Synthesis of 2-acetyl-6-methoxynaphthalene using mesoporous 
$SO_2^-/Al-MCM-41$ molecular sieves

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Abstract

The mesoporous molecular sieves Al-MCM-41 with Si/Al ratio equal to 16, was synthesized under hydrothermal conditions using cetyltrimethylammonium bromide (CTMA$^+Br^-$) as surfactant. The $SO_2^-/Al-MCM-41$(Si/Al = 16) material was synthesized using sulfuric acid under impregnation method, and the resulting material is sulfated Al-MCM-41 ($SO_2^-/Al-MCM-41$). The mesoporous materials viz. Al-MCM-41 and $SO_2^-/Al-MCM-41$ were characterized using several techniques e.g. ICP-AES, Nephelometer, XRD, FT-IR, TG/DTA, $N_2$-adsorption, solid-state-NMR, SEM, TEM and TPD-pyridine. By impregnating of sulfuric acid on silica surface, crystallinity, surface area, pore diameter and pore volume of $SO_2^-/Al-MCM-41$ decreased except wall thickness. While the Lewis acidity is increased because of the expelling aluminum from the Al-MCM-41 framework by impregnating sulfuric acid. The $SO_2^-/Al-MCM-41$ has been used for synthesis of 2-acetyl-6-methoxynaphthalene using 2-methoxynaphthalene with acetic anhydride as acylating agent and 1,2-dichloroethane as solvent. The catalytic results were compared with those obtained using 0.8 N sulfuric acid, amorphous silica–alumina, H-$b$, USY and H-ZSM-5 zeolites. From the catalytic results it was concluded that the conversion of 2-methoxynaphthalene and selectivity of 2-acetyl-6-methoxynaphthalene in the $SO_2^-/Al-MCM-41$ is higher than that in other catalysts due to higher number of Lewis acid sites. Thus the $SO_2^-/Al-MCM-41$ is found to be a highly active and recyclable heterogeneous catalyst while the catalyst is a very suitable for the synthesis of 2-acetyl-6-methoxynaphthalene. © 2005 Elsevier Inc. All rights reserved.

Keywords: Al-MCM-41; $SO_2^-/Al-MCM-41$; Lewis acidity; Conversion of 2-methoxynaphthalene; Selectivity of 2-acetyl-6-methoxynaphthalene

1. Introduction

Friedel-crafts acylation of aromatics is one of the most important reactions to produce aromatic ketones, which are useful intermediates for the synthesis of fine chemicals such as pharmaceutical ((S)-naproxen), fragrances and dye stuffs [1,2]. The conventional processes for the preparation of these aromatic ketones employ metal halides (AlCl$_3$, FeCl$_3$, etc.) or mineral acids (HF or polyphosphoric acid) as homogeneous catalysts [3]. Such process, however, consume near stoichiometric quantities of catalysts, and the recovery of products from reaction mixture is difficult. Most of these catalysts cannot be recycled and pose serious waste disposal problems. Because of current environmental restrictions, many research groups have tried to develop environmentally benign acylation processes using solid acid catalysts [4–10].

The acylation of 2-methoxynaphthalene (2MN) has been investigated over HY, ZSM-12 and BEA [11,12] and mordenite [13], and ZSM-5 [14]. In the acylation reaction, one of the major products is 2-acetyl-6-methoxynaphthalene (2A-6MN), the intermediate for an important anti-inflammatory drug, (S)-(++)-6-methoxy-α-methyl-2-naphthalencacetic acid, known as Naproxen.

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During the acylation of 2MN with acetic anhydride the linear 2A-6MN and the bulky 1-acetyl-2-methoxy-naphthalene (1A-2MN) can be formed. 2A-6MN can be created at the inner and outer surfaces of zeolites. 1A-2MN is too bulky and cannot enter the micropores [11]. Harvey et al. [11,15] reported that zeolite beta was the most effective catalysts among various zeolites in the acylation of 2MN. According to their results, the external surface played an important role in the catalytic activity for synthesis 1A-2MN. A disadvantages of zeolite catalysts are their limited pore (up to 1.0 nm), which renders useless as catalysts in the conversion of larger sized reactants.

The discovery of the mesoporous material MCM-41 [16,17] has greatly enlarged the window of porous materials applicable as catalyst for organic reactions. The typical characteristics of the materials, viz. highly ordered mesoporosity, large surface area, high hydrothermal stability and mild acidity, allude to the possibility of applying these materials as catalysts in the synthesis and conversion of large organic molecules. Unfortunately, the acid strength of MCM-41 resembles that of the amorphous silica aluminas rather than that of the more strongly acidic zeolites [18]. Although the materials are valuable for many organic conversions [19–24], enhancement of its acidity is desirable for extension of its applicability.

Gunnwegrh et al. [25] studied the acylation of 2MN catalysed by mesoporous molecular sieve such as MCM-41. They concluded that the higher selectivity of 1A-2MN is formed with small amount of undefined high molecular products at 100 °C over H-MCM-41. However, the molecular size of 1A-2MN is higher than that of 2A-6MN. So this catalyst is very suitable to 1A-2MN due to the catalyst pore size with the higher number of mild Bronsted acid sites.

Chen et al. (1999) first reported the details of the synthesis and characterization of sulfuric acid impregnated mesoporous Al-MCM-41 materials for synthesis of β-naphthyl methyl ether [26] and later, we also reported the synthesis, characterization of mesoporous materials with different Si/Al ratios for synthesis of nerolone [27,28] and dypnone [29]. Herein we report the synthesis and characterization of Al-MCM-41 with aluminum isopropoxide under hydrothermal conditions [29]. The synthesized Al-MCM-41 materials were modified with sulfuric acid and the resulting materials are known as sulfated Al-MCM-41 (SO$_3^-$/Al-MCM-41) materials. From the physicochemical characterization and some catalytic experimental results of the materials it was concluded that the SO$_3^-$/Al-MCM-41 have the higher number of Lewis acid sites, have good recyclability and suitable pore size to the synthesis of 2A-6MN. So the materials have used as catalyst for highly selective synthesis of 2A-6MN. The catalytic reaction was carried out under various reaction conditions using SO$_3^-$/Al-MCM-41 as catalyst. The catalytic results are correlated and compared with those of 0.8 N sulfuric acid solution and other solid acid catalysts such as Al-MCM-41, amorphous silica–alumina, H-β, USY and H-ZSM-5 zeolite.

2. Experimental

2.1. Materials

The syntheses of Al-MCM-41 and SO$_3^-$/Al-MCM-41 materials were carried out hydrothermally and by impregnation methods respectively and using tetraethylylorthosilicate (TEOS), aluminum isopropoxide (Al–[O–CH–(CH$_3$)$_3$]), cetyltrimethylammonium bromide (C$_{16}$H$_{33}$N+Br$^-$), tetraethylammonium hydroxide ((C$_2$H$_5$)$_4$NOH), sulfuric acid (H$_2$SO$_4$). The synthesis of 2A-6MN was carried out by liquid phase reaction and using 2-methoxy naphthalene (2MN) and acetic anhydride (AC$_2$O) as reactants, and cyclohexane, dichloromethane, 1,2-dichloroethane, nitrobenzene, sulfolane, nitromethane as solvents. All chemicals (AR grade) were purchased from Aldrich & Co., USA.

2.2. Commercial catalytic materials

Amorphous silica–alumina (Si/Al = 5.7, Strem), H-β (Si/Al = 25.7, Strem), USY (Si/Al = 27.5, PQ) and H-ZSM-5 (Si/Al = 25.5, PQ) were obtained from commercial sources. These catalysts were calcined at 500 °C for 6 h in air before catalytic reaction.

2.3. Synthesis of Al-MCM-41 and SO$_3^-$/Al-MCM-41

2.3.1. Synthesis of Al-MCM-41

For the synthesis of the Al-MCM-41 (Si/Al = 16) material, 22.3 mL (1 mol) of tetraethylylorthosilicate was mixed with 0.68 g (0.033 mol) of aluminum isopropoxide (dissolved in 5 mL of deionized water). The mixture solution was stirred for 30 min at a speed of about 250 rpm and tetraethylammonium hydroxide solution (10% water) was added with continuous stirring for another 30 min. at a speed of about 250 rpm until the gel formation (pH = 11). After that, 7.2 g (0.2 mol) of cetyltrimethylammonium bromide was added dropwise (30 mL/h) via a dual syringe pump so that the gel changed into suspension after further stirring for 1 h the resulting synthesis gel of composition 1SiO$_2$:0.033Al$_2$O$_3$:0.2CTMABr:100H$_2$O, it was transferred into Teflon-line steel autoclave and heated at 150 °C for 48 h. After cooling to room temperature, the material was recovered by filtration, washed with deionized water and ethanol, dried in air at 100 °C for 1 h and finally calcined at 540 °C for 6 h in the presence of air (calcination ramp rate is 100 °C/h).
2.3.2. Synthesis of SO$_2^-$/Al-MCM-41

The SO$_2^-$/Al-MCM-41 was prepared by impregnating 1 g of calcined Al-MCM-41 with 50 mL (0.8 N) of sulfuric acid with stirring 500 rpm for 3 h at room temperature. Then the sample was dried at 110 °C for 12 h.

2.4. Characterization

The Al content in SO$_2^-$/Al-MCM-41 and Al-MCM-41 was recorded using ICP-AES with allied analytical ICAP 9000. The SO$_2^-$ content in SO$_2^-$/Al-MCM-41 with barium chloride was recorded using Nephelometer with CL52D (Elanco Limited, India).

The crystalline phase identification and phase purity determination of the calcined samples of Al-MCM-41 (Si/Al = 16) and SO$_2^-$/Al-MCM-41 were carried out by x-ray diffraction (XRD, Philips, Holland) using nickel filtered CuKα radiation (λ = 1.5406 Å). The samples were scanned from 1° to 5° (2θ) angle in steps of 0.5°, with a count of 5 s at each point. In order to protect the detector from the high energy of the incident and diffracted beam, slits were used in this work.

N$_2$-adsorption isotherms were measured at −197 °C using a Micromeritics ASAP 2000. Prior to the experiments, the samples dried at 130 °C and evacuated overnight for 8 h in flowing argon at a flow rate of 60 mL/min at 200 °C until the vacuum pressure was below 8 mmHg. Surface area, pore size, pore volume and wall thickness was obtained from these isotherms using the conventional BET and BJH equations.

Infrared spectra were recorded with a Nicolet Impact 410 FTIR Spectrometer in KBr pellet (0.005 g sample with 0.1 g KBr) scan number 36, resolution 2 cm$^{-1}$.

Thermo gravimetric–differential thermal analysis was carried out in Rheometric Scientific (STA H$^+$) thermo balance. Ten to 15 mg of as-synthesized Al-MCM-41 and SO$_2^-$/Al-MCM-41 were loaded, and the airflow used was 50 mL/min. The heating rate was 20 K/min and the final temperature was 1000 °C.

The $^{27}$Al MAS NMR spectra were recorded at a frequency of 75.512 MHz and a spinning rate of 75.512 MHz and a frequency of 75.512 MHz and a spinning rate of 8 kHz with a pulse length of 4 μs, a pulse interval of 1 s and approximately 1000 scans. $^{27}$Al chemical shifts are reported relative to 1 M Al(NO$_3$)$_3$.

The SEM micrographs of a typical sample of MCM-41 materials were obtained on a JEOL 2010 microscope operated at 200 kV with 0.1 g KBr) scan number 36, resolution 2 cm$^{-1}$.

2.5. Experimental for synthesis of 2-acetyl-6-methoxynaphthalene

2.5.1. Catalytic reaction

The catalyst (0.2 g) was added to 2MN, acetic anhydride as acylating reagent and 1,2-dichloroethane as solvent while the reaction was performed in a stirred (600 rpm) and sealed batch autoclave reactor (100 mL, Autoclave Engineers) at reaction temperatures namely, 40, 80, 120, and 140 °C with atmospheric pressure, different time (h), AC2O/2MN ratio, different solvent and different catalysts. The reaction products were recovered from the reactor after cooling to 0 °C.

After reusing the MCM-41 its activity decreases and the catalyst needs to be regenerated by calcination. It can be reused after washing with dichloromethane and ethyl acetate at 40 °C followed by hot water to remove the organics and unreacted 2MN. The recycled SO$_2^-$/Al-MCM-41 catalyst was washed 5 times with dichloromethane and ethyl acetate. It was drying at 140 °C for overnight.

2.5.2. Analysis of reaction products

After the reaction, the catalyst (if a solid was used) was separated from the reaction solution and washed with small amount of dichloromethane and ethyl acetate using a centrifuge. Again small amount of above reagents was added to separate the catalyst. The catalyst solution centrifuge tube was tightly sealed and magnetic stirred at 25 °C for 1 h. This step was repeated 2–3 times. The supernatant solutions collected in the above steps were maintained at 0 °C for 1 h. The solution was evaporated to give a crude oil. This crude product was purified by preparative TLC (dichloromethane/ethyl acetate = 10/1) to afford 2A-6MN. 1A-2MN could also be purified by preparative TLC. The clear product solutions were analyzed with a GC (HP 5890 series II) using a flame-ionization detector on a 30-M HP-5 column. The products were also identified by GC-MS (Shimadzu, QP 2000 a).

Spectroscopic data of 2-acetyl-6-methoxynaphthalene: $^1$H NMR (CDCl$_3$) δ: 2.72 (s, 3H), 3.95 (s, 3H) 7.17 (d, J = 2.6 Hz, 1H), 7.22 (dd, J = 8.7, 2.6 Hz, 1H), 7.77 (d, J = 8.7 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 8.02 (dd, J = 8.7, 1.9 Hz, 1H), 8.40 (d, J = 1.7 Hz, 1H). $^{13}$C NMR (CDCl$_3$) δ: 26.5, 55.5, 105.8, 119.8, 124.7, 127.2, 127.9, 130.1, 132.2, 132.7, 137.31, 159.7, 197.9.
Spectroscopic data of 1-acetyl-2-methoxynaphthalene: $^1$H NMR (CDCl$_3$) $\delta$ 2.64 (s, 3H), 3.99 (s, 3H), 7.28 (d, $J = 9.1$ Hz, 1H), 7.38 (ddd, $J = 8.2$, 6.9, 1.2 Hz, 1H), 7.48 (ddd, $J = 8.1$, 6.9, 1.5 Hz, 1H), 7.77 (d, $J = 8.1$ Hz, 1H), 7.80 (d, $J = 8.1$ Hz, 1H), 7.89 (d, $J = 9.2$ Hz, 1H). $^{13}$C NMR (CDCl$_3$) $\delta$: 32.8, 56.4, 112.8, 123.6, 124.2, 125.2, 127.8, 128.2, 128.7, 128.9, 130.3, 131.5, 135.9, 205.3.

2.6. Leaching of sulfate experiment studies from $SO_2^2-/Al$-MCM-41

After the catalyst reaction, catalyst was equilibrated with distilled water for 1 week at 100°C (pH < 5), and kept in water bath and the supernatant was checked for $SO_2^2-$ using barium chloride. The experiment was repeated to verify reproducibility before reporting the results.

3. Results and discussion

3.1. ICP-AES

The Al content in both catalysts was found to be 0.28 g containing Si/Al = 16 using ICP-AES. The $SO_2^2-$ content was found to be 1960 ppm in the $SO_2^2-/Al$-MCM-41 using a Nephelometer.

3.2. X-ray diffraction

The X-ray diffractograms of the Al-MCM-41 and $SO_2^2-/Al$-MCM-41 materials are illustrated (Fig. 1), after calcination at 540°C for 6 h in air, contain, in addition to sharp $d_{100}$ reflection line near $2\theta = 1.93^\circ$, broad peaks near $2\theta = 3.33^\circ$ (110) and $3.83^\circ$ (200). The $SO_2^2-/Al$-MCM-41 material after having been dried at 110°C for 12 h, contains, in addition to the sharp $d_{100}$ reflection line near $2\theta = 2.0^\circ$, broad peaks near $2\theta = 3.48^\circ$ (110) and $3.98^\circ$ (200). The broadening effects of higher reflection lines can be due to small crystallites [31]. Physicochemical properties of these mesoporous materials are summarized in Table 1. The XRD patterns of calcined Al-MCM-41 with characteristic peaks of hexagonal symmetry and with $d_{100} = 45.73$ Å are shown in Fig. 1(a). The unit cell parameter ($a_0$) was 52.8 Å. The hexagonal unit cell parameter ($a_0$) was calculated using $2d_{100}/\sqrt{3}$ from $d_{100}$, which was obtained from the peak in the XRD pattern by Bragg’s equation ($2d\sin\theta = \lambda$, where $\lambda = 1.5406$ Å for the CuKx line). The value of $a_0$ was equal to the internal pore diameter plus one pore wall thickness. In general, in the synthesis condition used, the crystallization reaction is non-stoichiometric and the crystal’s Si/Al ratio is always greater than in the hydrogel containing aluminum [32]. Incorporation of aluminum into the silicate framework decreases the size of the unit cell when the source of Al is Al-isopropoxide. The data obtained for the calcined materials are in good agreement with those reported by Beck et al. [17]. Excess incorporation of aluminum (low Si/Al ratio) might lead to the collapse of the structure, as reported by Kim et al. (1997) for Al-MCM-41 (Si/Al = 10) prepared at a pH of 11 [33]. Impregnation of Al-MCM-41 with sulfuric acid results in the decrease of crystallinity, d-spacing value and unit cell parameter [26–29] and is as shown in Table 1.

3.3. Nitrogen adsorption isotherm

Fig. 2 shows the isotherm of nitrogen adsorption on the calcined Al-MCM-41 and $SO_2^2-/Al$-MCM-41 measured at liquid nitrogen temperature (~197°C). Three well-defined stages may be identified: (1) A slow increase in nitrogen uptake at low relative pressure, corresponding to monolayer–multilayer adsorption on the pore walls; (2) a sharp step at intermediate relative pressures indicative of capillary condensation within mesopores; and (3) a plateau with a slight inclination at high relative pressures associated with multilayer adsorption on the external surface of the crystals [34]. A fourth stage, characterized by a sharp rise in N$_2$ uptake as the pressure reaches saturation ($P/P_0 = 1$), may be identified in some
The pore diameter of Al-MCM-41 is higher than that of SO$_2$/$\text{Al-MCM-41}$ due to the presence of textural mesoporosity. Sulfuric acid treatment of Al-MCM-41 sample results in a decrease of surface area from 1099 to 698 m$^2$/g which is consistent by lower relative pressure ($P/P_0 < 0.3$). Thus, in the SO$_2$/$\text{Al-MCM-41}$ the surface area, pore diameter and pore volume are lower than that of Al-MCM-41 material while the sulfation of Al-MCM-41 results in a decrease of the pore volume from 1.48 to 0.84 cm$^3$/g. (Since the Kelvin equation is not valid for pores below 18 Å only the BJH approach can be used for mesoporous material.) This could be due to structure collapse due to arrangement of tetrahedral Al in non-frame work with impregnation of sulfuric acid.

3.4. Fourier transform infra red spectroscopy

Infra red spectroscopy had been used extensively for the characterization of zeolites. In the FTIR spectrum of calcined siliceous MCM-41, the asymmetric and symmetric stretching vibration bands of framework Si–O–Si bands, assigned by Sohn et al. [36] for zeolites, appeared at 1123 and 814 cm$^{-1}$. In as-synthesized Al-MCM-41, the IR spectrum was measured in 400–4000 cm$^{-1}$ range in a few steps during sample preparation and is shown in Fig. 3(a). The as-synthesized sample exhibits absorption bands around 2921 and 2851 cm$^{-1}$ corresponding to n-C–H and d-C–H vibrations of the surfactant molecules. The broad bands around 3650–3800 cm$^{-1}$ may be attributed to surface silanols and adsorbed water molecules, while deformational vibrations of adsorbed molecules cause the adsorption bands at 1623–1640 cm$^{-1}$ [37]. The absorption band at 1069 and 1223 cm$^{-1}$ are due to asymmetric stretching vibrations of Si–O–Si bridges, but in the opposite direction are observed for the 962 cm$^{-1}$ bands due to ᵈSi–OH or ᵈSi–O$^-$ vibrations in aluminum incorporation. When various metals are incorporated, the intensity of this band increases. This is generally considered to be proof of the incorporation of the heteroatom into the framework. Cambler et al. (1993) have reported similar stretching vibrations of Si–OH groups present at defect sites [38]. From disappearance of bands at 2851 and 2921 cm$^{-1}$, we can conclude that calcination of the original framework

![](image)
was completed. The vibration bands of calcined Al-MCM-41 can be shifted from 1 to 3 or 5 cm\(^{-1}\). An FTIR spectrum of calcined Al-MCM-41 is shown in Fig. 3(b).

IR spectrum was measured in 400–4000 cm\(^{-1}\) range for SO\(_2\)/Al-MCM-41 and is shown in Fig. 3(c). The sulfated sample exhibits absorption bands around 3500 cm\(^{-1}\), which may be attributed to surface silanol groups and adsorbed water molecules [36]. The adsorption bands at 1186, 876 and 585 cm\(^{-1}\) are due to strong stretching vibrations of HSO\(_4\) [39]. The SO\(_2\) deformation frequency has been assigned in the region 876 and 585 cm\(^{-1}\). The proposed structure to the SO\(_2\)/Al-MCM-41 material showing possible Lewis acid sites is shown in Fig. 4. If the aluminum-ions are non-framework by impregnating sulfuric acid while the sulfate groups are also having inductive effect with aluminum-ions, the strong Lewis acid sites (LA) can be generated on its surface. From the infrared analysis, the asymmetric and symmetric stretching of the S=O bond were determined in the 1215–1125 cm\(^{-1}\) and 1060–995 cm\(^{-1}\), respectively. The adsorption band at 1186 cm\(^{-1}\) is due to symmetric vibrations of S–O–Si-bridges, but in the opposite direction are observed for the 963 cm\(^{-1}\) bands due to ≡Si–O ≡ silanols. The absorption band at 799 cm\(^{-1}\) is due to the symmetric Si–O stretching vibration and band at 876 cm\(^{-1}\) is due to the symmetric S–O stretching vibrations.

3.5. Thermal analysis

Thermogravimetric analysis [40] of the crystals shows distinct weight losses that depend on the framework composition (Table 2). Representative thermogram is given in Fig. 5(a). The minor weight loss below 150 °C corresponds to the desorption of physisorbed water (or ethanol) in the voids formed by crystal agglomeration and in the mesopores. Weight losses in the temperature range 150–350 °C are attributed to the decomposition and removal of occluded organics. Weight losses in this temperature range are not as large as in the parent silicate because of stronger sorbate–sorbent interactions at the aluminosilicate surface. In the temperature range 280–340 °C, the oxidative decomposition of residual organic compounds occurs which is accompanied by exotherms whose number and intensity depends on the

<table>
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<th>Samples</th>
<th>Weight loss (wt%)</th>
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<tr>
<td></td>
<td>Total 50–150 °C</td>
</tr>
<tr>
<td>Al-MCM-41</td>
<td>44.11</td>
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<tr>
<td>SO(_2)/Al-MCM-41</td>
<td>67.51</td>
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aluminum content of the crystal. The 350–550 °C was the region of surfactant associated with Al–O. There was almost no exothermal peak after 550 °C, which indicated the surfactant, had been removed completely. The total weight loss at 1000 °C of the Al-MCM-41 sample is in 44.11%.

Representative thermograms for SO$_4^{2-}$/Al-MCM-41 are given in Fig. 5(b). The major endothermic reaction peak is assigned the minor weight loss below 150 °C corresponds to the desorption of physisorbed water in the voids formed by crystal agglomeration and also the minor endothermic peak occurring at the 200–300 °C is attributed to the decomposition of SO$_4^{2-}$ into SO$_2$ gas by absorption of entropy. Thus the total weight loss at 1000 °C of the SO$_4^{2-}$/Al-MCM-41 sample is 67.51%.

3.6. Solid-state NMR spectroscopy

Fig. 6 shows solid-state $^{27}$Al-MAS-NMR spectra of calcined Al-MCM-41 and SO$_4^{2-}$/Al-MCM-41 with Si/Al = 30. Chemical shift peak spectrum shows a strong and sharp signal at 53 ppm as well as a weak and broad signal at around 0 ppm regardless of the Al content in the Al-MCM-41 (Fig. 6(a)), but a sharp signal at around 0 ppm shows in the SO$_4^{2-}$/Al-MCM-41 (Fig. 6(b)). The structure collapse consequent upon the disappearance of tetrahedral aluminum after impregnation of sulfate in the reduction in the physical parameters is only resulted. The signal at around 53 ppm could be assigned to tetrahedrally coordinated framework aluminum (T$_d$-Al), which was observed in aluminosilicate zeolites [41]. The signal at around 0 ppm was ascribed to octahedrally coordinated (O$_h$) non-framework aluminum [41].

It is important to bear in mind these results when considering the use of these materials for acid-catalyzed reactions, in which the Bronsted acidity should be attributed to the presence of tetrahedral aluminum and also Lewis acidity should be attributed to the presence of octahedral aluminum. From the results it is concluded to the acid sites, however, the number of Lewis acid sites is higher in SO$_4^{2-}$/Al-MCM-41 than in Al-MCM-41 due to higher number of aluminum octahedral coordination on the silica surface by impregnation of sulfuric acid.
3.7. Scanning electron microscopy

Al-MCM-41 materials are having micellar rod-like shape hexagonal or spherical edges as shown in Figs. 7(a) and (b). In materials synthesized using cetyltrimethylammonium bromide as surfactant, Steel et al. (1994) postulated that CTMABr surfactant molecules assembled directly into the liquid crystal phase upon addition of the silicate species, based on $^{14}$NMR spectroscopy [42]. The size of micellar rod like shape and hexagonal phase is smaller in $\text{SO}_2^2-/\text{Al-MCM-41}$ than that of Al-MCM-41 materials because tetrahedral aluminum is forced into non-framework positions during impregnation with sulfuric acid.

3.8. Transmission electron microscopy

The TEM image of $\text{SO}_2^2-/\text{Al-MCM-41}$ (Fig. 8) exhibits ordered hexagonal arrays of mesopores with uniform pore size [16]. While the distance between mesopores are estimated by TEM image of the sample.

![Fig. 8. Transmission electron microscope images for $\text{SO}_2^2-/\text{Al-MCM-41}$.](image)

Both pore channels and hexagonal symmetry can be clearly identified in the TEM image for $\text{SO}_2^2-/\text{Al-MCM-41}$ samples which indicate that the MCM-41 samples have only one uniform phase as inferred from the XRD results. The pore sizes are observed by TEM analysis while the results are in agreement with the results obtained from N$_2$-adsorption measurements. The pore size is smaller in $\text{SO}_2^2-/\text{Al-MCM-41}$ than that in Al-MCM-41.

3.9. TPD-pyridine analysis

The acidities of the Al-MCM-41 and $\text{SO}_2^2-/\text{Al-MCM-41}$ samples were characterized by the TPD of pyridine. The strength appears to be rather moderate as nearly all the pyridine desorbed below 300 °C. The acidities (mmol/g) based on the pyridine desorbed by the samples beyond 100 °C are presented in Table 1. The number of acid sites is higher in the $\text{SO}_2^2-/\text{Al-MCM-41}$ than in Al-MCM-41 due to the impregnation of sulfuric acid on the Al-MCM-41.

3.10. Acylation of 2-methoxynaphthalene

In our experiments it was observed that the yield of 2A-6MN was higher than that of 1A-2MN, 1-acetyl-8-methoxynaphthalene and diacetylmethoxynaphthalene. The mechanism proposed by Guisnet et al. [43] for the formation of 2A-6MN from 2MN in strong acid medium involves the acylation of 2MN with acetic anhydride as acylating agent.

The acylation of 2-MN with acetic anhydride over $\text{SO}_2^2-/\text{Al-MCM-41}$ leads to a complex mixture of products, in which 2A-6MN is primary stable and 1A-2MN is primary unstable. It is well known that the presence of an electron-donating group like methoxy activates
the 1, 6 and 8 positions of the naphthalene ring. The 1-position is more active than the other two positions, and acylation of 2-methoxynaphthalene generally occurs at this kinetically controlled position. However, migration of the acyl group from 1 to 8 positions [2] and protodeacylation of the acyl group at the 1-position [44] results in the formation of the thermodynamically most stable 6-acylated isomer. Steric hindrance to acylation is in the order 1- > 8- > 6-position. Hence, the isomerization of the sterically hindered ketones like 1A-2MN to sterically less hindered isomers like 6- and 8-acetyl-2-methoxynaphthalene will be favored. 1A-2-MN can follow an intramolecular transacylation to yield other acetyl-methoxynaphthalenes (i.e.,1-acetyl-8 methoxynaphthalene) [43], while consecutive acylation of the products is also possible [45] providing different isomers of the diacetylmethoxynaphthalene and is shown in Fig. 9.

3.10.1. Influence of conversion of 2MN and selectivity of 2A-6MN

When the reaction was carried out at 120 °C in the presence of SO_4^2-/Al-MCM-41, the conversion of 2MN was 60.1% and selectivity of 2-acetyl-6-methoxynaphthalene was highest at 72.1%. Hence, all the subsequent experiments in different conditions were carried out only with SO_4^2-/Al-MCM-41 catalyst; the results are compared with that of various catalysts to synthesis of 2A-6MN, which resulted into higher yield (Table 3).

The rate of acylation of 2MN depends upon the pore structure and acidity behavior of the catalyst. The acidity of SO_4^2-/Al-MCM-41 and Al-MCM-41 are given in Table 1. As it was reported, the acidity is higher in the SO_4^2-/Al-MCM-41 than that of Al-MCM-41. Hence the yield of the final product 2A-6MN depends on the rate of acylation of conversion, which in turn depends on substrate and catalyst features (pore structure and acidity). This observation indicates that number of Lewis acid sites in SO_4^2-/Al-MCM-41 is higher but Bronsted acid sites is lower than that in Al-MCM-41 due to the higher number octahedral Al-ions coordinated on the silica surface. Thus, the selectivity of 2A-6MN is higher in SO_4^2-/Al-MCM-41 than that of other catalysts (Table 3).

3.10.2. Effects of reaction time

Acylation of 2MN was carried out with acetic anhydride to 2MN molar ratio = 2 and 50 mL of 1,2-dichloroethane as solvent on SO_4^2-/Al-MCM-41 catalyst at

![Chemical structures](image)

- most activated position for the electrophillic substitution on 2- methoxynaphthalene
- activated position
- low activated position

1-direct acylation; 2-intermolecular transacylation of 1-acetyl-2-methoxynaphthalene; 3- protodeacylation of 1-acetyl-2-methoxynaphthalene; 4- intramolecular transacylation of 1-acetyl-2-methoxynaphthalene; 5- consecutive acylation of monoacylated products.

Fig. 9. Reaction of 2MN and AC_2O in presence of SO_4^2-/Al-MCM-41.
In the range of time between 1–48 h and is as shown in Fig. 10. 2MN is mainly transformed into 1A-2MN and 2A-6MN. Small amounts of the other monoacylated methoxynaphthalene isomers (1-acetyl-8-methoxynaphthalene) are produced. As the reaction progresses, traces of diacylated compounds (i.e. diacetylmethoxynaphthalene) are formed. The conversion of 2MN is 33.4% at 1 h and then slowly levels off to a final value 60.1% at 24 h. Initially, 1A-2MN is formed with a slight selectivity over 2A-6MN. With longer reaction times, the opposite selectivity (2A-6MN) is observed (Fig. 10).

3.10.3. Effects of reaction temperature with reaction time

The acylation of 2MN over SO$_2$/Al-MCM-41 at various reaction temperature (40–140 °C) and reaction time (1–48 h) were carried out with acetic anhydride to 2MN molar ratio = 2 and 50 mL of 1,2-dichloroethane as solvent and the results are shown in Fig. 11. The conversion of 2MN and selectivity of 2A-6MN increases, but the 1A-2MN selectivity decreases significantly when the reaction time (24 h) was increased up to 120 °C.

| Reaction conditions: Catalyst, 2 g; reaction time, 24 h; reaction temperature, 120 °C; solvent, 50 mL of 1,2-dichloroethane; AC$_2$O/2MN ratio = 2; 1A-2MN, 1-acetyl-2-methoxynaphthalene; 6A-2MN, 6-acetyl-2-methoxynaphthalene, X, conversion of 2MN (%); S$_1$, selectivity of 1A-2MN (%); S$_2$, selectivity of 6A-2MN (%); others, 1-acetyl-8-methoxynaphthalene, diacetyl methoxynaphthalene.

![Figure 10. Variation of conversion of 2MN and selectivity of isomers with reaction time over SO$_2$/Al-MCM-41 at 120 °C (50 mL of 1,2-dichloroethane and AC$_2$O/2MN = 2).](image)

![Figure 11. Variation of conversion of 2MN (a), selectivity 1A-2MN (b), and selectivity of 2A-6MN (c) with reaction time over SO$_2$/Al-MCM-41 at different temperature (50 mL of 1,2-dichloroethane and AC$_2$O/2MN = 2).](image)
After 120 °C, when the reaction temperature was increased, the conversion of 2MN increases but the selectivity of 1A-2MN and 2A-6MN slightly decreases at 48 h. However, the small amounts of the other monocylated methoxynaphthalene isomers and traces of diarylated compounds are formed and may be due to the protiodeacylation of the acyl group. The increase in the temperature leads also to catalyst samples becoming darker in color after reaction and likely indicates increasing carbonaceous residue contents.

3.10.4. Effect of acetic anhydride (AC2O)/2MN molar ratio with reaction time

The acylation of 2MN over SO2/Al-MCM-41 at various volume of acetic anhydride to 2MN molar ratio and 50 mL of 1,2-dichloroethane as solvent was carried out at 120 °C reaction temperature. The results are shown in the Fig. 12. The ratio of acetic anhydride to 2MN was varied while a constant amount of 2MN and total reaction solution volume was maintained. At early reaction times, the concentration of the acylating agent has practically no influence on the conversion of 1A-2MN and 2A-6MN. Thus, the reaction order is close to zero order. At longer reaction time, the effect of the ratio of acetic anhydride to MN is different for the formation of 1A-2MN and 2A-6MN (Fig. 12). At longer reaction times, the conversion of 2MN and selectivity of 2A-6MN increases but the 1A-2MN decreases when the ratio of AC2O/2MN was increased. After AC2O/2MN ratio = 2, when the AC2O/2MN ratio was increased, the conversion of 2MN and selectivity of 2A-6MN decreases. This may be due to the catalyst rapidly turns into dark solid that is indicative of a large formation of heavy products and also small amounts of diarylated compounds are formed.

3.10.5. Effect of different zeolites and Al-MCM-41 as catalysts

Both the catalytic activity and the yield and selectivity of 2A-6MN follow: SO3/Al-MCM-41 > H-β > USY > H2SO4 > H-ZSM-5 > silica–alumina > Al-MCM-41 from the catalytic results in Table 3. Based on the results from FTIR of adsorbed pyridine, TPD of the ammonia and those reported elsewhere [46], the catalyst acid strength also exhibits a similar trend, except H-ZSM-5 zeolite. As the acylation of 2MN is an acid-catalyzed reaction; the conversion of 2MN is correlated to the catalyst acid strength and the conversion of 2MN with various catalysts was shown in Table 3. Although the acid strength of H-ZSM-5 is the highest among all solid catalysts, its low catalytic activity is due to the small pore size that hinders both the entry of 2MN and the formation of 2A-6MN. The 2A-6MN selectivity with various catalysts is shown in Table 3. The selectivity of 2A-6MN increases from 14.5 to 72.1 wt.% when Al-MCM-41 is impregnated with 0.8 N H2SO4, while, a value is so much higher than that obtained from sulfuric acid. Therefore, sulfuric acid modification of Al-MCM-41 enhances the catalyst activity. To investigate the reasons for such a result, the sulfated Al-MCM-41 was stirred and washed with deionized water. The filtrate was found via atomic absorption spectroscopy to contain aluminum cation. Therefore the non-framework aluminum existing in the intrachannel space is supposed to increase the catalyst activity due to the increase of Lewis acidity [47].
3.10.6. Effect of solvents

The solvents employed for acylation of 2MN exerted a significant effect on the conversion and selectivity of 2A-6MN with acetic anhydride as acylating agent and AC$_2$O/2MN = 2 at 120 °C for 24 h over SO$_2^\text{4}/$Al-MCM-41 and the results is shown in the Table 4. The selectivity of 2A-6MN follow: 1,2-dichloroethane > dichloromethane > nitrobenzene > cyclohexane > nitromethane > sulfolane from the catalytic results in Table 4. 1,2-dichloroethane and dichloromethane showed the higher activity and selectivity of 2A-MN, because the solvents can compete with reactants for adsorption on the surface acidic sites. A non-polar solvent (cyclohexane) or a very polar solvent (nitromethane) showed slightly lower selectivity of 2A-6MN compared with 1,2-dichloroethane and dichloromethane. Sulfolane showed unusually high selectivity toward 1A-2MN over SO$_2^\text{4}/$Al-MCM-41. Herein SO$_2^\text{4}/$Al-MCM-41 did not change its Si/Al ratio and sulfate content after acylation of 2MN with acetic anhydride in both sulfolane and 1,2-dichloroethane solvents. Consequently, it was concluded that the low selectivity of 2A-6MN in sulfolane was not due to the modified catalytic species but due to the properties of the solvent itself.

3.10.7. Recyclability

After the initial use, the SO$_2^\text{4}/$Al-MCM-41 usually suffers from the activity loss and hence the catalyst needs to be regenerated by calcination. In contrast, SO$_2^\text{4}/$Al-MCM-41 is excellent catalyst for the acylation of 2MN with acetic anhydride as acylating agent to 2A-6MN. It can be recycled by washing with dichloromethane and ethyl acetate at 40 °C followed by hot water to remove the organics and unreacted 2MN. The recycled SO$_2^\text{4}/$Al-MCM-41 catalyst was washed 5 times with dichloromethane and ethyl acetate. It was dried at 140 °C overnight. No loss of activity was observed after 4 runs. Instead, its selectivity is to remain constant with each cycling (Table 5). It was verified that the reaction did not occur in the absence of catalyst. Also, the sulfate ion in recycled samples confirmed that SO$_2^\text{4}/$Al-MCM-41 was resistant to leaching under reaction conditions tested in this study.

3.11. Leaching studies of SO$_2^\text{4}/$Al-MCM-41

From the experiments on leaching studies carried out using SO$_2^\text{4}/$Al-MCM-41 it was observed no leaching of SO$_2^\text{4}$ from the catalyst after catalytic reaction.

4. Conclusions

Mesoporous Al-MCM-41 and SO$_2^\text{4}/$Al-MCM-41 were synthesized under hydrothermal and sulfuric acid impregnation conditions, respectively. The materials were characterized using ICP-AES, Nephelometer, XRD, N$_2$-adsorption, FT-IR, TG-DTA, Solid-StateMAS-NMR, SEM, TEM and TPD-Pyridine techniques. Sulfuric acid treatment of Al-MCM-41 sample results in a decrease of surface area from 1099 to 698 m$^2$/g and pore volume from 1.48 to 0.84 cm$^3$/g. The number of Lewis acid sites is higher in SO$_2^\text{4}/$Al-MCM-41 than that of Al-MCM-41 materials. The materials were evaluated for their efficiency with respect to acylation of 2MN in the liquid phase for the

### Table 4

<table>
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<tr>
<th>Solvents</th>
<th>1 h</th>
<th></th>
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<th></th>
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<th></th>
<th></th>
<th></th>
<th>24 h</th>
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<td></td>
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<td>$S_1$</td>
<td>$S_2$</td>
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### Table 5

<table>
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<tr>
<th>Cycle (catalyst used)</th>
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<th>Selectivity (wt%)</th>
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<tr>
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<td>25.1</td>
</tr>
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</table>

Catalyst, 2 g of SO$_2^\text{4}/$Al-MCM-41; reaction time, 24 h; reaction temperature, 110 °C; solvent, 50 mL of 1,2-dichloroethane; 1A-2MN, 1-acetyl-2-methoxynaphthalene; 6A-2MN, 6-acetyl-2-methoxynaphthalene; others, 1-acetyl-8-methoxynaphthalene, diacetylaminobenzene.
production of 2A-6MN. The SO$_2$/$\text{Al-MCM-41}$ catalyst has much higher activity than other catalysts tested due to the higher catalytic activity. After the catalytic reaction, no leaching of SO$_2$ was detected.

Acknowledgment

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References