



ACID INDUCED MESOPOROUS Si-MCM-41 AS SOLID ACID CATALYST FOR FRIEDEL-CRAFTS ALKYLATION AND ACYLATION

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ABSTRACT

Mesoporous MCM-41 has been synthesized by sol-gel method at room temperature possessing good thermal stability, high surface area as well as retention of surface area at high temperature. The MCM-41 neutral framework has been modified and put to practical use. Al^{3+} has been incorporated in the siliceous MCM-41 framework and 12TPA (12-Tungstophosphoric acid) anchored onto MCM-41 by process of anchoring and calcination to induce Brønsted acidity in MCM-41 to yield Al-MCM-41 and 12TPA-MCM-41, respectively. The synthesized materials have been characterized for elemental analysis, ICP-AES, XRD, SEM, TEM, EDX, FTIR and TGA. Surface area has been determined by BET method and pore size and pore size distribution determined by BJH method. Surface acidity has been evaluated by NH_3 -TPD method. The potential use of Al-MCM-41 and 12TPA-MCM-41 as solid acid catalysts has been explored and compared by studying Friedel-Crafts alkylation and acylation as model reactions. Friedel-Crafts acylation of anisole and veratrole with acetic anhydride and alkylation of toluene with benzyl chloride have been performed to obtain 4-methoxy acetophenone (4-MA), 3,4-dimethoxy acetophenone (3,4-DMA) and parabenzyltoluene (PBT), respectively under solvent free condition, and several parameters such as catalyst amount, reaction time, reaction temperature, mole ratio of reagents, etc.

Key words: Mesoporous material, Si-MCM-41, Al-MCM-41, Heteropoly acid anchored onto MCM-41, Friedel-Crafts acylation and alkylation, Solid acid catalyst.

INTRODUCTION

Friedel-Crafts acylation of aromatic compounds is an omnipresent reaction in the production of aromatic ketones largely used as intermediates in the synthesis of pharmaceuticals, dyes, fragrances, agrochemicals, paint additives, photo initiators, plasticizers and other commercial products^{1,2}. The liquid phase benzylation of benzene and other aromatic compounds by benzyl chloride is important for the production of diphenylmethane and substituted diphenylmethanes which are industrially important compounds used as pharmaceutical intermediates and fine chemicals³.

Traditional Friedel-Crafts acylation uses acyl halides or anhydrides as acetylating agents, with soluble Lewis acids (anhydrous $AlCl_3$ and BF_3) and mineral acids (H_2SO_4 , HF) as catalysts, which are polluting and difficult to work with. These acids are consumed in more than stoichiometric amounts due to the formation of 1:1 molar adduct with the product. Besides, the subsequent separation of the product by hydrolysis is cumbersome and generates a large amount of environmentally hazardous and corrosive waste.

Friedel-Crafts alkylation reactions catalyzed by homogeneous Lewis acid catalysts generally give complex reaction mixtures. The formation of reactant (and product) catalyst complexes, the increased tendency of alkylated products towards further alkylation and isomerization, coupled with the long contact of the reactant with the catalyst, result in decreased product selectivity. The major drawback in these processes is that the Lewis acid is non-regenerable.

Owing to stringent and growing environmental regulations worldwide, there is a global effort to replace the conventional liquid acid catalysts by solid acids, which are less toxic, easily regenerable from the product, easy to handle and reusable. Many MCM-41 type materials have been used as solid acid catalysts for Friedel-Crafts alkylation and acylation. Benzoylation of benzene over sulfated zirconia supported onto MCM-41,⁴ alkylation of benzene with propylene over 12TPA (12-Tungstophosphoric acid) supported onto MCM-41 and -48 type mesoporous materials⁵, alkylation and acylation of ethylbenzene with ethyl acetate using Al-MCM-41, Fe, Al-MCM-41 and Zn, Al-MCM-41,⁶ veratrole acetylation using 12TPA supported over zirconia in mesoporous channels of MCM-41,⁷ benzoylation of aromatics with benzyl alcohols catalyzed by heteropoly acids (HPAs) such as tungstophosphoric acid, molybdophosphoric acid and tungstosilicic acid supported onto mesoporous silica such as MCM-41, FSM-16 and SBA-15⁸, are some good examples.

MCM-41 based materials have negligible catalytic activity due to framework neutrality, however with advantageous properties like mesoporous nature of the material, good thermal stability, high surface area and retention of surface area at high temperatures. Thus, the main aim of the present study was to encash the advantageous properties of MCM-41 and enhances its practicability in the area of catalysis using Green Chemistry principles. There are a number of ways by which catalytic activity can be generated into the MCM-41 neutral framework. (i) Substitution of M^{3+} cation e.g. Al^{3+} in the Si^{4+} framework, leading to negatively charged framework, followed by balancing these charges by H^+ ions (via NH_4^+ ion exchange and subsequent thermal decomposition to give H^+ and NH_3) to create Brønsted acid sites. (ii) Immobilization/anchoring/impregnation of homogenous acid catalyst e.g. HPAs onto MCM-41. HPAs have proved to be the alternative to traditional mineral acid catalysts due to both strong acidity and appropriate redox properties. However, limitations for HPAs to be used as solid acid catalysts are low thermal stability, low surface area (1-10 m^2/g) and difficulty in separation from reaction mixture due to their high solubility in polar solvents⁹. For HPAs to be effective as catalysts, they should be supported on a carrier with a large surface area. Owing to a very large surface area and a uniform large pore size, the MCM-41 materials can act as excellent supports that provide an opportunity for HPAs to be dispersed over a large surface area and hence, increased catalytic activity.

The present study involves the synthesis of siliceous mesoporous MCM-41 at room temperature by sol-gel method, using templates. Further, Al^{3+} has been incorporated in the siliceous MCM-41 framework and 12TPA (where 12 TPA = 12-Tungstophosphoric acid a HPA) has been supported onto MCM-41 by process of anchoring and calcination to induce Brønsted acidity in MCM-41 to yield Al-MCM-41 and 12TPA-MCM-41, respectively. All synthesized materials have been characterized for elemental analysis, ICP-AES, X-ray diffraction (XRD), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX), Surface area (BET method), Pore volume and pore distribution (BJH method), surface acidity by temperature programmed desorption (TPD) of ammonia, Diffuse reflectance spectroscopy (UV-DRS), Fourier transform infrared spectroscopy (FT-IR) and Thermogravimetric analysis (TGA).

The potential use of Al-MCM-41 and 12TPA-MCM-41 as solid acid catalysts has been explored and compared by studying Friedel-Crafts alkylation and acylation as model reactions. Friedel-Crafts acylation of anisole and veratrole with acetic anhydride and alkylation of toluene with benzyl chloride have been performed to obtain 4-methoxy acetophenone (4MA), 3,4-dimethoxy acetophenone (3,4 DMA) and

parabenzyltoluene (PBT) respectively under solvent free condition and several parameters such as catalyst amount, reaction time, reaction temperature, mole ratio of reagents, etc.

EXPERIMENTAL

Materials

Commercial grade sodium silicate (Na_2SiO_3) with composition 28% SiO_2 and 7.5% Na_2O was procured from Sapna Chemicals, Vadodara. Cetyl trimethyl ammonium bromide (CTABr), cetyl pyridinium bromide (CPBr), sodium hydroxide flakes, aluminium sulfate, ammonium nitrate and 12-tungstophosphoric acid (12TPA) were purchased from Loba Chemicals, Mumbai. Tetra ethylortho silicate (TEOS) and analytical grade sulphuric acid were obtained from E. Merck, Mumbai. All other chemicals and reagents used were of analytical grade. Double distilled water (DDW) was used for all studies.

Catalyst synthesis

Synthesis of MCM-41

MCM-41 has been synthesized by sol-gel method using templates varying several parameters such as silica source, templating agent/types, reaction conditions such as pH, time of reaction, aging, temperature etc. and these parameters were optimized, using surface area as an indicative tool in all cases. Table 1 describes the parameters that have been optimized for synthesis of MCM-41.

Table 1: MCM-41 Synthesis strategies-parameters optimized

Parameters	No	SiO ₂ source	Template source	Template mole	H ₂ O mole	Temp. (°C)	Aging time (hr)	pH	BET Surface area at different temp. (m ² /g)		
									550°C	700°C	900°C
Aging time	1	Na ₂ SiO ₃	CTABr	0.25	80	RT	1	10.5	640	490	370
	2	Na ₂ SiO ₃	CTABr	0.25	80	RT	3	10.5	770	510	342
	3	Na ₂ SiO ₃	CTABr	0.25	80	RT	6	10.5	820	550	446
	4	Na ₂ SiO ₃	CTABr	0.25	80	RT	18	10.5	900	570	428
	5	Na ₂ SiO ₃	CTABr	0.25	80	RT	24	10.5	917	612	433
Temperature	6	Na ₂ SiO ₃	CTABr	0.25	80	70	24	10.5	864	735	460
	7	Na ₂ SiO ₃	CTABr	0.25	80	100	24	10.5	974	820	300
Template mole	8	Na₂SiO₃	CTABr	0.5	80	RT	24	10.5	1136	1121	805
	9	TEOS	CTABr	0.5	40	RT	24	9.5	1126	1116	706
Template source	10	Na ₂ SiO ₃	CPBr	0.5	80	RT	24	10.5	736	593	483

SiO₂ mole = 1 mole; RT = Room Temperature (30±3 °C); % SiO₂ = 99.89 (ICP-AES)

Synthesis of MCM-41 at optimized conditions

The molar gel composition for MCM-41 is 1 SiO₂:0.5 CTABr: 0.25 Na₂O: 80 H₂O. The first step was preparation of the precursor solution. 63.02 g of Na₂SiO₃ was mixed with 183 g DDW under continuous stirring at room temperature for ~15 min. in a polypropylene container (A). An aqueous solution of CTABr was prepared by dissolving 54.14 g CTABr in 200 g DDW under continuous stirring at room temperature

(B). Template solution B was added to precursor solution dropwise and with continuous stirring within ~15 min. and then the solution further stirred for 15 min. The pH of the resultant solution was adjusted to ~10.5 using 1:1 H₂SO₄ (diluted 1:1 V/V). A gel was obtained at this stage, which was stirred further for 30 min. The polypropylene container was now closed and allowed to age at room temperature without stirring for 24 h. The resultant gel was filtered, washed with DDW to remove adhering ions and dried at 120°C, followed by calcination at 550°C for 6 h at a heating rate of 2°C/min. The final material obtained was used for all further studies.

Synthesis of Al-MCM-41

In the present synthetic endeavor the objective is to synthesize mesoporous Al-MCM-41 at room temperature with good thermal stability and high surface acidity. A sol-gel method has been used to achieve this objective. Several sets of materials were prepared varying silica to alumina ratios, apart from other conditions, where surface acidity has been used as an indicative tool in all cases. Table 2 describes parameters that have been optimized for synthesis of Al-MCM-41.

Table 2: Al-MCM-41 Synthesis strategies-parameters optimized

Parameters	No	SiO ₂ mole	Al ₂ O ₃ mole	SiO ₂ /Al ₂ O ₃ Input mole ratio	Template mole	Element analysis (ICP-AES)		SiO ₂ /Al ₂ O ₃ Output mole ratio	*Total acidity (mL/g)	BET Surface area at different temp. (m ² /g)		
						%	%			550°C	700°C	900°C
						SiO ₂	Al ₂ O ₃					
Template mole	1	1	0.01	100	0.5	98.59	1.35	124.15	0.86	1191	1028	554
	2	1	0.01	100	0.4	98.22	1.55	107.70	1.14	1220	1044	577
SiO ₂ /Al ₂ O ₃ Mole ratio	3	1	0.02	50	0.4	93.31	3.05	52.01	1.74	884	730	600
	4	1	0.033	30	0.4	94.90	4.90	32.92	3.03	580	510	470
	5	1	0.05	20	0.4	89.42	6.64	22.89	2.60	500	438	280

SiO₂ Source = Na₂SiO₃; Al₂O₃ source = Al₂(SO₄)₃; Template Source = CTABr; H₂O mole = 90; RT = (30±3 °C); pH = 10.5; Aging Time = 24 h *Details in Table 3

Synthesis of Al-MCM-41 at optimized conditions

The molar gel composition of Al-MCM-41 is 1 SiO₂: 0.033 Al₂O₃: 0.4 CTABr: 0.25 Na₂O: 90 H₂O. The first step was preparation of the precursor solution. 57.48 g of Na₂SiO₃ was mixed with 197.5 g DDW under continuous stirring at room temperature for ~15 min, in a polypropylene container, to which was added an aqueous solution of aluminium sulfate (prepared by dissolving 5.643 g aluminium sulfate in 40 g DDW) dropwise and with constant stirring within ~15 min. This is the precursor solution (A). An aqueous solution of CTABr was prepared by dissolving 39.5 g CTABr in 160 g DDW under continuous stirring at room temperature to give (B). Template solution (B) was added to precursor solution (A), dropwise and under constant stirring within ~15 min. The pH of the resultant solution was adjusted to ~10.5 using 1:1 H₂SO₄ (diluted 1:1 V/V). A gel was formed which was further stirred for 30 min. The polypropylene container was now closed and allowed to age at room temperature without stirring for 24 hrs. The resultant gel was filtered, washed with DDW to remove adhering ions and dried at 120°C followed by calcination at 550°C for 6h, at a heating rate of 2°C/min. After thermal treatment, the samples with various Silica : Alumina ratios Al-MCM-41-20, Al-MCM-41-30, Al-MCM-41-50, and Al-MCM-41-100 were subjected to

ion exchange by treating them with aqueous 1.0% NH_4NO_3 solution under continuous stirring for 3 h, followed by calcination at 550°C for 3 h at a heating rate of 2°C/min. in air flow. The sample Al-MCM-41-30 exhibits maximum surface acidity and was used for all further studies (Table 3).

Table 3: Acidity data of synthesized materials

Materials	Surface acidity (mL/g)				Total acidity volume (mL/g)	Pore volume (cc/g)
	Weak acid		Strong acid			
	Temp. (°C)	Volume (mL/g)	Temp. (°C)	Volume (mL/g)		
Siliceous MCM-41	171	0.15	470	0.06	0.21	0.72
10% 12TPA-MCM-41	209	1.67	651	3.74	5.41	0.57
20% 12TPA-MCM-41	201	1.60	662	5.78	7.39	0.55
30% 12TPA-MCM-41	200	2.40	609	2.90	5.30	0.43
40% 12TPA-MCM-41	188	2.50	620	2.50	5.00	0.36
Al-MCM-41-20	203	1.59	287	1.02	2.60	0.44
Al-MCM-41-30	207	2.91	287	0.12	3.03	0.27
Al-MCM-41-50	204	1.65	304	0.09	1.74	0.60
Al-MCM-41-100	201	1.09	311	0.05	1.14	0.91

For synthesis described, Na_2SiO_3 as a silica source is preferred to TEOS, reasons being higher cost of TEOS, thermal stability of final material obtained is better, and excess negative charge developed in the framework due to substitution of Si^{4+} by Al^{3+} , requires Na^+ for charge balance. While preparing, it is preferable to add template to precursor source. The pH of template being almost neutral and pH of precursor being >12, if template is added to precursor source, the pH variation window is narrowed down due to which pH of gel formation is easily adjusted. The pH in the synthesis was adjusted to ~10.5 because gel viscosity is maximum at this pH, which can also be stirred with ease for homogenization. Further, in Al-MCM-41 synthesis lower is the SiO_2 : Al_2O_3 ratio, higher will be Al^{3+} content and hence, better is the acidity generated in the resulting materials. At the optimized condition, surface acidity is high as well as surface area retention between 550-900°C is fairly good.

Synthesis of 12TPA supported MCM-41

The aim was to load different wt. % of 12TPA onto MCM-41 and induce acidity into the material, using surface acidity as an indicative tool in all cases. Four samples (12TPA supported onto MCM-41) of the catalyst were prepared with varying 12TPA loading (10-40 wt.%). In a typical setup (10% 12TPA loading) 1 g of 12TPA was dissolved in 100 mL DDW, to which 9 g of MCM-41 was added (synthesized as described earlier), and the resultant slurry was stirred continuously for 24 h at room temperature. The excess solution was removed under vacuum, dried and subsequently calcined at 350°C for 2 h at a heating rate of 2°C/min.

Instrumental methods of analysis

All synthesised materials were subjected to instrumental methods of analysis/characterization. Elemental analysis was performed on ICP-AES spectrometer (Thermo Scientific iCAP 6000 series). X-ray

diffraction pattern ($2\theta = 1^\circ - 40^\circ$) was obtained on X-ray diffractometer (Bruker D8 Focus) with Cu-K α radiation with nickel filter. FTIR spectra was recorded using KBr pellet on Shimadzu (Model 8400S). Thermal analysis (TGA) was performed on a Shimadzu (Model TGA 50) thermal analyzer at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$. SEM and EDX of the sample were scanned on Jeol JSM-5610-SLV scanning electron microscope. TEM was performed using Philips CM30 ST electron microscope operated at 300kv. Surface area measurements were determined using Micromeritics Gemini at -196°C using nitrogen adsorption isotherms. Surface acidity was determined by NH_3 -TPD method using Micromeritics Chemisorb 2720. UV-VIS.-diffuse reflectance spectra was obtained using Shimadzu (Model UV-DRS 2450).

EXPERIMENTAL

Experimental setup for Friedel-Crafts acylation and alkylation

The reactions were carried out in a two necked 50 mL round bottomed flask equipped with a magnetic stirrer under heating in an oil bath. In a typical set up, a mixture of anisole or veratrole (10 mmol) and acetic anhydride (15 mmol) for acylation and toluene (10 mmol) and benzyl chloride (15 mmol) for alkylation, along with the catalyst (0.2 g) were taken in a round bottomed flask and stirred at 110°C for three hours. In all the reactions, the substrates were used as solvents and hence the reaction temperature was kept according to solvent used (reflux temperature) for all the studies. The reactions were monitored by GC. After completion of reaction, the catalyst was separated by decantation, and reaction mixture was distilled to obtain the products 4-MA, 3,4-DMA and PBT, the boiling points being $\sim 273^\circ\text{C}$, 286°C and 300°C , respectively.

Regeneration of catalyst

During the course of the reaction, there is a possibility of adsorption of reacting molecules onto the surface of the catalyst. After separation of catalyst in reaction mixture by decantation, it is first refluxed in ethanol for 30 min to solubilise and remove adsorbed molecules, followed by drying at 120°C . This material was used as recycled catalyst. This regeneration procedure was followed in subsequent recycle reaction.

RESULTS AND DISCUSSION

Catalyst characterization

Characterization of MCM-41

The characterizations of MCM-41 and Al-MCM-41 are well investigated and presented in Figs. 1 to 19, which include XRD, TEM, SEM, EDX, FTIR, TGA, pore size and pore volume distribution, surface area using Nitrogen adsorption isotherm, surface acidity (NH_3 -TPD) and UV-DRS. The characterization indicate mesoporous nature of the materials.

Characterization of 12TPA supported onto MCM-41

12TPA supported onto MCM-41 with 20 wt.% 12TPA loading, abbreviated as 12TPA-MCM-41-20 has been used for characterization, as it exhibits highest surface acidity and used for all catalytic studies.

The three main reliable techniques used for characterization of 12TPA-MCM-41-20 are XRD^{10,11}, FTIR and surface acidity, which ensure the anchoring of HPA's onto MCM-41, wherein comparisons are made between pure HPA's, pure MCM-41 and a combination of these.

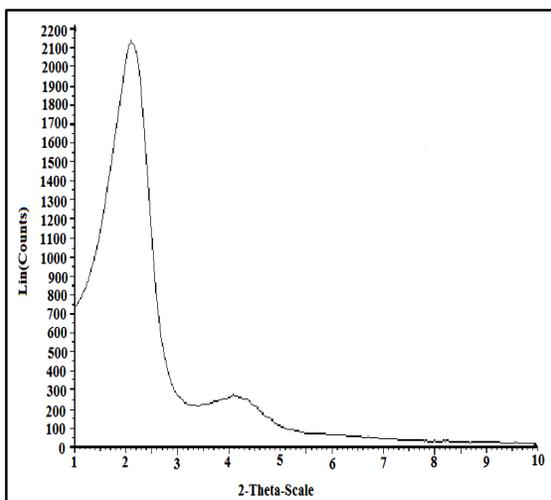


Fig. 1: XRD of MCM-41

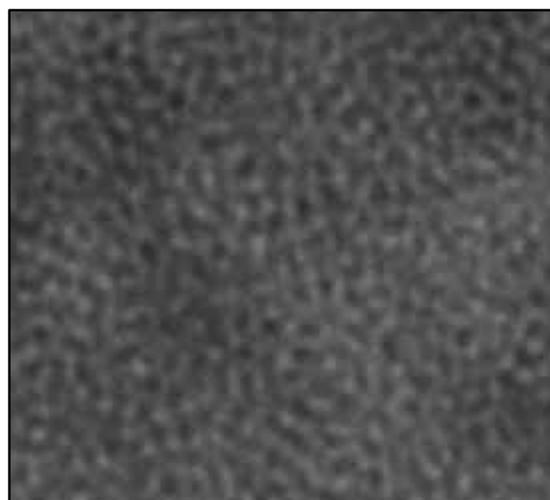


Fig. 2: TEM of MCM-41



Fig. 3: SEM of MCM-41

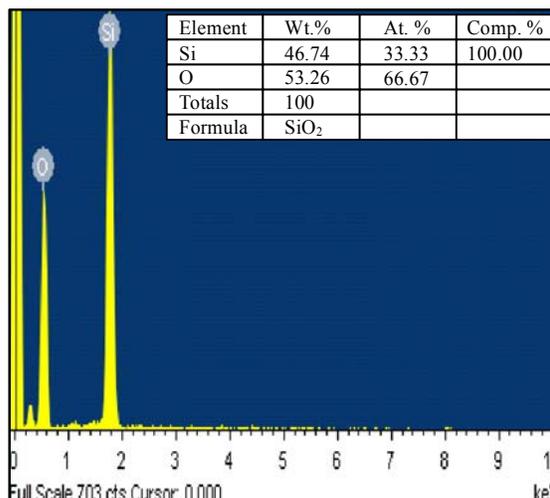


Fig. 4: EDX of MCM-41

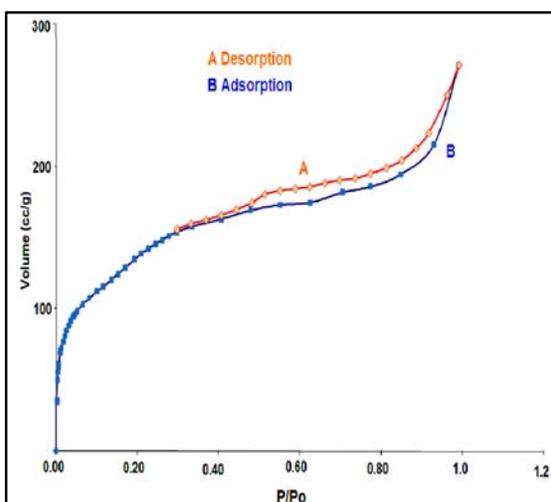


Fig. 5: Nitrogen adsorption isotherm of MCM-41

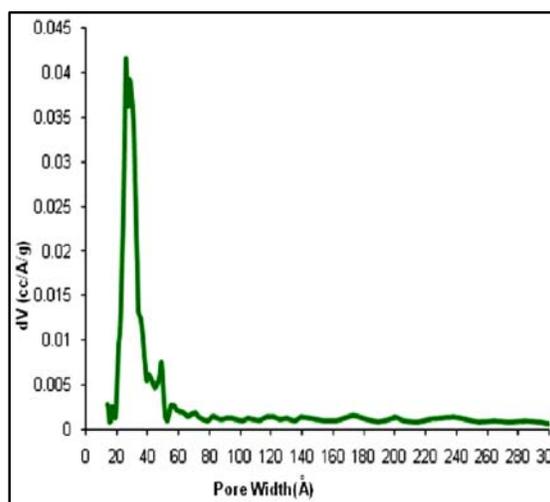


Fig. 6: Pore distribution of MCM-41

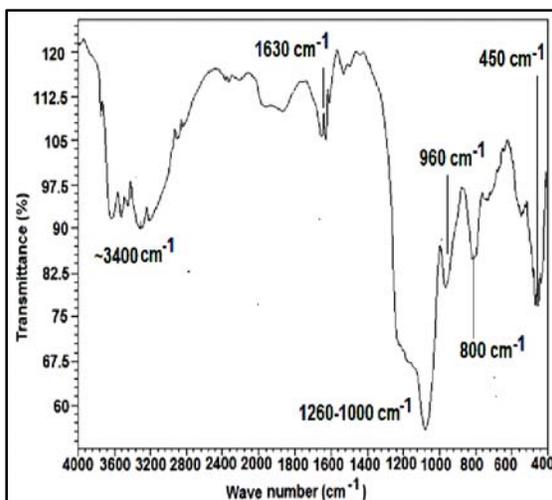


Fig. 7: FTIR of MCM-41

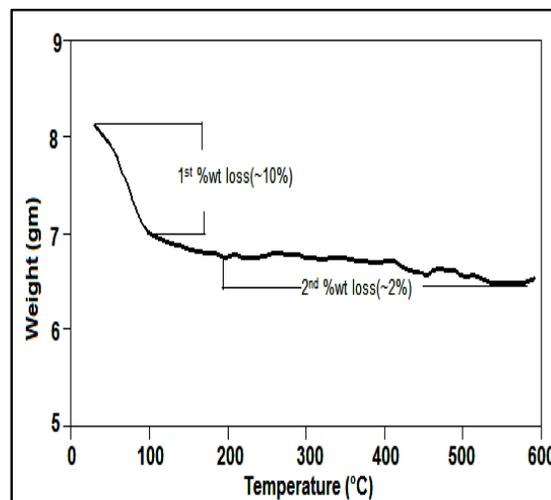


Fig. 8: TGA of MCM-41

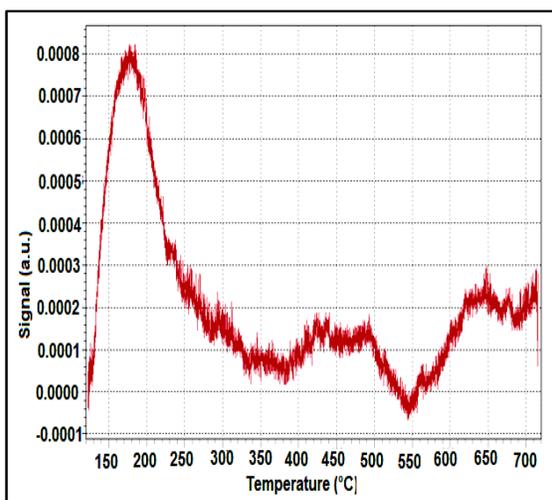


Fig. 9: Ammonia TPD of MCM-41

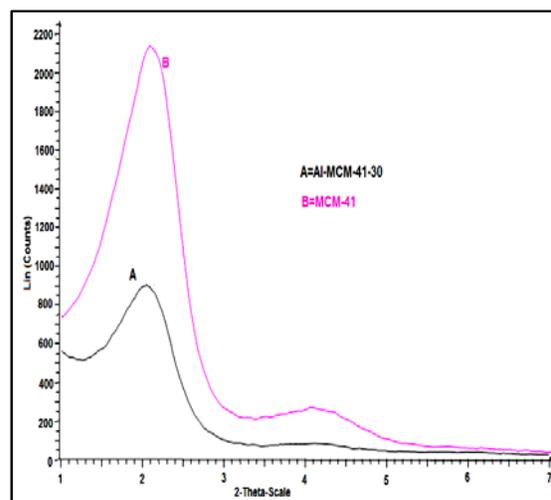


Fig. 10: XRD of Al-MCM-41-30

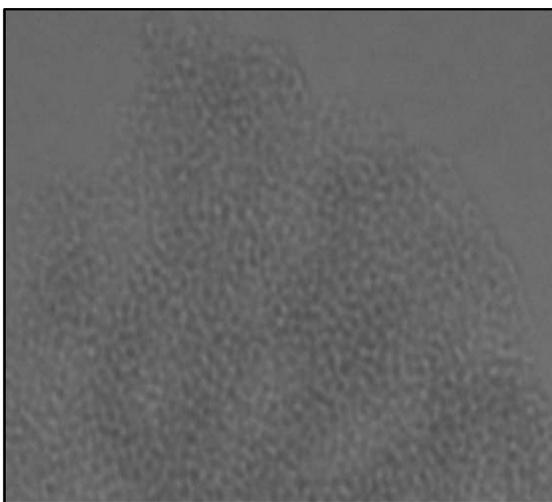


Fig. 11: TEM of Al-MCM-41-30



Fig. 12: SEM of Al-MCM-41-30

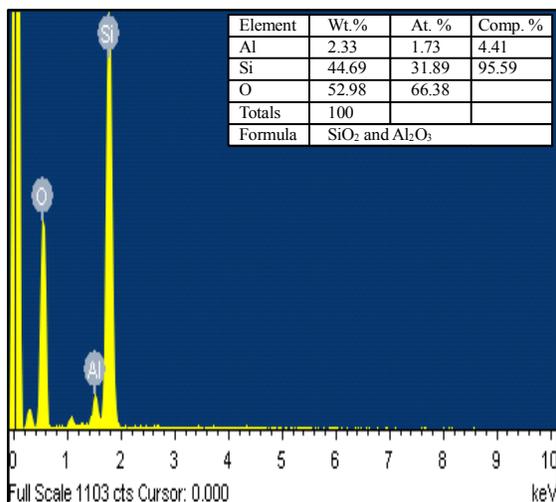


Fig. 13: EDX of Al-MCM-41-30

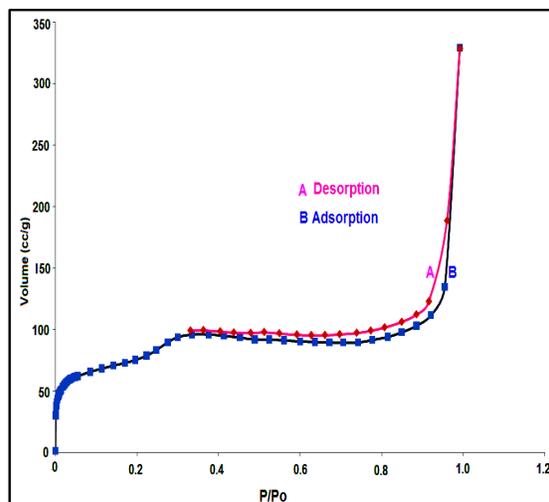


Fig. 14: Nitrogen adsorption isotherm of Al-MCM-41-30

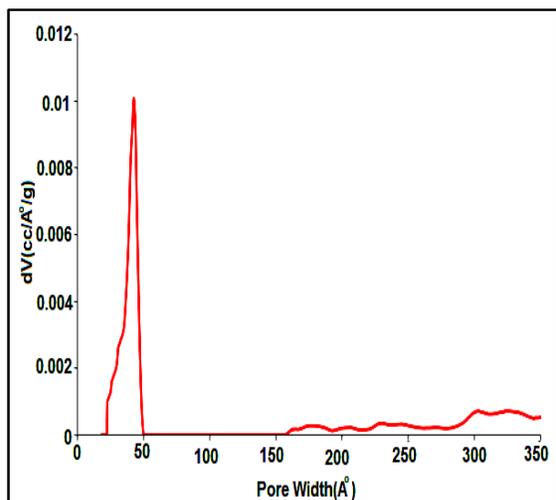


Fig. 15: Pore distribution of Al-MCM-41-30

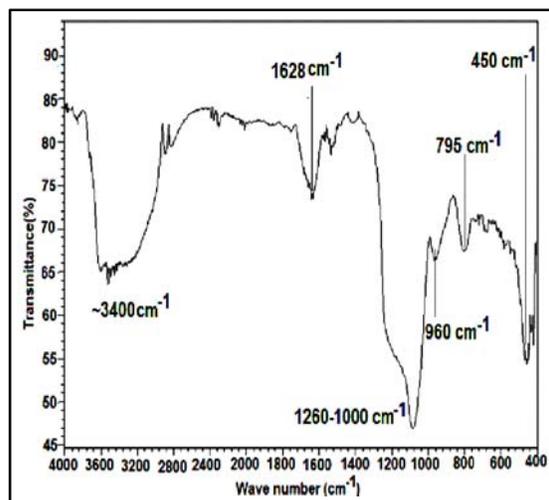


Fig. 16: FTIR of Al-MCM-41-30

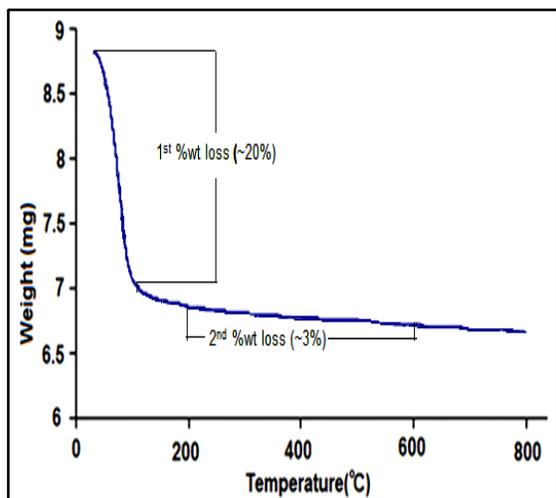


Fig. 17: TGA of Al-MCM-41-30

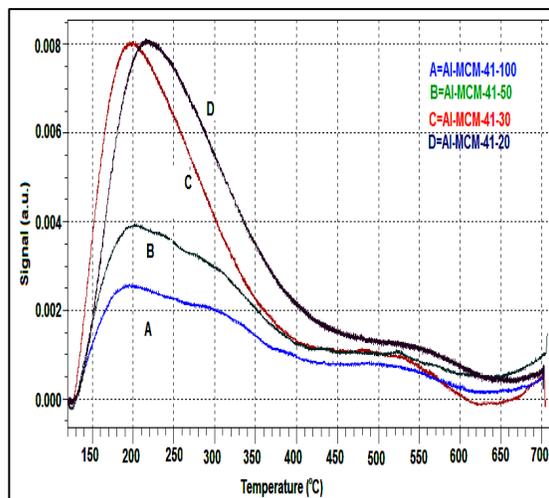


Fig. 18: Ammonia TPD of Al-MCM-41

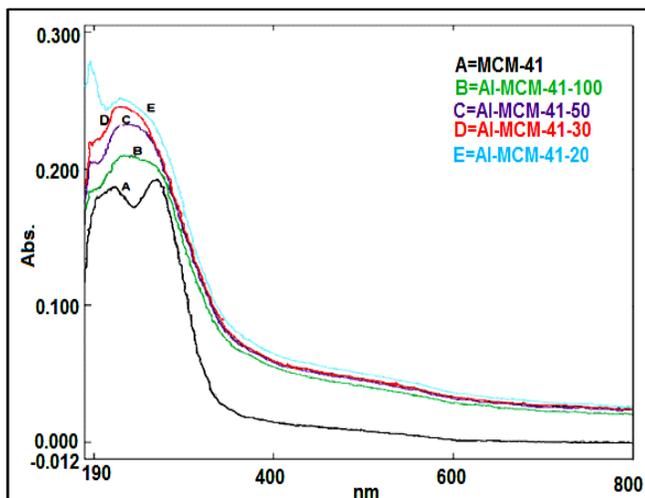


Fig. 19: UV-DRS of Al-MCM-41

XRD of different wt% loading of 12TPA-MCM-41 are presented in Fig. 20. With reference to MCM-41 (a) and 12TPA (f). (b), (c), (d) and (e) show that 12TPA is loaded onto MCM-41. e with the highest loading shows that the 12TPA remains on the surface and the X-ray pattern is close towards (f). The observed results coincide well with those reported in literature^{10,11}.

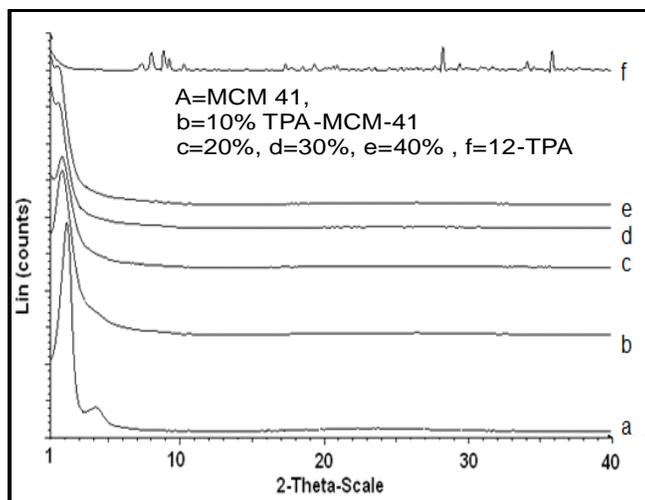


Fig. 20: XRD of 12TPA-MCM-41

SEM image of 12TPA-MCM-41-20 (Fig. 21) exhibits irregular particle size. TEM image (Fig. 22) shows porous structure of the material. EDX of 12TPA-MCM-41-20 (Fig. 23), shows the presence of W as atomic % = 2.20, Si atomic % = 30.44 and O atomic % = 67.40. Absence of P in EDX is probably due very low % of P in the original compound, which is probably not detected in EDX due to instrument limitations.

FTIR spectra of HPA supported onto MCM-41 have been discussed earlier¹²⁻¹⁵. The FTIR spectra (Fig. 24) with different 12TPA loading coincide well with those reported in literature¹²⁻¹⁵.



Fig. 21: SEM of 12TPA-MCM-41-20

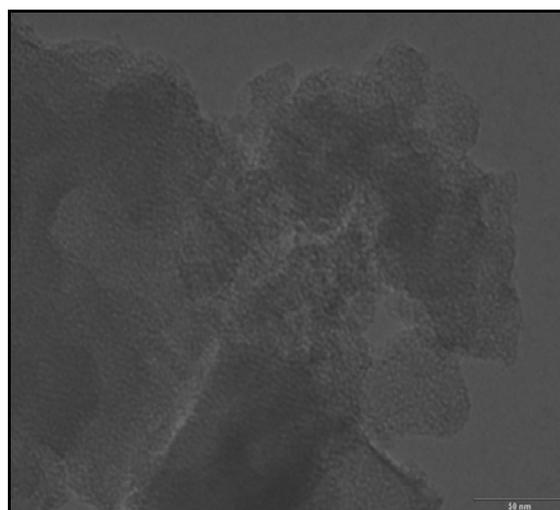


Fig. 22: TEM of 12TPA-MCM-41-20

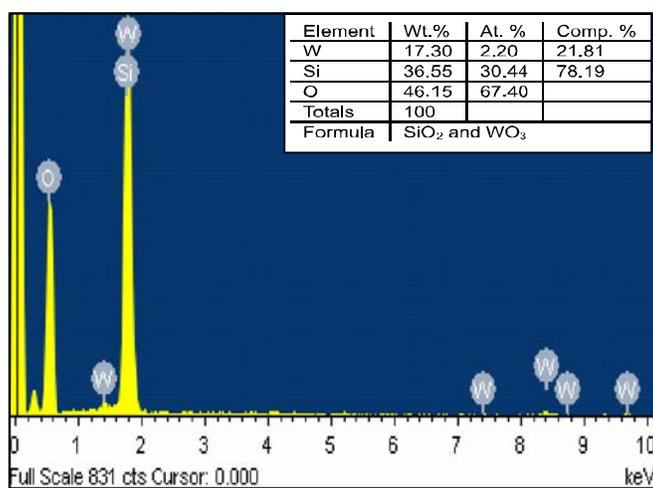


Fig. 23: EDX of 12TPA-MCM-41-20

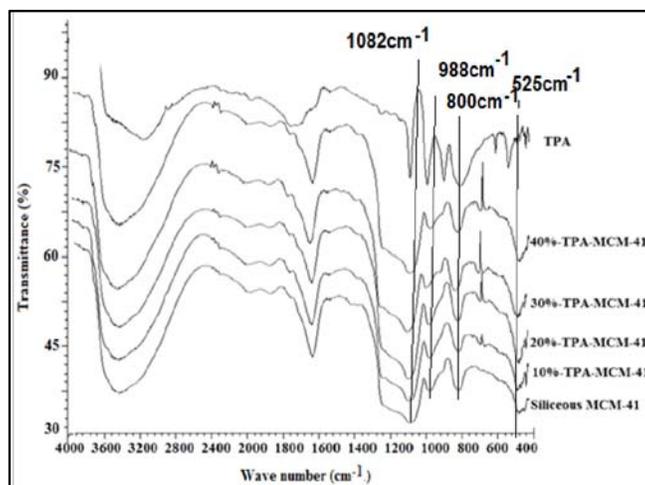


Fig. 24: FTIR of 12TPA-MCM-41

Comparative TPD pattern of MCM 41 samples with different 12TPA loading (Fig. 25) exhibits two distinct peaks at 200°C and 600°C indicating presence of medium and strong acid sites respectively in all the samples. The surface acidity increases gradually with increasing 12TPA loading from 10 to 20 wt.%, after which a decrease is observed (Table 3).

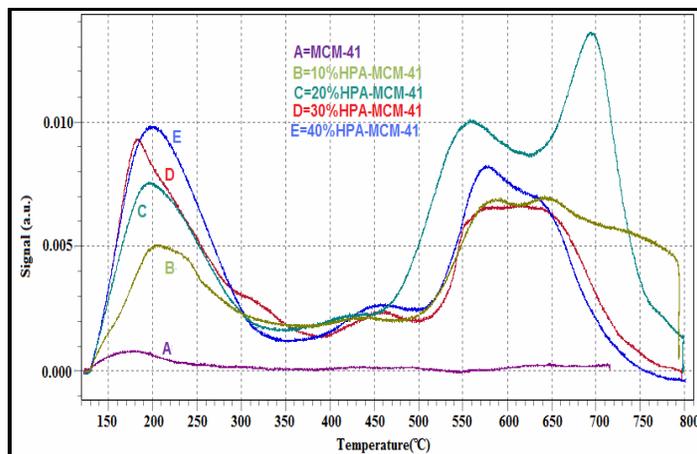


Fig. 25: Ammonia TPD of 12TPA-MCM-41

Friedel-Crafts acylation and alkylation

Firstly, reaction condition was optimized using 12TPA-MCM-41-20 as solid acid catalyst for 3,4-DMA synthesis by varying such parameters as catalyst amount, initial mole ratio of the reactants, reaction time and temperature. The results obtained have been presented in Table 4 and a graphical presentations (Figs. 26 to 29). Friedel-Crafts acylation of veratrole with acetic anhydride, gave selectively 3,4-DMA. It is observed that yield increases with reaction time until equilibrium is reached within 4 h. For the same reaction time, yield increases with increasing catalyst amount, since the number of active sites per g of substrate increases. The influence of reactant ratio (veratrole:acetic anhydride) was studied in the range from 1:0.75 to 1:2. It is observed that the % yield of 3,4-DMA was maximum with 1:1.5 mole ratio (Table 4).

Table 4: Optimization of reaction conditions for Friedel Crafts acylation and alkylation using 12TPA-MCM-41-20

S. No	Reactants with mole ratio	Catalyst amount (g)	Time (h)	Temp. (°C)	% Yield of 3,4-DMA
A					
Time variation					
1	V: AA (1:1.5)	0.10	1	70	47.4
2	V: AA (1:1.5)	0.10	2	70	53.6
3	V: AA (1:1.5)	0.10	3	70	55.6
4	V: AA (1:1.5)	0.10	4	70	61.5
5	V: AA (1:1.5)	0.10	5	70	60.8
6	V: AA (1:1.5)	0.10	6	70	61.3
B					
Catalyst amount variation					
7	V: AA (1:1.5)	0.15	4	70	69.4
8	V: AA (1:1.5)	0.20	4	70	74.3
9	V: AA (1:1.5)	0.25	4	70	74.4

Cont...

S. No	Reactants with mole ratio	Catalyst amount (g)	Time (h)	Temp. (°C)	% Yield of 3,4-DMA
C Mole ratio variation					
10	V: AA (1:0.75)	0.20	4	70	47.8
11	V: AA (1:1)	0.20	4	70	53.5
12	V: AA (1:2)	0.20	4	70	74.3
D Temperature variation					
13	V: AA (1:1.5)	0.20	4	100	73.4
14	V: AA (1:1.5)	0.20	4	120	72.4

A = Anisole; AA = Acetic Anhydride; V = Veratrole; T = Toluene; BzCl = Benzyl Chloride

It has been reported earlier that there is no significant effect of solvents in the acylation of anisole and veratrole and best results were obtained, when aromatic ethers were used as self solvents¹⁶. In the present study, therefore, anisole and veratrole (aromatic ethers) have been used both as substrates and solvent and for this reason, while optimizing reaction condition, concentration of only acylating agent was varied. Thus, the Green Chemistry principle 5, which states that the “use of solvents should be made unnecessary whenever possible and when used, innocuous” is implemented. Further, the boiling point of solvent was taken as reaction temperature. However, when reaction temperature is varied (100°C and 120°C), there is no significant change in % yield. Therefore, 70°C is optimized as reaction temperature for 3,4-DMA synthesis.

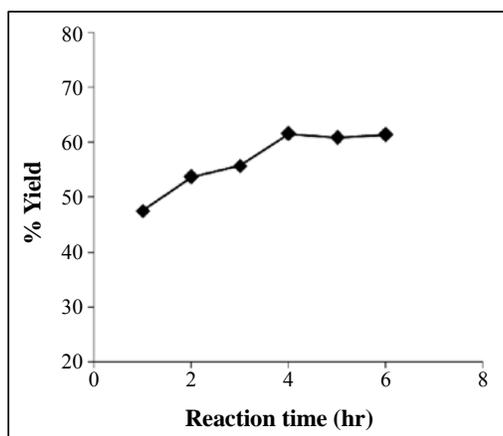


Fig. 26: Reaction time variation for 3,4-DMA

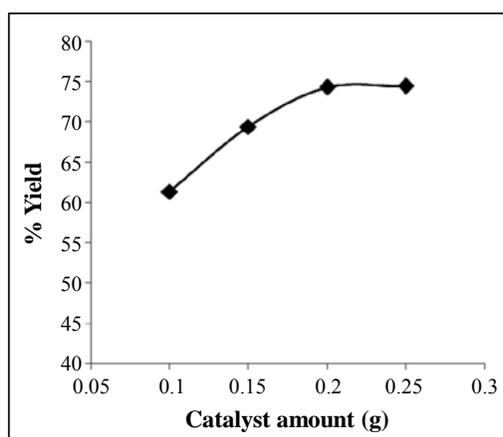


Fig. 27: Catalyst amount variation for 3,4-DMA

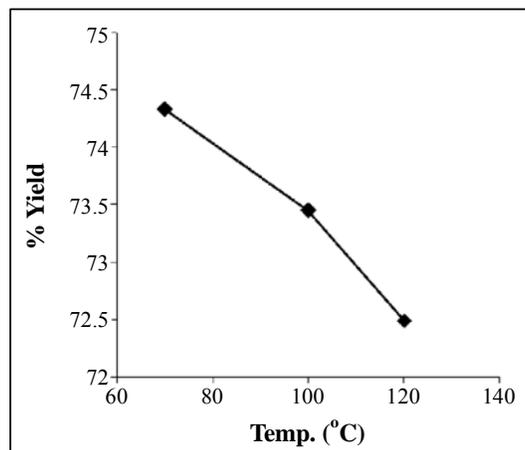


Fig. 28: Reaction temperature variation for 3,4-DMA

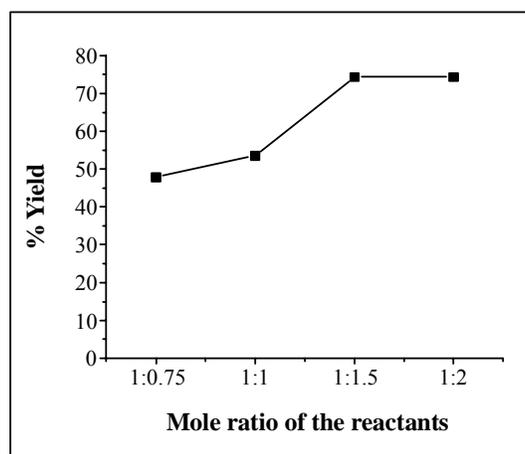


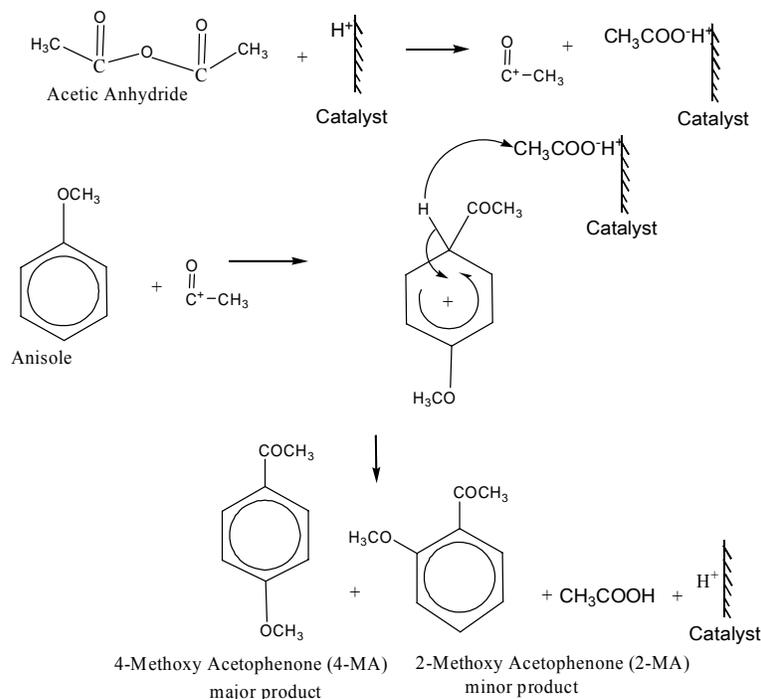
Fig. 29: Mole ratio variation for 3,4-DMA

At optimum condition (mole ratio of reactants, veratrole:acetic anhydride = 1: 1.5, amount of catalyst = 0.2 g, time = 4 h) 4-MA and PBT have been synthesized. Acylation of anisole with acetic anhydride gave selectively 4-methoxy acetophenone (4-MA) and alkylation of toluene with benzyl chloride gave selectively p-benzyl toluene (PBT) (Table 5). Further, for comparative study, at this optimized condition Al-MCM-41(30) is used as solid acid catalyst for synthesis of 3,4-DMA, 4-MA and PBT (Table 5).

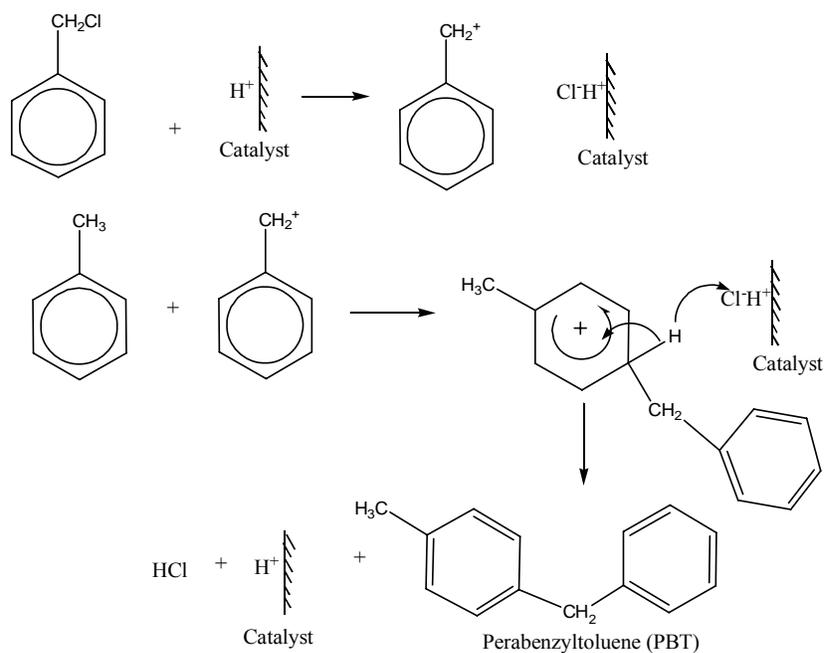
It is reported that the mechanism for Friedel-Crafts acylation and alkylation over solid acid catalysts is the same as in case of homogeneous system where Lewis acid catalysts are used^{14,17,18}. The proposed mechanism (**Scheme 1 and 2**) for the acylation and alkylation reaction on solid acid catalyst implies the formation of an adsorbed species by interaction of the acylating/alkylating agent with a Brønsted acid site^{4,6,17-20} (acyl/alkyl cation). The Brønsted acid site generates an acyl carbonium ion, which in turn affects the electrophilic substitution. A higher density of acid sites increases number of acyl cations enhancing activity of the reaction. Catalytic activity is a function of number as well as type of acid sites present on the catalyst surface. The acylation and alkylation reactions are thus driven by the surface acidity of the catalyst. Probably this is the reason, why 12TPA-MCM-41-20 gives higher yields compared to Al-MCM-41-30 due to higher surface acidity observed in case of the former catalyst.

When comparison is made between anisole and veratrole, the product yield and turn over number (TON) are higher for veratrole. The rate-determining step of the Friedel-Crafts acylation is the formation of

the electrophilic intermediate (**Scheme 1**). The presence of an additional electron donating methoxy group in veratrole makes it a more active compound for electrophilic substitution of acyl group in the para position than anisole due to an increased electron density at para position and resultant increased susceptibility for attack by the electrophile.



Scheme 1: Reaction mechanism of Friedel-Crafts acylation of anisole using solid acid catalyst



Scheme 2: Reaction mechanism of Friedel-Crafts alkylation of toluene using solid acid catalyst

% Yields obtained in recycled catalyst and % decrease in yields in subsequent cycles is presented in Tables 5 and 6 respectively, and a graphical presentation (Fig. 30).

Table 5: Friedel Crafts acylation and alkylation using 12TPA-MCM-41-20 and Al-MCM-41-30 at optimized condition

S. No	Reactants	Product	Temp. (C°)	12TPA-MCM-41-20		Al-MCM-41-30	
				% Yields	*TON	% Yields	*TON
1	V: AA	3,4-DMA	70	74.3	10.8	62.1	9.0
2	A: AA	4-MA	70	59.3	9.0	59.2	9.0
3	T: BzCl	PBT	110	72.0	9.8	58.9	8.9
A Catalyst reusability							
1	V: AA 1 st Cycle	3,4-DMA	70	72.8	10.6	59.4	8.6
2	V: AA 2 nd Cycle	3,4-DMA	70	68.3	10.0	56.1	8.1
3	A: AA 1 st Cycle	4-MA	70	56.4	8.2	56.0	8.0
4	A: AA 2 nd Cycle	4-MA	70	51.6	7.1	52.7	7.5
5	T: BzCl 1 st Cycle	PBT	110	66.1	9.0	54.3	7.4
6	T: BzCl 2 nd Cycle	PBT	110	61.7	8.4	47.9	6.5

A = Anisole; AA = Acetic Anhydride; V = Veratrole; T = Toluene; BzCl = Benzyl Chloride;
Catalyst amount = 0.20 g; reaction time = 4 h; mole ratio of the reactants = 1:1.5 (Veratrole/Anisole/Toluene: acylating/alkylating agent); *TON = Turn over number, gram of product formed per gram of catalyst

Table 6: % Decrease in yields of 3,4-DMA, 4-MA and PBT using recycled catalysts in subsequent cycles

Product	% Decrease in yields			
	12TPA-MCM-41-20		Al-MCM-41-30	
	1 st Cycle	2 nd Cycle	1 st Cycle	2 nd Cycle
3,4-DMA	2	4	3	3
4-MA	3	5	3	4
PBT	5	7	4	5

It is observed that in subsequent cycles decrease in % yields is less for Al-MCM-41 compared to 12TPA-MCM-41-20. This could be due to the leaching of 12TPA from surface of MCM-41. It is observed that the colour of the catalyst changes after each catalytic run. This gives an indication that during the course of the reaction the reacting molecules come onto the surface of the catalyst observed in FTIR spectra of used and regenerated catalysts (Figs. 31 and 32).

Some of them enter into reaction to give the product while a few of them get adsorbed on the surface, which is marked by the change in the colour of the catalyst. The fact that the reactant molecules are weakly adsorbed is evident from the catalyst regaining its original colour, when treated with ethanol. The possibility of molecules entering interstices cannot be ruled out. This is observed from the fact that the yields go down by 3-6% after every regeneration, leading to deactivation of the catalyst (Figs. 33-36). The deactivation of the catalyst might be due to the strongly adsorbed acetic acid and the product on the acid sites. It is known that acetic acid is generally strongly absorbed on the acidic sites. The above two reasons are responsible for decrease in % yield.

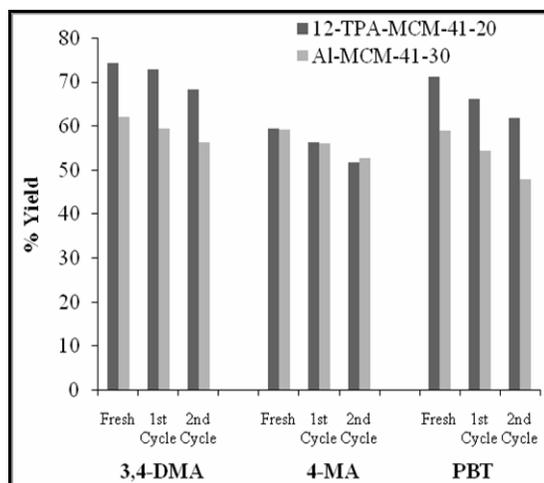


Fig. 30: Comparative catalyst performance in the Friedel-Crafts alkylation and acylation

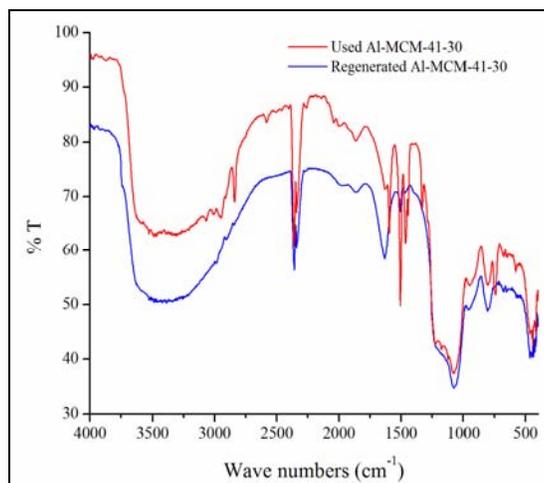


Fig. 31: FTIR spectra of used and regeneratd Al-MCM-41-30

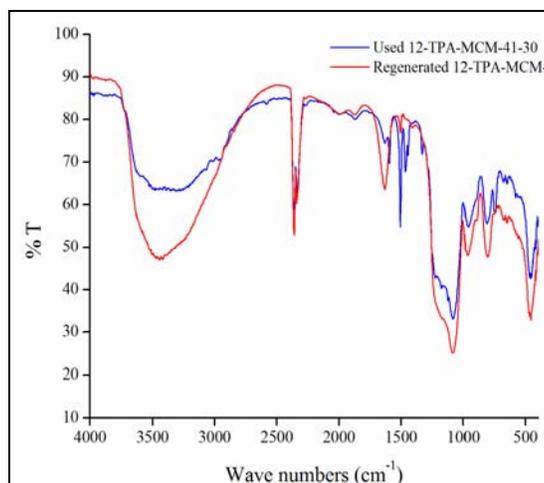


Fig. 32: FTIR spectra of used and regeneratd 12TPA-MCM-41-30

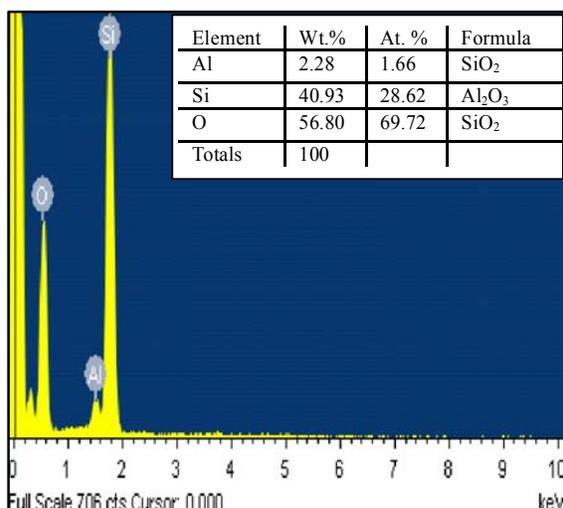


Fig. 33: EDX of used Al-MCM-41

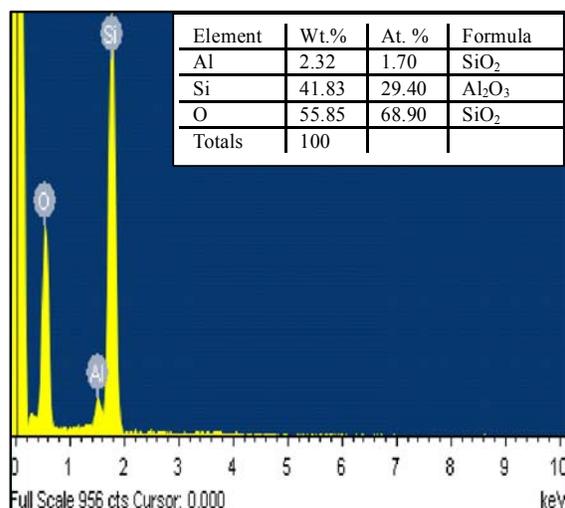


Fig. 34: EDX of regenerated Al-MCM-41

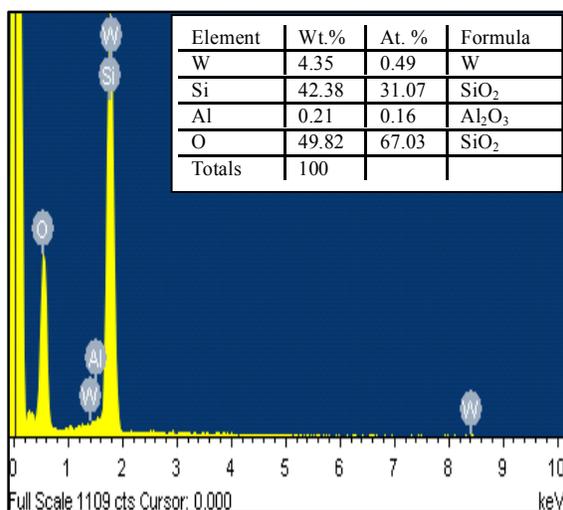


Fig. 35: EDX of used 12TPA-MCM-41-30

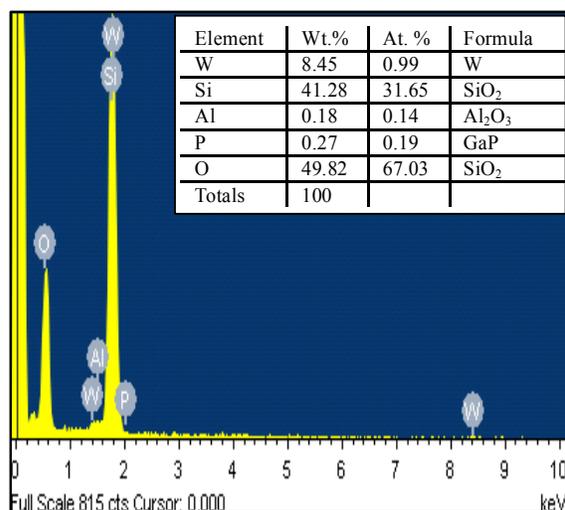


Fig. 36: EDX of regenerated 12TPA-MCM-41-30

CONCLUSION

In the present study, Green Chemistry goals have been achieved by using solid acid catalysts (replacing liquid acid catalysts used in conventional reactions) and under solvent free conditions with high selectivity of the products. The products formed can be simply distilled over. There is no catalyst contamination in product and no acid waste formed. The catalyst can be regenerated and reused. Finally, the MCM-41 neutral framework has been successfully modified and put to practical use.

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REFERENCES

1. M. L. Kantam, K.V.S. Ranganath, M. Sateesh, K. B. Shivakumar and B. M. Chaudary, *J. Mol. Catal. A: Chem.*, **15**, 225 (2005).
2. R. V. Jasra, *Bul. Catal. Soc. India*, **2**, 157 (2003).
3. A. Vinu, D. Sawant, K. Arigu, M. Harfmann and S. B. Halligudi, *Micro. Meso. Mat.*, **80**, 195 (2005).
4. A. H. Mohammed, W. Alledn and W. Apblett, *Catal. Sci. Technol.*, **1**, 621 (2011).
5. M. Gómez-Ruiz, J. A. Melo-Banda, C. E. R. Galván, S. E. López, R. R. Silva, R. I. Alamilla and J. M. Domínguez, *Adv. Mater. Res.*, **132**, 192 (2010).
6. S. Sudha, S. Vishnu, J. Priya, M. H. Mabel Palanichamy and V. Murugesan, *J. Porous Mater.* **16**, 215 (2009).
7. P. Dhanashri, A. Sawant, F. Vinub, C. Lefebvre and S. B. Halligudi, *J. Mol. Catal. A: Chem.*, **262**, 98 (2007).
8. G. Kamalakar, K. Komura, Y. Kubota and Y. Sugi, *J. Chem. Technol. Biotechnol.*, **81**, 981 (2006).
9. J. S. Beck, C. T. Kresge, M. E. Leonowicz, W. J. Roth and J. C. Vartuli, *Nature*, **359**, 710 (1992).
10. B. R. Jermy and A. Pandurangan, *Appl. Catal. A: Gen.*, **295**, 185 (2005).
11. J. C. Juan, J. Zhang and M. A. Yarmo, *J. Mol. Cat.*, **267**, 265 (2007).
12. V. I. Kozhevnikov, A. Sinnema, R. J. Jansen, K. Pamin and H. Van Bekkum, *Catal. Lett.*, **30**, 241 (1995).
13. Q. H. Xia, K. Hidajat and S. Kawi, *Mater. Lett.*, **42**, 102 (2000).
14. Y. Ma, Q. L. Wang, W. Jian, and B. Zuo, *Appl. Catal. A: Gen.*, **165**, 199 (1997).
15. K. J. Edler and J. W. White, *Chem. Mater.*, **9**, 1226 (1997).
16. C. Hu, T. Hashimoto, M. Okuhara and M. Misono, *J. Catal.*, **143**, 437 (1993).
17. K. Bachari and O. Cherifi, *Appl Catal A: Gen.*, **319**, 259 (2007).
18. K. Bachari and O. Cherifi, *Catal. Commum*, **7**, 926 (2006).
19. J. Kaur, K. Giffin, B. Harrison and I. V. Kozhevnikov, *J. Catal.*, **208**, 448 (2002).
20. Z. Ramli, D. Prasetyoko and S. Endud, *J. Teknologi.*, **36C**, 41 (2002).