Al-MCM-41 as an efficient heterogeneous catalyst in the acetalization of cyclohexanone with methanol, ethylene glycol and pentaerythritol

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Abstract

Mesoporous Al-MCM-41 molecular sieves in the Si/Al ratios 25, 50, 75 and 100 were synthesized under hydrothermal condition. They were characterised using powder X-ray diffraction (XRD), FT-IR and BET surface area analyser. The catalytic activity of these materials was tested for the slurry phase acetalization of cyclohexanone with methanol (MET), ethylene glycol (EG) and pentaerythritol (PEN) at 40–120 °C. MET conversion was found to be higher than that of EG and PEN. Hydrophobic property of catalyst and alcohols and also the steric properties of alcohols were suggested to play an important role in the acetalization. For MET and EG, Al-MCM-41 (100) was found to be more active than other catalyst but for PEN, Al-MCM-41 (25) was found to be more active. The reaction was also studied over $H_3PW_{12}O_{40}$ supported MCM-41, commercially available heteropolyacid ($H_3PW_{12}O_{40} \cdot nH_2O$) and zeolites (HM, Hβ and ZSM-5). Zeolites showed less activity for EG, PEN but comparable activity to MET. The requirement of Brönsted acid sites for the reaction was clearly established by running the reaction in the absence of catalyst.
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Keywords: Comparison; Acetalization; Al-MCM-41; Hydrophobicity; Methanol; Ethylene glycol; Pentaerythritol

1. Introduction

Acetals [1] are important in synthetic carbohydrate [2] and steroid chemistry [3]. In the phyto pharmaceutical, fragrances [4] and lacquers industries [5], acetals are used both as intermediates and as end products. Pentaerythritol acetals in general are applied as plasticizers and vulcanizers, as physiologically active substance and as potential protective groups for aldehydes and ketones. Protection of the carbonyl group of aldehyde or ketones can be accomplished by using five main types of reagents: alcohols [6], diols [7], orthoesters [8] even acetals [9] and scarcely oxiranes [10,11]. Several publications have described the protection of carbonyl compounds under acidic conditions [12,13]. However, these methods have not been entirely satisfactory, owing to the problems of corrosion, tedious workup, and environmental polluting catalysts. Consequently, there is a demand for environmentally friendly acid catalysts to synthesize diac-

etals under mild conditions. In this context, heterogeneous catalyst plays a dramatic role [14] with its easy workup in the case of separation of the catalyst by filtration, high purity of the products and the possibility of recycling catalyst. Different heterogeneous catalysts such as montmorillonite [15], sulfated zirconia [16] and envirocat EPZG [17], have been employed for the acetalization of carbonyl compounds and, in particular alumina/KSF [18], natural kaolinitic clay [19] and Y zeolite [20], have been proposed for the preparation of 1,3 dioxolanes. However, just one of these is reported as a reusable catalyst. Also the steric hindrance in ketones was known to have a large effect on the formation of cyclic acetals over solid acid catalysts [21]. For example, an acidic montmorillonite clay catalysed the formation of cyclic acetal of acetone with 70% yield, while the product yields for more hindered dibenzyl ketone and 2,4-dimethylpentan-3-one were 30 and 0%, respectively [22]. Interestingly, natural kaolinitic clay containing mostly Lewis acid sites (79% total acid sites) could catalyse the formation of cyclic acetals of aldehydes, but failed to catalyse the same reaction with ketones. Acetalization in the presence of solid catalysts such as resin [23] or zeolite [20] has been carried out

successfully with trialkyl orthoformate but with alcohol the reaction did not occur well [24]. For example, the acetalization of cyclohexanone with methanol in the presence of Al^{3+}-bentonite has been performed at room temperature for 30 min but with incomplete conversion (33% yield). The uses of relatively stable and strongly acidic heteropoly acids in acid catalysed reactions have attracted increasing attention for processes requiring higher acidity than that of the zeolites [25]. However, for heteropoly acids to be effective as catalysts they should be supported on a carrier with a large surface area due to the extremely small surface area ($<10 \, m^2/g$) of these non-porous materials [26]. Even though silica, alumina, resin, active carbon, clays and microporous zeolites are used as a supports [27–30], their non-uniform pore size and relatively small surface area limit their potential for catalysing bulky molecules because of diffusion problems. MCM-41 mesoporous materials which have attracted a great deal of attention due to their regular pore structure, uniform pore diameter and high surface area [31], has been employed successfully for typical acid catalysed reactions like isomerization [32], alkylation [33], debenzylation [34] and esterification [35,36] but not been extensively investigated as potential alternative catalysts for acetal formation because they found to be less efficient catalysts owing to their low acidity. We report herein, Al-MCM-41 with various Si/Al ratios as an efficient heterogeneous catalyst for the direct condensation of cyclohexanone with methanol, ethylene glycol and pentaerythritol under slurry phase. This process is an efficient, clean, economic and solvent less technique, inconstrast to conventional method, where the standard conditions for acetalization often fail for diaryl ketones, making the desired compounds available only via indirect routes. Acetals of 4,4′-dichloro- and 4,4′-dimethoxybenzophenone, for example, are usually prepared by alkoxy-halogen exchange from the appropriate dihalodiarylmethanes [37].

2. Experimental

2.1. Materials

The syntheses of Al-MCM-41 materials were carried out by hydrothermal method using sodium metasilicate ($Na_2SiO_3 \cdot 5H_2O$), aluminum sulfate ($Al_2SO_4 \cdot 18H_2O$), cetyltrimethylammonium bromide ($C_{16}H_{33}(CH_3)_2N^+Br^-$) and sulfuric acid ($H_2SO_4$). The chemicals used were of AR grade purchased from M/s Aldrich, USA. Methanol, ethylene glycol and cyclohexanone used were of AR grade procured from Merck. Pentaerythritol was obtained from SRL Pvt. Ltd.

2.2. Commercial catalytic materials

H–M (Si/Al = 12, PQ), H–β (Si/Al = 8, PQ), H-ZSM-5 (Si/Al = 15, PQ), $H_3PW_{12}O_{40} \cdot nH_2O$, were obtained from Sud Chemie India Ltd.

2.3. Synthesis of Al-MCM-41

The Al-MCM-41 with various Si/Al ratios 25, 50, 75 and 100 was synthesised according to the previous report [38] using a hydrothermal method with the gel composition of $SiO_2:XAl_2O_3:0.2CTAB:0.89H_2SO_4:120H_2O$ using sodium meta silicate as the silicon source, H_2SO_4, cetyltrimethylammonium bromide as the structure directing agent and aluminium sulphate as the aluminium source. 21.21 g of sodium meta silicate was dissolved in 80 ml of water and allowed to stir for half an hour. Then required quantity of aluminium sulphate, which was dissolved in 15 ml of water, was added and allowed to stir for 1 h. Then 40 ml of 4N sulphuric acids was added drop by drop until the gel formed. The stirring was continued for 2 h. Exactly 7.28 g of cetyltrimethylammonium bromide (CTAB), dissolved in 25 ml of water, was added and stirring was continued for further 2 h. After that, the gel was transferred to an autoclave and it was kept in a hot air oven at 145 °C for 36 h. Then the product obtained was filtered, washed several times with double distilled water and dried at 80 °C in an air oven for 2 h. Then it was calcined in a muffle furnace at 550 °C for 6 h to remove the template.

### 2.4. Synthesis of PW/MCM-41 catalysts

One gram of predried Si-MCM-41 was dispersed under vigorous stirring into a solution of the desired amount of PW crystals in 12 ml of water. After evaporating the water at 70 °C, the solid was dried in an oven at 96 °C overnight. Three PW (x%)/MCM-41 catalysts, where x% is the respective PW content of 10, 15 and 20 wt.%, were prepared according to the above procedure.

2.5. Catalytic runs

Acetalization reactions were carried out under slurry phase reaction conditions using a conventional oil bath attached with condenser in the temperature range of 40–120 °C under nitrogen atmosphere. A typical reaction mixture in the 50 ml round bottom flask contained cyclohexanone (0.1 mol), alcohol (0.1 mol) and a freshly activated catalyst (0.1 g). Activation of the catalyst was done by calcinations at 500 °C in air for 5 h. The oil bath temperature was then slowly raised to 40, 60, 80, 100 and 120 °C as required and maintained at the desired temperature during the specified reaction periods. The effect of temperature, reaction period, the molar ratios of the reactants and the amount of catalyst required on cyclohexanone conversions and product selectivity was studied (Scheme 1).

2.6. Analysis

The reaction mixture was collected from the round bottom flask after cooled to room temperature. This solution was removed from the catalyst by filtration. The reaction mixture was analysed by a Perkin-Elmer Clarus 500 gas chromatograph using a SE-30 capillary column with FID detector. The product analysed by GC revealed the formation of acetals with 100% selectivity. The formation of the product was further confirmed by GC–MS. The formation of diacetals of pentaerythritol was confirmed by extracting with dichloromethane solvent and isolated by distillation and purified through recrystallisation to give consistent MS (JEOL DX-303), ^1H NMR (300 MHz in $CDCl_3$,
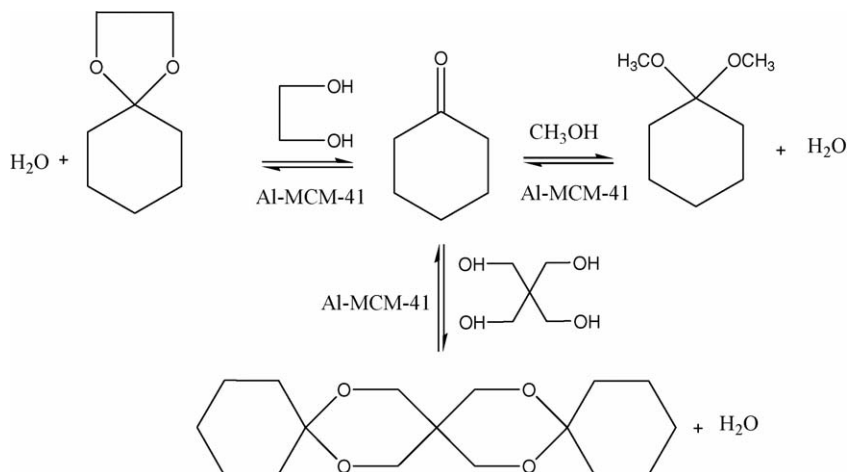
Scheme 1. Al-MCM-41 catalysed acetalization of cyclohexanone with methanol, ethylene glycol and pentaerythritol.

internal standard TMS) and FT-IR (Nicolet Avatar 360 FT-IR) spectra. The percentage conversion calculation is based on the GC analysis. The conversion of the reactant is expressed as the difference between the initial and final percentage weight of the reactant divided by initial weight percentage of the reactant.

$$\text{Conversion}\,(\%) = \frac{\text{initial wt.\%} - \text{final wt.\%}}{\text{initial wt.\%}} \times 100$$

2.7. Characterisation

Mesoporous materials, in general are characterised by a variety of techniques including XRD (Rigaku, D-Max/111-VC model) using nickel filtered Cu Kα radiation λ = 1.5406 Å. 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 mesopores volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.5 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. Mid-infrared spectra of as-prepared and calcined MCM-41 molecular sieves were recorded on a Nicolet (Avatar 360) instrument by KBr pellet technique. About 4 mg of the sample was ground with 200 mg of spectral grade KBr to form a mixture, which was then made into a pellet using a hydraulic press. This pellet was used to record the infrared spectra in the range 4000–400 cm^{-1}. Thermal analysis was carried out in Mettler TA 3001 analyser. Zeolites used in this study were procured from Sud Chemie India Ltd.

2.8. Acidity measurements

The acidity of Al-MCM-41 and PW/MCM-41 materials was analysed by pyridine adsorption followed by FT-IR spectroscopy. Finely ground catalyst sample (10–15) was pressed for 2 min at 10 t/cm^2 pressure under vacuum into a

self-supporting wafer. The wafers were calcined under vacuum (133.322 × 10^{-3} N/m^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 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 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.

3. Results and discussion

3.1. Characterisation of Al-MCM-41

3.1.1. XRD

The XRD diffraction patterns for calcined Al-MCM-41 and PW/MCM-41 materials are shown in Fig. 1 and the data are presented in Table 1. The patterns show the characteristics of a typical mesoporous MCM-41 structure. The d_{100} reflections of calcined Al-MCM-41 have been shifted to higher values compared to its as-synthesized analogue. This is in agreement with Borade and Clearfield [39], suggesting the framework substitution of alumina in MCM-41 structure.

During calcinations at 550 °C, the d values are generally shifted towards the lower values or higher 2θ values, though to a smaller extent, implying shrinkage in the unit cell as a result of the removal of the surfactant molecules used as templates [40]. Fig. 1. Illustrates the effect of the PW loading on the XRD of MCM-41 samples. PW has a striking effect on the width and intensity of the main reflection at high d_{100} spacing and this line becomes broader and weaker as the loading increases. This suggests that the long-range order of Si-MCM-41 is decreased noticeably by the presence of PW.

3.1.2. Nitrogen adsorption isotherms

BET surface area, pore size and pore volume of calcined materials are presented in Table 1. Adsorption and desorption isotherms and pore size distribution for calcined materials (BJH

Table 1
Textural properties of the calcined catalysts

Catalysts	Calcined		Surface area (m^2/g)	Pore size BJH$_{Ads}$ (nm)	Pore volume BJH$_{Ads}$ (cm^3/g)
	d_{100} (Å)	Unit cell-a_0 (nm)			
Si-MCM-41	44.21	5.10	938	2.60	0.60
Al-MCM-41 (25)	35.38	4.09	950.8	2.50	0.94
Al-MCM-41 (50)	40.60	4.69	976.6	2.53	0.94
Al-MCM-41 (75)	42.50	4.90	1018	2.63	0.95
Al-MCM-41 (100)	42.50	4.90	1023	2.64	0.95
10 wt.% PW/MCM-41	42.15	4.86	526	2.55	0.32
15 wt.% PW/MCM-41	38.45	4.44	265	2.40	0.12
20 wt.% PW/MCM-41	35.37	4.08	235	1.90	0.11
HM (12)	–	–	431	–	–
Hβ (8)	–	–	694	–	–
HY (4)	–	–	821	–	–
HZSM-5 (15)	–	–	393	–	–

method) coincide with the reported values [41,42]. It can be seen that MCM-41 presents the highest surface area and pore volume, with all pore being in the mesopore range. The pore size distribution of calcined MCM-41 shows a unique peak centered at about 25 Å diameter as given in literature [43]. With increasing PW loading, a reduction in the pore volume and a notable compression of the pore size distribution was observed. The BET surface areas were calculated by fitting the straight part of the $p/x(p - p_o)$ versus p/p_o curve (where p is the presence of nitrogen and x is the number of grams of adsorbed nitrogen per gram of solid). The resulting surface area ranged from 393 to 1023 m^2/g. Pyridine adsorbed FT-IR spectroscopy spectra for Al-MCM-41 (25), Al-MCM-41 (50), Al-MCM-41 (75), Al-MCM-41 (100) and PW/MCM-41 samples containing adsorbed pyridine are reported in our earlier literature [44] and presented in Table 2. A typical sharp peak appeared at 1545 cm^{-1} is due to the indication of pyridine adsorbed on Brönsted and a small peak at 1455 cm^{-1} and a high-intensity peak around 1620 cm^{-1} are due to Lewis acid sites. In case of PW/MCM-41 samples the acidity increases gradually with increasing PW loading.

3.1.3. FT-IR spectroscopy

The FT-IR spectra of the samples are given in Fig. 2. In the FT-IR spectrum of samples, broad envelope due to –OH stretch of water in the higher energy region and the corresponding –OH$_2$ bending mode around 1637 cm^{-1} very well correlate with the water adsorption property (hydrophilic property) of the catalysts. Pure HPA with a Keggin structure with four strong

Table 2
Brönsted and Lewis acidity values of mesoporous molecular sieves

Catalysts	423 K	
	B.A.[a]	L.A.[a]
AlMCM-41 (25)	7.8	9.0
AlMCM-41 (50)	7.0	8.9
AlMCM-41 (75)	3.6	5.5
AlMCM-41 (100)	3.4	1.1
15 wt.% PW/MCM-41	8.0	9.5
20 wt.% PW/MCM-41	8.2	9.2

[a] Acidity (μmol py/g catalyst).

bands, at 1082 cm^{-1} (P–O), 988 cm^{-1} (W=O) and 800 cm^{-1} (W–O–W), and one weak band at 525 cm^{-1} (W–O–P) [45] are observed. The framework bands of Si-MCM-41 at 1236, 1090, 965, 800, 564 and 465 cm^{-1} [46] easily overlap with those of PW. For 10 wt.% PW/MCM-41, none of the PW bands was observable except for a slight increase in the intensity of the 800 cm^{-1} band. For 15 wt.% PW/MCM-41, the bands at 988 and 891 cm^{-1} became visible. With 20% of PW loading, the 1082 cm^{-1} band became sharper and the intensity of the two bands at 988 and 891 cm^{-1} increased. Furthermore, it was observed that the intensity of the 800 cm^{-1} band was almost proportional to the increase in the amount of PW on MCM-41 due to the greater number of oscillators. The FTIR spectra of the Keggin structure of PW/MCM-41 with different PW loading clearly coincide from those reported in the literature.

3.2. Application of Al-MCM-41 (25), Al-MCM-41 (50), Al-MCM-41 (75) and Al-MCM-41 (100) catalysts to the acetalization of cyclohexanone with methanol (MET), ethylene glycol (EG) and pentaerythritol (PEN)

3.2.1. Variation with reaction temperature

The reaction was carried out at various reaction temperatures, ranging from 40 to 120 °C at a given ketone to alcohol ratio of 1:4 for 8 h over Al-MCM-41 with various Si/Al ratios ranging 25, 50, 75 and 100 and the results are given in Table 3. The activities for EG and PEN were compared at 120 °C, while that for MET was compared at 100 °C. The activation energy may be required to reduce intermolecular association of cyclohexanone for dispersed adsorption and to avoid clustering of cyclohexanone around the Brönsted acid sites by hydrogen bonding. A common trend in conversion over all the catalysts is increase of ketone conversion to a maximum of 87.8, 75.1 and 66.0% for MET, EG and PEN, respectively, with increase in temperature, which suggest that the low rate of hemiacetal formation was accelerated with increase in the temperature and the conversion was higher than reported, where 33% yield was obtained after performing the reaction at room temperature for 30 min [47]. The rate determining step for acetalization is the formation of a cation from the protonated hemiacetal. While the presence
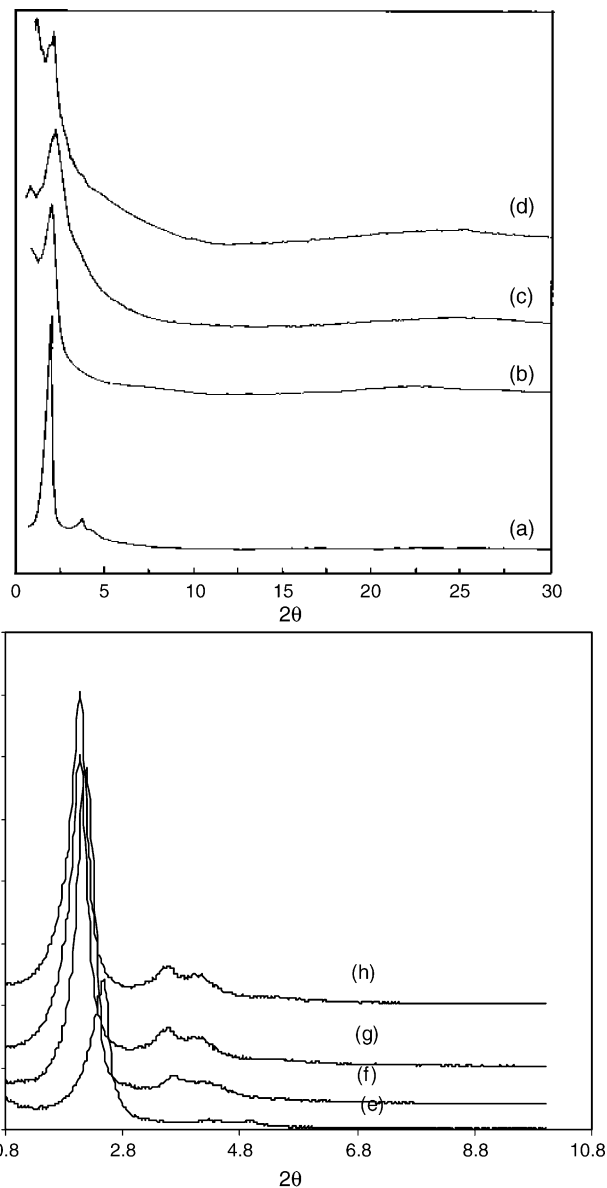
Fig. 1. X-ray diffraction pattern of calcined materials: (a) Si-MCM-41, (b) 10 wt.% PW/MCM-41, (c) 15 wt.% PW/MCM-41, (d) 20 wt.% PW/MCM-41, (e) Al-MCM-41 (25), (f) Al-MCM-41 (50), (g) Al-MCM-41 (75) and (h) Al-MCM-41 (100).
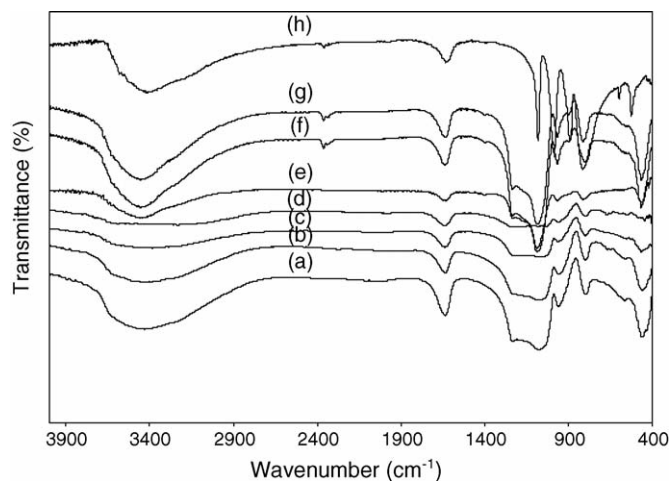

Fig. 2. FT-IR spectra of mesoporous materials (using KBr method): (a) Al-MCM-41 (25), (b) Al-MCM-41 (50), (c) Al-MCM-41 (75), (d) Al-MCM-41 (100), (e) 10 wt.% PW/MCM-41, (f) 15 wt.% PW/MCM-41, (g) 20 wt.% PW/MCM-41 and (h) PW.

of two aryl groups should enhance the rate of acetalization by stabilizing the intermediate cation, the overall reaction may be more strongly affected by the steric crowding which would occur during initial hemiacetal formation [48]. The increased conversion observed with Al-MCM-41 might be due to its mesoporous nature, where an increase in the temperature might force the reactant to get accessed to all the acid sites available in the catalysts particularly inside the pores for the formation of acetals. For each catalyst, the conversion at the particular temperature decreases in the order MET > EG > PEN, the steric factor may be important to account of the difference in their conversion. The plausible reaction mechanism for the formation of cyclic acetals with respect to larger nucleophiles like EG and PEN might involve six steps as given in Scheme 2. (A) Adsorption of carbonyl compound on the Brönsted acid site, (B) nucleophilic attack of the glycol, (C) formation of hemiacetal, (D) readsorption of the hemiacetal on the Brönsted acid site, (E) cyclodehydration reaction and (F) desorption of the reaction product from the Brönsted acid site. Since MET is pose less steric hindrance compare to that of EG and PEN, the conversion of cyclohexanone with MET becomes higher than other alcohols. Hence it may also be inferred that in addition to the rate-determining step of carbonium ion, the steric factor and reactivity of alcohols is also important when acetalization is carried out in heterogeneous catalysis. Since temperature employed in this reaction is sufficiently high, the rate of formation of carbonium ion may not be the slow step in the acetalization. For each temperature, the activity of the catalysts for MET, and EG follows the order: Al-MCM-41 (100) > Al-MCM-41 (75) > Al-MCM-41 (50) > Al-MCM-41 (25), which is reverse to the order of the density of acid sites of the catalyst. The high yield inspite of his low density of acid sites with respect to Al-MCM-41 (100) might be due to its more hydrophobic with which it can expel water out of the pores as and when it is formed in the reaction. For PEN, the order of the catalysts is Al-MCM-41 (25) > Al-MCM-41 (50) > Al-MCM-41 (75) > Al-MCM-41 (100). In this case, the lower yield in the presence of Al-MCM-41 with high Si/Al ratios might be due to its high hydrophobic property, with which it can retain most of the large reactant inside the pores thereby resulting in blocking of product to diffuse out of the pores.

3.2.2. Influence of reaction time

The effect of reaction period on the acetalization was studied on Al-MCM-41 (100) at the optimised temperature of 100 and 120 °C with the feed ratio of 1:4 for MET and EG, Al-MCM-41 (25) for PEN at 120 °C and presented in Fig. 3. Conversion with respect to MET increases from 61.0% at 2 h to a maximum of 87.5% at 10 h. Similarly, the conversion with respect to EG was 63% at 2 h to a maximum of 72.3%. For PEN, the conversion at 2 h was 23.6% after 10 h it is 68.0%. A gradual arise in the conversion was seen with increase in the duration of the reaction

Table 3
Catalytic activity of Al-MCM-41 (25, 50, 75 and 100) for acetalization of cyclohexanone with various alcohols

Catalyst	Temperature (°C)	Conversion of cyclohexanone with MET (%)	Conversion of cyclohexanone with EG (%)	Conversion of cyclohexanone with PEN (%)
Al-MCM-41 (100)	40	47.4	55.4	9.7
	60	71.0	64.8	11.0
	80	74.5	63.9	15.5
	100	86.8	68.5	28.8
	120	87.8	75.1	28
Al-MCM-41 (75)	40	40.8	56.9	11.8
	60	70.4	51.1	16.0
	80	79.1	60.9	21.1
	100	86.2	62.8	32.8
	120	85.1	64.8	32.0
Al-MCM-41 (50)	40	48.3	51.9	18.0
	60	69.8	65.9	11.8
	80	71.0	58.0	38.0
	100	72.3	65.4	42.1
	120	74.2	70.8	43.5
Al-MCM-41 (25)	40	51.6	59.4	13.3
	60	76.2	73.5	16.8
	80	78.2	41.4	53.1
	100	72.6	69.7	54.0
	120	76.0	72.3	66

Time = 8 h, feed ratio = 1:4 (aldehyde:alcohol).

period. Though this observation is a normal feature for reaction procedures of this kind, the low time of reaction is a matter of consideration. As seen from the table, in the case on MET, 6 h of reaction time completes 82.8% of the reaction, whereas at the end of 10 h only 87.5% of the reaction is complete. This shows that between 6 and 10 h only a meagre increase of 5.0 wt.% is seen. Similarly in the case of EG and PEN, only 5.0 wt.% increase in the conversion for each was found to occur after 10 h. This observation illustrates the lower time requisite for the reaction to attain equilibrium.
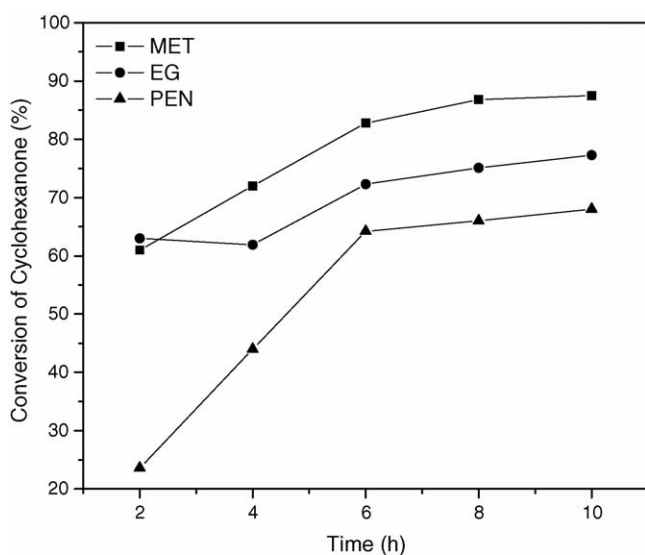

Fig. 3. The effect of reaction time on the acetalization of cyclohexanone over Al-MCM-41 (100) for MET and EG, Al-MCM-41 (25) for PEN, respectively. *Reaction conditions*: Temperature = 100 °C for MET; 120 °C for EG and PEN; feed ratio = 1:4 (aldehyde:alcohol).

3.2.3. Influence of mole ratio of the reactants

The effect of feed ratio on the acetalization of cyclohexanone was studied with different feed ratios over Al-MCM-41 (100) for MET at 100 °C and EG for 120 °C at 6 h. In the case of PEN, the reaction condition involves the use of Al-MCM-41 (25) for 120 °C at 6 h. The results are presented in Table 4. When the alcohol feed is increased from 1:2 to 1:5, a non-linear trend in cyclohexanone conversion was observed. Initially, the conversion increased with increase in mole rations of the reactants. The conversion increased from 78.7% for a mole ratio of ketone:alcohol 1:2 to 86.8% for 1:4. With further increase in the mole ratio to 1:5, a decrease in conversion of about 81.9% was observed. The formation of acetal with 100% selectivity for all the feed ratios is observed. The effect of mole ratio over the conversion can be attributed with the occupancy of ketone over the active sites and the availability of alcohol molecules for further acetalization. At the mole ratio of 1:2, the ketone is chemisorbed on the active sites to form carbonium ion. The attack of these stable carbonations by the alcohol to form acetals is least effect at this molar ratio stage. Further, when the concentration of alcohol is double from 1:2 to 1:4, the approach of nucleophiles to the carbocation is to be enhanced. When the mole ratio is increased to 1:5, a decrease in conversion due to the flooding of active sites with alcohol molecules rather than the ketone causing the dilution of ketone takes place and hindrance in being protonated at the active sites. The similarly trend in ketone conversion was also observed for EG and PEN. The optimum feed ratio for MET, EG and PEN was found to be 1:3. Although the optimum feed reaction for MET is 1:4, 1:3 might be sufficient as the increase in conversion for the change of feed ratio from 1:3 to 1:4 was only about 1%. The reaction was also studied by taking more ketone content in the feed from 2:2 to 5:2. A steady decrease in the
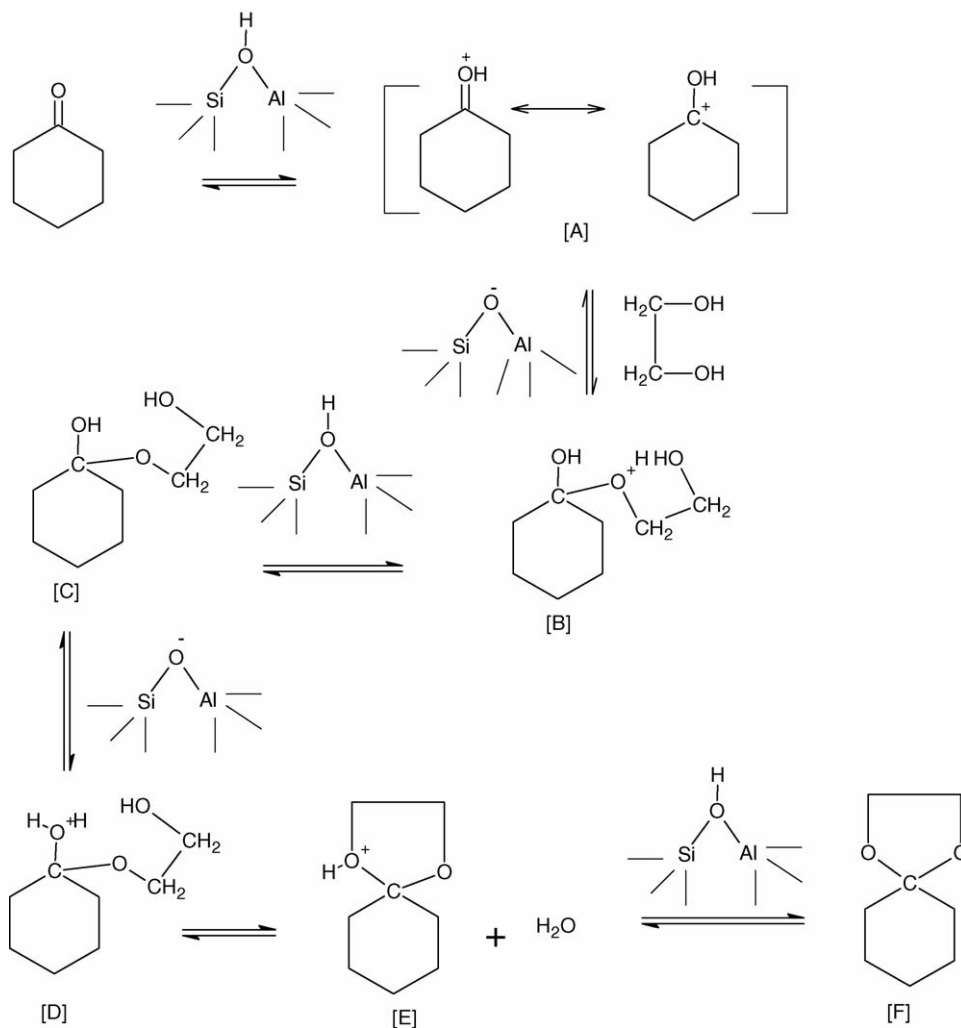
Scheme 2. A plausible mechanism for the formation of cyclic acetals from cyclohexanone with ethylene glycol over Al-MCM-41.

conversion was observed for the feed ratio from 2:2 to 5:2 in the case of MET. Although the increase in ketone content might be expected to increase conversion there might be dilution of alcohol hence the expected increase in conversion must balanced by decrease in conversion due to increase in dilution of alcohol. The conversion of cyclohexanone with EG for similar variation in the feed ratio from 2:2 to 5:2 decreased the conversion from 52.5 to 24.7%. The same trend was also observed for the conver-sion of ketone with PEN, where the conversion declined from 43.0 to 11.1%. Hence in both the cases there might be dilution of alcohol.

3.2.4. Influence of the catalyst loading

The effect of catalyst loading on ketone conversion was stud-ied at various optimised conditions over Al-MCM-41 (100) for MET and EG at the ketone:alcohol feed ratio of 1:3 for 100 and

Table 4
Effect of feed ratio on acetalization of cyclohexanone over Al-MCM-41 (100) for MET and EG, Al-MCM-41 (25) for PEN

S. no.	Mole ratio (ketone:alcohol)	Conversion of cyclohexanone with MET (%)	Conversion of cyclohexanone with EG (%)	Conversion of cyclohexanone with PEN (%)
1	1:2	78.7	92.7	68.6
2	1:3	85.2	85.9	69.3
3	1:4	86.8	75.1	66.0
4	1:5	81.9	78.0	50.4
5	2:2	51.2	52.5	43.0
6	3:2	43.4	34.4	41.5
7	4:2	32.6	27.9	23.7
8	5:2	39.1	24.7	11.1

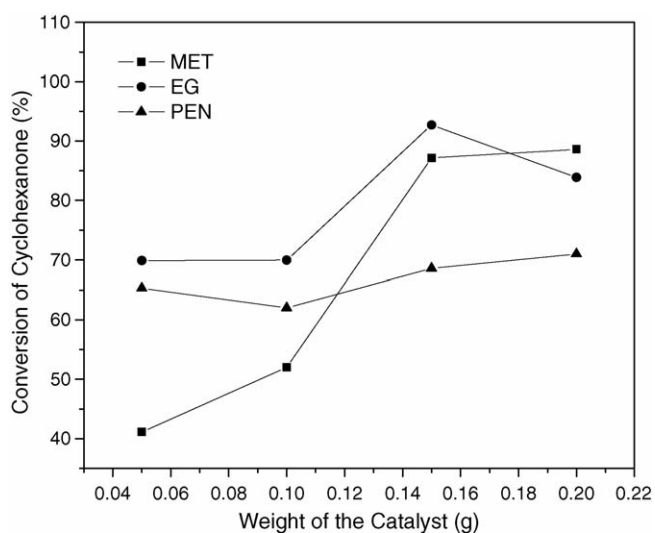Temperature = 100 °C for MET; 120 °C for EG and PEN; time = 6 h.

Fig. 4. . The effect of amount of catalyst on the acetalization of cyclohexanone over Al-MCM-41 (100) for MET and EG, Al-MCM-41 (25) for PEN, respectively. *Reaction conditions*: Temperature = 100 °C for MET; 120 °C for EG and PEN; feed ratio = 1:3 for MET, EG, PEN; time = 6 h.

120 °C, respectively, Al-MCM-41 (25) at 120 °C with the feed ratio of 1:3 for PEN at 6 h. The results are presented in Fig. 4. With increase in catalyst loading the conversion increased. The increase in conversion with increase in catalyst loading with respect to MET was high ranging from 41.1 to 88.6% while for EG and PEN, the conversion ranges from 69.9 to 83.9 and 65.3 to 71.0%, respectively. The optimum loading can taken as 0.15 g where a maximum conversion of cyclohexanone of 87.2, 92.7 and 68.6% was obtained with respect to MET, EG and PEN, respectively. Their requirement of high catalyst loading for these three reactants MET, EG and PEN might be due to the effect of hydrophobic property of the alcohols, which could be reduced by increase in the catalyst loading. There might be to some extent prevention of adsorption of cyclohexanone on the catalyst surface at low loading.

3.2.5. Comparative study on various zeolites

The acetalization of cyclohexanone with various alcohols was also tested with different catalyst at optimised temperature over Al-MCM-41 (100) for MET and EG at the ketone:alcohol feed ratio of 1:3 for 100 and 120 °C, respectively, Al-MCM-41 (25) at 120 °C with the feed ratio of 1:3 for PEN at 6 h (Table 5, entries 1–12). In the case of zeolites, it is possible to see that the conversion of cyclohexanone with respect to MET was very high comparable to that of heteropolyacids. On the other hand as pointed out earlier, the pore diffusion limitation induced by the large molecular size of the reactants played an important role in the acetalization reaction using zeolite catalysts. The catalytic activity of the zeolite catalysts decreases when the size of the reactant increased. This reduction is remarkable for the acetalization of cyclohexanone with EG and PEN, which might be due to the steric hindrance to diffuse into the pores as well as the bulkier reaction products to diffuse out of the pores (entries 6–8). The catalytic activity of the mesoporous molecular sieves studied shows a greater activity regardless of the size of the reactants used as the acetalization agent (entries 1–4). The activity of HPA supported MCM-41 showed a lower activity irrespective of the size of the reactant used, due to the blockage of pores of MCM-41 due to the dispersion of HPA (entries 10–12). The HPA catalyst showed nearly same activity as that of Al-MCM-41 molecular sieves for all the three alcohols used (entry 5). This observation clearly supported molecular concession free acetalization inside the pores of MCM-41. The reaction was also performed with as-prepared Al-MCM-41 (100) under the same condition mentioned above. The alcohol conversion found to be very less for all the three alcohols. This clearly establishes occurring of the reaction within the pores of Al-MCM-41 molecular sieves. In addition, Al-MCM-41 (100) and Al-MCM-41 (25) was tested for its recyclability by running the reaction five times where no change in the conversion was observed up to three cycles and a slight decrease in the fourth and five cycles was observed illustrating the stability of the catalyst. In order to verify the active influence of the catalysts, the reaction was also studied in the absence of the catalyst under the optimum conditions, feed ratio of 1:3 at 120 °C for EG and PEN, 100 °C at the feed ratio of 1:3 for MET for 6 h. After running the reaction for 6 h, the reaction mixture was analysed and the cyclohexanone conversion for MET, EG and PEN was found to be 7, 10 and 0% (entry 9). It is 81, 82 and 71% less than in the presence of cat-

Table 5
Effect of various catalysts on acetalization of cyclohexanone for MET, EG and PEN

S. no.	Catalyst	Conversion of cyclohexanone with MET (%)	Conversion of cyclohexanone with EG (%)	Conversion of cyclohexanone with PEN (%)
1	Al-MCM-41 (25)	72.6	72.3	68.6
2	Al-MCM-41 (50)	71.3	70.8	43.5
3	Al-MCM-41 (75)	86.2	64.8	32.0
4	Al-MCM-41 (100)	87.2	92.7	32.0
5	$H_3PW_{12}O_{40} \cdot nH_2O$	70.4	72.7	76.6
6	HM (12)	75.0	60.4	38.2
7	Hβ (8)	71.0	54.0	22.3
8	HZSM-5 (15)	50.8	60.2	25.4
9	Without catalyst	7.0	10.1	0
10	10 wt.% PW/MCM-41	56.1	28.1	49.1
11	15 wt.% PW/MCM-41	52.1	36.8	53.2
12	20 wt.% PW/MCM-41	54.1	37.9	68.0

Temperature = 100 °C for MET; 120 °C for EG and PEN; time = 6 h. Feed ratio = 1:3 for MET, EG and PEN; catalyst loading = 0.15 g.

alyst. This observation therefore clearly establishes the active role of the catalyst for this reaction. Further in order to know whether the reaction occurs mainly inside the pore, outside the pore or on both, the study was carried out with as-synthesised catalyst. As this catalyst is incapable of permitting the reaction inside the pore due to template blocking, the outer surface sites alone can catalyse the reaction. 25, 11 and 12% cyclohexanone conversion was obtained which is 63, 81 and 60% less than that of calcined sample. So the reaction is more prone to occur within the pores of the catalyst rather than on the outer surface.

4. Conclusion

From the studies the following conclusions were drawn. Al-MCM-41 molecular sieves can be conveniently exploited for the acetalization of cyclohexanone with MET, EG and PEN. For MET and EG, Al-MCM-41 (100) was found to be more active where as Al-MCM-41 (25) was found to be more active for PEN. The hydrophobicity of the catalyst surface and the hydrophobicity of the alcohol are also found to be the deciding factor. The activity of Al-MCM-41 was comparable to heteropoly acids catalyst. Zeolites were found to be active in the case of MET but their activity decreases when bulky reactants such ethylene glycol and pentaerythritol were used as acetalization agent with cyclohexanone. The reaction over as-prepared catalyst showed 60, 64 and 54% less conversion than that of calcined sample. Hence the reaction is proposed to occur mainly within the pores of the catalyst. This observation indirectly proves planting of Brönsted acid sites insides the pores of the catalyst.

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