

Esterification of alkyl acids with alkanols over MCM-41 molecular sieves: Influence of hydrophobic surface on condensation reaction

S. Ajaikumar^a, A. Pandurangan^{a,b,*}

^a Department of Chemistry, Anna University, Guindy, Chennai-600 025, India

^b Center for Applied Energy Research, University of Kentucky, Lexington, KY 40511-8410, USA

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Abstract

The Al-MCM-41 mesoporous materials with Si/Al ratios 29, 52, 74 and 110 were synthesized by hydrothermal method and characterized by powder X-ray diffraction (XRD), nitrogen adsorption–desorption measurements (BET), ²⁹Si-MAS-NMR, ²⁷Al-MAS-NMR, DRIFT, SEM and TGA–DTG techniques. The XRD studies indicated ordered hexagonal structure for all the samples. The specific surface area, pore volume, and pore size distribution of the samples were comparable to mesoporous molecular sieves. The catalytic activity of these materials was tested for the esterification of acetic acid (AA) with 1-hexanol (HeOH), 2-ethyl-1-hexanol (2E-1HOH), isoamyl alcohol (IAOH), and propionic acid (PA) with isoamyl alcohol under autogenous conditions. The effects of temperature from 75 to 150 °C, initial molar feed ratios, acid:alcohol, 1:1, 1:2, 2:1, 3:2 and 5:2, amount of catalyst and the reaction time were also investigated. The yield of the product ester was observed with higher for the feed ratio 5:2. Under the experimental conditions, Al-MCM-41 (110) a hydrophobic material showed higher alcohol conversion with acetic acid at 125 °C than the other catalysts. The conversion with respect to the alcohols followed the order HeOH (88.4%) > IAOH (87.7%) > 2E-1HOH (84.4%). All the product esters showed selectivity close to 100%. The hydrophobic properties of the catalysts were suggested to play important role in the esterification reaction.

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1. Introduction

Organic esters are very important class of chemicals which have applications in different areas of chemical industry such as perfumes, flavours, pharmaceuticals, plasticisers, solvents and intermediates [1]. The ester of isoamyl alcohol, namely, isoamyl acetate, finds wide industrial applications. It is used in large quantities as artificial flavouring (preservative in sodas, soft drinks, etc., banana-flavoured food items, artificially pear-flavoured food articles), as additive in cigarettes, and as solvent for tannins, nitrocellulose, lacquers, celluloid, and camphor. It is also used for the manufacture of celluloid cements, waterproof varnishes, artificial silk, leather, pearls, photographic films, bronzing liquids and metallic paints, perfuming shoe polish and dyeing, and finishing textiles [2].

The esterification reaction is a liquid-phase process, where the limiting conversion of the reactants is determined by equilibrium. Typically, esterification reactions are very slow; it requires several days to attain the equilibrium in the absence of catalyst. Therefore, the reaction is enhanced by an added catalyst. Account to literatures, the use of many acidic catalysts such as fluorhydric, sulfuric acids, *p*-toluene sulphonic acid (Brønsted acidic) and other mineral acids [3–8] creates many disadvantages to commercialize the process. As these substances are miscible with the reaction medium it is difficult to separate them. Furthermore, at higher catalyst concentrations equipment corrosion can occur. Where as metal-containing Lewis acid catalyst like Sn-octoate [9] needs to be removed carefully after reaction. Hence, there is a need to develop an environmentally benign method for the esterification of acids using more active, selective and reusable solid acid catalyst. But, sulphated oxides [10–12], hydrous zirconium oxide [13] and alumina catalysis (Lewis acid) reaction shows that higher conversion of alcohols on dehydration rather than the esterification. Other solid acids like cationic

* Corresponding author. Tel.: +91 44 22203158; fax: +91 44 22200660.
E-mail address: pandurangan_a@yahoo.com (A. Pandurangan).

exchange resins shows better activity towards esterification but it has poor heat resistance that deactivates a lot as the reaction proceeds [14,15]. Hence the overall activities of these catalysts are far less than those of sulphuric acids. Heteropolyacids [16] are the active heterogeneous which have common disadvantages like low thermal stability and low surface area. In the case of porous materials like large-pore zeolites such as X and Y for catalyzing the esterification has recently been suggested by Bergk [17] and no relationship between the activity and its surface acidity was observed.

For economic and ecological reasons, organic synthetic chemists face an increasing obligation to optimize their synthetic methods in order to produce the desired product in high yield and selectivity through a safe and environmentally acceptable process [18]. So, the challenge was to replace them by solid MCM-41 acids, which are easier to separate from the products, reusability, and higher acid strength, hydrophilic and hydrophobic properties. The main drawback of esterification reactions using alcohol is that water is formed as a by-product, requiring azeotropic distillation to remove water during the reaction which otherwise would deactivate the catalyst [19]. On the other hand, because of the low values of the equilibrium constants of the esterification reactions, it is well known that in order to obtain higher yield of esters, the reactions must be forced to completion by removing the water which was formed during the course of reaction and/or by operating with an excess of one of the two reactants (acid or alcohol). The effective segregation of water needs a high reaction rate, that is, a very active catalyst such as sulfuric acid. However, the rate of zeolite-catalyzed esterification reactions is much lower than that of the reactions catalyzed by sulfuric acid [20,21]. The possibility to segregate the water formed during the esterification reaction over zeolite molecular sieves has not yet been achieved.

The objective of this work is to study the role of hydrophobic and hydrophilic nature of the catalyst for the esterification of alkyl acids with alcohols using higher and lower hydrophobic mesoporous Al-MCM-41 molecular sieves. Lower % of aluminium containing Al-MCM-41 (110) has higher hydrophobic nature and higher hydrothermal stability towards water that is formed during the reaction. Higher hydrophobic nature prevents ester hydrolysis, which in turn prevents the backward reaction. Less acidic MCM-41 does not have extra-framework Lewis acid aluminium, which reduces the dehydration of alcohols. Hence, it avoids some of the by-products, thereby improving the reaction product selectivity.

2. Experimental

2.1. Materials

The chemicals used for the synthesis of Al-MCM-41 with various Si/Al ratio: 29, 52, 74 and 110 were sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$), aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), cetyl trimethyl ammonium bromide ($\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+\text{Br}^-$), and sulfuric acid (H_2SO_4). All chemicals used were AR grade, purchased from E-Merck India Limited. Acetic acid, propionic acid, 2-ethyl-1-hexanol, 1-hexanol, isoamyl alcohol were used

for the reaction. These chemicals were bought from SRL chemicals with a claimed purity.

2.2. Synthesis of Al-MCM-41

Al-MCM-41 (Si/Al = 29, 52, 74 and 110) samples were synthesised hydrothermally using a molar gel composition of $\text{SiO}_2 : x\text{Al}_2\text{O}_3 : 0.2 \text{ CTAB} : 0.89\text{H}_2\text{SO}_4 : 120\text{H}_2\text{O}$ (x = varies with Si/Al ratio). Sodium metasilicate and aluminium sulphate were used as the sources for silicon and aluminium, respectively. Cetyl trimethyl ammonium bromide (CTAB) was used as the template. In a typical synthesis, 10.6 g of sodium metasilicate in water was combined with an appropriate amount of aluminium sulphate in distilled water and the pH of the solution was adjusted to 10.5 by adding 1 M H_2SO_4 with constant stirring to form a gel. After 30 min, an aqueous solution of CTAB was added to it and the mixture was stirred for 1 h at room temperature. The suspension was then transferred into a 300 ml stainless steel autoclave, sealed and heated in a hot air oven at 145°C for 48 h. After cooling to room temperature, the product that formed was filtered, washed with deionised water and dried. The dried materials were calcined at 550°C for 1 h in nitrogen atmosphere and for 5 h in air. The calcined materials were converted into H-form by repeated ion-exchange with aqueous 1 M NH_4Cl solution, followed by calcination at 550°C for 5–6 h.

2.3. Catalyst characterization

The XRD powder diffraction patterns of the calcined mesoporous Al-MCM-41 (Si/Al = 29, 52, 74 and 110) molecular sieves were obtained with a Stereoscan diffractometer using nickel-filtered $\text{Cu K}\alpha$ radiation and a liquid nitrogen cooled germanium solid-state detector. The diffractograms were recorded in the 2θ range of 0.7 – 10.7° in the steps of 0.02° with a count time of 15 s at each point for MCM-41 molecular sieves. Surface area, pore volume and pore size distribution were measured by nitrogen adsorption at 77 K using an ASAP-2010 porosimeter from Micromeritics Corporation, GA. The samples were degassed at 623 K and 10^{-5} Torr overnight prior to the adsorption experiments. The mesopore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.5 (p/p_0) by assuming that all the mesopores were filled with condensed nitrogen in the normal liquid state. Pore size distribution was estimated using the Barrett, Joyner and Halenda (BJH) algorithm (ASAP-2010) available as built-in software from Micromeritics. ^{29}Si -MAS-NMR spectra were recorded with a DRX-500 FT-NMR Spectrometer at a frequency of 59.64 MHz, spinning speed of 8 kHz, pulse length of $2.50 \mu\text{s}$ (45° pulse), delay time of 10 s and spectral width of 335 ppm. Two thousand scans were acquired with reference to trimethylsilylpropanesulfonic acid (TSP). Solid-state ^{27}Al -MAS-NMR spectra were recorded at a frequency of 104.22 MHz, spinning rate of 8 kHz, pulse length of $1.0 \mu\text{s}$, delay time of 0.2 s and spectral width of 330 ppm. The total number of scans was 150 and the line broadening was 50 Hz. The ^{27}Al chemical shifts are reported in relation to the solution of aluminium nitrate. The SEM images of typical samples of mesoporous Al-MCM-41 materials were obtained with

a JEOL 640 instrument. Samples were gold coated using an Instrumental Scientific Instrument PS-2 coating unit. The SEM pictures were developed on thin photographic paper.

The acidity of Al-MCM-41 was analyzed by pyridine adsorption followed by FT-IR spectroscopy. Finely ground catalyst sample (10–15 mg) was pressed for 2 min at 10^{-7} Torr cm^{-2} pressure under vacuum into a self-supporting wafer. The wafers were calcined under vacuum (133.322×10^{-3} Nm $^{-2}$) at 500 °C for 2 h, followed by exposure to pyridine vapour at ambient temperature for 1 h to allow the pyridine to permeate the samples. The wafers were then allowed to cool to ambient temperature and evacuated to remove the physisorbed pyridine. The thin wafer was placed in the FT-IR cell and the spectrum was recorded in absorbance mode on a Nicolet 800 (AVATAR) FT-IR spectrometer, fully controlled by the OMNIC software, and in an all-glass high-vacuum system. The difference between the spectra of pyridine adsorbed on the samples and that of the reference was obtained by subtraction.

2.4. Catalytic runs and analysis of the product

Esterification reactions were carried out in a stainless steel autoclave (10 ml) in the temperature range 75–150 °C under autogenous pressure. A typical reaction mixture in the reactor contained acid (0.1 mmol) and alcohol (0.1 mmol). To this mixture, 0.05 g of freshly activated catalyst (particle diameter close to 0.12–1.0 μm) was added. Activation of the catalyst was done by calcination at 550 °C in air for 5 h. The autoclave temperature was then raised to 100, 125 and 150 °C as required and maintained at the desired temperature during the reaction period of 5 h. After the reaction, the autoclave was cooled to room temperature, the reaction mixture was collected from the autoclave and the catalyst was removed by filtration. The effect of reaction period, molar ratios of the reactants, and amount of catalyst required on alcohol conversion and product selectivity were studied. Analysis of the products was carried out in gas chromatograph (Shimadzu GC-17A, DB-55 capillary column with FID detector) using nitrogen as the carrier gas. The identification of products was performed on a Shimadzu GC-MS-QP 5000 with a PE-5 capillary column: scan mode 40–400 amu.

3. Results and discussion

3.1. Characterization

3.1.1. XRD

The low angle X-ray diffraction patterns of calcined mesoporous Al-MCM-41 samples with Si/Al ratios 29, 52, 74 and 110 are shown in Fig. 1. All the above materials exhibit a strong peak in the 2θ range of 1.9–2.4° due to 100 reflection lines and weak broad signals between 2.5° and 4° (2θ) due to (1 1 0), (2 0 0), and (2 1 0) reflections, indicating the formation of well-ordered mesoporous materials with hexagonal regularity [22–24]. The d_{100} spacing and the lattice parameter (a_0) calculated as per the literature procedure are presented in Table 1. The calcined materials possess well-defined pore structure due to the condensation of Si–OH groups. These XRD patterns mesoporous

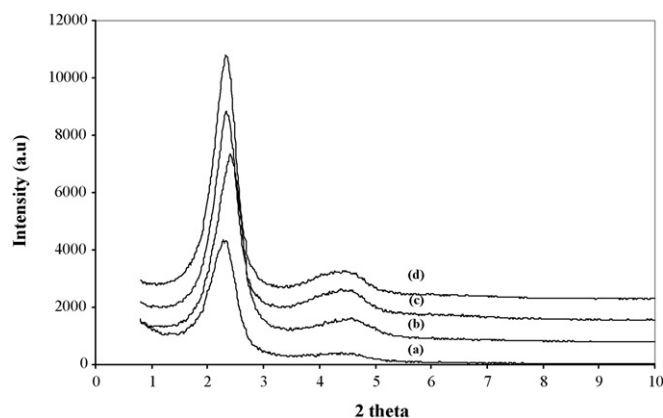


Fig. 1. X-ray diffraction pattern of Al-MCM-41 molecular sieves obtained before calcination: (a) Al-MCM-41 (29), (b) Al-MCM-41 (52), (c) Al-MCM-41 (74) and (d) Al-MCM-41 (110).

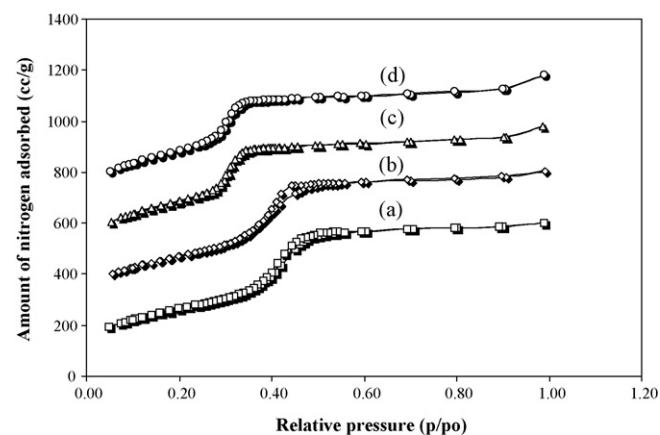


Fig. 2. Adsorption isotherms of Al-MCM-41 molecular sieves: (a) Al-MCM-41 (110), (b) Al-MCM-41 (74), (c) Al-MCM-41 (52) and (d) Al-MCM-41 (29).

aluminosilicate molecular sieves coincide well with the data already reported in the literature [25].

3.1.2. Nitrogen adsorption isotherms

BET surface area, pore size and pore volume of all these samples are summarized in Table 2. It is seen that the surface area decreases as the Si/Al ratio decreases. Fig. 2 shows the N₂ adsorption–desorption isotherms of the materials show a sharp inflection at relative pressures (p/p_0) in the range of 0.27–0.42. This corresponds to capillary condensation of N₂ in the mesopores with completely reversible isotherms but with little hysteresis, characteristic of ordered mesoporous materials.

Table 1
Textural properties of the catalysts

Catalysts	Si/Al	ICP	Calcined		Uncalcined	
			d_{100}	Unit cell, a_0 (nm)	d_{100}	Unit cell, a_0 (nm)
Al-MCM-41 (29)	25	29	37.81	4.37	38.47	4.44
Al-MCM-41 (52)	50	52	37.45	4.32	38.47	4.44
Al-MCM-41 (74)	75	74	37.45	4.32	38.19	4.41
Al-MCM-41 (110)	100	110	37.81	4.36	38.19	4.41

Table 2
Surface area, pore size and pore volume of the catalysts

Catalysts	Surface area (m ² /g)	Surface area BJH _{Ads} (m ² /g)	Surface area BJH _{Des} (m ² /g)	Pore size BJH _{Ads} (nm)	Pore size BJH _{Des} (nm)	Pore volume BJH _{Ads} (cm ³ /g)	Pore volume BJH _{Des} (cm ³ /g)
Al-MCM-41 (29)	955	1167	1163	2.671	2.630	0.959	0.933
Al-MCM-41 (52)	978	1205	1198	2.660	2.625	0.956	0.934
Al-MCM-41 (74)	1037	1345	1295	3.194	3.263	0.977	0.972
Al-MCM-41 (110)	1044	1334	1274	3.482	3.352	0.969	0.962

The sharpness of the inflection reflects the uniformity of the pore sizes and the height indicates the pore volume. Fig. 3 shows the pore size distribution of the mesoporous part is centered at about 26.2–33.5 Å and this is attributed further to the mesopore ordering with well-defined pore structures, the data obtained coincide well with those already reported in the literature [26,27].

3.1.3. Thermal analysis

The thermal properties of the samples were investigated by TGA and DTG (Fig. 4). The initial weight loss from 50 to 120 °C is due to the desorption of physically adsorbed water on the mesopores. The weight loss from 120 to 350 °C is due to the removal of organic template. The minute quantity of weight loss above 350–550 °C is related to water loss from the condensation of adjacent Si–OH groups to form siloxane bonds [22]. The individual values of weight losses for all the four catalysts are presented in Table 3.

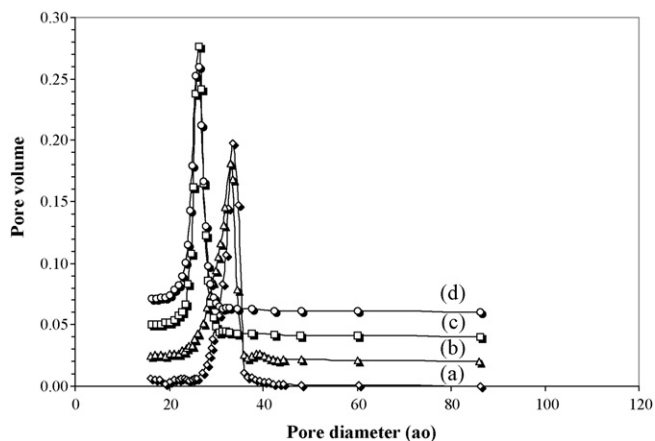


Fig. 3. Pore size distribution in Al-MCM-41 (adsorption isotherms): (a) Al-MCM-41 (110), (b) Al-MCM-41 (74), (c) Al-MCM-41 (52) and (d) Al-MCM-41 (29).

Table 3
TGA and DTG spectral data of uncalcined mesoporous Al-MCM-41 molecular sieves: Al-MCM-41 (29, 52, 74 and 110)

Catalyst	Weight loss (wt.%)			
	Total	40–100 °C	100–300 °C	300–600 °C
Al-MCM-41 (29)	33.14	3.76	16.74	12.64
Al-MCM-41 (52)	43.10	5.57	26.17	11.36
Al-MCM-41 (74)	45.01	5.72	32.61	5.68
Al-MCM-41 (110)	46.25	5.28	37.34	5.63

3.1.4. ²⁹Si-, ²⁷Al-MAS-NMR

The ²⁹Si-MAS-NMR spectra of the calcined Al-MCM-41 materials are shown in Fig. 5. The broad signal at –111 ppm in the spectra can be assigned to Si(OSi)₄. The shoulder in the range between –103 and –108 ppm is due to Si(OAl). These spectral features coincide well with those reported by previous researchers [28,30,31]. The ²⁷Al-MAS-NMR spectra of the samples are shown in Fig. 6. The peak around 54 ppm is attributed to the presence of aluminum in tetrahedral coordination [28,29]. ²⁷Al-MAS-NMR spectra of the calcined Al-MCM-41 (29, 52

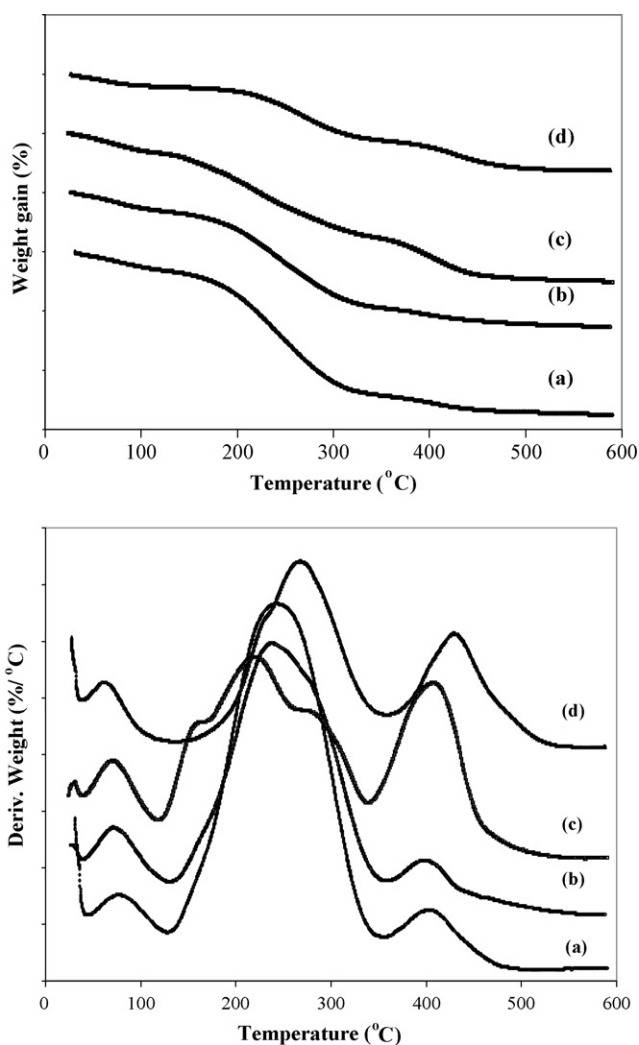


Fig. 4. TGA and DTG curves for as-synthesised mesoporous Al-MCM-41 molecular sieves: (a) Al-MCM-41 (110), (b) Al-MCM-41 (74), (c) Al-MCM-41 (52) and (d) Al-MCM-41 (29).

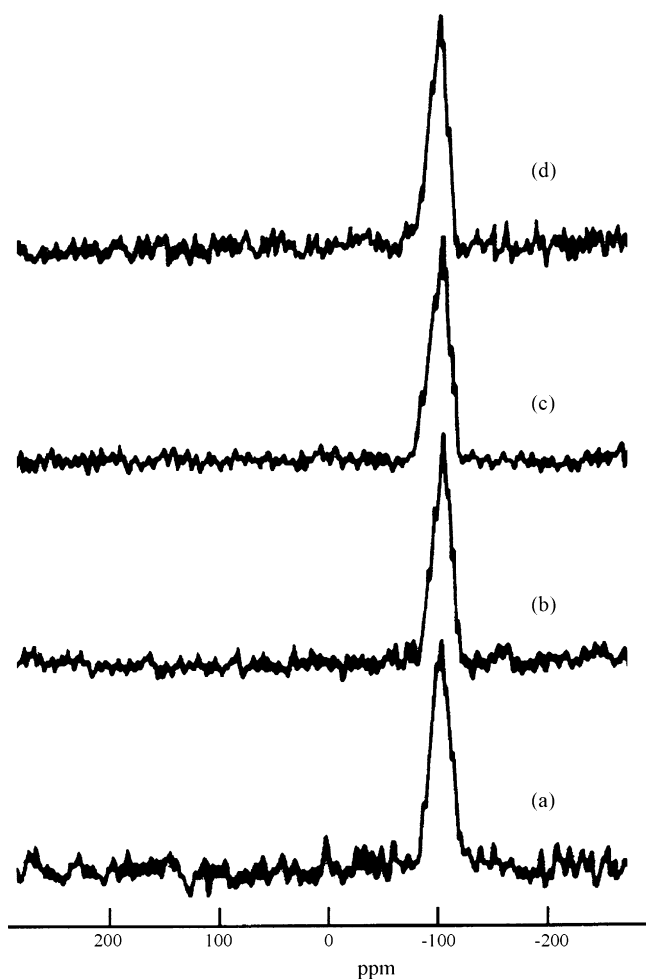


Fig. 5. ^{29}Si -MAS-NMR spectra of calcined mesoporous Al-MCM-41 molecular sieves: (a) Al-MCM-41 (110), (b) Al-MCM-41 (74), (c) Al-MCM-41 (52) and (d) Al-MCM-41 (29).

and 74) shows a less intense peak around 0 ppm. This peak is due to the extra framework aluminum species in octahedral coordination and it is expected to arise out of the framework dealumination during calcination [31].

3.1.5. Pyridine FT-IR analysis

The distribution of both Brönsted and Lewis acid sites on the mesoporous materials was confirmed by FT-IR techniques. Fig. 7 shows the pyridine adsorbed FT-IR spectra of mesoporous Al-MCM-41 materials. The samples exhibit expected bands around $1450\text{--}1650\text{ cm}^{-1}$ due to the adsorbed pyridine on both Lewis and Brönsted acid sites. The peak appeared at 1545 cm^{-1} indicates the adsorption of pyridine on Brönsted acid sites, and a peak appeared at 1455 and 1623 cm^{-1} attributed to pyridine adsorbed on Lewis acid sites. A broad peak that appeared around 1500 cm^{-1} is the combination band of both Brönsted and Lewis acid sites. These data coincide well with those already reported in the literature [32,33].

3.1.6. SEM analysis

The SEM photographs showed the size and morphology of the mesoporous catalysts with highly ordered hexagonal crys-

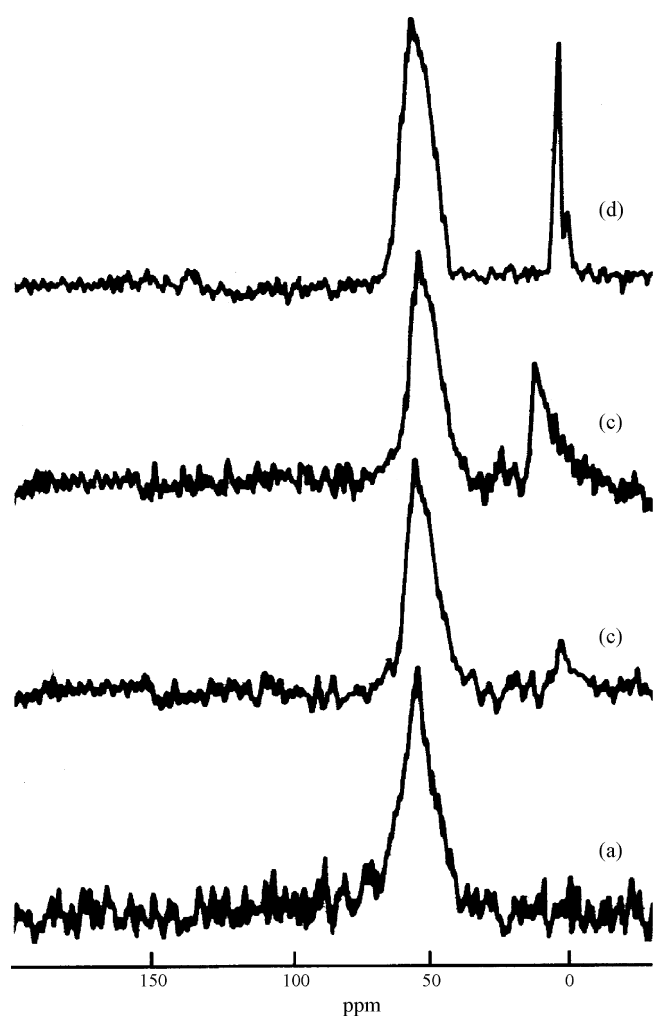


Fig. 6. ^{27}Al -MAS-NMR spectra of calcined mesoporous Al-MCM-41 molecular sieves: (a) Al-MCM-41 (110), (b) Al-MCM-41 (74), (c) Al-MCM-41 (52) and (d) Al-MCM-41 (29).

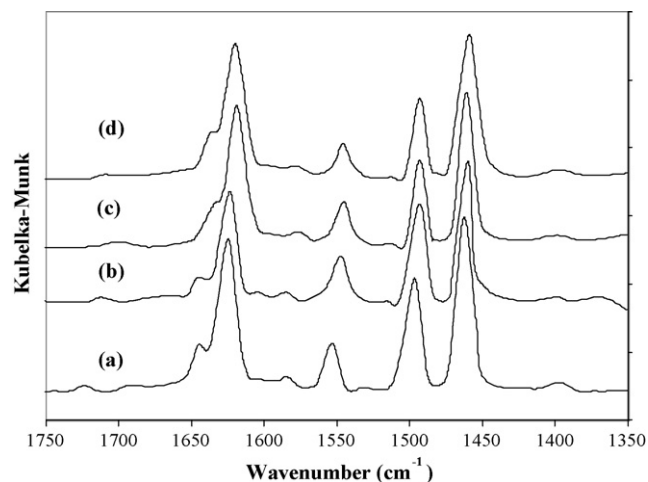


Fig. 7. DRIFT spectra of pyridine adsorption region of mesoporous materials: (a) Al-MCM-41 (29), (b) Al-MCM-41 (52), (c) Al-MCM-41 (74) and (d) Al-MCM-41 (110).

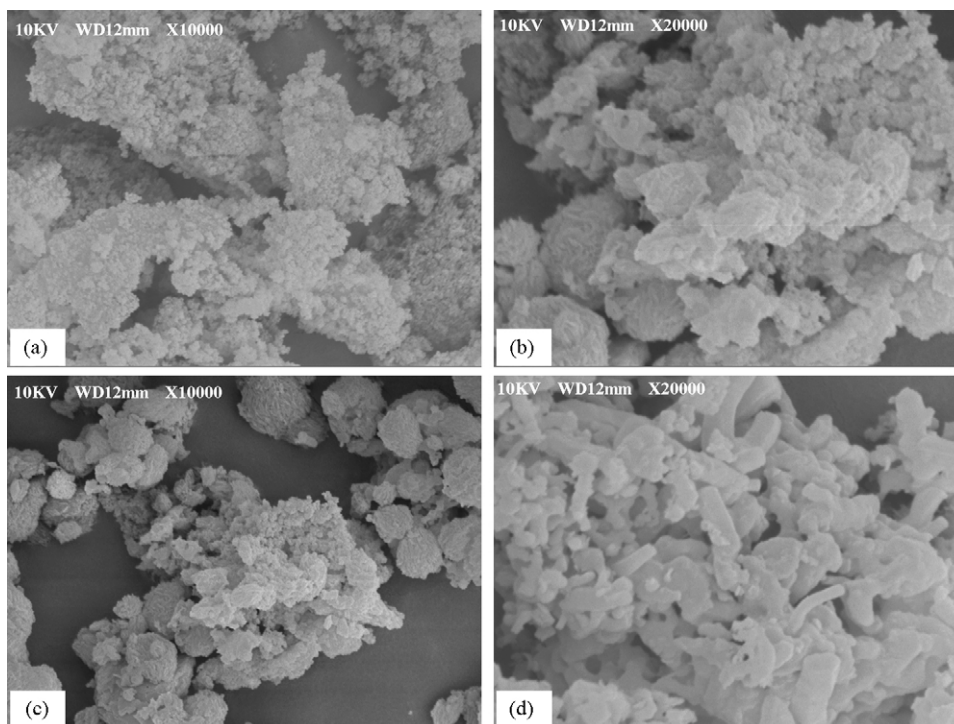


Fig. 8. SEM pictures of Al-MCM-41 molecular sieves: (a) Al-MCM-41 (29), (b) Al-MCM-41 (52), (c) Al-MCM-41 (74) and (d) Al-MCM-41 (110).

tals of mesoporous molecular sieves. The SEM pictures of these catalysts are presented in Fig. 8. The pictures also show the orderly growth of pure hexagonal phase with well-defined sites.

3.1.7. ICP–AES analysis

The aluminum content in Al-MCM-41 for various Si/Al ratios 29, 52, 74 and 110 was recorded using various ICP-AES with Allied Analytical ICAP 9000. The results of Si/Al ratios of the materials are given in Table 1.

3.2. Applications of Al-MCM-41 (29), Al-MCM-41 (52), Al-MCM-41 (74) and Al-MCM-41 (110) catalysts to esterification of alkanols with alkyl acids

3.2.1. Catalytic process

Esterification of acetic acid with 1-hexanol, 2-ethyl-1-hexanol, isoamyl alcohol, and propionic acid with isoamyl alcohol were studied using mesoporous Al-MCM-41 molecular sieves with various Si/Al ratios 29, 52, 74 and 110. Table 4 summarizes the catalytic performances of Al-MCM-41 over esterification of alkanols with alkyl acids. Acid catalyst (generally a mineral acid) protonates the carbonyl group of the acid making it more readily attacked by the nucleophilic oxygen of the alcohol. In the case of solid acid catalyst, the Brønsted acid sites associated to tetrahedrally coordinated Al are the only active ones for the production of esters. The mechanism of the esterification reaction given in Scheme 1 shows that the carbo-cationic species is the common intermediate for producing esters. During esterification in the presence of acid sites, a molecule of water is then eliminated and the ester is formed.

At reflux temperatures and in the presence of an acid catalyst, both the forward and reverse esterification reactions are rapid and the system comes to equilibrium within a few minutes. In order to obtain more amount of ester more amount of alcohol was reacted under the conditions of equilibrium. One technique for accomplishing this is to use a large amount of one of the reagents. Another method is to remove one (or more) of the products as it is formed (e.g., azeotropic distillation of water).

3.2.2. Influence of temperature

The esterification of 1-hexanol (HeOH), isoamyl alcohol (IAOH) and 2-ethyl-1-hexanol (2E-1HOH), using acetic acid (AA) and propionic acid (PA) were studied over Al-MCM-41 (Si/Al = 29, 52, 74, 110). The reaction conducted in autogenous pressure using 0.05 g of catalyst with reactant ratio of 2:1 (alcohol/acid) for a period of 5 h. The reaction yielded four esters namely: hexyl acetate (HXA), 2-ethyl-1-hexyl acetate (2E-1HA), isoamyl propionate (IAP) and isoamyl acetate (IAA). The reaction yields major amount of esters ($\geq 95\%$ selectivity) along with minor amount of dehydrated and etherified products ($\leq 5\%$ selectivity). From Table 4, it can be inferred that alcohol-conversion increases with increase in temperature; Al-MCM-41 (110) shows better conversion than other Si/Al ratios. This may due to the hydrophobic nature of the catalyst, which alters the conversion. The reaction is discussed based on alcohol-conversion, which is in the order of: HXA > IAA > IAP > 2E-1HA. But conversion of alcohol is less than 50% due to the usage of lower % of acid (mole ratio is 2:1 (alcohol/acid)) in this reaction.

The reaction shows better conversion with chain length of alcohol. Climent et al. reported that increase in the carbon chain

Table 4
Influence of temperature on synthesis of esters over Al-MCM-41 (Si/Al=29, 52, 74 and 110) molecular sieves

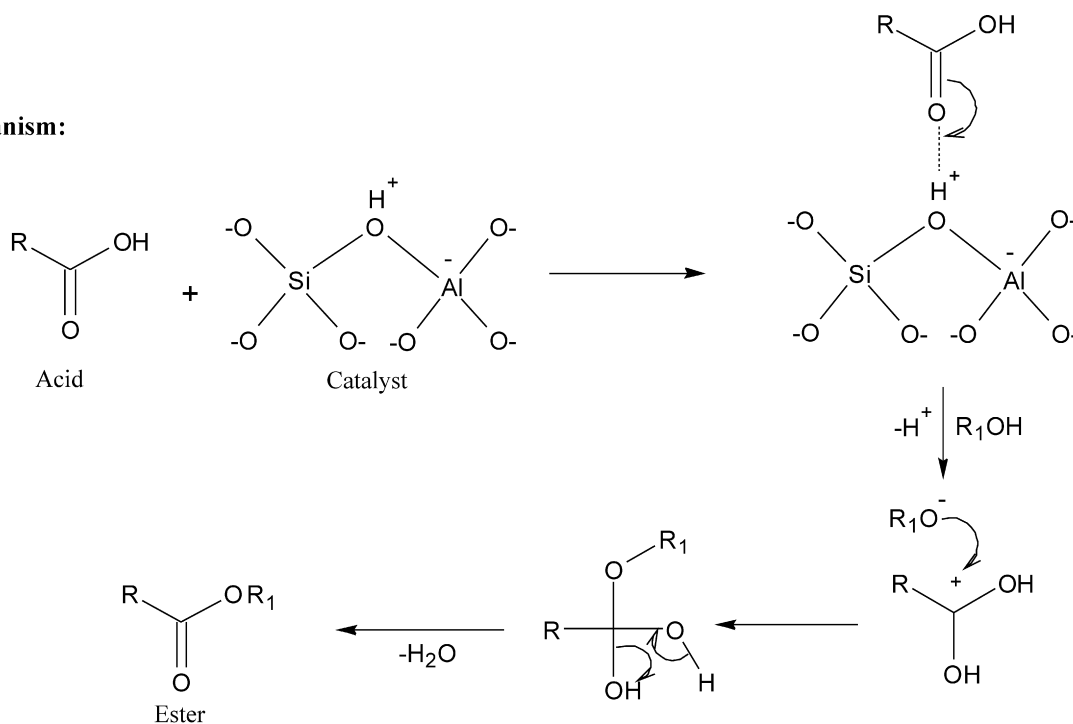
Catalyst	Temperature	2E-1HA (2E-1HOH:AA)		HXA (HeOH:AA)		IAP (IAOH:PA)		IAA (IAOH:AA)	
		Con-alcohol	Selectivity to 2E-1HA	Con-alcohol	Selectivity to HXA	Con-alcohol	Selectivity to IAP	Con-alcohol	Selectivity to IAA
Si/Al=29	75	8.3	96.5	11.3	96.7	9.4	97.1	10.7	96.5
	100	20.8	95.2	26.0	95.5	23.4	96.3	26.5	95.3
	125	29.6	94.6	36.7	94.1	32.8	96.0	34	95.0
	150	38	93.4	43.5	93.8	41.0	95.2	44.5	94.0
Si/Al=52	75	8.7	97.6	11.2	97.8	10.0	98.2	10.8	97.3
	100	20.4	95.6	22.8	95.3	20.8	97.3	21.9	96.5
	125	30.5	95.1	35.9	95.0	30.6	97.2	33.9	96.1
	150	40.1	94.6	42.5	93.2	40.6	95.1	43.8	96.0
Si/Al=74	75	10.4	99.5	13.4	98.5	10.9	99.2	9.3	98.4
	100	18.5	98.2	21.8	98.0	20.5	98.3	21.2	98.2
	125	33.9	96.2	34.6	97.5	34.6	97.8	34.8	97.5
	150	42.7	95.7	46.3	94.1	43.6	96.3	45.9	97.1
Si/Al=110	75	10.9	100	13.6	100	13.8	100	11.2	100
	100	20.1	100	30.6	99.5	22.3	100	23.3	100
	125	30.1	99.5	35.1	99.3	33.7	99.5	37.1	99.5
	150	41.3	99.1	47.3	98.8	44.3	99.3	46.5	99.0

Reaction condition: weight of the catalyst = 0.05 g; reaction period = 5 h; pressure = autogenous pressure; reactor = autoclave; mole ratio = 2:1 (ROH:ACOH).

length, increases the hydrophobicity of alcohol [34]. Hydrophobicity of the catalyst will increase the adsorption of alcohol on the active sites; there by increasing the alcohol-conversion. Table 4 illustrates the increase in the acid chain length with

decrease the alcohol-conversion. This can be compared by the reaction with propionic acid and acetic acid esterification with isoamyl alcohol. The reaction with propionic acid shows lower alcohol-conversion than the reaction conducted with acetic acid.

Mechanism:



$R = CH_3-$; CH_3CH_2-

$R_1 = (CH_3)_2CH(CH_2)_2-$; $CH_3(CH_2)_5-$; $CH_3(CH_2)_3CH(C_2H_5)CH_2-$

Scheme 1. The esterification mechanism of acid and alcohol over catalytic active sites.

The chain length of propionic acid has higher homologue of carbon than acetic acid; this electron-donating tendency of propionic acid reduces the alcohol conversion.

The reaction trend also shows the influence of alcohol. In the first case, when compared with yield of IAA and IAP, IAA shows higher yield than IAP. This is mainly due to higher chain length of propionic acid than acetic acid, which shows considerable influence on the yield of IAP [3]. In the second case, though 2E-1HOH and HeOH have similar chain length (C_6), 2E-1HOH shows lower yield than HeOH. This can be concluded from two different aspects: (a) If inductive effect plays a major role then 2E-1HOH shows higher positive inductive effect (electron donating nature) than HeOH, electron-donating nature enhances the protonation of alcohol on the active sites, which induces the product yield. (b) If steric hindrance play a major role, the 2E-1HA shows lower yield (2E-1HOH used reaction) than the HXA yield (HeOH used reaction) and this might be due to steric hindrance of ethyl group (branched group creates more steric crowded) in the second carbon, which reduces the percentage of alcohol availability in the active sites thereby reduces the 2E-1HA yield. The over all reaction trend shows that increase in the chain length of alcohol, which increases the alcohol-conversion, whereas branched group decreases the alcohol-conversion [3].

3.2.3. Discussion of hydrophilic and hydrophobic nature of the catalyst

The aim of this particular experiment is to explain the hydrophobic nature of the catalyst on the esterification reactions. The hydrophobic character of MCM-41 has been clearly demonstrated by carrying out the adsorption of cyclohexane and water, and benzene and H_2O [22]. The results obtained show that in a hydrophilic zeolite, such as faujasite, the adsorption of H_2O is larger than that of benzene, and when the same adsorbates were used on a sample of siliceous MCM-41, adsorption of benzene is larger than that of H_2O . This clearly indicates that the formation of water (by-product in the condensation reactions) largely influences the product formation. Ma et al. reported that, higher amount of acid sites shows the hydrophilicity, which is confirmed by the results of dealumination process and they proposed that the framework dealuminated catalyst has more hydrophobic nature than the parent catalyst [35].

Based on the previous results, this reaction illustrates the hydrophilic and hydrophobic properties of the mesoporous material. According to Nijhuis et al. water acts as an adsorp-

tion poison over solid acid catalysts [36]. All the products show better yield in the higher Si/Al ratio when compared with lower Si/Al ratio containing Al-MCM-41. The catalytic activity of the different catalysts on esterification reaction follow the order: Al-MCM-41 (110) > Al-MCM-41 (74) > Al-MCM-41 (52) > Al-MCM-41 (29), which shows that, catalyst having lower Si/Al ratio chemisorbs the water molecule due to its hydrophilicity. From the above observation further optimization was conducted with lower % aluminum containing Al-MCM-41.

3.2.4. Influence of mole ratio

By considering the economic factor, since acid is cheaper than alcohol, the reaction was conducted with excess of acid in the feed, which increases the conversion of ester. The reaction was examined with 1:1, 3:2, 2:1 and 5:2 (ACOH:ROH) and the reaction was optimized with higher hydrophobic Al-MCM-41 (110) catalyst of 0.05 g at 125 °C. The reaction was conducted for 5 h under autogeneous condition. The results are presented in Table 5. The alcohol-conversion at 1:1 (ACOH:ROH) shows lower value, whereas the mole ratio; 5:2 (ACOH:ROH) shows the higher alcohol-conversion. This might be due to higher % of acid in the reaction mixture, which facilitates the esterification reaction. The same trend was also observed in all the cases. The trend of alcohol-conversion is shown to increase with decrease in mole ratio in the feed. This can be compared with two mole ratios of 1: 1 and 5: 2 (2.5:1). The ratio 1: 1 shows 65.0% of alcohol-conversion for the preparation of HXA, whereas the same reaction with 2.5:1 (5:2) shows 87.7%, which concludes that higher % of acid in the feed encourages the esterification reactions.

3.2.5. Influence of reaction time

The effect of the reaction time on the esterification of alcohol by acid on Al-MCM-41 (Si/Al = 110) was studied at the optimized temperature of 125 °C using reactant mole ratio of 2:1 (ACOH:ROH) with a reaction time of 1–8 h. The results are presented in Table 6. All the four reactions show that the alcohol-conversion increases with increase in reaction time. From the first hour to second hour of reaction time, the alcohol-conversion increases rapidly, but after the second hour the conversion increases gradually. But, the sixth hour to seventh hour shows only marginal increase in conversion. The seventh to eighth hour shows no change in alcohol-conversion, thereby the seventh hour is considered as the optimized time for the maximum yield of

Table 5
Influence of mole ratio on synthesis of esters over Al-MCM-41 (110) molecular sieves

Mole ratio (ACOH:ROH)	2E-1HA (2E-1HOH:AA)		HXA (HeOH:AA)		IAP (IAOH:PA)		IAA (IAOH:AA)	
	Con-alcohol	Selectivity to 2E-1HA	Con-alcohol	Selectivity to HXA	Con-alcohol	Selectivity to IAP	Con-alcohol	Selectivity to IAA
1:1	56.8	97.5	61.7	97.2	60.0	98.0	65.0	98.5
3:2	58.1	98.1	77.2	97.6	67.6	98.7	76.6	98.8
2:1	78.5	99.5	83.5	98.7	74.9	99.6	81.3	99.0
5:2	84.4	100	88.4	99.0	77.8	100	87.7	99.2

Reaction condition: temperature = 125 °C; weight of the catalyst = 0.05 g; reaction period = 5 h; pressure = autogenous pressure; catalyst = Al-MCM-41 (110); reactor = 10 ml autoclave.

Table 6
Influence of time on synthesis of esters over Al-MCM-41 (110) molecular sieves

Hour (h)	2E-1HA (2E-1HOH:AA)		HXA (HeOH:AA)		IAP (IAOH:PA)		IAA (IAOH:AA)	
	Con-alcohol	Selectivity to 2E-1HA	Con-alcohol	Selectivity to HXA	Con-alcohol	Selectivity to IAP	Con-alcohol	Selectivity to IAA
1	29.4	99.7	40.7	99.5	34.1	100	39.2	100
2	37.4	99.7	54.5	99.5	45.9	99.9	50.5	100
3	45.4	99.5	65.8	99.3	54.2	99.9	61.3	99.9
4	51.7	99.7	76.3	99.3	62.3	99.7	71.8	99.7
5	57.2	99.6	84.4	99.3	67.8	99.2	78.6	99.7
6	61.0	99.4	90.4	99.3	73.8	99.3	84.6	99.5
7	64.3	99.4	94.6	99.2	78.6	99.3	89.1	99.5
8	64.7	99.4	94.9	99.1	79.0	99.4	89.5	99.5

Reaction condition: temperature = 125 °C; weight of the catalyst = 0.07 g; pressure = autogenous pressure; mole ratio = 2:1 (ACOH:ROH); catalyst = Al-MCM-41 (110); reactor = 10 ml autoclave.

Table 7
Influence of catalyst weight on synthesising of esters over Al-MCM-41 (110) molecular sieves

Wt. catalyst	2E-1HA (2E-1HOH:AA)		HXA (HeOH:AA)		IAP (IAOH:PA)		IAA (IAOH:AA)	
	Con-alcohol	Selectivity to 2E-1HA	Con-alcohol	Selectivity to HXA	Con-alcohol	Selectivity to IAP	Con-alcohol	Selectivity to IAA
Without catalyst	49.1	99.9	50.7	99.5	46.0	100	48.1	100
0.03 g	63.7	99.8	67.4	100	64.6	100	61.0	99.5
0.05 g	67.5	99.5	72.3	100	68.1	99.2	70.6	99.9
0.07 g	75.3	100	82.5	99.5	77.1	99.4	80.1	99.5
0.09 g	82.5	100	90.5	99.6	86.8	99.6	87.3	100
0.11 g	89.6	99.6	94.2	99.5	90.5	99.7	91.4	100

Reaction condition: temperature = 125 °C; mole ratio = 2:1 (ACOH:ROH); catalyst = Al-MCM-41 (110); reaction period = 5 h; pressure = autogenous pressure; reactor = 10 ml autoclave.

esterification reaction for all the four reactions. The kinetics data under pseudo-first-order conditions are also derived; the results are presented in Fig. 9. The rate constants derived by the first-order plot for all the four products are 0.1376, 0.1360, 0.1339 and 0.1300, respectively. The rate constants also follow the order $K_1\text{HXA} > K_3\text{IAA} > K_4\text{IAP} > K_2\text{2E-1HA}$, which also matches the activity of the catalyst.

3.2.6. Influence of amount of the catalyst

The influence of catalyst is account with varying the amount of catalyst in the reaction. The reaction was conducted with and

without catalyst (0.03–0.11 g), at 125 °C for 5 h with Al-MCM-41 (110) under autogeneous conditions. The results are presented in Table 7; the system conducted in the absence of catalyst shows alcohol-conversion around 50 wt.%, it shows that 50% of reaction going via auto catalytic pathway. The alcohol-conversion was increased with increase in the weight of catalyst. The 0.03 g of catalyst shows ~60% of alcohol-conversion whereas 0.11 g catalyst shows ~90% of alcohol-conversion. From 0.09 to 0.11 shows only marginal increment of alcohol-conversion, thereby 0.09 g of Al-MCM-41 (110) with mole ratio of 2:1 (AcOH:ROH) at 125 °C is the optimum condition for the synthesizing 2E-1HA, HXA, IAP and IAA esters.

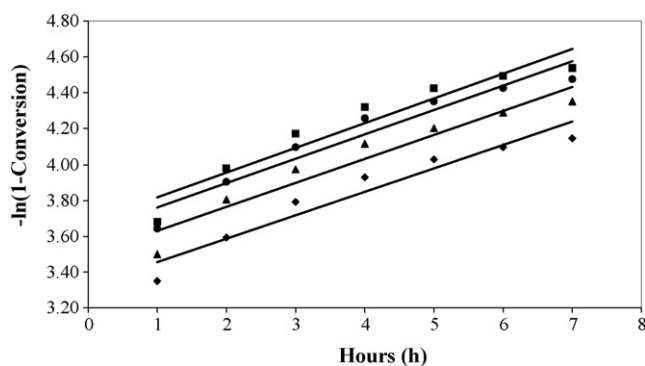


Fig. 9. Relation between $-\ln(1 - \text{conversion})$ and time (h) on esterification of isoamyl alcohol, 1-hexanol and 2-ethyl-1-hexanol. Reaction condition: temperature = 125 °C; weight of the catalyst = 0.07 g; pressure = autogenous pressure; mole ratio = 2:1 (ACOH:ROH); catalyst = Al-MCM-41 (110).

4. Conclusion

Through this study, it can be inferred that Al-MCM-41 catalyst could be the convenient eco-friendly alternative to the conventional hazardous mineral acid catalyst for esterification reactions. The higher % silicon containing Al-MCM-41 molecular sieves confirms the hydrophobic nature of all the four-esterification reactions. The carbon chain length and branching of side chain in the alcohols show much influence on the yield of products. The increase in the chain length of alcohol increases the yield of esters, whereas increase in the chain length of acid decreases the product yield. The reaction with higher amount of catalyst and higher % of acid shows more alcohol-conversion. Maximum conversion and products selec-

tivity can be attained with 0.07 g of Al-MCM-41 (110) with mole ratio of 2:1 (AcOH:ROH) at the end of 8 h at 125 °C, which can be achieved sufficiently, only by the specific nature of the solid acid catalyst.

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