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Catalytic Performance of Al-MCM-41 Catalyst for the Allylation of Aromatic Aldehydes with Allyltrimethylsilane: Comparison with TiCl₄ as Lewis acid

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Graphical Abstract



Highlights

- Mesoporous Al-MCM-41 molecular sieve with Si/Al ratio equal to 12.5 was synthesized under hydrothermal condition.
- Pyridine coupled FT-IR spectroscopy analysis showed the existence of a high concentration of Lewis acid sites in Al-MCM-41.
- In presence of Al-MCM-41 using mild conditions, homoallyl silyl ether is obtained.
 With TiCl₄, the reactions require temperature of -85 °C and the products obtained are the diallylation.
- To explain this different allylation in the presence of the Al-MCM-41 or TiCl₄, two plausible reaction mechanisms are proposed.

Abstract

Mesoporous Al-MCM-41 molecular sieve with Si/Al ratio equal to 12.5 was synthesized under hydrothermal condition using cetyltrimithylammonium bromide (CTAB) as surfactant. This solid was characterized using several techniques e.g. powder X-ray diffraction (XRD), N₂ adsorption-desorption, FT-IR, TG/DTG and pyridine adsorption-desorption followed by IR spectroscopy. The catalytic performance of Al-MCM-41 catalyst as Lewis acid was used without treatment and was compared with TiCl4 in the allylation of aromatic aldehydes with allyltrimethylsilane. The results showed that in presence of Al-MCM-41, homoallyl silyl ether is obtained regardless of the nature of aromatic aldehydes at a temperature of 35 °C. When TiCl4 was used, the reactions require temperature of -85 °C and all the products obtained were due to the diallylation. To explain this different allylation in the presence of the Al-MCM-41 or TiCl4, two plausible reaction mechanisms are proposed. The Al-MCM-41 was used in four consecutive experiments without important loss of activity, confirming it stability. Finally, a new method for preparing single allylation in the short timeframe and mild conditions is presented.

Keyword:

Al-MCM-41, TiCl₄, aromatic aldehydes, allyltrimethylsilane, Lewis acid.

1. Introduction

Allylation of aromatic aldehydes with allylmethylsilane reactions is an important tool for the formation of different carbon-carbon bond, using homogeneous Lewis acids such as BF₃ [1], Sc(OTf₃) [2], InCl₃ [3], YbCl₃ [4], FeCl₃ [5] and TiCl₄ [6-9] as catalysts, which and is commonly practiced in organic synthesis.

However, the commonly used homogeneous Lewis acids pose several problems, such as difficulty in separation and recovery, disposal of spent catalyst, corrosion, high toxicity and they are not reused for catalytic runs. For these reasons, more recyclable or environmentally benign catalysts have been developed. The replacement of homogeneous acids by easily separable heterogeneous solids in the allylation of aromatic aldehydes reactions is, therefore, of great practical importance for the production of industrially important chemicals [10-12], from the standpoint of so-called "green chemistry".

Although zeolitic materials have important catalytic properties for use in different reactions [13], they are not used when the size of the reactants is greater than pore size. For this reason, in the past, efforts were directed towards the synthesis of similar structures which led to the discovery of a novel family of materials called M41S [14,15]. Thus the discovery of mesoporous materials MCM-41 belonging to the M41S family of catalysts opens new possibilities for using uniform mesopores, whose access is possible for large molecules such as those commonly used in the production of fine chemicals and petroleum chemistry. The obvious advantage of these materials compared to zeolites is in the size of their pores which can be adjusted from 20 to 100 Å in diameter, a surface area that can reach 1500 m²/g and a pore volume which is of the order of $1.2 \text{ cm}^3/\text{ g}$.

MCM-41 pure silica possesses a neutral framework, which limits its application as a catalyst. However, the isomorphous substitution of silicon by a variety of metals such as Al, Ga or Fe [16,17] gives rise to acidic properties. The catalytic activity of Al-MCM-41 is attributed to the presence of the acid sites resulting AlO₄ tetrahedral units in the structure. These acid sites are Brönsted or Lewis according to the nature of the treatment. The acid sites of these solids were used in several applications as acetalization [18,19], alkylation [20-22], esterification [23], Mukaiyama aldol reactions [24], Strecker-type synthesis [25] and Beckmann rearrangement [26]. The Lewis acid sites of Al-MCM-41 were tested in different reactions, such as in the synthesis of diphenylmethane [27], Michael addition of indole to α , β -unsaturated ketones [28], gas phase m-cresol alkylation with methanol [29], production of 5-hydroxymethylfurfural from glucose [30], etc.

In our preliminary communication [7], the TiCl₄ was used as Lewis acid in the reaction of the allylation of aromatic aldehyde using allyltrimethylsilane to afford the corresponding diallylation. In this work the efficiency of the Al-MCM-41 as catalyst Lewis acid in the allylation of aldehyde aromatic by allyltrimethylsilane is explored and a comparison with TiCl₄ is discussed.

2. Experimental

2.1. Catalyst preparation

2.1.1. Starting materials

Sodium aluminate (54%Al₂O₃; 41%Na₂O; 5%H₂O; Aldrich) was used as the aluminium source, colloidal silica (ludox 40%, Prolabo) served as a silicon source, cetyltrimethylammonium bromide (C₁₉H₄₂NBr; CTAB, Merck; 99%) as a surfactant, tetramethylammonium hydroxide (TMAOH.5H₂O, 97%, Aldrich) was utilized as a base and the demineralized water as a solvent.

2.1.2. Synthesis of Si-MCM-41

Sample of Si-MCM-41 was prepared by using the direct synthesis method hydrothermal [31]. The molar chemical composition was: 1SiO₂:0.25CTABr:0.2TMAOH:40H₂O. The mixtures were prepared by adding an amount of the surfactant (CTAB) under continuous stirring to a basic solution tetramethylammonium hydroxide. 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 100 °C. Thereafter, the product was washed several times with demineralized water, filtered and dried at 100 °C overnight, afterwards calcined under air at 550 °C for 12 h.

2.1.3. Synthesis of Al-MCM-41

The Al-MCM-41 was synthesized according to the procedure described in a previous paper [32]. For this method three solutions were prepared, the first one contains a source of aluminum mixed with an organic hydroxide of quaternary ammonium type (S1), the second one a source of silica (S2) and a surfactant agent for the last one (S3). The solvent used in the solutions demineralized three is water. The molar composition was 1SiO2:0.25CTAB:0.2TMAOH: 0.04Al2O3:40H2O. The obtained gel was kept in a Teflonlined stainless steel autoclave and heated at 100 °C for two days for crystallization. The solid product obtained was washed, filtered and dried overnight at 100 °C. The as-synthesized samples were calcined at 550 °C in air for 12 h.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were carried out using a Bruker D5005 diffractometer using Cu Karadiation (wavelength =1.15406 Å), with scanning step 0.0358 2theta between 1° and 10° 2theta. N₂ gas sorption measurements were performed at -196 °C with a Nova 1000e. For the N₂ adsorption–desorption, the sample was degassed under vacuum at 200 °C over 24 hours prior to adsorption. The specific surface area was determined by the BET formula [33] from data in the relative pressure range from 0.04 to 0.2. The transmission infrared spectra was recorded on a Nicolet Avartar 360 spectrometer, and the sample content in KBr wafers was 1%. The thermogravimetric analysis of the as-synthesized Si-MCM-41 and Al-MCM-41 were obtained in the air from 20 °C to 800 °C at the heating rate of 10 °C/min in SDT Q600 Instruments apparatus. The energy dispersion X-ray analysis (EDX) jointed to Philips ESEM XL 30 FEG scanning electron microscope was used to calculate the Si/Al ratio of the aluminum containing MCM-41. The surface acidity of the Al-MCM-41 was characterized by in situ pyridine adsorption FT-IR spectroscopy. A self-supporting wafer with 20 mg catalyst was put into the in situ cell and was activated at 200 °C for 4 hours under 0.267 Pa. The sample was cooled to room temperature, and pyridine adsorption was performed in excess pure pyridine for 15 min followed by evacuation. FT-IR spectra were then recorded at room temperature of 50, 150, 250 and 350 °C respectively. To determine the concentration of both types of acid sites, the extinction coefficients [34] used were $\varepsilon_{\rm B} = 0.73$ cm μ mol⁻¹ and $\epsilon_L = 1.11$ cm μ mol⁻¹, for Brönsted and Lewis acid sites, respectively.

2.3. General procedure for the allylation of aromatic aldehydes with allyltrimethylsilane2.3.1. In the presence of TiCl4

A flame-dried, three-necked, round-bottomed flask equipped with a magnetic stirring bar, a thermometer and an argon outlet were charged with anhydrous CH₂Cl₂ (20 mL) and MeNO₂ (1.2 mL, 20 mmol). The solution was cooled at-60 °C, TiCl₄ (1 mL, 8.1 mmol) and aldehyde (5.0 mmol) in CH₂Cl₂ (2 mL) was then added. After 15 min of stirring, the mixture was cooled at -90 °C and allyltrimethylsilane (2.4 mL, 15 mmol, 3 equiv.) in CH₂Cl₂ (2 mL) was slowly added. The mixture was stirred at -85°C for 3 h and then warmed to -60 °C. After completion of the reaction (TLC; 5–15 h), the mixture was poured into a saturated solution of NH₄Cl. After the usual workup, the crude product was purified by flash chromatography on silica-gel (petroleum ether then petroleum ether–ether 25:1). The product gave a satisfactory ¹H NMR and ¹³C NMR spectra.

2.3.2. In the presence of Al-MCM-41

In a two-necked, round-bottomed flask equipped with a magnetic stirring bar, under an atmosphere of argon was charged with aldehyde (0.106 g, 1.0 mmol, 1 equiv.) and Al-MCM-41 (25 mol%, dried prior to use at 300 °C for 1h under vacuum) in dichloromethane (2 mL),the mixture was stirred at 35 °C. After 5 min of stirring, the allyltrimethylsilane (0.228 g, 2 mmol, 2 equiv.) in CH₂Cl₂ (0.5 mL) was slowly added, the reaction mixture was stirred at 35°C. Upon completion of the reaction (TLC; 25min-24 h), the catalyst was removed by filtration. After the filtrate was concentrated under reduced pressure, only pure homoallyl silyl ether was obtained, thus further purification by silica-gel column chromatography (petroleum ether then petroleum ether-ether 28:1) was necessary. The product gave a satisfactory ¹H NMR and ¹³C NMR spectra.

2.3.3. Analytical data for compounds 3a, 3c, 3e, 3l

Proton nuclear magnetic resonance (¹H) spectra and carbon-13 (¹³C) spectra were recorded at 400 and 100 MHz, respectively. The proton signal of residual, non-deuterated solvent (δ 7.26 ppm for CHCl₃) was used as an internal reference for ¹H spectra. For ¹³C spectra, chemical shifts are reported relative to the δ 77.23 ppm resonance of CDCl₃. Coupling constants are reported in Hz. Trimethyl(1-phenylbut-3-enyloxy)silane (**3a**): colorless oil; ¹H NMR (300 MHz, CDCl₃) δ 7.39–7.28 (m, 5H), 5.84 (m, 1H), 5.11 (t, *J* = 9 Hz, 2H), 4.75 (dd, *J* = 5.41, 7.42 Hz, 1H), 2.50 (m, 2H), 0.11 (s, 9H); ¹³C NMR (75MHz, CDCl₃) δ 144.90, 135.33, 128.12, 127.08, 125.94, 116.86, 74.95, 45.18, 0.18.

1-Chloro-4-[1-[(trimethylsilyl)oxy]-3-buten-1-yl]benzene (**3c**): colorless oil; ¹H NMR (300 MHz, CDCl3) δ 7.31 (m, 4H), 5.78 (m, 1H), 5.09-5.05 (m, 2H), 4.70 (m, 1H), 2.45 (m, 2H), 0.11 (s, 9H); ¹³C NMR (75MHz, CDCl3) δ 143.50, 134.79, 132.70, 128.31, 127.30, 117.28, 74.26, 45.19, 0.16.

4-[1-[(trimethylsilyl)oxy]-3-buten-1-yl]benzonitrile (**3e**): colorless oil; ¹H NMR (300 MHz, CDCl3) δ 7.60 (d, J = 8.43Hz, 2H), 7.42 (d, J = 8.06 Hz, 2H), 5.71 (m, 1H), 5.01 (m, 2H), 4.74 (dd, J = 5.15, 7.35 Hz, 1H), 2.39 (m, 2H), 0.05 (s, 9H); ¹³C NMR (75MHz, CDCl3) δ 150.29, 134.06, 131.98, 126.57, 118.91, 117.72, 110.80, 73.98, 44.78, 0.02.

1,3-bis(1-(trimethylsilyloxy)but-3-enyl)benzene (**3l**): pale yellow oil; ¹H NMR (300 MHz, CDCl3) δ 7.31–7.23 (m, 4H), 5.81 (m, 2H), 5.06 (m, 4H), 4.70 (m, 2H), 2.58-2.41 (m, 4H), 0.07 (s, 18H); ¹³C NMR (75MHz, CDCl3) δ 144.74, 135.23, 127.88, 124.71, 123.66, 116.81, 75.07, 45.27, 0.16.

3. Results and discussion

3.1. Catalyst characterization

3.1.1.X-ray diffraction analysis

The diffraction patterns of the as-synthesized and calcined Si-MCM-41and Al-MCM-41 catalysts are given in Fig. 1. The main peaks of the XRD patterns of all the samples are consistent with the characteristic peaks of the hexagonal structure of the MCM-41 mesoporous molecular sieves [35-37]. The as-synthesized Si-MCM-41 material (Fig. 1a) exhibit a strong peak, at 2theta = 2.21 due to (100) reflection lines and three weak signals around 3.79, 4.35 and 5.72 (2theta) corresponding to (110), (200) and (210) reflections, indicating the formation of well-ordered mesoporous materials with hexagonal regularity [38]. For the as-synthesized Al-MCM-41 (Fig. 1b), the characteristic reflection (100) is broadened as a result of the insertion of amount of Al. This suggests more disordered arrangement of channels for the Al-MCM-41, but keeping a hexagonal structure with good regularity. However, when the MCM-41 mesoporous molecular sieves are submitted to the calcinations process, the (100) reflection becomes sharper and more intense.

In the case of Si-MCM-41, we can observe the disappearance of peak (210); this is probably due to reduction of the order of the structure. After calcinations, the 2theta positions for all samples are shifted to a higher value, which indicated a contraction of the unit cell parameter a used by template removal and subsequent condensation of the silanol groups. The unit cell parameter aois calculated from $ao = 2d_{100}/\sqrt{3}$, where the d-spacing values are calculated by $n \lambda = 2d \sin\theta$. The observed d spacing and unit cell parameter results (Fig. 1) are well-matched with the hexagonal p6mm space group. We notice that the calculated cell parameters are 42 and 44 Å for Si- or Al-MCM-41 solids, respectively; these results are consistent with the literature, where it has been shown that the incorporation of a heteroatom in the structure of MCM-41 increases the unit cell parameter [32,39]. This difference is probably due to the bond length of Al-O (183.6 pm) being higher than Si-O (158 pm) as consequence of the larger ionic radius of Al³⁺ than Si⁴⁺ [32]. The change in d-spacing and unit cell parameter compared to siliceous MCM-41 proved the incorporation of aluminum in the framework. It is important to note that after the calcinations process of the samples an expected contraction of the unit cell parameter (Δao) is observed (Table 1).

Higher degree of lattice contraction has occurred when the aluminum is incorporated in the framework. According to Gaydhankar et al. [40], this indicates that the population of Si-OH units in the channel wall increases in the order: Al-MCM-41 > Si-MCM-41. The quantity of

aluminum incorporated in the framework was obtained by EDX analysis. According to the chemical composition used for the synthesis of Al-MCM-41, a nominal value of Si/Al = 12.5 was expected. However, the Si/Al ratio, as determined by EDX in the calcined MCM-41, is a little higher, indicating that the amount of heteroatom incorporated in the structure is a little less than expected (Table 1).

3.1.2. N2 adsorption-desorption

Fig. 2 shows the N₂ adsorption–desorption isotherms of the calcined Si- or Al-MCM-41and Table 1 summarizes the textural proprieties of theses catalysts. 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 [41].

The type IV isotherm is defined by three stages: at low relative pressures, a slow increase of nitrogen corresponding to monolayer-multilayer adsorption on the pore walls (P/P₀ < 0.24). At intermediate relative pressures, a sharp step indicates capillary condensation with in mesopores ($0.24 < P/P_0 < 0.40$). In the last stage (P/P₀ > 0.40), a final plate with a slight inclination associated with multilayer adsorption on external surface of the particles. It could be seen from Table 1 that the pore diameter of Al-MCM-41 higher than Si-MCM-41, on the other hand, the pore volume and BET surface area decreased for Al-MCM-41, which suggested generally that heteroatoms incorporation would result in a shift to higher pore size and decreased in specific surface areas [39]. The wall thickness in the case of Al-MCM-41 is around (8.4Å) and higher than that found for Si-MCM-41 (ca. 7.6Å). This can be explained by the incorporation of aluminium species (Si/Al = 13.47) [42].

3.1.3. FT-IR analysis

The IR spectra in the 500-1600 cm⁻¹ range, named the fingerprint zone of the materials for the KBr-pelletized calcined Si-MCM-41 and Al-MCM-41 samples are shown in Fig. 3. The main bands described in the literature for MCM-41 are found in our samples [43,44]. The peaks between 1244 and 1081 cm⁻¹are attributed to the asymmetric stretching of the T-O-T (T is Al or Si) groups. The symmetric stretching mode of the T-O-T (T is Al or Si) groups is observed at approximately 802 cm⁻¹. The pure silica MCM-41 presents a band at 964 cm⁻¹attributed to the Si-O stretching vibration in the Si-OH groups at the defect sites present in the mesoporous structure [45].

3.1.4. TG-DTG analysis

Thermogravimetric analysis of uncalcined samples prepared with CTAB as template, presented typical MCM-41 TG-DTG curves. The thermograms of the samples are presented in Fig. 4. The TGA curves show three weight losses at 30-120 °C, 120-350 °C and 350-600 °C. The weight loss in the first step is due to desorption of physically adsorbed water. The second mass loss is caused by the oxidative decomposition of organic surfactant. The final step is mainly due to the water loss formed by the condensation of adjacent silanol groups to form siloxane bonds.

The loss in mass varies according to the following order Si-MCM-41 > Al-MCM-41. From the TGA results, the peaks of surfactant removal for the Al-MCM-41 are shifted towards higher temperature compared to the pure silica MCM-41. According to Hui and Chao [42], Al-MCM-41 has a much stronger interaction of the organic template cations with aluminium species than with SiO⁻.

3.1.5. Pyridine FT-IR analysis

The acidity of Al-MCM-41 was measured by adsorption of pyridine coupled FT-IR spectroscopy, for detect the presence and nature of acid sites. The corresponding FT-IR spectra (Fig. 5) shows the presence of both types of acid sites, as inferred from the intense bands at 1454 cm⁻¹ and 1545 cm⁻¹ due to Lewis and Brönsted acid sites respectively. The integration of the area under these bands quantified the concentration of the acid sites [46].

The concentrations were determined after evacuation at different temperatures (Table 2), thus corroborates that the catalyst is strong acid solid. It can be seen that Al-MCM-41 gave priority to with Lewis acid and the concentration of this site still remained even after evacuation at $350 \,^{\circ}$ C.

3.2. Allylation of aromatic aldehydes with allyltrimethylsilane catalyzed by TiCl₄ or Al-MCM-41

In our previous communication, TiCl₄ was used to catalyze the allylation of aromatic aldehydes with allyltrimethylsilane [7]. We have observed that benzaldehyde, naphthaldehydes and benzaldehydes substituted by electron- donor and electron withdrawing groups twice undergo allylation by treatment with allylsilane and titanium tetrachloride, giving rise to 1,6-heptadien-4-yl-substituted arene compounds (Table 3). In contrast, the use of phthalaldehyde gives a single allylation of each carbonyl moiety in modest yield (Table 3,

entry 10). This moderate yield is explained by the instability in a reaction condition of the product.

In the presence of the Al-MCM-41(Table 4), we have used the same conditions, namely the temperature and the amount of allyltrimethylsilane in the condensation reactions of allyltrimethylsilane with benzaldehyde and 2,4-dichlorobenzaldehyde, and TiCl₄ was replaced by Al-MCM-41. At low temperature (-85 °C to -10 °C), the condensation reaction does not give any product (Table 4, entries 1 and 8), while in the presence of TiCl₄ excellent yields were obtained (Table 3, entries 1-7).When we increased the reaction temperature from 0 to 24 °C, only trace amount of the product were obtained (Table 4, entry 2),whereas at a higher temperature of 35 °C, the best yields were obtained (Table 4, entries 3 and 9). NMR analysis H¹ and C¹³ confirmed that these products are the result of a single allylation. Increasing the amount of allyltrimethylsilane to 5 equivalent (Table 4, entry 4) does not yield the diallylated product, however, when TiCl₄ was used as the Lewis acid and in the presence of only 3 equivalent of allyltrimethylsilane, the diallylated products were obtained regardless the substituted aromatic aldehydes (Table 3).

A reaction of various aldehydes with allyltrimethylsilane using Al-MCM-41 at 35°C gives rise to a single allylation (homoallyl silyl ether) (Table 5). We have observed that electron-deficient aromatic aldehydes are allylated in excellent yields (Table 5, entries 1-7, 10-13). However, in aromatic aldehydes bearing electron-donating groups such as p-anisaldehyde and p-tolualdehyde, the desired products were obtained in moderate yields (Table 5, entries 8 and 9).

On the other hand, when the heteroaromatic aldehydes were used as allylation with allyltrimethylsilane no reaction occurred (Table 5, entries 14 and 15). This may be due to the low stability of the furfural ring and thiophene ring when exposed to Lewis acids. Whereas, the reaction of crotonaldehyde gave the allylated products in moderate yields (Table 5, entry 16).

To explain this difference allylation in the presence of the MCM-41 or TiCl₄, two plausible reaction mechanisms are proposed, involving the role of Lewis acid sites of Al-MCM-41 and the role of TiCl₄ in allylation of different benzaldehydes in the presence of allyltrimethylsilane (scheme 1). Upon the addition of benzaldehyde to the different catalysts, a strong chelation is created between the oxygen of the aldehyde and the Lewis acid site of Al-MCM-41 (A), the appearance of the brown color indicates that chelation O-TiCl₄ (A') has

occurred [47], which makes the addition of allyltrimethylsilane easier and thereby forming a carbon-carbon bond (Scheme 1, B and B'). The reorganization of the electrons in the intermediate (C) gives rise to a formation of an allylic motif for obtaining homoallyl silyl ethers (D), thereby freeing the Lewis site of Al-MCM-41 for the following cycle. The stage between (C) and (D), shows that the attack of the second allyltrimethylsilane is not permitted, it is for this reason that diallylated products were not detected in this catalytic system.

However, the reorganization of the electrons in the intermediate (C'), is first made by the expulsion of the chloride anion of the intermediate (B') due to the coordination of nitromethane with TiCl₄. The chloride anion will be captured by trimethylsilane for regeneration of allyl motif [48]. The intermediate (D') reacts rapidly with excess allyl trimethylsilane via the formation of gem-diallyl derivative (E) and the expulsion of the catalyst in the form of titanium oxychloride [49]. The condensation in the presence of Al-MCM-41 of allyltrimethylsilane is very rapid, compared to the first allylation catalyzed TiCl₄, which is known to be a slow step [50]. This can be observed by comparing the time of the reaction of terephthalaldehyde with allyltrimethylsilane. Using Al-MCM-41, the homoallyl silyl ethers (100% yield) was obtained after only 25 minutes (Table 5, entry 7), whereas the diallylation of the same aldehyde was obtained after 5 hours of reaction at low temperature with a 85% yield (Table 3, entry 5).

3.3. Catalyst reusability

Reusability of the catalyst has been studied in the reaction of benzaldehyde with allyltrimethylsilane in the presence of Al-MCM-41. Upon completion of the reaction, Al-MCM-41 is recovered by simple filtration, washed by dichloromethane three times to confirm the complete removal of any residual material, then dried and activated before use for the next cycle. The catalyst could be reused three times with-out a significant loss of catalytic activity (Fig. 6).

4. Conclusion

The solid catalyst Al-MCM-41 was synthesized by hydrothermal method with Si/Al atomic ratio of 12.5. The structural and textural properties of this catalyst were measured using various analytical instruments.

Pyridine coupled FT-IR spectroscopy analysis showed the existence of a high concentration of acid sites, with both Brönsted and Lewis sites. The concentrations determined after evacuation at different temperatures gave priority to Lewis acid. The site acids of Lewis of Al-MCM-41 are highly efficient for the allylation of various aldehydes with

allyltrimethylsilane. Similar to TiCl₄ the Lewis acid promotes the formation of the diallylation, whereas in the presence of Al-MCM-41, the single allylation was obtained using mild conditions. To explain this different allylation in the presence of the MCM-41 or TiCl₄, a reaction mechanism is proposed. The catalyst can be regenerated and reused for three times without significant loss of activity.

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Fig.1. XRD patterns of as-synthesized and calcined Si-or Al-MCM-41. (a) Si-MCM-41, (b) Al-MCM-41.



Fig.2. Nitrogen adsorption–desorption isotherms of calcined Si- or Al-MCM-41 mesoporous materials.



Fig.3. FT-IR spectra of calcined Si- or Al-MCM-41 mesoporous materials.



Fig.4. TG and DTG curves of as-synthesized Si- or Al-MCM-41. (a) Si-MCM-41, (b) Al-MCM-41.



Fig.5. FTIR spectra of pyridine desorbed on calcined Al-MCM-41 under vacuum 3 Torr pressure at (a) 50 °C, (b) 150 °C, (c) 250 °C, (d) 350 °C.



Fig. 6. Reusability of Al-MCM-41. *Reaction conditions*: benzaldehyde (1 mmol), allyltrimetylsilane (1.5 mmol), Al-MCM-41 (25 mol%), CH₂Cl₂ (2 mL), 35 °C, reaction period = 4h.



Scheme 1. Plausible mechanism of role of Al-MCM-41 as a Lewis acid (a) catalyst in allylation of various aldehydes with allyltrimethylsilane in compared with TiCl₄ as a Lewis acid (b).

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Table 1

Catalysts	Si/Al ^a	Si/Al ^b (EDX)	ao (Å)	Δa_0^c	S_{BET}^{d} (m ² /g)	V_{meso}^{e} (cm ³ /g)	D _p ^f (Å)	Wt ^g (Å)
Si-MCM-41	-	-	41.60	9.8	1154	0.84	34.0	7.6
Al-MCM-41	12.50	13.47	43.94	12.0	983	0.76	35.6	8.4

Physical characteristics of calcined mesoporous catalysts.

^a Molar ratio in the initial gel.

^bMolar ratio determined by EDX analysis.

 $^{c}\Delta a_{0}$ (%) = ([a₀ (as-synthesized)- a₀ (calcined)]/a₀ (as-synthesized)).100

^d Specific surface area.

^e Mesoporous volume.

^f Pore diameter determined by BJH.

^g Wall thikness, $a_0 - D_p$.

Table 2

Brönsted (C_B) and Lewis (C_L) acidity of the Al-MCM-41 sample measured by FTIR spectroscopy combined with pyridine adsorption and desorption at different temperatures.

Acid proprieties (µmol.g ⁻¹)	50 °C	150 °C	250 °C	350 °C	Total acidity
Total acidity	295.62	372.21	402.52	344.42	1414.77
Brönsted acidity (CB)	92.13	124.79	142.78	85.89	445.59
Lewis acidity (CL)	203.49	247.42	259.74	258.53	969.18
$C_{L^{\prime}} \; C_{B}$	2.21	1.98	1.82	3.01	2.17

Table 3

Allylation of various aldehydes with allyltrimethylsilane catalysed byTiCl4^a.

R	H + H SiMe ₃	TiCl ₄ CH ₂ Cl ₂ - CH ₃ NO ₂ -85°C to -10°C	
Entry	Aldehyde	Product	Yield ^b (%)
1	⟨ → ⊣ [°] _H		74
2	Me – Contraction Me	Me	85
3	MeO – K	MeO	85
4	Br - H	Br	95
5	$\overset{O}{\xrightarrow}_{H} \overset{O}{\longrightarrow} \overset{O}{\xrightarrow}_{H}$		85
6	O H		88
7	° H		75
8	о Н Н		35
9	MeO H	MeO	76
10	O H H O		30

^a Reaction conditions: aldehyde (5 mmol), allyltrimethylsilane (15 mmol), TiCl₄ (8.1 mmol), CH₂Cl₂ (20 mL) and MeNO₂ (1.2 mL), -85 to -10 °C, 5-15 h. ^b Isolated yield after column chromatography.

Table 4

The effect of reaction temperature in the presence of Al-MCM-41 as catalyst^a.

$R' \longrightarrow R' + K' = R' - R$	
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Entry	R,R'	Temperature	SiMe ₃	Time	Yield ^b
		(°C)	(equiv)	(h)	(%)
1	H, H	-85 to -10	3	-	n.r.
2	Н, Н	0 to 24	3	24	Traces
3	Н, Н	35	3	4	99
4	Н, Н	35	5	4	99
5	Н, Н	35	1.5	4	99
6 ^c	Н, Н	35	1.5	4	54
7^d	Н, Н	35	1.5	4	35
8	Cl, Cl	-85 to -10	3	-	n.r.
9	Cl, Cl	35	3	45 min	100
10	Cl, Cl	35	1.5	45 min	100

^aReaction conditions: aldehyde (1 mmol), Al-MCM-41 (25 mol%), CH₂Cl₂ (2 mL).

^b Isolated yield after column chromatography.

^c 10 mol% of Al-MCM-41 is used.

^d 5 mol% of Al-MCM-41 is used.

Table 5

Allylation of various aldehydes with allyltrimethylsilane catalysed by Al-MCM-41^a.

$R \stackrel{O}{\underset{H}{\leftarrow}}_{H} + \underbrace{\qquad SiMe_{3}}_{2} \xrightarrow{A1-MCM-41} R \stackrel{OSiMe_{3}}{\underset{CH_{2}Cl_{2}, 35^{\circ}C}{\leftarrow}} R \xrightarrow{\qquad OSiMe_{3}}_{3a-3n}$								
Entry	Aldehyde	Time (h)	Product	Yield	^b (%)			
1	⟨ → ⊣ [°]	4	OSiMe ₃	3a	99			
2	$Br \longrightarrow H$	3	Br OSiMe ₃	3b	98			
3	CI – L	2		3c	99			
4	F - H	< 2	F-COSIMe ₃	3d	99			
5		1	NC-	3e	98			
6	O ₂ N - C	0.5	O2N O2N	3f	99			
7	°→→→→→ H	25 min	OSiMe ₃ OSiMe ₃	3g	100			
8	Me - H	4	Me	3h	40			
9	MeO \longrightarrow H	4	MeO - OSIMe3	3i	36			
10	$\sim H$	1	O ₂ N	3ј	98			



Table 5 (continued)

Entry	Aldehyde	Time (h)	Product	Yield ^b	(%)
12	H O H	45 min	OSiMe ₃ OSiMe ₃	31	98
13		45 min	Cl – OSiMe ₃	3m	100
14	K [™] [™] [™]	24	OSiMe ₃	-	
15	K ^O → ^O H	24	OSiMe ₃	-	
16	° H	7	OSiMe ₃	3n	55

^a Reaction conditions: aldehyde (1 mmol), allyltrimethylsilane (1.5 mmol), Al-MCM-41 (25 mol%), CH₂Cl₂ (2 mL), 35 °C.

^b Isolated yield after column chromatography.