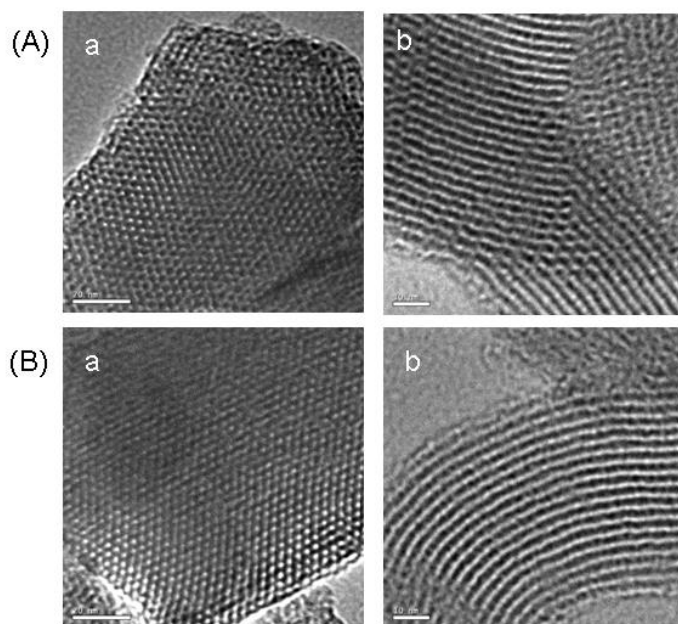
In order to study the local environment of aluminum species and to distinguish the aluminum coordination to establish the degree of aluminum substitution in the silica framework <sup>27</sup>Al MAS NMR was used and results are presented in Figure 4. The as-synthesized sample shows a strong and sharp signal at 53 ppm corresponding to tetrahedrally coordinated framework aluminium. Upon calcination, the additional weak signals were appeared at 0 ppm which is assigned to extra-framework aluminium formed by dealumination during calcination.<sup>20</sup>

The defective pentacoordinated peak was also observed at 27 ppm.<sup>21</sup> The intensities of these signals increased with increasing Al content in the initial gel. However, the intensity of peak at 53 ppm is much higher than the peak at 0 and 27 ppm, indicating that the aluminium is mainly incorporated in tetrahedral framework of Al-MCM-41 developed by this present ultrasonic method. This result suggests that the amount of Td-Al in the MCM-41 structure can be regulated by controlling the ratio of silica to alumina. Samoson et al observed the non-framework tetrahedral coordinated aluminium at 30–40 ppm as an Al residue in dealuminated zeolites.<sup>22</sup> was not observed in the present study. The TEM images (Figure 6) clearly show that Al-MCM-41 samples exhibited an ordered hexagonal mesostructure, which is consistent with the previous reports for MCM-41 synthesized under basic media.<sup>13,17</sup> This image indicates the possibility of aluminum incorporation while retaining the hexagonal pore structure of MCM-41



**Figure 4.** <sup>27</sup>Al MAS NMR spectra of (a) as-synthesized and (b-d) calcined Al-MCM-41-x, where x = (a) 10 (b) 10, (c) 5 and (d) 2.





**Figure 5.** TEM images of (A) Al-MCM-41-2 and (B) Al-MCM-41-5 in a direction of (a) parallel and (b) perpendicular to the pore axis.

The advantages associated in the present study are the Al-MCM-41 can be prepared in extremely short synthesis time about five minutes via ultrasonic irradiation. The present synthesis route effectively reduces the total synthesis time from days to few minutes. In the conventional method, the obtained Al-MCM-41 was reacted with aqueous ammonia solution at 80 °C for 6 h and deammoniated was done at 500 °C for 6 h to increase the acid sites of materials.<sup>23</sup> These multisteps are being avoided in this study as Al-MCM-41 prepared in the presence of NH<sub>4</sub>OH. Further, the protonated form of Al-MCM-41, which contains higher acid sites and can be used directly for catalytic reactions, is being prepared in this study in single step. In the conventional method, most of the Al-MCM-41 prepared in the presence of sodium ion either as sodium salt or NaOH medium, which is catalytically less active. The NH<sub>4</sub>OH medium used in this study favors for longer micelle, which yields the materials with higher surface area and longer cylindrical pores. In addition, extremely higher loadings of aluminium is possible in this study without disturb its original structure. It is of great interest to explore what would happen if the sample prepare without ultrasonic irradiation. Therefore, Al-MCM-41-10 prepared under same condition in the absence of ultrasonic irradiation. The resultant material shows the poor quality and disorder structure. However, it is speculated that long synthesis time might required to obtain a highly mesostructured Al-MCM-41 without ultrasonic irradiation

## CONCLUSIONS



In summary, we have successfully applied ultrasonic technique for the synthesis of mesoporous silica Al-MCM-41 with highly ordered hexagonal pore-arrangement within a much shorter hydrolysis–condensation period compared to the conventional technique. The developed materials possess the high surface area, large pore volume and pore diameter compared to conventional synthesis. It is demonstrated in this work that the sonochemical mediated synthesis of Al-MCM-41 is not only can reduce the synthesis time from days to a few hours, but also can provide well ordered materials with highly consolidated frameworks. Considering the simplicity of this study it is pointing out that the sonochemical technique can serve as a general method for the synthesis various type of mesoporous materials.

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