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Synthesis, Characterization and Catalytic Application of Acid Functionalized Mesoporous Silica

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ABSTRACT

MCM-41 materials were synthesized by room temperature co-precipitation method by mixing a silica precursor to a clear solution of surfactant which acts as structure directing agent. In order to increase acidic sites, it is functionalized with sulphonic acid and phosphotungestic acid to yield SO_3HMCM-41 and PWMCM-41 respectively. The synthesized materials were characterized by XRD, BET, FTIR and SEM-EDAX techniques. Materials have been found to have mesoporous character. PXRD studies confirmed the hexagonal arrangement and SEM images revealed spherical morphology of the materials. The catalytic behaviour of MCM-41 and acid functionalized MCM-41 has been investigated towards the synthesis of imines. SO_3HMCM-41 is found to be an efficient catalyst for the synthesis of imines giving moderate to excellent yields with very short reaction times.

Keywords: Functionalized MCM-41, mesoporous character, catalysis, imine synthesis.

INTRODUCTION

Mesoporous solids synthesized using micelles as structure directing agents have been found to posses' large specific surface area, large pore volume, regular order of pore structure and tuneable pore characteristics [1, 2]. These properties make mesoporous solids as potential green catalysts for variety of organic reactions by allowing fast diffusion of reactants and products through their pores [3, 4]. Mesoporous MCM-41 has been widely used as a heterogeneous solid catalyst in the synthesis of fine chemicals [5, 6]. It is possible to modify surfaces of these materials by covalent anchoring of different organic moieties [7]. Functionalization of MCM-41 with acidic groups enhances its surface acidic character due to the incorporation of acid containing moieties onto the frame work. Although there are reports on acid functionalized MCM-41 materials, studies on their catalytic applications in organic transformations are very few [8].

In continuation of our efforts to find suitable heterogeneous catalysts for one pot organic reactions, we carried out synthesis of imines using acid functionalized MCM-41 as catalyst. Imines have been found to have a wide range of biological activities such as lipoxygenase inhibition, anti-inflammatory [9] and anti-cancer behaviour [10]. They are also used as versatile components in the formation of optically active α-alkyl aldehyde [11], preparation of secondary amines by hydrogenation [12], nucleophilic addition with organometallic reagents [13] and cycloaddition reactions [14]. Imines, have been usually prepared by a reversible condensation reaction between a primary amine and a carbonyl compound

[15]. Some recent methods for the preparation of imines include use of different Lewis acids, like $ZnCl_2$, P_2O_5/SiO_2. These methodologies often require complex procedures, long reaction times, huge quantities of organic solvents, high reaction temperatures, and large amounts of expensive dehydrating agents [16, 17].
In this paper, we report our studies on the preparation of sulphonic acid and phosphotungestic acid functionalized MCM-41 by a simple method at room temperature and their catalytic behaviour towards synthesis of imines in solvent free conditions.

MATERIALS AND METHODS

Chemicals: n-Hexadecyltrimethylammonium bromide (CTAB) was obtained from SD fine chemicals Ltd., India, Ammonia (reagent grade, 25%) and ethyl alcohol (reagent grade). Sulphuric acid (98%) and phosphotungestic acid were obtained from SRL laboratories, India. Tetraethylorthosoilicate (TEOS, reagent grade, 98%) was obtained from Sigma-Aldrich India. All the chemicals were used as obtained without further purification. Double distilled water was used in all the reactions.

Synthetic procedures

Synthesis of MCM-41: Modified classical synthetic procedure was adopted for the preparationof MCM-41 under mild conditions in terms of temperature and surfactant quantity [18]. 2.4 g of Cetyltrimethylammonium Bromide (CTAB) was dissolved in 50 ml of distilled water and stirred continuously employing a mechanical stirrer until a clear homogeneous solution was obtained. 76 ml of ethyl alcohol followed by 13 ml of 25 wt. % aqueous ammonia was added to this homogeneous solution while continuing stirring. 10 ml of TEOS was added drop by drop to the above mixture. The solution turns milky and a gel is formed due to the hydrolysis of TEOS. The gel is stirred further for about 2 hours to completely hydrolyze TEOS. White precipitate thus formed was filtered and washed consecutively with distilled water and methanol. The product was dried overnight at 110 ^{O}C. Solid product thus obtained was calcined at 550 °C in air atmosphere for 5 hours to remove the trapped surfactant.

Synthesis of Sulphonic Acid Functionalized MCM-41(SO_3HMCM-41): 1 g of calcined MCM-41 sample was treated with 30 ml of 0.5 N sulphuric acid and the mixture was stirred at room temperature for about 2 hours. This mixture was evaporated by heating the slurry at 70 ^{O}C for 30 minutes. Resultant sample was dried at 110 ^{O}C for 5 hours and then calcined at 550 ^{O}C for 5 hours.

Synthesis of Phosphotungestic Acid Functionalized MCM-41 (PWMCM-41):1 g of calcined MCM-41 is treated with methanolic solution of 40 wt% phosphotungestic acid. The resultant suspension was stirred at room temperature for 22 hours. The gel formed was evaporated and dried at 110 ^{O}C for 30 minutes followed by calcination at 200 ^{O}C for 2 hours.

Characterization of the Synthesized Materials: Synthesized MCM-41, SO_3HMCM-41 and PWMCM-41 materials were characterized by low angle XRD, BET, SEM–EDAX and FTIR. The X-Ray diffraction patterns were recorded in air atmosphere at room temperature on Philips X'Pert X-Ray diffractometer equipped with Cu K_α (λ = 1.5406 A^{O}) radiation operating at 40 kV and 40 mA between 2θ angle range from 0.5 to 10 degree with a scan speed of 0.02^{o} s^{-1}. Nitrogen Adsorption – Desorption isotherms of the synthesized materials were carried out by using quntachrome surface area and particle size analyzer equipped with Nova win2 software using liquid Nitrogen as the adsorbent. Prior to the adsorption-desorption studies the samples were degassed at 150 ^{O}C under nitrogen atmosphere for 5 hours. SEM-EDAX studies were carried out by using Jeols electron microscope. The FTIR spectra of the materials were recorded on Shimadzu FTIR 8201 spectrophotometer equipped with Hyper IR software by KBr pelleting technique.

General procedure for the synthesis of imines: A mixture of aromatic amine (10 mmol) and benzaldehyde (10 mmol) was taken in a mortar. 0.005g of catalyst was added to this mixture. The reaction mixture was subjected to grinding at room temperature. The progress of the reaction was monitored through thin layer chromatography using Hexane: Ethyl acetate as solvent system. After completion of the reaction, the product was dissolved in hot ethanol and filtered. The filtrate was then evaporated under reduced pressure to give the crude product. The catalyst was recovered and washed with methanol for several times and dried at 150 ^{O}C. Pure product was obtained by recrystallisation using ethanol. Melting points of the products were found to be identical to their literature values. Products were authenticated by FTIR studies.

RESULTS AND DISCUSSION

Low Angle XRD Studies: The XRD pattern of MCM-41 and acid functionalized MCM-41 samples are shown in Fig.1. Only one low-angle peak for d_{100} plane corresponding to the mesophase at 2θ value of 2.2° is observed. This is characteristic of the long range hexagonal structure of MCM-41. Low value of 2θ is mainly due to the length of the carbon chain of micelle forming surfactant used as template for synthesis of MCM-41 [19]. With the incorporation of acid groups into the frame work of mesoporous materials, the intensity of low angle peak decreased. This indicates the occupancy of acid groups on the surface. No considerable change in the peak position of the XRD patterns was observed due to the introduction of acidic groups on MCM-41. This reveals that the lattice structure of acid functionalized MCM-41 remains mesoporous and is similar to that of parent material.

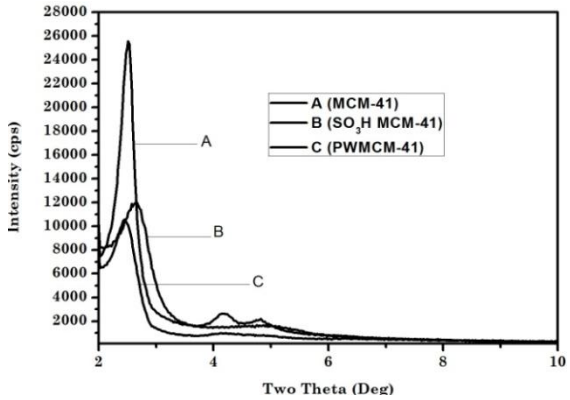


Fig. 1: XRD patterns of MCM-41, SO_3H MCM-41 and PWMCM-41

Nitrogen Adsorption – Desorption Studies: The surface areas of the synthesized MCM-41 and acid functionalized MCM-41 materials were calculated by applying BET adsorption isotherm and were found to be in the range of 600-1000 m^2g^{-1}. The Nitrogen Adsorption- Desorption isotherms of MCM-41 and acid functionalized MCM-41materials are shown in Fig.2. From the figure, it can be observed that the adsorption follows typical type-IV adsorption isotherm indicating mesoporous character of the materials [20]. The pore volume and pore radius of the materials were calculated from BET surface area measurements using BJH method. The pore volume and pore radius have been calculated from the desorption branch of multipoint BET isotherms. The surface area of the functionalized MCM-41 materials was found to decrease with the loading of acidic functional group into the frame work. The textural properties of these materials are shown in Table1.

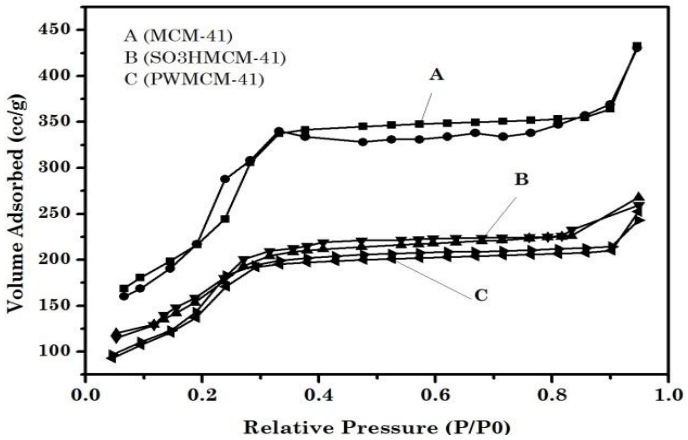


Fig.2: BET Adsorption Desorption isotherms of MCM-41, SO_3HMCM-41 and PWMCM-41

Table1: Textural properties of synthesized materials

Material	S_{BET} (m^2g^{-1})	Pore Size (A^o)	Pore Volume (cc g^{-1})
MCM-41	1023.5	17.2	0.28
SO_3HMCM-41	862.3	15.6	0.16
PWMCM-41	631.12	16.3	0.15

FTIR Studies: The FTIR spectra of MCM-41and functionalized MCM-41 materials are shown in Fig.3. The FTIR spectra of the MCM-41 samples reveal the absorption bands close to 1643.2 cm^{-1} due to the bending vibration of adsorbed water molecules. The asymmetric stretching vibrations of Si-O-Si are observed by the absorption bands at 1072 and 1228.6 cm^{-1}. The band at 964.3 cm^{-1} can be attributed to Si-OH vibrations. The absorption peaks around 450 to 795 cm^{-1} are mainly due to bending vibration of Si-O-Si bonds and the band at 794 cm^{-1} corresponds to the presence of free silica. The presence of sulphur groups and W-O-P linkages can be confirmed from the corresponding peaks in the FTIR spectrum.

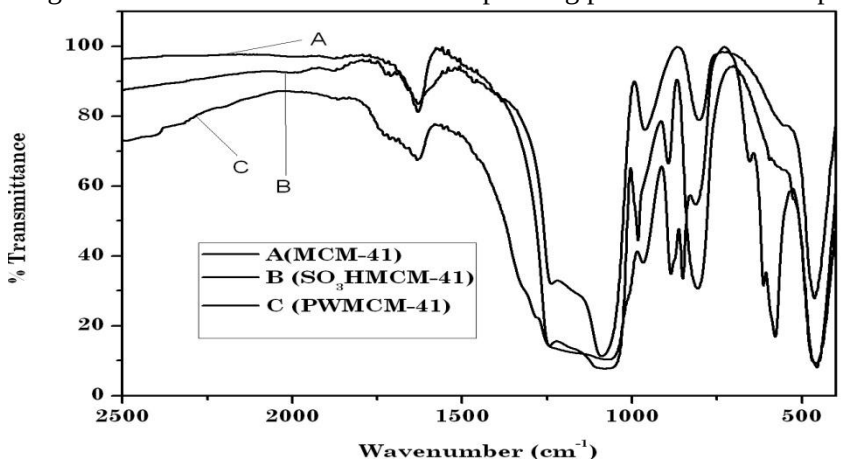
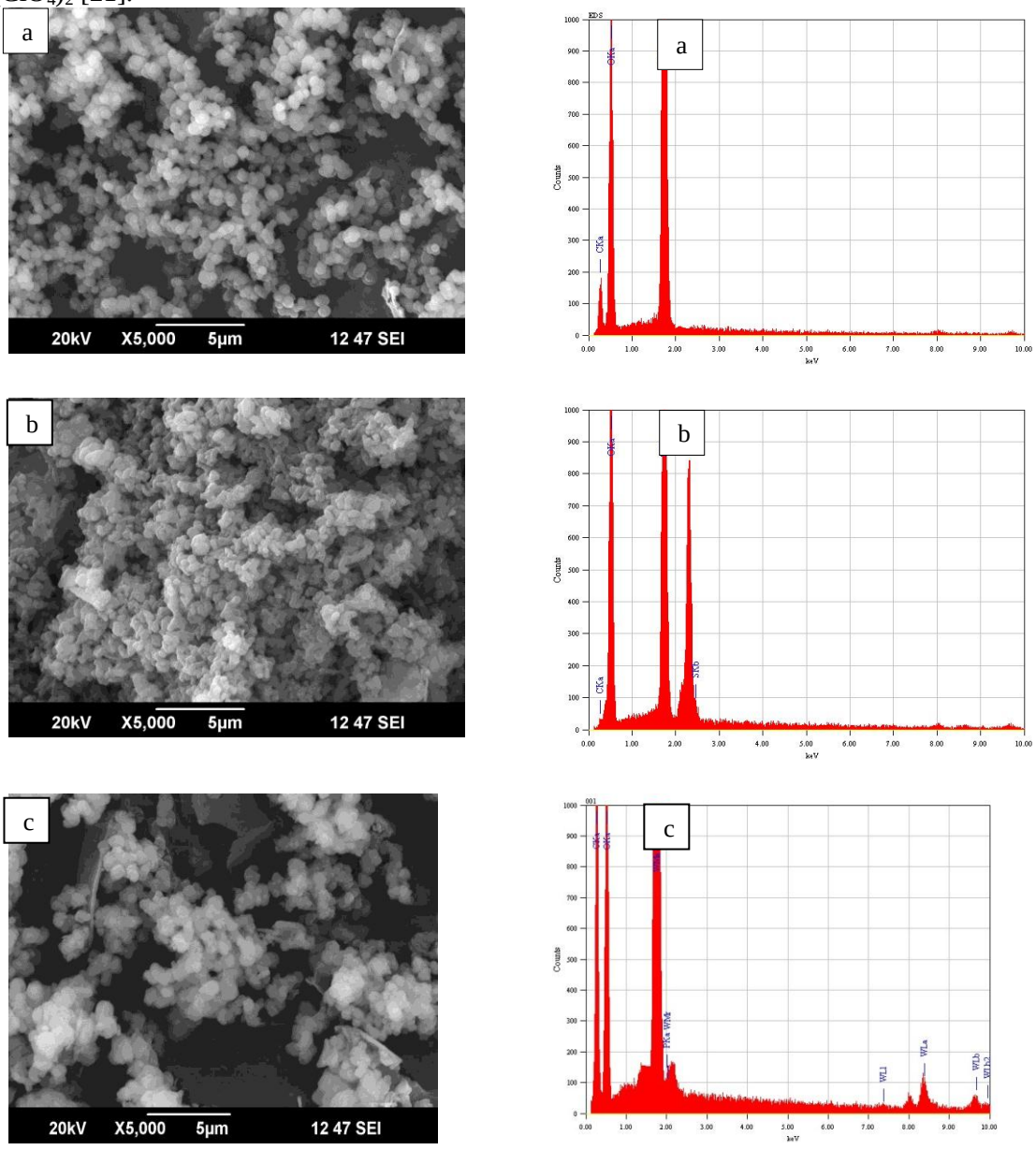


Fig.3: FTIR Spectrum of MCM-41, SO_3HMCM-41 and PWMCM-41.

SEM – EDAX Studies: SEM images reveal spherical morphology of the material. It can be observed that the morphology remains unaltered after the modification with acid groups. The particle size is found to be uniform on the surface. EDAX results show the presence of acid groups in the frame work of the materials. The SEM-EDAX images are shown in Fig.4a, 4b and 4c.

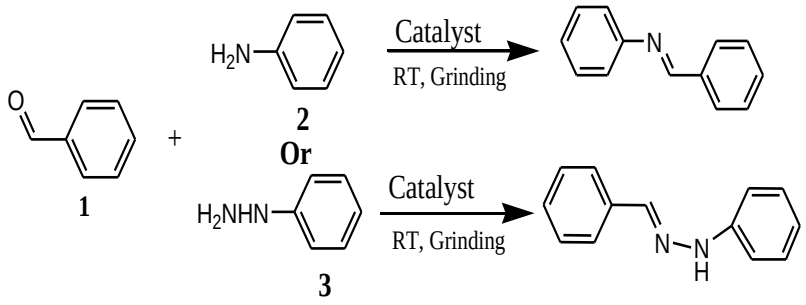
Catalytic Studies: The catalytic effect of acid functionalized MCM-41 towards the synthesis of imines has been studied at room temperature and solvent free conditions (Fig. 5).
It is observed that acid functionalization of MCM-41 increases the catalytic effect of the materials and results in high yields in short reaction time. The reaction time using acid functionalized MCM-41 as catalyst has decreased drastically from 8 hrs to 15 minutes when compared with the conventional catalyst $Mg(ClO_4)_2$ [21].



(I) (II)

Fig. 4: SEM (I) - EDAX (II) images of a) MCM-41, b) SO_3HMCM-41 and c) PWMCM-41.

Among functionalized catalysts, sulphonic acid functionalization exhibited higher catalytic activity by giving higher yields. This may be attributed to the presence of larger number of sulphonic acid moieties on the surface compared to the bulkier phosphotungestic acid groups. Since the reactions are carried out without any solvent at room temperatures using reusable heterogeneous catalyst, this synthetic procedure is environmental friendly.



Catalyst = MCM-41 or SO_3HMCM-41 or PWMCM-41

Fig. 5: Synthesis of imines over MCM-41 and acid functionalized MCM-41

Table 2: Effect of catalysts on the synthesis of imines

Entry		Catalyst	Solvent	Time	Yield
1	**2**	$Mg(ClO_4)$ [21]	DCM	8 Hr	80.3%
		MCM-41	Nil	15 mins	45.5%
		SO_3HMCM-41	Nil	15 mins	83.3%
		PWMCM-41	Nil	15 mins	74.0%
1	**3**	$Mg(ClO_4)_2$ [21]	DCM	8 Hr	90%
		MCM-41	Nil	15 mins	37.5%
		SO_3HMCM-41	Nil	15 mins	95.5%
		PWMCM-41	Nil	15 mins	80.3%

APPLICATION

The synthesized materials contains silica in the frame work and acid groups on the surface of the material. These materials act as heterogeneous catalyst for the synthesis of imines. The protocol discussed in this communication is a green chemical and efficient route for the synthesis of fine chemicals.

CONCLUSIONS

MCM-41, sulphonic acid functionalized MCM-41 and phosphotungestic acid functionalized MCM-41 are synthesized at room temperature by modified condensation method. They are characterized for their properties by XRD, SEM, FTIR and BET studies. The ordered arrangement of pores has been confirmed from XRD studies. The mesoporous character of the materials is revealed from BET studies. SEM images of the materials have shown spherical morphology. EDAX shows the presence of sulphur, phosphorous and tungsten in the samples. The incorporation of acid groups in the frame work is confirmed from FTIR studies. These materials were investigated for their catalytic application towards the efficient and green synthesis of imines at room temperature. It is observed that acid functionalization of MCM-41 increases

the effectiveness of the material as catalysts for the synthesis of imines under solvent free conditions by way of giving high yields in a short reaction time. SO_3HMCM-41 is found to be more efficient catalyst than PWMCM-41 for the synthesis.

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