



Reaction of benzaldehyde with various aliphatic glycols in the presence of hydrophobic Al-MCM-41: A convenient synthesis of cyclic acetals

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ABSTRACT

The reaction of benzaldehyde with aliphatic glycols was performed over Al-MCM-41 with various Si/Al ratios. The effects of various parameters like temperature, mole ratio, reaction time and catalyst amount on the formation of acetals were optimized. The mesoporous Al-MCM-41 (Si/Al ratio 36, 57, 81 and 108) were synthesized by hydrothermal method. The synthesized catalysts were characterized by X-ray diffraction (XRD), nitrogen adsorption–desorption isotherm (BET), thermo gravimetric–differential thermal analysis (TGA-DTA) and TEM techniques. The acidity of the catalysts was measured by pyridine adsorption followed by FT-IR analysis. TEM analysis showed that the honeycomb-like regular arrangement of hexagonal pores on the molecular sieves. The highly hydrophobic Al-MCM-41 (108) showed higher activity than the other Si/Al ratios. The activity of the catalysts showed the following order Al-MCM-41 (108) > Al-MCM-41 (81) > Al-MCM-41 (57) > Al-MCM-41 (36). The hydrophobicity and nucleophilicity of the glycols highly influences the conversion of benzaldehyde, it followed the order; hexylene glycol (HG) > propylene glycol (PG) > ethylene glycol (EG). The results showed that mole ratio of 1:3 (aldehyde:glycol) gave higher yield than the other mole ratios.

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1. Introduction

Cyclic acetals are imperative class of chemicals which is widely used for the production of perfumes, flavours, fragrances [1,2], pharmaceuticals [3], plasticizers [4], food and beverage additives, solvents and intermediates [5,6]. Acetalization is also a well-known synthetic procedure for the protection of carbonyl groups in multistage synthesis [7], and is achieved by treatment of aldehydes or ketones with an alcohol or diol in the presence of Brønsted or Lewis acids [8–11]. Generally, the production of cyclic acetals was carried out by the condensation of glycols with aromatic aldehydes using mineral acids. However, the usages of these acid catalysts are toxic, corrosive and in addition, are hard to remove from the reaction medium. Most methods described so far are lengthy procedures involving high catalyst/substrate ratios and high temperatures. For economic and ecological reasons, organic synthetic chemists face an increasing obligation to optimize their synthetic methods in order to produce the desired product with high yield and selectivity through a safe and environmentally acceptable process. So, the challenges was to replace them by solid catalysts such as zeolites, alumina or resins, which are ecofriendly and easier to separate

from the products. Zeolites are a class of solid acids, which have been widely studied as viable alternatives to conventional acids. The use of zeolites as catalysts for organic reactions began in the early 1960s. Different homogeneous catalysts [12–16] and heterogeneous catalysts such as montmorillonite [17], sulfated zirconia [18] and envirocat EPZG [19], alumina/KSF [20], natural kaolinitic clay [21] and Y zeolites [22], have been employed for the acetalization of carbonyl compounds. Even though silica, alumina, resin, active carbon, clays and microporous zeolites are used as supports [23–26], their non-uniform pore size and relatively small surface area, limit their potential for catalysing bulky molecules because of diffusion problems. The mesoporous materials MCM-41 which have attracted a great deal of attention in organic transformation due to their regular pore structure, uniform pore diameter and high surface area [27].

An acetalization reaction is a reaction between an aldehyde and ethylene glycol (EG), leading to the formation of cyclic acetal and a water molecule. This reaction is an equilibrium reaction and it can be displaced towards the product by removal of water or by the use of an excess of one of the reactants. Further, acetalization is a reversible reaction catalyzed by an acid environment and is usually performed in the liquid phase, which leads to the elimination of water as a by product, thereby requiring azeotropic distillation to remove the water formed during the reaction, or else leading to the deactivation of the catalyst. The objective of this work is to

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study the role of hydrophobic and hydrophilic nature of the catalyst for the acetalization of benzaldehyde with aliphatic glycols using Al-MCM-41 molecular sieves. The influence of nucleophilicity and hydrophobicity of glycols on the conversion of aldehyde was also studied. Al-MCM-41 (108) has higher hydrophobic nature and higher hydrothermal stability towards water that is formed during the reaction. Higher hydrophobic nature prevents hydrolysis, which in turn prevents the backward reaction. So the use of heterogeneous solid acid Al-MCM-41 catalysts could provide much cleaner technology for the production acetals. In the present study we have found excellent catalytic activity of Al-MCM-41 for the acetalization of benzaldehyde with ethylene glycol, propylene glycol (PG) and hexylene glycol (HG) under autogeneous pressure in the batch process.

2. Experimental

2.1. Materials

The chemicals used for the synthesis of Al-MCM-41 with various Si/Al ratio: 36, 57, 81 and 108 were sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$), aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), cetyltrimethylammonium 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 Qualigens Fine Chemicals (India). Benzaldehyde, ethylene glycol, propylene glycol and hexylene glycol 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 = 36, 57, 81 and 108) 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 meta silicate and aluminium sulphate were used as the sources for silicon and aluminium, respectively. Cetyltrimethylammonium bromide (CTAB) was used as the template. In a typical synthesis, 10.6 g of sodiummetasilicate 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 X-ray diffraction patterns of the calcined mesoporous Al-MCM-41 (Si/Al = 36, 57, 81 and 108) 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 1.03–9.99° 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. Thermal analysis was carried out in Mettler TA 3001 analyser. 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 ($133.322 \times 10^{-3} \text{ N m}^{-2}$) 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 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. The TEM images of typical samples of mesoporous Al-MCM-41 materials were obtained using a JEOL 3010 electron microscope operated at 300 kV. Samples for TEM were prepared by placing droplets of a suspension of the sample in acetone on a polymer micro grid supported on a Cu grid.

2.4. Catalytic runs and analysis of the product

Acetalization reactions of benzaldehyde with various glycols were carried out under batch reaction conditions using an autoclave in the temperature range of 50–150 °C, in 15 ml stainless steel batch reactors under autogeneous pressure conditions. A typical reaction mixture in the reactor contained benzaldehyde 5 mmol, glycol 15 mmol 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 autoclave temperature was then slowly raised to 50, 70, 90, 120 and 150 °C as required and maintained at the desired temperature during the specified reaction periods. 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. 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 36, 57, 81 and 108 are shown in Fig. 1. All the above materials exhibit a strong peak in the 2θ range of 2.05–2.65° due to 100 reflection lines and weak signals around 4.15, 4.79 and 6.37° (2θ) due to 110, 200, and 210 reflections, indicating the formation of well-ordered mesoporous materials with hexagonal regularity [28–30]. 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 of mesoporous aluminosilicate molecular sieves coincide well with the data already reported in the

Table 1
Physico-chemical properties of the catalysts

Catalysts	Si/Al ratio ^a	Fresh catalyst		Spent catalyst		Surface area ^b (m ² /g)	Pore size, ^b <i>D</i> (nm)	Pore volume ^b (cm ³ /g)
		<i>d</i> -Spacing ^c (Å)	Unit cell, <i>a</i> ₀ ^c (nm)	<i>d</i> -Spacing ^c (Å)	Unit cell, <i>a</i> ₀ ^c (nm)			
Al-MCM-41 (25)	36	34.73	4.20	34.41	4.27	896	2.82	0.95
Al-MCM-41 (50)	57	34.82	4.26	34.61	4.19	920	2.81	0.94
Al-MCM-41 (75)	81	36.14	4.36	36.65	4.21	951	2.79	0.95
Al-MCM-41 (100)	108	36.21	4.47	36.41	4.29	989	2.81	0.96

^a The results obtained from ICP-AES.

^b The values obtained from N₂ adsorption–desorption studies.

^c The results obtained from XRD analysis.

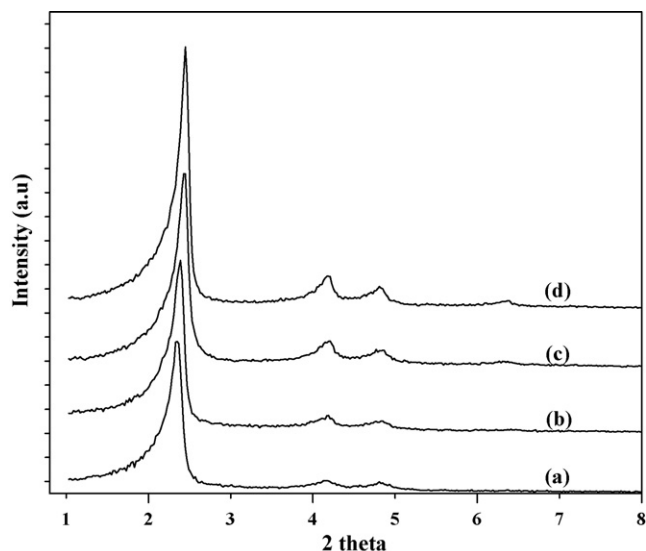


Fig. 1. X-ray diffraction pattern of fresh Al-MCM-41 mesoporous molecular sieves: (a) Al-MCM-41 (36), (b) Al-MCM-41 (57), (c) Al-MCM-41 (81) and (d) Al-MCM-41 (108).

literature [31]. In order to study the stability of the catalysts, the spent catalysts are also subjected to the XRD analysis. The results are presented in Fig. 2 and Table 1. The XRD patterns of the spent catalyst also showed that there is no remarkable change in the

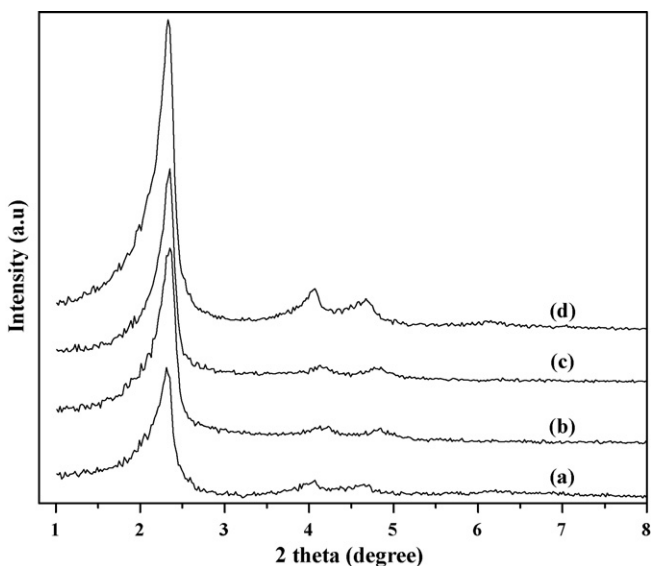


Fig. 2. X-ray diffraction pattern of spent Al-MCM-41 mesoporous molecular sieves: (a) Al-MCM-41 (36), (b) Al-MCM-41 (57), (c) Al-MCM-41 (81) and (d) Al-MCM-41 (108).

intensity and *d*-spacing values and it is well retained after the reaction.

3.1.2. Nitrogen adsorption–desorption isotherms

BET surface area, pore size and pore volume of all these samples are summarized in Table 1. It is seen that the surface area decreases as the Si/Al ratio decreases. Fig. 3 shows the N₂ adsorption–desorption isotherms of the materials show a sharp inflection at relative pressures (*p/p*₀) in the range of 0.27–0.40. This corresponds to capillary condensation of N₂ in the mesopores with completely reversible isotherms but with little hysteresis, characteristic of ordered mesoporous materials. The sharpness of the inflection reflects the uniformity of the pore sizes and the height indicates the pore volume. Fig. 4 shows the pore size distribution of the mesoporous part is centered at about 25.0–30.5 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 [32,33].

3.1.3. Thermogravimetric analysis

To study the hydrophobic nature of catalysts, thermogravimetric analysis was carried out for benzene-adsorbed catalysts [34]. The applied procedure involved, contacting of calcined Al-MCM-41 catalysts (0.5 g dried at 150 °C prior to adsorption) with benzene (10 ml) under constant stirring for 12 h at room temperature. After 12 h the benzene-adsorbed catalyst was filtered and subjected to surface drying under 250 W lamp followed by thermogravimetric

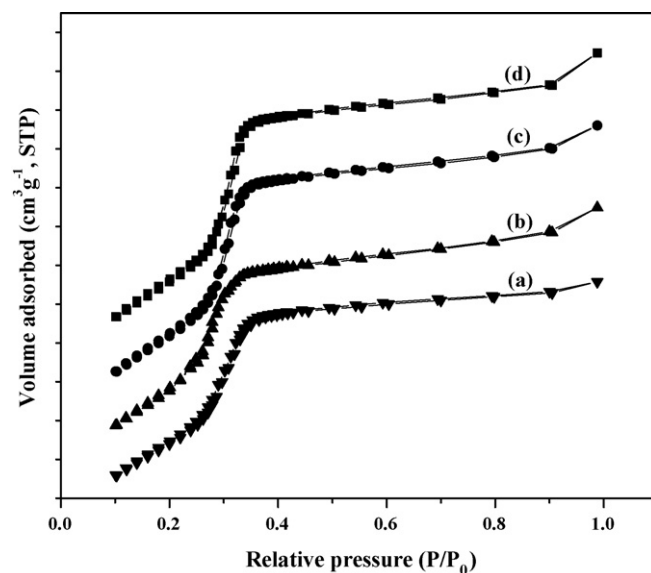


Fig. 3. Nitrogen adsorption–desorption isotherms of Al-MCM-41 molecular sieves: (a) Al-MCM-41 (36), (b) Al-MCM-41 (57), (c) Al-MCM-41 (81) and (d) Al-MCM-41 (108).

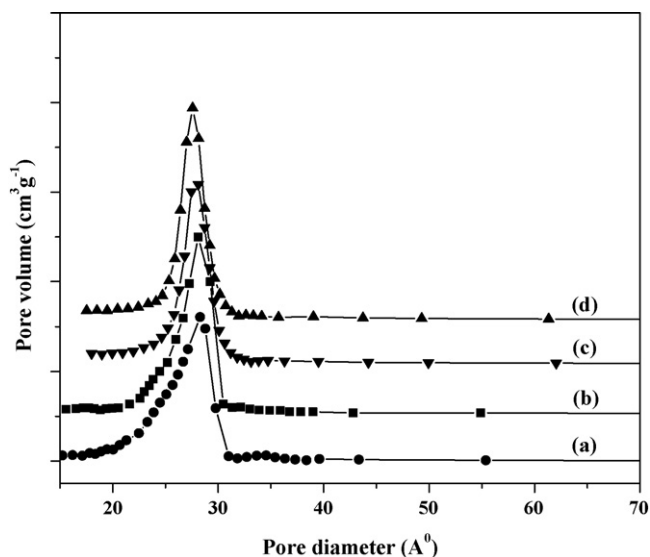


Fig. 4. Pore size distribution of Al-MCM-41 mesoporous materials: (a) Al-MCM-41 (36), (b) Al-MCM-41 (57), (c) Al-MCM-41 (81) and (d) Al-MCM-41 (108).

analysis in the temperature range of 30–600 °C. The obtained TGA-DTA results are shown in Fig. 5. The TGA patterns of Al-MCM-41 (108) showed total weight loss of 27.59% in the temperature range from 30 °C to 600 °C where as Al-MCM-41 (36) showed only 23.38% weight loss. Al-MCM-41 (108) was observe to take 4.21% extra benzene than Al-MCM-41 (36). The TGA result clearly illustrates higher hydrophobic properties for materials with high Si/Al ratios.

3.1.4. Pyridine FT-IR analysis

The distribution of both Brönsted and Lewis acid sites on the mesoporous materials was confirmed by FT-IR techniques. Fig. 6 shows the pyridine adsorbed FT-IR spectra of mesoporous Al-MCM-41 materials. The samples exhibit expected bands around 1450–1650 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 cm^{-1} 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

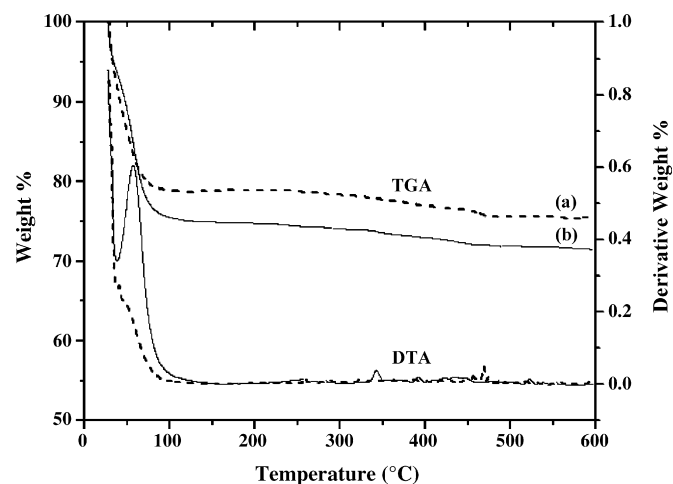


Fig. 5. Thermogravimetric analysis of benzene adsorbed Al-MCM-41 catalysts: (a) Al-MCM-41 (36) and (b) Al-MCM-41 (108).

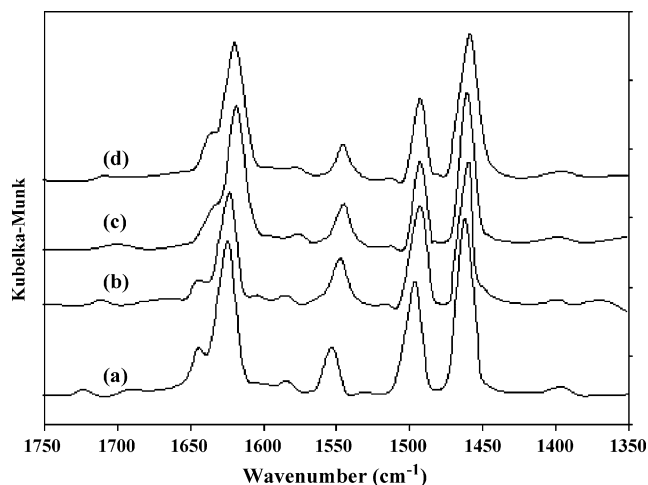


Fig. 6. DRIFT spectra of pyridine adsorption region of mesoporous materials: (a) Al-MCM-41 (36), (b) Al-MCM-41 (57), (c) Al-MCM-41 (81) and (d) Al-MCM-41 (108).

data coincide well with those already reported in the literature [35,36].

3.1.5. TEM analysis

The TEM photographs showed that the size and morphology of the mesoporous catalysts with highly ordered honeycomb-like regular arrangement of hexagonal pores on the molecular sieves. The TEM pictures of these catalysts are presented in Fig. 7. The pictures also show the orderly growth of pure hexagonal phase with well-defined sites.

3.2. Applications of Al-MCM-41 (36), Al-MCM-41 (57), Al-MCM-41 (81) and Al-MCM-41 (108) catalysts for the formation of cyclic acetals

3.2.1. Influence of reaction temperature

The reaction of benzaldehyde with various glycols of different molecular sizes namely ethylene glycol, propylene glycol and hexylene glycol were carried out over Al-MCM-41 with various Si/Al ratios (Si/Al=36, 57, 81 and 108) at various temperatures, ranging from 50 to 150 °C. The mole ratio of the reactants 1:3 (aldehyde:glycol), the reaction period 5 h were kept constant for all the reactions and the results are given in Table 2. The reaction yielded three cyclic acetals namely: 2-phenyl-1,3-dioxolane (PD), 4-methyl-2-phenyl-1,3-dioxolane (MPD) and 4-butyl-2-phenyl-1,3-dioxolane (BPD). Acid catalyst (generally a mineral acid) protonates the carbonyl group of aldehyde making it more readily attacked by nucleophilic oxygen of the alcohol. In the case of solid acid catalyst, the bronsted acid sites associated to tetrahedrally coordinated Al are the only active ones for the production of acetals.

The mechanism of the acetalization reaction is given in Scheme 1. It shows that the formation of carbocation on the carbonyl group of aldehyde takes place over the bronsted acid sites associated to tetrahedrally coordinated aluminium. The formed carbo cationic species were combined with nucleophilic oxygen of the glycol and hemiacetal is formed in the first step. In the second step, the formed hemiacetal is readsorbed on the acid sites followed by the cyclodehydration to eliminate a molecule of water and acetal is formed. Table 2 summarizes the catalytic performances of Al-MCM-41 over the formation of cyclic acetals. The aldehyde conversion over all the catalysts increases with increase in temperature. Al-MCM-41 (108) shows better conversion than other Si/Al ratios. This may be due to the hydrophobic nature of the catalyst,

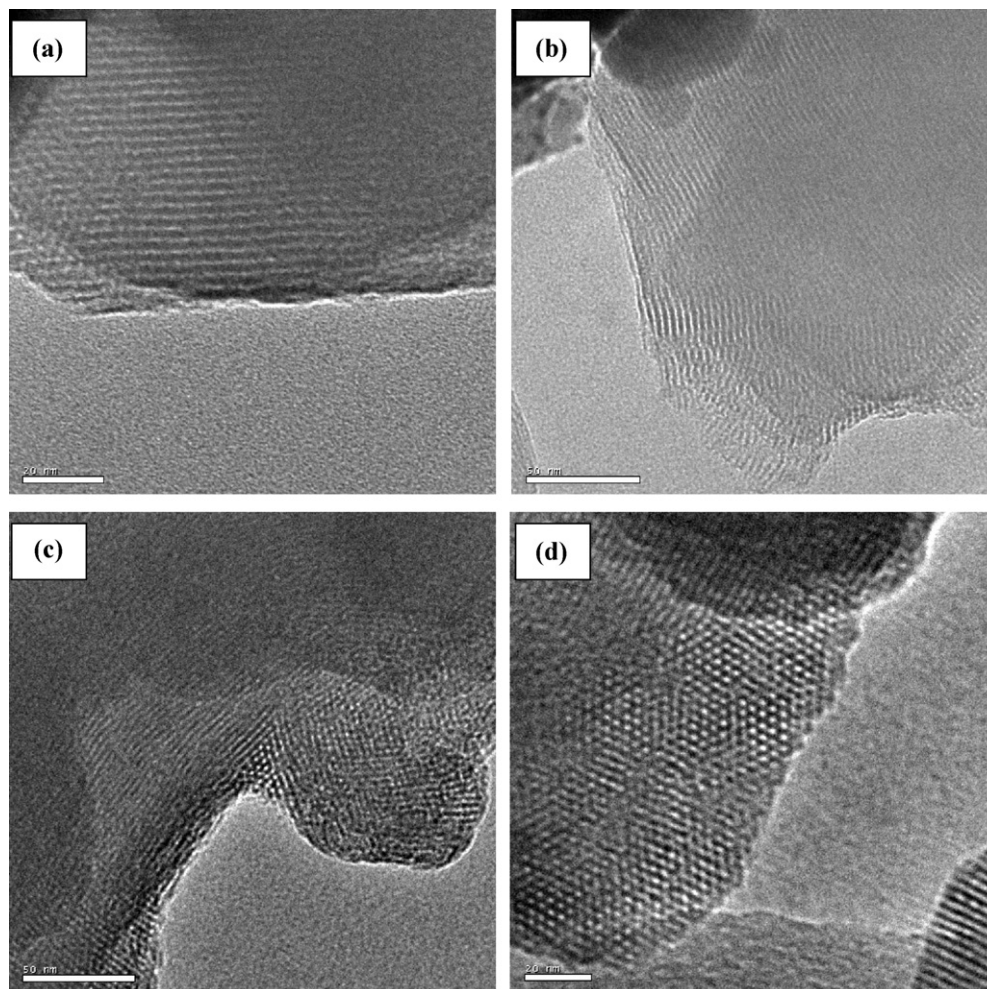


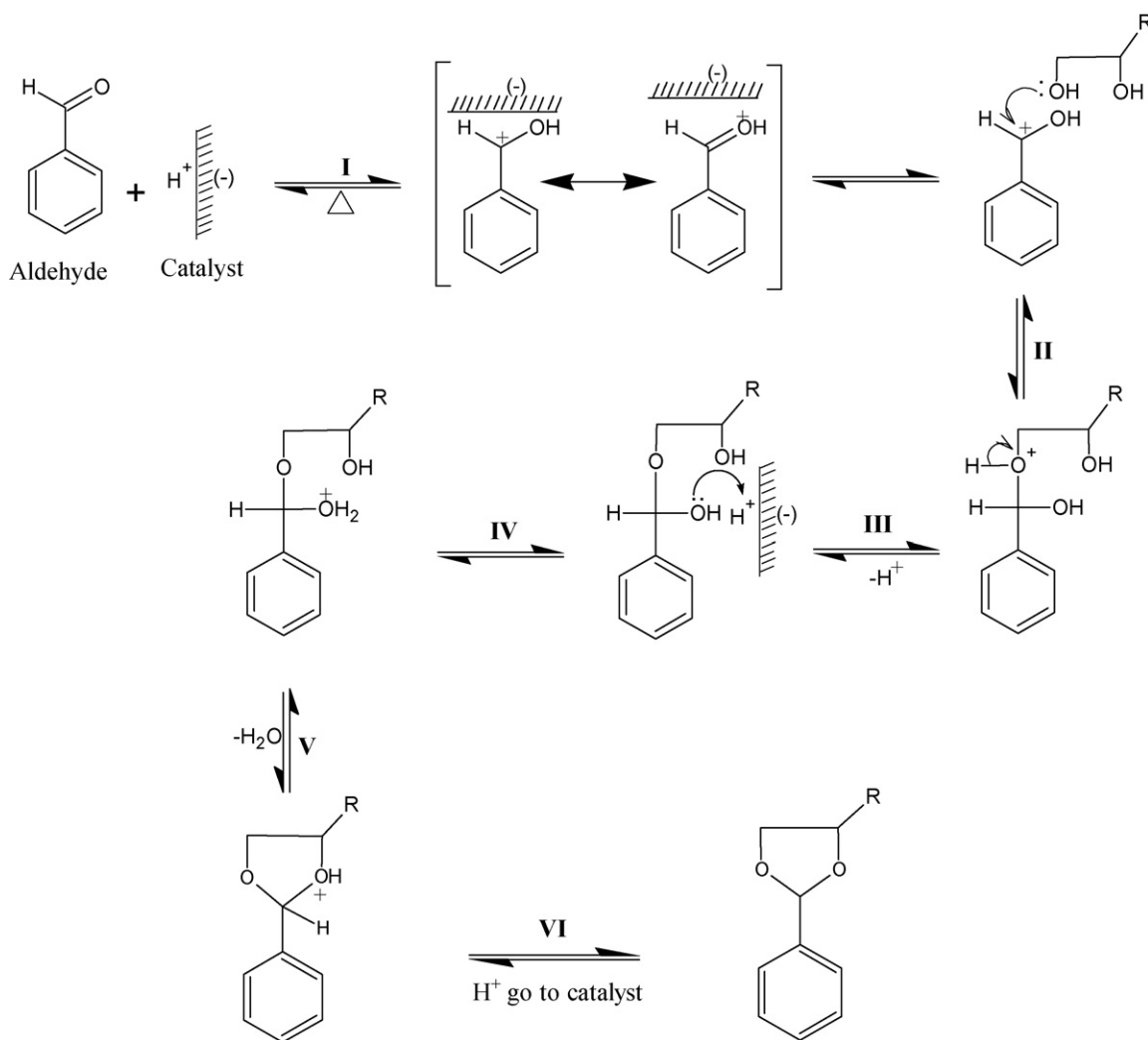
Fig. 7. TEM pictures of Al-MCM-41 molecular sieves: (a) Al-MCM-41 (36), (b) Al-MCM-41 (57), (c) Al-MCM-41 (81) and (d) Al-MCM-41 (108).

Table 2

Influence of temperature on the synthesis of acetals over Al-MCM-41 (Si/Al = 36, 57, 81 and 108) molecular sieves

Catalyst	Temperature (°C)	2-Phenyl-1,3-dioxolane		4-Methyl-2-phenyl-1,3-dioxolane		4-Butyl-2-phenyl-1,3-dioxolane	
		%Conversion of benzaldehyde	Selectivity to PD	%Conversion of benzaldehyde	Selectivity to MPD	%Conversion of benzaldehyde	Selectivity to BPD
Si/Al = 36	50	33.5	99.5	41.1	99.1	53.8	91.1
	70	40.1	99.5	51.9	99.2	68.3	91.2
	90	53.1	99.4	66.5	98.9	82.1	90.9
	120	60.7	99.1	78.1	98.7	85.1	89.9
	150	68.3	98.8	83.3	98.6	87.9	89.8
Si/Al = 57	50	31.9	99.5	41.9	99.2	53.3	92.2
	70	39.7	99.4	52.6	99.1	69.9	92.3
	90	52.7	99.4	67.2	99.2	83.5	91.9
	120	63.5	99.2	78.8	99.0	88.9	91.9
	150	67.5	99.3	84.5	99.0	89.9	91.8
Si/Al = 81	50	34.9	99.7	44.5	99.6	55.1	93.1
	70	43.9	99.7	55.5	99.6	71.3	93.2
	90	55.6	99.6	69.8	99.7	85.7	93.1
	120	64.4	99.7	80.6	99.6	87.7	92.8
	150	68.3	99.3	83.8	99.5	90.6	92.7
Si/Al = 108	50	38.7	99.9	46.3	99.9	56.4	96.3
	70	49.5	99.9	59.8	99.8	73.4	96.0
	90	61.4	99.9	73.2	99.8	89.8	95.6
	120	69.2	99.7	83.7	99.5	91.1	93.5
	150	72.9	99.8	85.8	99.6	92.7	92.3

Reaction conditions: mole ratio = 1:3 (aldehyde:glycol); weight of the catalyst = 0.10 g; reaction period = 5 h; reactor = 10 ml autoclave.



Scheme 1. Mechanism for the formation of cyclic acetal.

which can drive out the water which is formed during the reaction from the meso pores of the catalyst. This can be evidenced by the previous literatures. The hydrophobic character of MCM-41 has been clearly demonstrated by carrying out the adsorption of cyclohexane–water and benzene–H₂O [28]. The results obtained shows that in a hydrophilic zeolite, such as faujasite, the adsorption of H₂O 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 H₂O. 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 [37]. In our study, the activity of the catalyst clearly indicates that the conversion is directly proportional to the hydrophobicity of the catalyst. All the reactions show better conversion of aldehyde for higher Si/Al ratio when compared with lower Si/Al ratio containing Al-MCM-41. This shows that the catalytic activity of the catalysts following the order Al-MCM-41 (108) > Al-MCM-41 (81) > Al-MCM-41 (57) > Al-MCM-41 (36) over the formation of all acetals. All the Si/Al ratios showed that the maximum conversion of aldehyde is attained at 120 °C for all three

reactions. For example the activities of EG, PG and HG for the conversion of aldehyde over Al-MCM-41 (108) were compared at 120 °C. The aldehyde conversion with good selectivity reaches to a maximum of 69.2, 83.7 and 91.1% for EG, PG and HG, respectively. All the catalysts shows the conversion of aldehyde following the order HG > PG > EG at all temperatures. The conversion of benzaldehyde increased from EG to HG. Generally, acetalization reaction starts with initial nucleophilic attack on the aldehyde by the primary alcoholic group of the glycol followed by the intramolecular cyclisation to yield the target product. The increase in conversion from EG to HG, suggests increase in nucleophilicity is due to the alkyl group present in PG and HG. Presence of alkyl group increases the nucleophilicity of both the primary and secondary alcoholic groups. The presence of alkyl groups also provide hydrophobic environment to facilitate the removal of water once the nucleophilic attack is over. This facilitates the further condensation and improves the product yield.

3.2.2. Influence of reaction time

The effect of reaction time on the acetalization reaction was studied over 0.10 g of Al-MCM-41 (108) with constant mole ratio of 1:3 at optimized temperature of 120 °C. The results are presented in Fig. 8. All the three reactions show that the aldehyde conversion

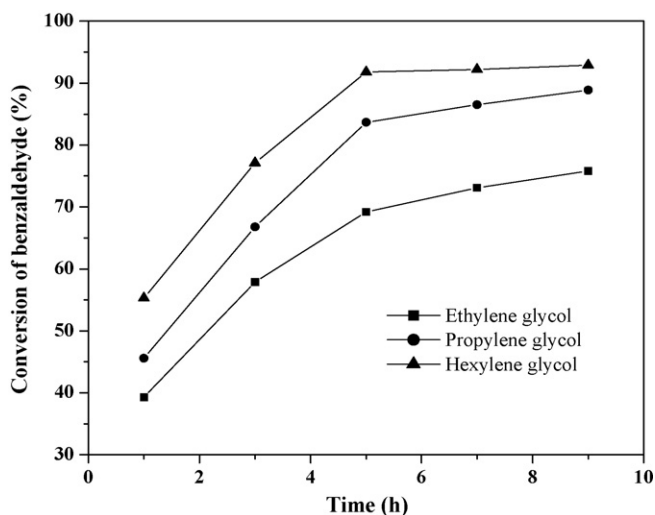


Fig. 8. Influence of reaction time on the acetalization of benzaldehyde over Al-MCM-41 (108). Reaction conditions: temperature = 120 °C; weight of the catalyst = 0.10 g; mole ratio = 1:3 (aldehyde:glycol); reactor = 10 ml autoclave.

increases with increase in reaction time. For example in the case of reaction with HG, the aldehyde conversion increases rapidly from 1st hour (55.3%) to 3rd hour (77.1%) of reaction time, and reaches optimum at 5 h (91.8%). At the end of 9th hour 92.9 wt.% is the conversion. From 5th hour to 9th hour there is only 1.1% conversion was observed. The similar trend is also followed for EG and PG. After the 5th hour it shows only marginal increase in conversion, thereby the reaction period of 5 h is the optimum time for the better conversion of aldehyde for all the three reactions.

3.2.3. Influence of mole ratio

The influence of various mole ratios of the reactants (aldehyde:glycol) in the acetalization reaction was studied over Al-MCM-41 (108) with constant reaction period (5 h) at optimized temperature of 120 °C. The mole ratios 1:1 to 1:5, 2:1 and 3:1 (aldehyde:glycol) were examined. The conversion and product selectivity are presented in Table 3. The aldehyde conversion increases from 1:1 to 1:3 then it decreases. From the reaction of HG with benzaldehyde, the benzaldehyde conversion is 74.3 wt.% for mole ratio 1:1; further increase in mole ratio 1:3, the conversion reaches maximum to 91.1% then it decreases to 86.7 wt.% for the mole ratio 1:5. The similar trend in aldehyde conversion was also observed for EG and PG. The increase in mole ratio (higher glycol ratio) increases the aldehyde conversion up to certain extent then it decreases. This might be due to dilution in the availability of carbonyl group of the aldehyde nearer to the bronsted acid sites of the catalyst which reduces the formation of carbocation. The mole ratio 1:3 is the optimum level for better conversion of aldehyde in all the three reactions. The reaction was also studied by taking more aldehyde content in the feed. The aldehyde conversion is very less in the feed ratio of 2:1 (42.9%) and 3:1 (40.5%) in the case of HG. The observed decrease in conversion might be due to the dilution of alcohol by excess of aldehyde; it prevents the availability of the nucleophilic oxygen of glycol nearer to the formed carbocation of the aldehyde. The same trend was also observed for EG and PG.

3.2.4. Influence of catalyst loading

The influence of catalyst loading on the conversion of aldehyde was studied with varying the amount of catalyst in the reaction. The reaction was studied over Al-MCM-41 (108) with mole ratio of 1:3 and reaction period of 5 h at optimized temperature of 120 °C.

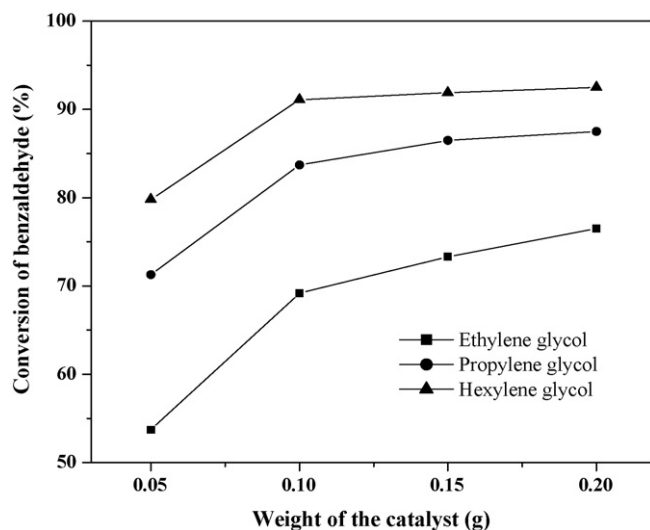


Fig. 9. Influence of catalyst loading on the acetalization of benzaldehyde over Al-MCM-41 (108). Reaction conditions: temperature = 120 °C; mole ratio = 1:3 (aldehyde:glycol); reaction period = 5 h; reactor = 10 ml autoclave.

The results are presented in Fig. 9. The aldehyde conversion was increased with increase in the weight of catalyst. In the case of reaction with PG, conversion increases from 0.05 g (71.3%) to 0.20 g (87.5%), whereas 0.10 g catalyst shows 83.7% aldehyde conversion. From 0.10 g to 0.20 g, it shows only marginal increase in aldehyde conversion. This observation shows that 0.10 g of Al-MCM-41 (108) is enough to catalyze the reaction.

3.2.5. Reusability of the catalyst

Reusability of the catalyst was studied for the reaction of benzaldehyde with hexylene glycol as the model substrates. The reaction was carried out under optimized reaction conditions using Al-MCM-41 (108) as the catalyst. After completion of the reaction, the reaction mixture was centrifuged at 4000–6000 rpm for 10 min, and the deposited catalyst was washed with acetone three to four times to confirm the complete removal of any residual material. The recovered catalysts were activated and used for further catalytic reaction cycle. The same process was repeated after each reaction cycle to isolate and reuse the catalyst. The reaction proceeded smoothly with a yield of 91.4–89.8% (Fig. 10). The results showed that the Al-MCM-41 could be reused at least five times without lowering the catalytic activity. The structural stability of the spent catalysts were also examined by XRD and TEM techniques. The XRD patterns of the used catalysts showed that the hexagonal

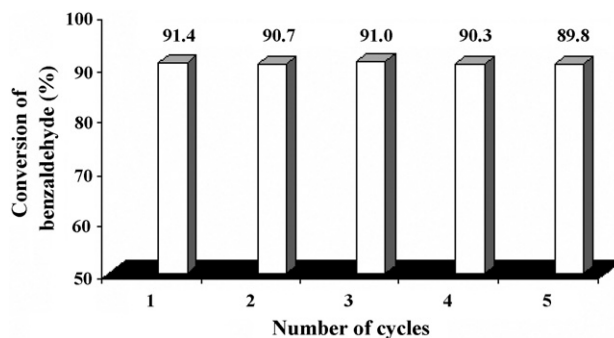


Fig. 10. Reusability of the catalyst. Reaction conditions: mole ratio = 1:3 (aldehyde:glycol); catalyst: Al-MCM-41 (108); weight of the catalyst = 0.10 g/10 mmol of benzaldehyde; reaction period = 5 h; reactor = 10 ml autoclave.

Table 3
Influence of mole ratio on synthesis of acetals over Al-MCM-41 (108) molecular sieves

Mole ratio (aldehyde:glycol)	2-Phenyl-1,3-dioxolane		4-Methyl-2-phenyl-1,3-dioxolane		4-Butyl-2-phenyl-1,3-dioxolane	
	%Conversion of benzaldehyde	Selectivity to PD	%Conversion of benzaldehyde	Selectivity to MPD	%Conversion of benzaldehyde	Selectivity to BPD
1:1	55.8	97.5	65.6	99.3	74.3	94.5
1:2	65.1	99.7	76.9	99.6	87.9	96.3
1:3	69.2	99.7	83.7	99.5	91.1	95.6
1:4	65.3	99.8	81.3	99.6	88.2	95.1
1:5	61.0	99.7	79.8	99.6	86.7	95.9
2:1	28.7	99.8	33.7	99.7	42.9	96.1
3:1	25.1	99.7	29.6	99.5	40.5	96.0

Reaction conditions: temperature = 120 °C; weight of the catalyst = 0.10 g; reaction period = 5 h; reactor = 10 ml autoclave.

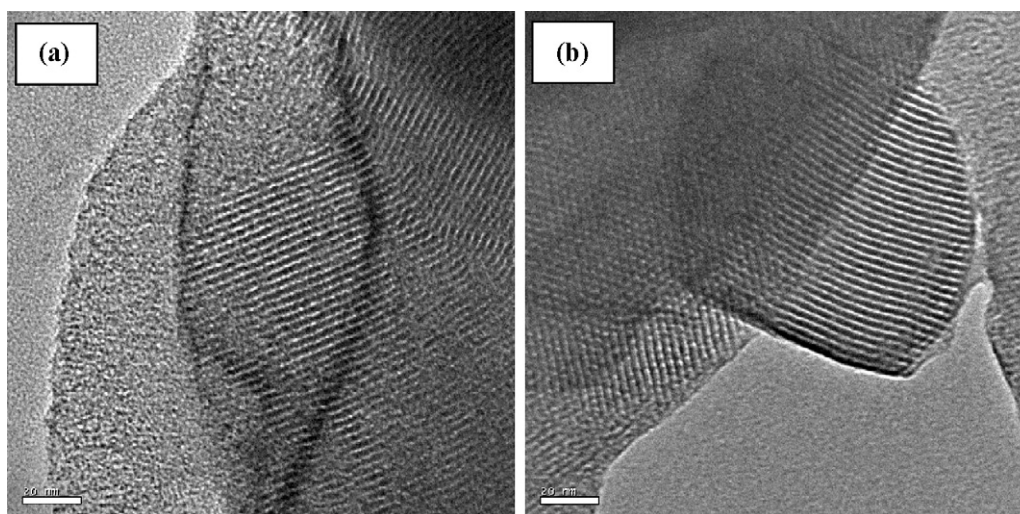


Fig. 11. TEM pictures of the spent catalysts: (a) Al-MCM-41 (36) and (b) Al-MCM-41 (108).

regularity of the materials is not affected; it is similar to that of the fresh catalysts (Fig. 2). The TEM images of the spent catalysts also showed that the uniform pore structure is not affected on recycling of the catalysts (Fig. 11). The above results indicating that the activity and stability of the catalyst is well retained on recycling.

4. Conclusion

The acetalization of benzaldehyde with various glycols were carried out over Al-MCM-41 with different Si/Al ratios. Cyclic acetals are the only product over all the catalysts. Highly hydrophobic Al-MCM-41 (108) facilitated the formation of cyclic acetals. The increase in the chain length of glycol increases the nucleophilicity and hydrophobicity of the glycols; this shows much influence on the conversion of benzaldehyde. All the catalysts shows the conversion of aldehyde following the order HG > PG > EG. From this study, the conditions like 0.1 g Al-MCM-41 (108) with reactant mole ratio 1:3 (aldehyde:glycol), the reaction period of 5 h and the temperature 120 °C were optimum for the better formation of cyclic acetals, which can be achieved only by the specific nature of the solid acid catalyst. It can be depicted that Al-MCM-41 catalyst could be the convenient eco-friendly alternative to the conventional hazardous mineral acid catalyst for acetalization reactions. Moreover the spent catalyst was very well regenerated even after five reaction cycles under these experimental conditions.

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