

Sulfonic acid functionalized mesoporous silicas and organosilicas: Synthesis, characterization and catalytic applications

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Abstract

Ethane bridged mesoporous organosilicas and MCM-41 having sulfonic acid groups in the pore channels were prepared by co-condensation method as well as grafting method, using 3-mercaptopropyltriethoxysilane (3-MPTS) as the sulfur precursor. TEM and N₂ sorption isotherm analysis revealed that the mesoporous structural ordering is retained after the functionalization and modifications of organic groups while FT-IR, Raman, XPS and solid-state ¹³C CP MAS NMR shows the presence of sulfonic acid groups and the stability of the mesoporous framework. The catalytic activity of the developed materials was evaluated in the liquid phase Claisen–Schmidt condensation reaction of acetophenone with benzaldehyde, to probe the effect of mesoporous support surfaces as well as the role of preparation methods. Results showed that sulfonic acid functionalized ethane–silica samples were more active, selective and stable than the conventional sulfonic acid containing mesoporous catalysts. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

In recent years, the use of organically functionalized mesoporous materials as catalysts for organic synthesis has received considerable attention, due to their high surface areas and larger pore channels [1–3]. However, the poor hydrothermal stability of mesoporous silica under drastic reaction conditions made them less promising in the field of catalysis. Among the different methods to increase the stability of mesoporous materials, the recent discovery of periodic mesoporous organosilicas is considered as a major breakthrough. Periodic mesoporous organosilicas (PMOs) are an attractive family of mesoporous materials that combine the properties of organic and inorganic components in a composite material. Since the framework of PMOs consists of a homogeneous distribution of the organic groups, the pore wall provides smooth accessibility for the reactant molecules and opens a wide range of new and exciting opportunity for designing materials, having better hydrother-

mal stabilities than the conventional M41S silicates [4–6]. So far, PMOs containing bridging organic groups like ethane, ethylene, benzene, biphenyl and thiophene and bifunctional PMO (BPMO) having different organic groups in the pore channels as well as in the frame wall have been reported [7]. However, akin to mesoporous silica, pristine PMO materials shows limited catalytic activity due to the lack of active catalytic sites and hence ample surface modifications are necessary to make them attractive in the field of catalysis.

Heterogeneous catalysis is widely accepted as an environmentally friendly alternative for the synthesis of fine chemicals, since their use allows easier separation, recovery and recycling of the catalyst from the reaction mixture. In this regard, the fabrication of sulfonic acid functionalized materials with different acid strengths, have attracted much research attention because of their applications as solid acid catalysts [8–10]. Many researchers had well demonstrated the fabrication of propylsulfonic acid functionalized mesoporous materials by either grafting on the preformed mesostructure or direct co-condensation during synthesis [11–15]. The high catalytic activity of these sulfonic acid functionalized mesoporous materials can be attributed to their high surface area and the high

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accessibility of the acid centers to the reactants. However, incorporating organic moieties on mesoporous silica materials via grafting technique commonly leads to nonuniform distribution of the functional groups, with higher concentration on the external surfaces instead of the internal surfaces. Therefore, the direct co-condensation synthesis technique in which the mesostructure and functional group is simultaneously introduced is widely accepted as the desirable route for incorporating functional groups because this method increases the concentration of the organic groups homogeneously, relative to grafting.

Claisen–Schmidt condensation of acetophenone with benzaldehyde to produce α - β -unsaturated ketones called chalcones attracts attention due to the wide applications of chalcones as photo protectors in plastics, pharmaceuticals, solar creams and food additives [16–18]. Traditionally Claisen–Schmidt condensation reactions were carried out using alkaline hydroxides as catalysts, but the poor selectivity, generation of wastes and laborious separation techniques make these catalysts practically inconvenient. Hence, solid catalysts like magnesium oxide, potassium carbonate, barium hydroxide and alkali-exchanged zeolites have been used as alternatives for the conventional homogeneous alkaline hydroxides. Even though, the solid basic catalysts provide advantages due to its heterogeneous nature, the major drawback is associated with the poor selectivity to chalcone due to the competitive Cannizzaro reaction of the aldehyde and other undesired side reactions like Michael addition at the strong basic sites [19,20]. Herein, an acid catalysis-approach was adopted to produce chalcones by the selective Claisen–Schmidt condensation reaction between substituted benzaldehyde and acetophenone using propylsulfonic acid functionalized ethane–silica PMO and MCM-41 samples, by co-condensation method and post-synthesis grafting method.

2. Experimental

2.1. Synthesis

In a typical synthesis procedure, an aqueous solution of cetyltrimethylammonium bromide (C_{16} -TMA, 3.7 g) in sodium hydroxide (1.8 g), Solution A, is prepared. To this solution, 1,2-bis(triethoxysilyl)ethane (BTEE, 5 g) and required amounts of 3-mercaptopropyltriethoxysilane (3-MPTS, $\sim 10\%$ or 30%) was added with vigorous stirring. The final gel was stirred for 12 h at ambient temperature and then allowed to reflux for an additional 48 h at 373 K. Thiol functionalized MCM-41 counterparts were synthesized by using TEOS as silicon source instead of the BTEE silicon source. The surfactant inside the pores of these materials was completely removed by stirring the as-synthesized material with HCl–EtOH mixture at 70°C for 8 h (Fig. 2a). The thiol-functionalized samples were then converted into the sulfonic acid groups by oxidation of –SH groups with aqueous H_2O_2 as an oxidant, under N_2 atmospheres [9]. Here after, the direct synthesized thiol and sulfonic acid functionalized mesoporous ethane–silica samples were denoted as ES-SH- x and ES-SO- x and the corresponding MCM-41 samples were denoted as MM-SH- x and MM-SO- x (where, x denotes the percentage of 3-MPTS loading, viz. 10% or 30%). For comparison, 30%

sulfonic acid containing ethane–silica, MCM-41 and silica gel samples were also synthesized by a grafting route as described in ref. [9] and the samples were denoted as ES-SO- 30% -G, MM-SO- 30% -G and SG-SO- 30% , respectively.

2.2. Characterization

FTIR spectra of the solid samples were taken in the range of 4000 – 400 cm^{-1} in a Shimadzu FTIR 8201 instrument by diffuse reflectance scanning disc technique. Raman spectra of the powdered samples were recorded at room temperature using a Raman microscope (InVia Reflex, Renishaw) equipped with deep-depleted thermoelectrically cooled CCD array detector. A near infra red laser (785 nm , 55.7 mW) was used as an excitation source. Spectra were recorded in the region of 100 – 3200 cm^{-1} at 4 cm^{-1} resolution and exposure time of 120 s. Solid-state ^{13}C CP MAS NMR was recorded on a Bruker MSL 300 NMR spectrometer with a resonance frequency of 75.5 MHz and was referenced to glycine. Analysis of the organic material incorporated on the solid silica materials were carried out by using EA1108 Elemental Analyzer (Carlo Erba Instrument). XPS measurements were performed on a VG Microtech ESCA 3000 instrument. The general scan and the core level spectra of S 2p were recorded with non-monochromatized Mg K radiation at a pass energy of 50 eV and an electro take off angle of 60° . The correction of binding energy was performed by using the C 1s peak of carbon at 284.9 eV as reference. TEM images were recorded on a JEOL JEM-1200 EX instrument at an acceleration voltage of 120 kV . Prior to TEM analysis, the powdered samples were dispersed in isopropanol, followed by depositing two drops on a holey carbon film supported by a copper grid. SEM micrographs of the hybrid samples were obtained on JEOL-JSM-5200 scanning microscopy. The specific surface area, total pore volume and average pore diameter were measured by N_2 adsorption–desorption method using NOVA 1200 instrument (Quantachrome). Pore size distribution (PSD) was obtained by applying the BJH pore analysis applied to the desorption branch of the nitrogen adsorption–desorption isotherms.

2.3. Catalytic reaction

The Claisen–Schmidt condensation reactions were carried out in a round-bottom flask fitted with a reflux condenser. In a typical reaction, 20 mmol of benzaldehyde was reacted with 20 mmol of acetophenone in presence of 50 mg of catalyst at 150°C . After reaction, the samples were analyzed on a gas chromatograph (HP 6890) equipped with a flame ionization detector and a capillary column ($5\text{ }\mu\text{m}$ cross-linked methyl silicon gum, $0.2\text{ mm} \times 50\text{ m}$) and the products were further confirmed by GC–MS analysis.

3. Results and discussion

3.1. Characterization results

Anchoring of 3-MPTS groups in the pore channels of mesoporous materials is identified by the methylene stretching bands

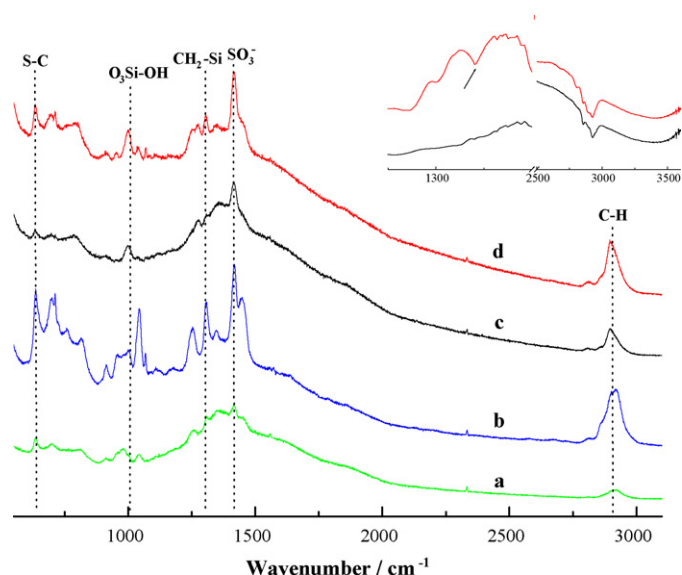


Fig. 1. Raman spectra of sulfonic acid containing mesoporous samples (a) ES-SO-10%, (b) ES-SO-30%, (c) MM-SO-10% and (d) MM-SO-30%. Inset shows the FTIR spectra of ES-SH-30% (black line) and ES-SO-30% (red line) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article).

in the $2950\text{--}2850\text{ cm}^{-1}$ region, from IR experiments. The band for the thiol (--SH) stretching vibrations are observed at 2575 cm^{-1} and its intensity gets increased with an increase in the percentage of 3-MPTS loading. A complete disappearance of this band was noted after H_2O_2 treatment, with the subsequent formation of new bands at 1350 cm^{-1} , which is assigned for the asymmetric stretching band of the SO_2 moieties, confirming the formation of sulfonic acid species after oxidation reactions (Fig. 1, inset) [9]. The nature of sulfur species formed over the mesoporous materials was further explored using Raman spectroscopy which is more sensitive than conventional FT-IR towards S–H vibrations. Prior to the thiol oxidation step, both the mesoporous materials showed a strong peak at 2585 cm^{-1} characteristic of the thiol group in the 3-MPTS groups. Akin to FT-IR results, after H_2O_2 oxidation, the --SH groups disappeared with the subsequent formation of new bands at 1040 and 1100 cm^{-1} , which are attributed to the symmetric and asymmetric vibrational modes of SO_3^- (Fig. 1) [21–23]. The presence of sharp peaks in the range $2800\text{--}3000\text{ cm}^{-1}$ shows the presence of anchored organic groups arising from the propyl chain of the organic linker. In addition, the bands at 1000 and 795 cm^{-1} can be assigned to the stretching modes of surface silanols ($\text{O}_3\text{Si--OH}$) and siloxane bridges (Si--O--Si). The band at 1450 cm^{-1} can be assigned to the $\text{C--CH}_2\text{--C}$ vibrational mode, the band at 650 cm^{-1} relates to the C--S stretching mode vibrations and the presence of bands at 1250 and 1300 cm^{-1} , attributes to the $\text{CH}_2\text{--S}$ and $\text{CH}_2\text{--Si}$ wagging mode vibrations [10,24]. All these results confirm the integrity of the propyl chain sulfonic acid groups within the support samples.

For a better identification of the anchored organic groups, ^{13}C CP MAS NMR experiments were conducted over the thiol and sulfonic acid functionalized PMO samples (Fig. 2). ^{13}C CP MAS NMR of solvent extracted ethane–silica sample showed a sin-

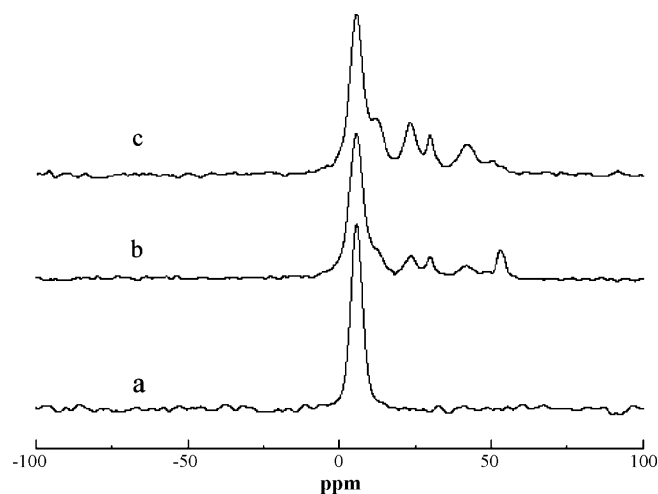


Fig. 2. ^{13}C CP MAS NMR results of (a) surfactant-extracted ethane–silica, (b) sulfonic acid functionalized ethane–silica and (c) thiol functionalized ethane–silica sample.

gle, sharp signal at 5.6 ppm corresponding to the $\text{--CH}_2\text{--CH}_2\text{--}$ groups integrated inside the porous network and the absence of peaks in the range $10\text{--}30\text{ ppm}$ suggests that the surfactant species are completely removed after extractions (Fig. 2a). In addition, CHN analysis confirmed the absence of nitrogen in the surfactant extracted samples, which further shows that the surfactant molecules can be completely removed after solvent extractions. The presence of functionalized propyl thiol groups is confirmed by the formation of peaks at 22.5 ppm for the carbon atom (C^1) adjacent to the thiol moiety and that at 29.5 ppm for the central (C^2) carbon atom while the carbon atom (C^3) bonded to the silicon shows a broad band at 12.3 ppm of $\equiv\text{Si--}^1\text{CH}_2\text{--}^2\text{CH}_2\text{--}^3\text{CH}_2\text{--SH}$ groups. Upon oxidation, the peaks obtained earlier for the C^1 , C^2 and C^3 carbon gets changed due to the transformation of thiol groups to sulfonic acid groups. The resonance at 5.9 ppm retained due to the ethane moiety while the new resonances at 12.5 , 19.1 and 54.6 ppm are assigned to C^1 , C^2 and C^3 carbon species of $\equiv\text{Si--}^1\text{CH}_2\text{--}^2\text{CH}_2\text{--}^3\text{CH}_2\text{--SO}_3\text{H}$, respectively. All these results demonstrate that the $\text{--(CH}_2)_2\text{--}$ groups are incorporated into the mesoporous framework of ethane–silica PMO samples with thiol or sulfonic acid groups in the pore channels and the surfactant is completely removed after solvent extraction. X-ray photoelectron spectroscopy analysis of ethane–silica and MCM-41 sulfonic acid samples show peaks at 169.2 eV , for the binding energy levels of S 2p of oxidized sulfur viz. $\text{--SO}_3\text{H}$ [25]. No peak corresponding to the --SH binding energy at 164 eV was observed, confirming the complete oxidation of --SH to $\text{--SO}_3\text{H}$.

The percentage incorporation of 3-MPTS groups into the pore channels of ethane–silica PMO and MCM-41 materials were determined by elemental analysis. As expected, with an increase in the percentage of 3-MPTS an increase in sulfur loading was observed, however the increment was not similar for the two classes of mesoporous samples (Table 1). This discrepancy arises due to the difference in the hydrolysis and condensation rates between BTEE and 3-MPTS than between TEOS and 3-MPTS, in one-pot synthesized catalysts. In addition, elemen-

Table 1
Properties of sulfonic acid functionalized silica samples

Sample	% of 3-MPTS ^a		S_{BET} (m^2g^{-1})	Pore diameter (\AA)	Pore volume (ccg^{-1})
	Input	Output			
ES-SO-10%	10	8.0	710	26.4	0.597
ES-SO-30%	30	22.0	643	21.6	0.347
ES-SO-30%-G	30	23.5	617	24.5	0.388
MM-SO-10%	10	8.5	927	30.4	0.735
MM-SO-30%	30	23.0	805	25.4	0.553
MM-SO-30%-G	30	26.0	733	n.d.	n.d.
SG-SO-30%	30	25.0	368	n.d.	n.d.

n.d., not determined.

^a Determined by CHS elemental analysis.

tal analysis result also shows that after oxidation with aqueous H_2O_2 , the sulfonic acid samples show lesser sulfur content than their corresponding thiol-containing materials due to the solubilization of some surface anchored thiol groups. Interestingly, irrespective of the support material, the percentage loading of 3-MPTS as well as sulfonic acid groups were more in the grafted samples than the samples prepared by co-condensation method. This result agrees with the general concept that a greater percentage of functional groups can be loaded over porous supports by employing the grafting method; while the distribution of the functionalized species matters if they are applied as catalysts, where site isolation and the accessibility of the reactive sites to the reactants molecules demands more.

TEM analysis confirms the structural regularity of the sulfonic acid functionalized PMO samples. For instance, TEM photographs of ES-SO-30% sample clearly shows the presence of hexagonally arranged pore structures, when viewed along the pore direction, with a pore diameter of ~ 2.2 nm and the presence of parallel lattice fringes, on a side view analysis (Fig. 3). The presence of equidistant parallel fringes shows the nature of separation between the layers and the well-packed pore arrangement of the ethane–silica PMO samples. Thus, images parallel and perpendicular to the channel axes confirm the 2D-hexagonal mesoporous structure of the sulfonic acid functionalized ethane–silica molecular sieves. Nitrogen adsorption–desorption isotherms of sulfonic acid functionalized

organosilicas and MCM-41 samples were of type IV with a typical capillary condensation step in the relative pressure (P/P_0) range of 0.3–0.5 (Fig. 4). This indicates that both the materials possess well-defined mesoporous structures and relatively narrow pore-size distributions. The textural properties such as the specific surface area, average pore size and pore volume of all the mesoporous samples are given in Table 1. The pristine mesoporous silica supports shows a high surface area of >800 m^2g^{-1} and with the percent of sulfonic acid loading the surface area gets systematically decreased. The BET surface area of the samples ES-SO-10%, ES-SO-30%, MM-SO-10% and MM-SO-30% are 710, 643, 907 and 805 m^2g^{-1} , respectively. The pore sizes of the samples determined by BJH analysis shows values of 26.4, 21.6, 30.4 and 25.4 \AA for ES-SO-10%, ES-SO-30%, MM-SO-10% and MM-SO-30% samples, respectively. These data indicate that the surface area and pore diameter of the samples decrease with higher loading of sulfonic acid groups.

3.2. Catalytic condensation of ketones with aldehydes

The effect of support (ethane–silica, MCM-41 and silica gel), percentage of sulfonic acid group loading (10% or 30%) as well as the development of sulfonic acid groups (co-condensation method or grafting method) over the catalytic properties was evaluated in the Claisen–Schmidt condensation reactions. The blank reaction carried without any sulfonic acid groups con-

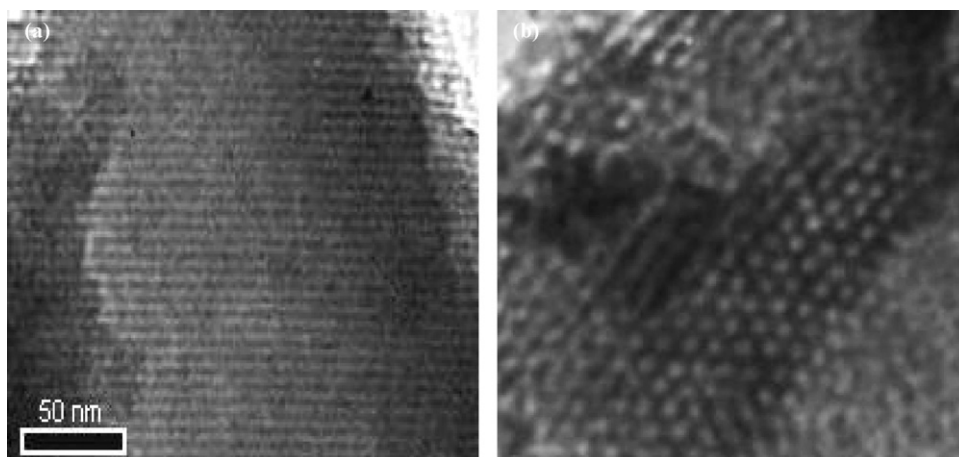


Fig. 3. TEM images of ES-SO-30% sample; (a) side on view analysis and (b) along the pore direction.

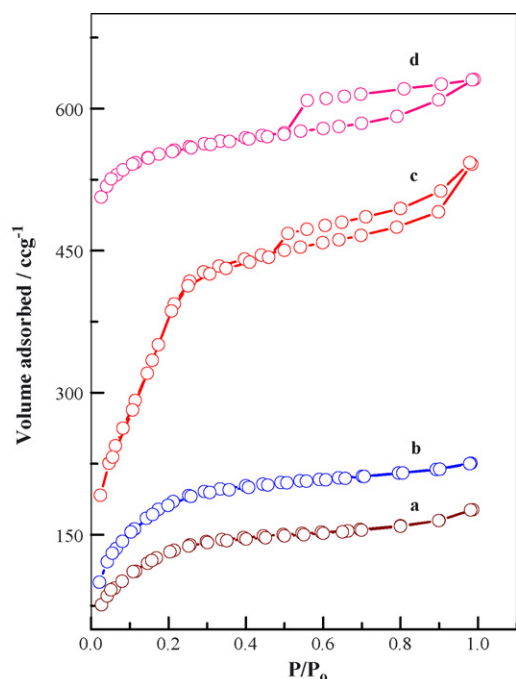


Fig. 4. N_2 adsorption–desorption isotherms of (a) ES-SO-10%, (b) ES-SO-30%, (c) MM-SO-10% and (d) MM-SO-30% sample. The isotherms are shifted along the y-axis for clarity.

taining samples showed a conversion less than 10% and, as expected, with the percentage of sulfonic acid groups the yield of condensed product (chalcone) increases. Among, the direct synthesized sulfonic acid catalysts, the maximum conversion was obtained over the ES-SO-30% catalyst and the conversion follows the order ES-SO-30% > MM-SO-30% > ES-SO-10% > MM-SO-10% catalysts (Table 2). However, for the post-synthesis grafted catalysts the conversion follows the order, MM-SO-30%-G > SG-SO-30%-G > ES-SO-30%-G samples. Interestingly, the conversion of acetophenone over SG-SO-30% catalyst was slightly greater than that over the ES-SO-30% catalyst and the lesser conversion obtained with the organosilica sample may result from the lower loading of the propyl sulfonic acid groups than the silica gel samples. But the

Table 2

Catalytic activity of sulfonic acid catalysts in the condensation reaction between acetophenone and benzaldehyde

Catalyst	Conversion ^a (%)	Chalcone selectivity (%)
Blank	<10	90
ES-SO-10%	43	96
ES-SO-30%	72	95
ES-SO-30% ^b	60	96
ES-SO-30%-G	61	95
MM-SO-10%	35	97
MM-SO-30%	61	93
MM-SO-30% ^b	43	94
MM-SO-30%-G	55	91
SG-SO-30%	64	81
SG-SO-30% ^b	38	84

Reaction conditions: catalyst (mg), 50; T ($^{\circ}C$), 150; acetophenone (20 mmol); benzaldehyde (20 mmol); time (h), 6.

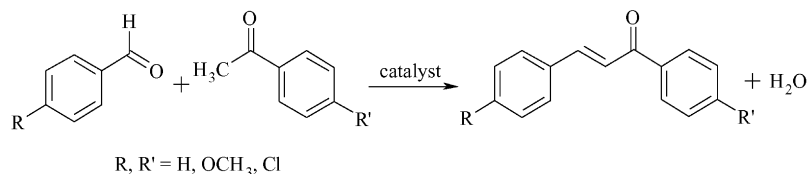
^a Conversion is based on acetophenone.

^b During third run.

selectivity for chalcone was greater with mesoporous samples (>95%) than in the amorphous silica gel sample (<80%) and this point out the need for ordered mesoporous structures for better selectivity in targeted reactions. Even though, ES-SO-30% and MM-SO-30% catalysts show higher conversion, improved chalcone selectivity was observed over lower sulfonic acid functionalized ES-SO-10% and MM-SO-10% catalysts. This result demonstrates that the structural ordering of the mesoporous materials play a role in acid catalyzed organic transformations. The linear dependence of reaction rate with sulfonic acid loading over both class of the mesoporous materials show that by increasing the MPTS:TEOS ratio only the number and not the nature of the resultant active sites changed. In this context, it is worth meaning to note that the conversion of acetophenone was more over the direct synthesized sulfonic acid samples than the post-synthesis modified samples, even though both materials contain almost similar sulfur contents. A tempting explanation arises from the diffusional limitations or due to the difference in the active site accessibility in the preparation process and hence all the sulfonic acid sites are not equally accessible for the diffused reactant molecules. The functionalities introduced

Table 3

Reactions of substituted benzaldehyde and acetophenone over ES-SO-30% catalyst



R	R'	Conversion (%) ^a	Selectivity (%)
H	H	72	95
OCH ₃	H	81	91
Cl	H	64	95
H	OCH ₃	80	94
H	Cl	77	96

Reaction conditions same as in Table 2.

^a Conversion is based on acetophenone.

to the mesoporous material by grafting always lead to irregularly distributed functionalities and thus most of the functionalities are distributed on the surface or near the pore mouth of the mesoporous materials [26]. In contrast, $-\text{SO}_3\text{H}$ functionalized mesoporous materials synthesized by co-condensation have uniformly distributed sulfonic acid sites. The effect of substituting groups in the para position of benzaldehyde as well as acetophenone was probed to know the role of ring substituents in condensation reactions. Results showed that the presence of electron donating groups in the para position of benzaldehyde or acetophenone had a positive effect in the conversion while the presence of electron withdrawing groups in the para positions decreased the conversion (Table 3). However, the selectivity of chalcone is almost similar in all cases, which may be due to the large pore size of the organosilica materials as steric effects does not play any role as observed over zeolites or hydrotalcites.

The reusability of the ES-SO-30% and MM-SO-30% catalysts were further probed to verify the role of integrated organic groups in the frame wall positions. Results showed that the ethane bridged mesoporous catalysts are more resistant to leaching under the present reaction conditions due to their special physical and chemical properties acquired by the presence of organic moieties in the frame work positions, than the MCM-41 based catalysts. The conversion of acetophenone decreased to 60% during the third reuse of ES-SO-30% catalyst while the MM-SO-30% catalyst shows a sharp decrease to 43%, after third reuse. Thus, the hybrid catalyst can be reused three times with out any appreciable change in activity; however, the MCM-41 based sulfonic acid catalyst showed a sharp decrease in the conversion during the reuse. The decrease in catalytic activity during reuse relates to the leaching of the active sulfonic acid moieties. Thus, the high activity and stability of the sulfonic acid functionalized PMO samples, possibly relates to the tight anchoring of the propyl $-\text{SO}_3\text{H}$ groups in the inner pore walls as well as due to the hydrophobic environments imparted inside due to the presence of bridging organic groups.

4. Conclusions

In short, mesoporous ethane–silica and MCM-41 functionalized with various amounts of 3-MPTS groups was prepared by grafting methods and a one pot co-condensation method using 3-MPTS groups as the sulfur precursor in presence of a structure orientor. The mercaptopropyl groups were then oxidized into sulfonic acid groups using aqueous H_2O_2 as an oxidizing agent. Various systematic characterizations revealed the successful formation of sulfonic acid groups with the retainment of mesoporous structural ordering. The sulfonic acid functionalized organosilica materials were active, selective and stable

in the Claisen–Schmidt condensation of aldehydes and ketones than the conventional MCM-41 samples and an amorphous silica gel.

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