



Research Article

Comparison of Lewis Acidity between Al-MCM-41 Pure Chemicals and Al-MCM-41 Synthesized from Bentonite

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Abstract

This study focused on the Lewis acidity of Al-MCM-41 prepared from bentonite (Al-MCM-bentonite) as silica and aluminum source simultaneously. This acidity was compared with Al-MCM-41 synthesized from pure chemicals reagents (Al-MCM-standard). Structural analysis showed that the substitution of the silicon atom by the aluminum atom decreases the structural order of Al-MCM-standard, whereas Al-MCM-bentonite has a better structural organization. The Lewis acidity of the Al-MCM-bentonite was evaluated in allylation reaction of benzaldehyde with allyltrimethylsilane and pyridine adsorption experiments. The results showed that the difference in acidity between Al-MCM-standard and Al-MCM-bentonite is due to the amount of aluminum incorporated into the framework of our mesoporous materials. According to the EDX analysis, the incorporation of aluminum in Al-MCM-standard (Si/Al = 13.47) is more important than in Al-MCM-bentonite (Si/Al = 43.64). This explains the low acidity of Al-MCM-bentonite, and the moderate yields in the allylation reactions of benzaldehyde with allyltrimethylsilane. Copyright © 2019 BCREC Group. All rights reserved

Keywords: Mesoporous materials; Al-MCM-41; Algerian bentonite; Lewis acid; Allylation of benzaldehyde

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1. Introduction

Many organic syntheses require catalytic reactions involving homogeneous Lewis acid, such

as: BF₃ [1], Sc(OTf)₃ [2], InCl₃ [3], YbCl₃ [4], FeCl₃ [5], and TiCl₄ [6,7]. The challenge for this type of reaction is to replace these homogeneous acids by heterogeneous acids which are environmentally benign catalysts, such as: MCM-41 mesoporous materials, which is the best known member of the family of materials called M41S [8,9]. This material has a uniform pore size dis-

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tribution in the mesopore range tunable between 20 Å and 100 Å, a high specific surface area of up to 1500 m²/g, and a high porosity, which is of the order of (1.2 cm³/g).

The synthesis of MCM-41 requires very reactive starting reagents such as silicate sources and aluminum sources [10-14]. In recent years and for economical and environmental considerations, researchers have been studying the possibility of replacing these laboratory reagents with raw materials that are widely available and inexpensive. Therefore, studies have reported the synthesis of mesoporous materials from halloysite [15], diatomite [16], kaolin [17], bentonite [18,19], coal fly ash [20], bottom ash [21,22], iron-ore tailing [23], copper-ore tailing [24], photonic waste [25,26], resin ash [27], husk ash [28,29], sedge ash [30], miscanthus ash [31], and volclay [32].

The use of bentonite as a silica and aluminum source for the preparation of mesoporous materials is very rare in the literature, and has been studied [18,19]. In this work, we focus on the study of the Lewis acidity of Al-MCM-41 synthesized from bentonite (Al-MCM-bentonite). The Lewis acidity of aluminum-containing MCM-bentonite was evaluated using allylation reaction of aromatic aldehydes with allyltrimethylsilane and this acidity was compared with that of the material prepared by laboratory reagents (Al-MCM-standard). We studied a number of parameters, namely the effect of temperature and the effect of amount of the catalyst (*X* mol%).

2. Materials and Methods

2.1 Materials

The natural bentonite used in this study was obtained from Maghnia mine (Hammam Boughrara, 600 km west of the capital Algiers) and used as obtained. The other reactants applied were cetyltrimethylammonium bromide (C₁₉H₄₂NBr; CTAB, Merck, 99%), ammonium hydroxide (NH₃, Aldrich, 25%), acetic acid (min. 99.8%, Aldrich), sodium aluminate (54% Al₂O₃; 41% Na₂O; 5% H₂O, Aldrich), colloidal silica (ludox 40%, Prolabo), and tetramethylammonium hydroxide (TMAOH.5H₂O, 97%, Aldrich).

2.2 Synthesis of Al-MCM-bentonite

The synthesis of Al-MCM-bentonite material evaluated in this work was previously reported [19]. The preparation of Al-MCM-41 from Algerian bentonite requires the following steps; firstly the alkaline melting of the

bentonite, in this step the mixture of bentonite and sodium hydroxide was prepared (using a weight ratio bentonite/NaOH = 1/1.2), and then calcined at 550 °C in air for 1 hour. The obtained solid was cooled at room temperature and then milled. An amount of water was added to the resultant material such that the weight ratio bentonite/water was 1/4. The mixture was stirred for 24 h at room temperature and then the supernatant was recovered by centrifugation.

The second step requires the preparation of a solution containing 15 mL of distilled water, NH₄OH (0.75 g) and 0.867 g of CTABr which were mixed with 40 mL of supernatant (obtained in the first step). The pH of the mixture was adjusted with acetic acid (1 M) until pH = 9.5 followed by stirring for 1h at room temperature and then hydrothermally treated at 100 °C for 48 hours. The final product was filtered washed, dried for 24 hours at 100 °C and calcined at 550 °C for 12 hours. The resulting material was named Al-MCM-bentonite.

2.3 Synthesis of MCM-standard

The synthesis and characterization the Si- or Al-MCM-standard, were given elsewhere [7,33]. The molar chemical composition used was: SiO₂ : 0.25 CTAB : 0.2 TMAOH : 0.04 Al₂O₃ : 40 H₂O. The mesoporous material Al-MCM-41 was synthesized by hydrothermal route. Firstly, three solutions were prepared, the first solution containing distilled water, TMAOH and sodium aluminate. The second solution contains only distilled water and colloidal silica. Both solutions were added dropwisely into the third solution containing distilled water and CTABr, the reaction mixture was stirred vigorously for 1 hour at room temperature. The mixture was transferred to an autoclave and then hydrothermally treated at 100 °C for 48 hours. The product was filtered washed and dried for 48 hours at 100 °C and then calcined in air for 12 hours at 550 °C. The obtained material was named Al-MCM-standard.

The mesoporous silica Si-MCM-41 was obtained according to the following steps; firstly, the surfactant CTABr was mixed with a solution containing distilled water and TMAOH. After stirring for 30 min, ludox as silica source was added dropwisely and stirred for 2 hours at room temperature. This mixture was hydrothermally treated at 100 °C for 48 hours. Finally, the obtained product was washed dried at 100 °C for 24 hours and then calcined at 550 °C

during 12 hours. The final product was named Si-MCM-standard.

2.4 Samples Characterization

The mesoporous materials were characterized by powder X-ray Diffraction (XRD, Bruker D5005 diffractometer, Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$), scanning step 0.0358° between 1° and 10° (2θ)), N $_2$ gas sorption (Nova 1000e, the

measurements were performed at -196°C , the sample was degassed under vacuum at 200°C over 24 hours prior to adsorption, the specific surface area was determined by using the BET method [34] from data in a relative pressure range from 0.04 to 0.2). The local chemical composition of the mesoporous aluminosilicates was examined by analytical Transmission Electron Microscopy (TEM) combined with an Energy Dispersive X-ray spectroscopy (EDX), (Philips ESEM XL 30 FEG), and the acid properties of the solid were measured using Nicolet Avartar 360 with pyridine adsorption / desorption (FT-IR spectra were then recorded at different temperature: 50, 150, 250, and 350°C).

2.5 Catalytic Performance

The procedure experimental of allylation of benzaldehyde with allyltrimethylsilane has been described in detail in our previous work [7]. The catalysts (Al-MCM-bentonite or Al-MCM-standard) were dried under vacuum at

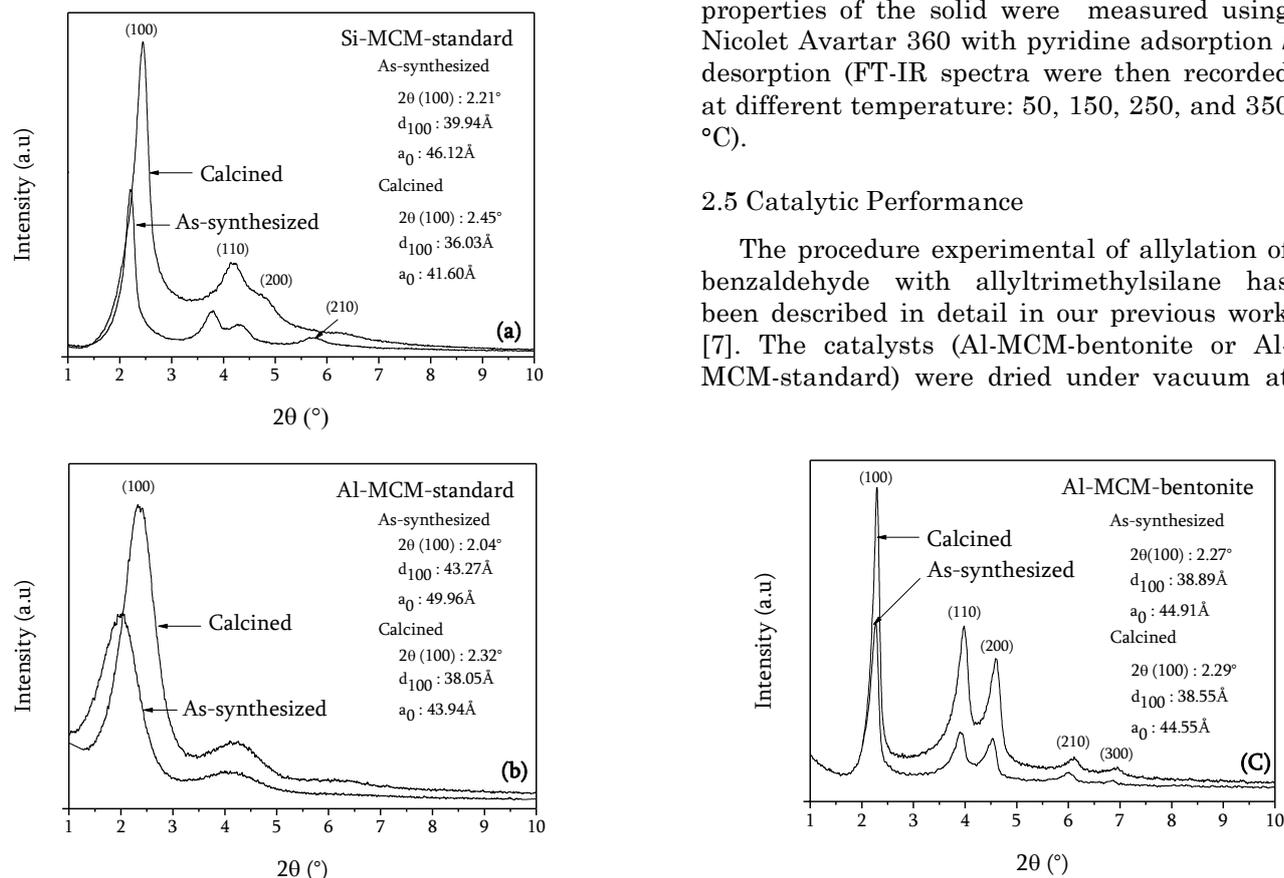


Figure 1. XRD patterns of Si-MCM-standard (a), Al-MCM-standard (b) and Al-MCM-bentonite (c)

Table 1. XRD diffraction results

Sample	As-synthesized				Calcined				Δa_0^d (%)
	I_{100}^a (a.u.)	2θ (100)	d_{100}^b (\AA)	a_0^c (\AA)	I_{100} (a.u.)	2θ (100)	d_{100} (\AA)	a_0 (\AA)	
Al-MCM-41 from bentonite	5369	2.27	38.89	44.91	9359	2.29	38.55	44.51	0.9
Al-MCM-41 standard	5994	2.04	43.27	49.96	9276	2.32	38.05	43.94	12.0
Si-MCM-41 standard	13645	2.21	39.94	46.12	25718	2.45	36.03	41.60	9.8

^a Intensity of the reflection peak (100).

^b XRD (100) interplanar spacing, $n\lambda = 2d_{100} \sin \theta$.

^c Unit cell determined for a hexagonal symmetry, $a_0 = 2d_{100} / \sqrt{3}$.

^d Δa_0 (%) = $(a_0(\text{as-synthesized}) - a_0(\text{calcined})) / a_0(\text{as-synthesized}) \times 100$.

300 °C for 1 hour prior to the catalytic test. Approximately, 0.106 g (1 mmol) of benzaldehyde, 2 mL of dichloromethane and 25 mol% of catalyst was added in a two-necked flask under an argon atmosphere. After 5 min of stirring at 35 °C, the solution containing allyltrimethylsilane (0.228 g, 2 mmol, 2 equiv) and CH₂Cl₂ (0.5 mL) was slowly added under constant temperature (35 °C) and the reaction product was followed by TLC. At the end of the reaction the catalyst was separated by a simple filtration. The filtrate was purified by silica-gel column chromatography using petroleum ether:ether of 28:1. The obtained product was characterized by ¹HNMR and ¹³CNMR.

3. Results and Discussion

3.1. Structural Discussion of Catalyst

The isomorphic substitution of the silicon atom by the aluminum atom (Si/Al = 12.5) (Figure 1b and Table 1) decreases the structural order of Al-MCM-standard, compared with Si-MCM-standard. In the Al-MCM-standard, the reflection peaks (110) and (200) observed in Si-MCM-41 were not well developed, indicating more disordered arrangement of channels for the Al-MCM-standard, however an hexagonal

structure with good regularity was kept. It has already been proved that the introduction of an heteroatom affect the structural order of mesoporous solids and more the aluminium content is high more the structural effect is high [35]. In contrast, the synthesis of Al-MCM-bentonite from the dissolution of the silicon and aluminum species that exist in bentonite using the fusion method provides a well-ordered mesoporous material with hexagonal regularity characterized by better resolved of the peaks (110), (200), (210), and (300).

Table 1 shows that the contraction of the unit cell ($\Delta a_0 = 0.9\%$) and the enlargement of the peak (100) of Al-MCM-bentonite are negligible after calcination at 550 °C for six hours. The presence of the diffraction peak (300) indicates that the high hexagonal uniformity is maintained after calcinations (Figure 1c).

Figure 2 shows the N₂ adsorption-desorption isotherms of the calcined Si-, Al-MCM-standard, and Al-MCM-bentonite, and Table 2 summarizes the textural proprieties of these samples. The obtained isotherms are typical for MCM-41 phase. The corresponding isotherm is of type IV, characteristic of the mesoporous solids according to the IUPAC nomenclature. The Table 2 clearly illustrates that

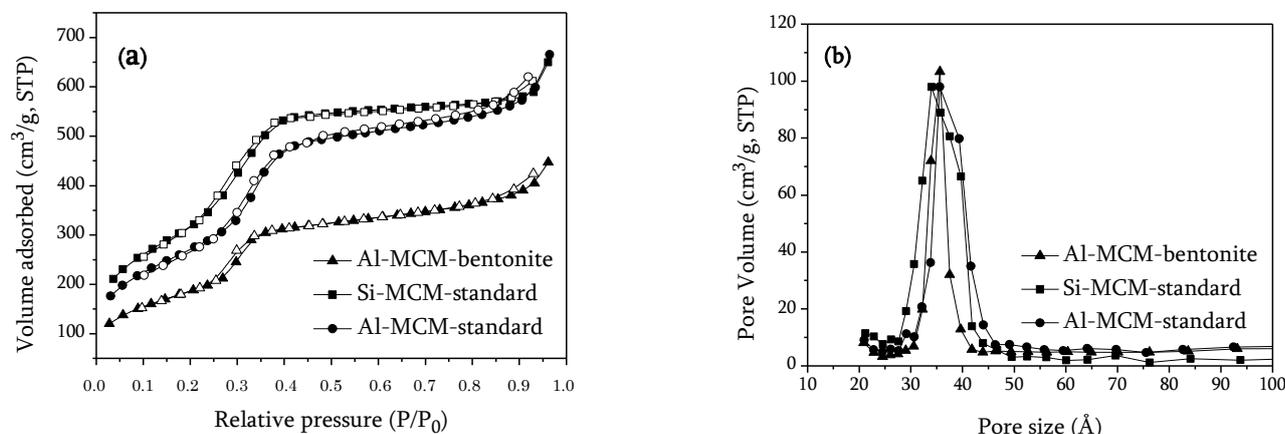


Figure 2. (a) Nitrogen adsorption-desorption isotherms of calcined samples and (b) BJH pore size distribution

Table 2. Textural properties of the samples

Sample	a_0 (Å)	Δa_0 (%)	S_{BET}^a (m ² /g)	V_{meso}^b (cm ³ /g)	D_p^c (Å)	W_t^d (Å)
Al-MCM-bentonite	44.51	0.9	674	0.42	35.6	8.9
Al-MCM-standard	43.94	12.0	983	0.76	35.6	8.4
Si-MCM-standard	41.60	9.8	1154	0.84	34.0	7.6

^a Specific surface area.; ^b Mesoporous volume.; ^c Pore diameter determined by BJH.; ^d Wall thickness, $a_0 - D_p$.

the incorporation of aluminum species in the mesoporous framework affects the structure and the texture of these materials. The pore diameter and the wall thickness of Al-MCM-standard and Al-MCM-bentonite are higher than Si-MCM-standard. This can be explained by the incorporation of aluminum species [36]. On the other hand, the pore volume together with the BET surface area decreased for Al-MCM-standard and Al-MCM-bentonite, which suggested generally that heteroatoms incorporation would result in a shift to higher pore size and decrease in specific surface areas [37].

The structural and textural comparison of Al-MCM-standard and bentonite derived Al-MCM-41 compared to pure silica MCM-41 showed that the incorporation of aluminum species decreases the structural order of Al-MCM-standard, whereas Al-MCM-bentonite has better structural organization. However, this interesting structural order of Al-MCM-bentonite does not reflect its textural properties: S_{BET} of 674 m²/g and mesoporous volume of 0.42 cm³/g, compared to those of Al-MCM-standard (S_{BET} of 983 m²/g and mesoporous volume of 0.76 cm³/g). This confirms the utility of the characterizing of X-ray diffraction and nitrogen adsorption at 77 K jointly.

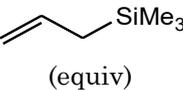
3.2. Allylation of Aromatic Aldehydes with Allyltrimethylsilane in the Presence of Al-MCM-bentonite or Al-MCM-standard

In our previous work [7], the catalytic performance of Al-MCM-41 prepared from pure chemicals was tested as a Lewis acid in the allylation of aromatic aldehydes with allyltrimethylsilane. The results showed that homoallyl silyl ether is obtained at a temperature of 35 °C. In this work, the Lewis acidity of the Al-MCM-41 prepared from bentonite was further evaluated using allylation of aromatic aldehydes with allyltrimethylsilane reaction and compared with Al-MCM-41 pure chemicals. We have studied a number of parameters, namely the effect of temperature and the effect of amount of the catalyst (X mol %).

3.2.1 Effect of reaction temperature

In order to study the effect of reaction temperature, we have used the same conditions of previous work [7]. Table 3 depicts the results using MCM-bentonite or Al-MCM-standard as catalysts Lewis acid. By reaction of benzaldehyde (1 equiv) with allyltrimethylsilane (3 equiv), using a catalytic amount (25 mol%) of MCM-bentonite or Al-MCM-standard, and at low temperature (-85 °C to 10 °C), the condensation reaction does not give any product

Table 3. Allylation of aromatic aldehydes with allyltrimethylsilane: effect of reaction temperature in the presence of Al-MCM-bentonite or Al-MCM-standard as a catalyst^a

Entry	R, R'	Temperature (°C)	 (equiv)	Al-MCM-standard		Al-MCM-bentonite	
				Time (h)	Yield ^b (%)	Time (h)	Yield ^b (%)
1	H, H	-85 to -10	3	-	n.r.	-	n.r.
2	H, H	0 à 24	3	24	traces	24	traces
3	H, H	35	3	4	99	24	20
4	H, H	35	1.5	4	99	20	20
5	Cl, Cl	-85 to -10	3	-	n.r.	-	n.r.
6	Cl, Cl	35	3	45min	100	20	36
7	Cl, Cl	35	1.5	45min	100	20	36
8	H, NO ₂	35	1.5	30 min	99	20	17

^a Reaction conditions: aldehyde (1 mmol), catalyst (25 mol%), CH₂Cl₂ (2 mL).

^b Isolated yield after column chromatography.

(entries 1 and 5). We have carried out several tests by increasing the reaction temperature to 35 °C. If the reaction temperature was raised from 0 to 24 °C, the catalytic activity of our materials was very low and only traces of the product were obtained (entry 2), whereas at a higher temperature (35 °C), the best yields were obtained in the presence of Al-MCM-standard (entry 3: 99% yield, 4 h reaction time and entry 6: 100% yield, 45 min reaction time). In the presence of Al-MCM-bentonite, moderate yields were noted (entry 3: 20% yield, 24 h reaction time and entry 6: 36% yield, 20 h reaction time). The reduction of the quantity of allyltrimethylsilane to 1.5, has not an impact on the reaction yield (entries 4, 7, and 8).

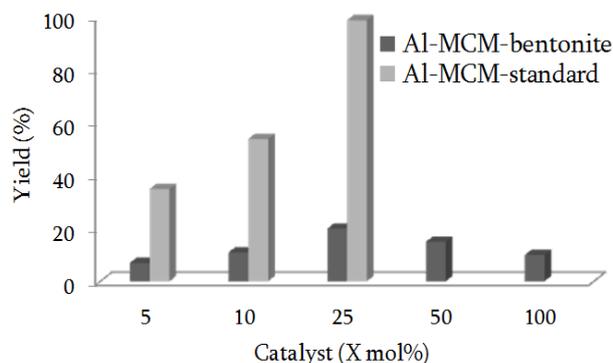


Figure 3. Effect of the amount of Al-MCM-bentonite or Al-MCM-standard on the yield of the allylation reaction of benzaldehyde with allyltrimethylsilane

3.2.2. Effect of the amount of catalyst

In the order to understand the influence of the heterogeneous catalyst and the improvement of the yield in the presence of Al-MCM-bentonite on the allylation of aromatic aldehydes with allyltrimethylsilane reaction, reactions between benzaldehyde (1 equiv) with allyltrimethylsilane (1.5 equiv) were performed using different amounts of catalyst (Table 4, Figure 3).

Using 5 mol% (entry 1, Table 4), the Al-MCM-bentonite led to a very low yield of 7% for 24 h reaction time, when Al-MCM-standard is used the yield is 35% for 4 h reaction time. We notice in Table 4 and Figure 3 that increasing the amount of catalyst has an impact on the reaction yield for Al-MCM-standard, which was not the case for Al-MCM-bentonite. Indeed, a 4 h reaction time led to a 54% yield using 10 mol% (entry 2, Table 5) and 99% yield using 25 mol% of Al-MCM-standard (entry 3, Table 5). However, in the presence of Al-MCM-bentonite the yield does not exceed 20% even after 20 h reaction time. This is confirmed by entries 4 and 5 in the Table 4. To explain this difference in yield using these mesoporous materials Al-MCM-standard or Al-MCM-bentonite as heterogeneous catalysts, it was necessary to study the acidity of these solids.

3.3 Evaluation of the Surface Acidity

The Lewis acidity of the Al-MCM-standard and Al-MCM-bentonite was also evaluated by measuring the IR spectra of pyridine adsorbed on the samples, for detecting the presence and the nature of acid sites. Figure 4A and 4B

Table 4. Allylation of benzaldehyde with allyltrimethylsilane: effect of the amount of catalysts^a

Entry	Catalyst (X mol%)	Al-MCM-standard		Al-MCM-bentonite	
		Time (h)	Yield ^b (%)	Time (h)	Yield ^b (%)
1	5	4	35	24	7
2	10	4	54	24	11
3	25	4	99	20	20
4	50	-	-	-	15
5	100	-	-	24	10

^a Reaction conditions: aldehyde (1 mmol), allyltrimethylsilane (1.5 mmol), CH₂Cl₂ (2 mL), 35°C.

^b Isolated yield after column chromatography.

shows the FT-IR spectra of the calcined Al-MCM-bentonite and Al-MCM-standard, respectively, recorded after subsequent evacuation at 50, 150, 250, and 350 °C. The samples exhibit expected bands around 1450-1650 cm^{-1} due to the adsorbed pyridine on both Lewis and Brönsted acid sites. For Al-MCM-standard, the peaks at 1545 cm^{-1} and 1636 cm^{-1} indicate the adsorption of pyridine on Brönsted acid sites, while those at 1456 cm^{-1} and 1622 cm^{-1} attribute the adsorption of pyridine on Lewis acid sites. The peak at 1490 cm^{-1} can be assigned to pyridine associated with Brönsted and Lewis acid sites [38]. However, these peaks are intense and clearly distinguished, their intensity

persists as the evacuation temperature is increased. This shows that Al-MCM-standard has a stable acidity even upon evacuation at 350 °C. On the other hand, in the Al-MCM-bentonite spectra we find the bands that characterize the presence of the acid sites, these bands have a very low intensity and it is difficult to distinguish them.

It is known that pyridine can form hydrogen bonds with the silanol groups present in the structure. Thus, for Al-MCM-bentonite, we note the appearance of new bands which correspond to silanol bonded pyridine (Py-H) at 1445 cm^{-1} and 1596 cm^{-1} [39-41]. These bands completely vanish after evacuation at 250 °C.

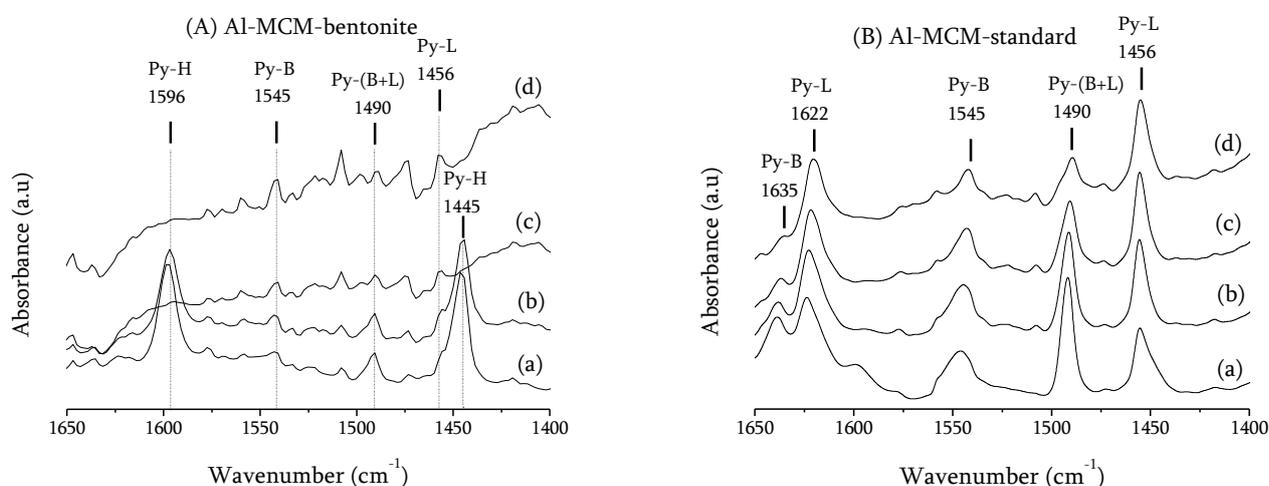


Figure 4. FTIR spectra of pyridine desorbed on calcined (A) Al-MCM-bentonite and (B) Al-MCM-standard under vacuum 3 Torr pressure at (a) 50 °C, (b) 150 °C, (c) 250 °C, (d) 350 °C

Table 5. Lewis (C_L) and Brönsted (C_B) acidity of the Al-MCM-bentonite and Al-MCM-standard samples measured by FTIR spectroscopy combined with pyridine adsorption and desorption at different temperatures

Acid proprieties (mmol.g ⁻¹)	Catalysts	50 °C	150 °C	250 °C	350 °C	Total acidity (2) ^b
Total acidity (1) ^a	Al-MCM-standard	295.62	372.21	402.52	344.42	1414.77
	Al-MCM-bentonite	31.13	42.17	47.37	52.1	172.77
Brönsted acidity (C_B) ^c	Al-MCM-standard	92.13	124.79	142.78	85.89	445.59
	Al-MCM-bentonite	26.79	30.10	31.20	33.03	121.12
Lewis acidity (C_L) ^c	Al-MCM-standard	203.49	247.42	259.74	258.53	969.18
	Al-MCM-bentonite	4.34	12.07	16.17	19.07	51.65
C_L/C_B	Al-MCM-standard	2.21	1.98	1.82	3.01	2.17
	Al-MCM-bentonite	0.16	0.40	0.51	0.57	0.42

^a Total acidity (1): the sum of the concentrations ($C_L + C_B$) at a fixed evacuation temperature.

^b Total acidity (2): the sum of the total acidity (1) for different evacuation temperatures.

^c To determine the concentration of both types of acid sites, the extinction coefficients [46] used were $e_B = 0.73 \text{ cm} \cdot \mu\text{mol}^{-1}$ and $e_L = 1.11 \text{ cm} \cdot \mu\text{mol}^{-1}$, for Brönsted and Lewis acid sites, respectively.

Lewis (Py-L) and Brönsted (Py-B) acid site concentrations were calculated by the integration of the IR bands at 1456 cm^{-1} and at 1545 cm^{-1} , respectively. These concentrations were determined after evacuation of our mesoporous materials at different temperatures (Table 5).

The C_L/C_B ratios show that Al-MCM-standard presents mainly Lewis acid sites. However, for Al-MCM-bentonite this ratio gives priority to Brönsted acid sites. By increasing the outgassing temperature of Al-MCM-standard to $350\text{ }^\circ\text{C}$, we note that the concentration of the Lewis acid sites remains almost stable, while that of Brönsted has decreased significantly. This confirms that Al-MCM-41 pure chemicals present stronger acid sites mainly of Lewis nature. In general, the Lewis and Brönsted acid sites are attributed to tetrahedrally coordination Al ions into the aluminosilicate framework and their concentrations increase with the amount of aluminum incorporated [38,42-45]. The difference in acidity between Al-MCM-standard and Al-MCM-bentonite is due to the amount of aluminum incorporated into the framework of our mesoporous materials. Effectively, according to the EDX analysis, the incorporation of aluminum in Al-MCM-standard ($\text{Si}/\text{Al} = 13.47$) is more important than in Al-MCM-bentonite ($\text{Si}/\text{Al} = 43.64$). Kumar *et al.* [46] studied and compared the acidity properties of the Al-MCM-41 prepared from coal fly ash and pure chemicals us-

ing the cumene cracking reaction, they found that all the aluminum present in the Al-MCM-41 prepared from fly ash is not catalytically active. This is due to the partial inaccessibility of the aluminum due to its incorporation in a separate aluminum phase.

To better estimate the rate of aluminum incorporated in Al-MCM-41 prepared from bentonite, it was necessary to make a difference between the Si/Al in the amorphous part and the hexagonal part. The analysis XRD of Al-MCM-bentonite in the 2θ range scanned ($2\theta = 1-40^\circ$) shows that existence of amorphous phase is less important than the hexagonal phase as illustrated in Figure 5. Thus, the evaluation of the acidity of the amorphous phase could be negligible compared to the acidity of the hexagonal phase. As shown in Table 6, the Si/Al ratio of mesoporous material prepared from the bentonite is 13.0 for the amorphous part. This ratio is higher than the Si/Al of natural bentonite (4.7) and close to fused bentonite (8.07). From that we can say that, the synthesis conditions and the aluminosilicate source (supernatant solution due to alkaline fusion) of the bentonite used to obtain Al-MCM-bentonite does not allow to control and to incorporate of aluminum in sufficient quantity in this material, which is characterized by $\text{Si}/\text{Al} = 44$ in the hexagonal part. This is the cause of the low acidity of Al-MCM-bentonite, which gave moderate yields using it as Lewis acid in the allylation reactions of aromatic aldehydes with allyltrimethylsilane.

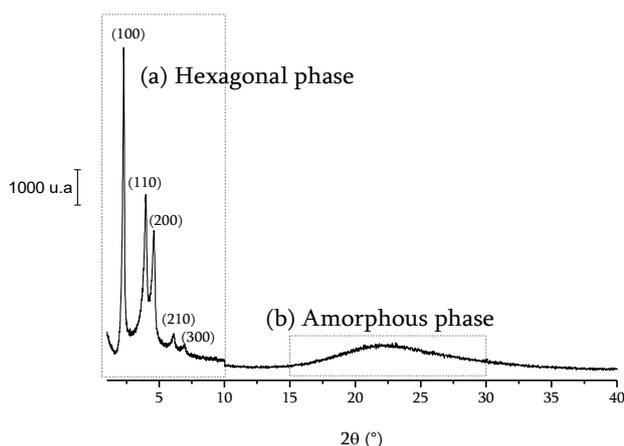


Figure 5. XRD pattern of calcined Al-MCM-bentonite: (a) low angle and (b) high angle

4. Conclusions

In summary, aluminum modified mesoporous molecular sieve with MCM-41 structure was synthesized from the bentonite low-cost mass material as Si and Al source. Its Lewis acidity is compared with that of Al-MCM-41 prepared from pure chemicals reagents. The isomorphic substitution of the silicon atom by the aluminum atom decreases the structural order of Al-MCM-standard, whereas Al-MCM-bentonite has better structural organization. However, this interesting structural order of Al-MCM-bentonite does not reflect its textural properties (S_{BET} of $674\text{ m}^2/\text{g}$ and mesoporous volume of $0.42\text{ cm}^3/\text{g}$), compared to those of Al-

Table 6. EDAX results

Sample	Natural bentonite	Fused bentonite	Al-MCM-bentonite	
			Hexagonal phase	Amorphous phase
Si/Al	4.76	8.07	43.64	12.43

MCM-standard (S_{BET} of 983 m²/g and mesoporous volume of 0.76 cm³/g).

The evaluation of Lewis acidity by the catalytic reaction of allylation of aromatic aldehydes by allylsilane showed that Al-MCM-standard gives a the best yield (99%) after four hours reaction time, while the yield does not exceed 20% even after a reaction time of 20 h for Al-MCM-bentonite. The increase in the amount of the Al-MCM-bentonite catalyst to 100 mol%, has not improved the reaction yield. The Lewis acidity of the Al-MCM-standard and Al-MCM-bentonite was also evaluated by measuring the IR spectra of pyridine adsorbed on the samples. This analysis of these materials revealed a very low Lewis acidity on Al-MCM-bentonite, whereas on Al-MCM-standard confirmed the existence of the Brönsted and Lewis acid sites. Concentrations of these sites have given priority to Lewis acid sites. The difference in acidity between Al-MCM-41 standard and MCM-bentonite is due to the amount of aluminum incorporated into the framework of our mesoporous materials. Effectively, according to the EDX analysis, the incorporation of aluminum in Al-MCM-41 standard (Si/Al = 13.47) is more important than in Al-MCM-bentonite (Si/Al = 43.64).

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