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Functionalized mesoporous materials as efficient organocatalysts for the syntheses of xanthenes

John Mondal^a, Mahasweta Nandi^{a,b}, Arindam Modak^a, Asim Bhaumik^{a,*}

^a Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur 700032, India

^b Integrated Science Education and Research Centre (ISERC), Visva-Bharati University, Santiniketan, Birbhum, West Bengal 731235, India

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ABSTRACT

Highly efficient and recyclable heterogeneous organocatalysts containing acidic functional groups such as $-CO_2H$ and $-SO_3H$ have been synthesized by post-synthesis modification of 2D-hexagonal mesoporous silica materials SBA-15 and MCM-41, respectively. The $-CO_2H$ functionalized material is obtained *via* Schiff-base condensation of 3-aminopropyl grafted SBA-15 with 4-formylbenzoic acid, whereas $-SO_3H$ functionalized material is prepared *via* partial oxidation of 3-mercaptopropyl grafted MCM-41 with dilute aqueous H_2O_2 . These functionalized mesoporous materials have been thoroughly characterized by powder X-ray diffraction (PXRD), nitrogen adsorption/desorption studies, transmission electron microscopy (TEM) and UV visible diffuse reflectance spectroscopy. Both these materials have highly ordered 2D-hexagonal mesoporous structures with high surface areas and well-defined pore sizes. These acid functionalized materials have been used as heterogeneous catalysts for the condensation of aromatic aldehydes with 2-napthol under mild conditions in the presence or absence of a solvent affording high yields of the value added xanthenes.

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1. Introduction

Heterogeneous catalysts bearing active metal centers have been studied extensively during the past few decades [1-4]. Although metal catalysis occupies a prominent position in synthetic organic chemistry, owing to the toxic effects associated with metal-containing catalysts, increasing interests have been paid for the development of catalysts devoid of metal and these catalytic reactions are broadly known as organocatalysis [5]. Despite being known for many decades, organocatalysis remained mostly unrecognized [6]. But in the recent years there has been a rapid development in this field, attributed to the versatile opportunities of catalyst design offered by organocatalytic systems. Although such transformations can be considered as a green process, however, contrary to metal based catalytic systems, organocatalytic reactions are mostly homogeneous in nature [7,8]. Thus catalyst recovery and its reuse is an important drawback associated with these organocatalytic reactions. Apart from economic advantages it is also very essential to elude the accumulation of unwanted waste products to make the processes environmentally benign. The most extensively practiced technique to avoid this problem is to transform a homogeneous catalyst to a heterogeneous one by immobilizing the former over high surface area insoluble solid supports [9]. In this context functionalized mesoporous silicas can be very promising support due to their exceptionally high surface area, tunable nanoscale pores and wide range of compositional variations [10-15]. Design and synthesis of surface functionalized ordered mesoporous silica materials have attracted particular attention for their application in catalysis [16–19], adsorption [20,21], ion-exchange [22], sensing [23] and so on. Rational design of these materials using suitable organic functionalities give rise to smart mesoporous materials [24], which can have potential applications in many other frontier areas of science. Thus the syntheses of organically modified mesoporous materials containing active functional groups are highly desirable. One of the convenient approach to synthesize these functionalized mesoporous materials is by anchoring the desired functionalities on silica matrices with high specific surface area. In such cases, a covalent interaction could be established between the organic functional group and the silica framework, which prevents the leaching of the active centers in the reaction medium [25].

Xanthenes are a class of compounds, which are hugely recognized in the field of medicine and organic chemistry due to their antibacterial [26], anti-inflammatory activities [27] and photodynamic therapy [28]. They are the source of a class of brilliant fluorescent dyes and are used extensively in laser technology and pH sensitive fluorescent materials [29]. Various methods for the syntheses of substituted xanthenes have been achieved

^{*} Corresponding author. *E-mail addresses:* msab@iacs.res.in, abhaumik68@yahoo.co.in (A. Bhaumik).

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-COOH functionalized organocatalyst, AFS-1

Scheme 1. Schematic diagram for the preparation of -CO₂H functionalized SBA-15.

including the cycloacylation of carbamates [30], trapping of benzynes by phenol [31], cyclocondensation between 2-hydroxy aromatic aldehydes and 2-tetralone [32], and intramolecular phenyl carbonyl reaction of aldehydes with 2-naphthol by dehydration [33]. Most of these syntheses procedures have been carried out by metal containing catalysts [34] but the drawbacks associated with these reactions are long reaction time, low product yield, vigorous reaction conditions, toxic effect of metals and their leaching during the course of reaction [35]. Absence of the possibility of metal leaching, low toxicity, simple reaction process and reusability make heterogeneous organocatalysts potentially more useful over conventional metal-based catalysts.

In this paper we will discuss about two acid functionalized organocatalysts supported on mesoporous silica backbone using two different synthetic approaches. In one approach surface carboxylic acid (-CO₂H) functionalized mesoporous silica has been prepared via Schiff-base condensation of 3-aminopropyl grafted SBA-15 [36]. In the other case sulfonic acid (-SO₃H) functionalized mesoporous silica has been prepared from 3-mercaptopropyl grafted MCM-41 via partial oxidation with hydrogen peroxide (H_2O_2) . Both the acid functionalized materials can be used as catalyst for the condensation reaction of aromatic aldehyde and 2-naphthol to prepare different value added xanthene derivatives. The -CO₂H functionalized mesoporous silica can be used as a catalyst under ambient conditions in the presence of dichloromethane (DCM) as the solvent, whereas for the -SO₃H functionalized material catalysis proceeds under solvent-free conditions at 363 K.

2. Experimental

2.1. Preparation of mesoporous acid functionalized materials

2.1.1. Synthesis of –CO₂H functionalized SBA-15 (AFS-1)

Synthesis of $-CO_2H$ functionalized mesoporous silica, AFS-1 has been carried out as described in our previous communication (Scheme 1) [36].

Mesoporous silica, SBA-15 is synthesized at first through evaporation induced self-assembly (EISA) method using non-ionic pluronic F127 (Sigma–Aldrich) as the structure directing agent. Trimethyl benzene (TMB) (E-Merck) has been used as the additive and tetraethyl orthosilicate (TEOS) as the silica source. In a typical synthesis, 6 g conc. HCl (E-Merck) is added to 25 ml of water. To it 0.5 g F127 is added under stirring, followed by the addition of 0.6 g TMB. To the homogeneous solution obtained after stirring for 2 h, 2.1 g TEOS is added and the mixture is stirred for 24 h. The resulting synthesis gel is autoclaved at 373 K for 24 h and the solid product is recovered by filtration, washed several times with water and dried under vacuum in a lypholyzer. The template-free mesoporous SBA-15 is obtained by calcination of the as-synthesized material at 723 K for 6 h in flow of air. This was further functionalized via condensation with organosilane precursor 3-aminopropyltriethoxy silane (3-APTES) by stirring 0.1 g of SBA-15 with 0.18g 3-APTES in chloroform at room temperature under nitrogen atmosphere for 12 h. Then this aminopropyl functionalized mesoporous SBA-15 is refluxed with 0.15 g of 4formylbenzoic acid in 20 ml methanol for 6 h to undergo Schiff base condensation. The final product is collected by filtration and repeatedly washed with hot methanol to remove any unreacted acid precursor.

2.1.2. Synthesis of -SO₃H functionalized MCM-41 (AFS-2)

Synthesis of $-SO_3H$ functionalized mesoporous silica, AFS-2 has been carried out by oxidation of thiol group in MCM-41 prepared *in situ* using a mixture of organosilane precursor 3-mercaptopropyltrimethoxy silane (3-MPTMS) and TEOS in 1:3 molar ratio as silica precursor (Scheme 2).

In a typical synthesis procedure, 2.73 g of cetyltrimethylammonium bromide (CTAB, Loba Chemie) is dissolved in an aqueous solution of tartaric acid (0.6 g in 30 g H₂O) and the resulting mixture is stirred for about 30 min to obtain a clear solution. To it 0.98 g of 3-MPTMS is added, stirred for another 30 min and followed by the addition of 3.18 g of TEOS. The reaction mixture is stirred for another 2 h to obtain a gel and then NaOH (2 M) solution is added drop wise into it until the pH reaches ca. 12.0. The gel is aged overnight under continuous stirring, transferred into a Teflonlined steel autoclave and kept at 348 K for 72 h. After hydrothermal treatment the solid product is isolated by filtration, washed several times with water and dried under vacuum. The CTAB template is removed from the as-synthesized material by extracting the solid thrice in a mixture of acid/ethanol. Then the thiol groups (-SH) of this template-free material are converted into -SO₃H group by treating with excess H₂O₂ at 333 K for 24 h [37]. Then it is filtered, washed with water and ethanol and acidified with 0.1 M H₂SO₄ to obtain the -SO₃H functionalized MCM-41.



-SO₃H functionalized organocatalyst, AFS-2

Scheme 2. Schematic diagram for the preparation of —SO₃H functionalized MCM-41.

2.2. Catalysis

2.2.1. Synthesis of xanthene derivatives catalyzed by acid functionalized mesoporous organocatalysts

In a typical procedure (Scheme 3), a mixture of 2 mmol β -naphthol and 1 mmol aromatic aldehyde is well stirred with 20 mg of AFS-1 organocatalyst in the presence of 5 ml dry dichloromethane (DCM) at room temperature for suitable time.

After completion of reaction, the solid catalyst is filtered of from the reaction mixture and washed thoroughly with DCM. Then the filtrate is evaporated to dryness under reduced pressure to give the solid product. The crude product is crystallized from ethanol and characterized by ¹H and ¹³C NMR spectroscopy.

2.2.2. Synthesis of xanthene derivatives catalyzed by $-SO_3H$ functionalized mesoporous organocatalyst under solvent free condition

In a typical catalytic cycle (Scheme 4), a mixture of 2 mmol β naphthol and 1 mmol of aromatic aldehyde is heated at 353 K in the presence of 20 mg of AFS-2 organocatalyst in an oil bath for the necessary time (determined by product analysis using thin layer chromatography (TLC)). Then the reaction mixture is cooled, diluted with 10 ml DCM and the catalyst is separated from the reaction mixture by filtration followed by thorough washing with DCM. Then the filtrate is evaporated to dryness under reduced pressure to get the crude product which is then crystallized from ethanol. The crystallized products are characterized by ¹H and ¹³C NMR spectroscopy.

2.2.3. Recovery of the catalyst

After the reaction is over, the reaction mixture is separated by filtration and washed four times with DCM followed by three times with diethyl ether. Then the catalyst is dried at 348 K for 6 h and used for further reaction cycles. The –COOH and –SO₃H functionalized organocatalyst have been recycled for six consecutive times for the condensation reaction between β -naphthol and 4-chlorobenzaldehyde.

2.3. Instrumentation

Powder X-ray diffraction patterns of the samples are recorded on a Bruker AXS D8 Advanced diffractometer using Cu K α $(\lambda = 1.5406 \text{ Å})$ radiation. TEM images are recorded in a Jeol JEM 2010 transmission electron microscope. N₂ adsorption/desorption isotherms of the sample have been recorded on a Beckman Coulter SA 3100 automatic gas adsorption apparatus, at 77 K. Prior to the measurement, the samples are degassed at 373 K for 6 h under high vacuum. UV-visible diffuse reflectance spectra have been obtained by using a Shimadzu UV 2401PC spectrophotometer with an integrating sphere attachment. BaSO₄ pellet is used as background standard. Thermogravimetry (TG) and differential thermal analysis (DTA) of the samples are carried out on a TA instrument Q600 DSC/TGA thermal analyzer. The solid NMR spectra of the samples are measured using Bruker MSL 500 spectrometer. Liquid state NMR spectra of the products obtained during catalysis have been measured on a Bruker Avance DPX 300 NMR (300 MHz) spectrometer using TMS as the internal standard.

3. Results and discussion

The small-angle powder X-ray diffraction (XRD) patterns of mesoporous SBA-15, carboxylic acid functionalized SBA-15 before and after using it as a catalyst are shown in Fig. 1. For SBA-15 (Fig. 1a) four well-resolved diffraction peaks in the 2θ region of 0.6–2.07 can be observed which can be indexed to the 100, 110, 200 and 210 reflections [10] corresponding to a two-dimensional hexagonal mesostructure. When the silica framework is grafted with 3-APTES followed by its functionalization with 4-formylbenzoic acid a decrease in the intensity of the peaks is observed (Fig. 1b), however the 2D-hexagonal ordering is retained. This decrease in the peak intensities is attributed to the lowering of local order, viz. variations in the wall thickness or reduction of scattering contrast between the channel walls of the silicate framework [38]. The PXRD pattern of AFS-1 after its use as a catalyst for six reaction cycles (Fig. 1c) shows that it retains its mesoporous structure, although the ordering of the pores becomes quite disordered. Further, as seen from Fig. 1c that peak has been significantly shifted. Possibly during six repetitive reaction cycles contraction of



Scheme 3. General procedure for the synthesis of xanthene over -CO₂H functionalized SBA-15.



Scheme 4. General procedure for xanthene synthesis over —SO₃H functionalized MCM-41.



Scheme 5. Reaction of thiophene 2,5-dialdehyde and 2-naphthol over -CO₂H functionalized SBA-15.

pore-wall occurs, which could be responsible in decrease in *d*-spacing. Similar results can be seen for the powder X-ray diffraction of the MCM-41 based materials. 3-MPTMS-MCM-41 shows a highly order two-dimensional mesoporous structure (Fig. 1d),



Fig. 1. Small angle powder XRD patterns of SBA-15 (a), —CO₂H functionalized SBA-15 (b), —CO₂H functionalized SBA-15 after six reaction cycles (c), 3-MPTMS-MCM-41 (d), —SO₃H functionalized MCM-41 (e) and —SO₃H functionalized MCM-41 after six reaction cycles (f).

whereas the material after treatment with hydrogen peroxide to give the -SO₃H functionalized MCM-41, losses some of its ordering (Fig. 1e). The PXRD pattern of this material (Fig. 1f) after six reaction cycles shows that the material retains its mesoporous structure after repeated use. Fig. 2 depicts the representative transmission electron microscopy (TEM) images of mesoporous SBA-15 (Fig. 2a) and AFS-1 (Fig. 2b). The uniform and long range ordering of the large mesopores are clearly seen throughout the respective specimens. The corresponding FFT diffractogram for the mesoporous SBA-15 material has been shown in the inset of Fig. 2a which also indicates the presence of hexagonally arranged pores [39,40]. The TEM images of 3-MPTMS-MCM-41 (Fig. 2c) and AFS-2 (Fig. 2d), also show similar hexagonally ordered mesoporous structure, but the size of the pores here are smaller (ca. 2 nm) compared to the SBA-15 analogs. The hexagonal arrangement of pores can also be confirmed from the FFT diffractogram of 3-MPTMS-MCM-41 given in the inset of Fig. 2c.

Nitrogen sorption at 77 K over $-CO_2H$ functionalized mesoporous SBA-15 (not shown here) shows type IV adsorption-desorption isotherms with very large H2 type hysteresis loop in the 0.5–0.8 *P*/P₀ range. Such type of isotherm suggests the presence of large uniform mesopores connected by windows of small cage-like pores and confirms the mesoporous nature of the sample [39]. The BET (Brunauer–Emmett–Teller) surface area and pore volume of the material are 250 m² g⁻¹ and 0.199 cm³ g⁻¹, respectively. The values of *P*/P₀ near the inflection point are closely related to the pore-widths, which lie in the mesopore range and the sharpness of these steps indicates the uniform size distribution of the mesopores [39]. Pore size of the sample estimated employing the Barett–Joyner–Halenda (BJH) method is *ca.* 9.16 nm, which is in good agreement with the pore widths depicted by the TEM

image analysis and XRD studies. The nitrogen sorption isotherm for AFS-2 is shown in Fig. 3. The sharp increase in N₂ uptake for adsorption is observed at a lower P/P_0 ca. 0.05–0.2 compared to the AFS-1 sample based on MCM-41 structure. The surface area for this material is $320 \text{ m}^2 \text{ g}^{-1}$ and the pore volume $0.135 \text{ cm}^3 \text{ g}^{-1}$. The pore size distribution plot for this material obtained by using non-local density functional theory (NLDFT) is given in the inset of Fig. 3. The average pore width of this material was ca. 1.84 nm, which is also supported by the PXRD and TEM analyses.

IR spectroscopy has been employed to characterize the presence of -CO₂H and -SO₃H groups in the functionalized mesoporous organocatalysts. In Fig. 4 FTIR spectra of AFS-1 and 2 samples are shown. As seen from the figure that the weak absorbance at 1470 and 1420 cm⁻¹ is observed with the introduction of 3-mercaptopropyltrimethoxysilane functionality in AFS-2. These peaks could be assigned to the bending vibrations of methylene groups. Further, absorbance in the range of 2850–2930 cm⁻¹ corresponding to the methylene stretching vibrations of the propyl chain appeared, indicating the incorporation of the organic moiety in AFS-2. Before the oxidation of the mercaptopropyl group a very weak peak at 2567 cm⁻¹ (Fig. 4a, inset) was observed. This peak could be assigned to the S–H stretching, which disappeared upon H_2O_2 treatment, demonstrating that the thiol group gets completely oxidized into -SO₃H group (Fig. 4b) [41]. The peaks corresponding to the S=O stretching vibrations of sulfonic acid are normally observed in the range of 1000–1200 cm⁻¹. However, these peaks cannot be resolved due to their overlap with the absorbance of the Si-O-Si stretch in the 1000–1130 cm⁻¹ range and that of the Si–CH₂–R stretching in the $1200-1250 \text{ cm}^{-1}$ range (Fig. 4b). The spectra for silica show peaks in the range of $3600-3200 \,\mathrm{cm}^{-1}$ attributed to the hydroxyl stretching of the hydrogen bonded internal silanol



Fig. 3. Nitrogen adsorption (filled symbol)/desorption (empty symbol) isotherm of AFS-2 at 77 K. Inset: corresponding pore size distribution using NLDFT method.

groups. The bands at *ca.* 1200, 1100 and 800 cm^{-1} are the characteristic bands of SiO₂ assigned to the Si–O stretching vibrations while the bands at 950 and 470 cm⁻¹ are assigned to the bending vibrations of the surface silanols and Si–O, respectively. For the –CO₂H functionalized organocatalyst (AFS-1) the peaks in the range 1693 cm⁻¹ are attributed for the C=O stretching frequency (Fig. 4c). On the other hand the peaks at 1394 cm⁻¹ and 3400 cm⁻¹



Fig. 2. Transmission electron microscopy images of SBA-15 (a), -CO₂H functionalized SBA-15 (b), 3-MPTMS-MCM-41 (c) and -SO₃H functionalized MCM-41 (d).



Fig. 4. FTIR spectra of —SH functionalized mesoporous organosilica (a), —SO₃H functionalized organocatalyst AFS-2 (b) and —CO₂H functionalized organocatalyst AFS-1 (c). S-H signal at 2567 cm⁻¹ has been expanded in the inset.

(broad) correspond to the C—O—H bending and —OH stretching vibrations, respectively. Further, the peak at 1646 cm⁻¹ could be assigned to the C=N stretching frequency of AFS-1 (Fig. 4c). Thus FTIR spectroscopic results suggested the grafting of the respective organic functionalities in AFS-1 and -2 materials (Schemes 1 and 2).

Quantitative determinations of the amount of the organic moieties have been estimated to calculate the total number of acid sites present in these materials. It is directly related to the active sites participating in the catalytic reactions and thus we could estimate the turn over frequency (TOF) of the catalytic reactions based on this acidity data. The results of the titrimetric analyses show that the loading of the $-CO_2H$ and $-SO_3H$ groups in these acid functionalized mesoporous materials is 4.5 and 3.7 mmol g⁻¹, respectively.

3.1. Catalysis: synthesis of xanthenes

The acid functionalized mesoporous materials have been used as catalysts for the synthesis of xanthene *via* condensation reaction between aromatic aldehydes and 2-naphthol. The condensation reaction of various aromatic aldehydes (**1a–j**) with 2-naphthol (**2**) in the presence of optimized amount of $-CO_2H$ functionalized organocatalyst under mild reaction condition gave 14-aryl-14*H*dibenzo [*a*, *j*] xanthenes (**3a–j**) (Scheme 1) [42]. It has been found that 0.02 g of $-CO_2H$ functionalized SBA-15 is the optimum amount of catalyst required to carry out the reactions. Increasing the amount of catalyst does not improve the yield of the products any further, whereas decreasing the amount of catalyst leads to decrease in the product yield. Under optimized reaction conditions



Scheme 6. Reaction of terephthaldehyde and 2-naphthol over —CO₂H functionalized SBA-15.



Fig. 5. Recycling efficiency of functionalized mesoporous organocatalysts AFS-1 (a) and AFS-2 (b).

yield of the products and time taken for maximum conversion of the substrates in each case, are listed in Table 1.

The reaction when performed with 1-naphthol instead of 2naphthol, keeping the other conditions same, did not produce any xanthene product. The aldehydes with both electron donating (Table 1, entries 3 and 4) and electron withdrawing groups (Table 1, entries 2, 5, 6, 7, 8, 9 and 12) participated in the condensation reaction with equal efficiency. Thus, the nature and position of substitution in the aromatic ring did not affect the reactions much. The meta-substituted aromatic aldehydes (Table 1, entry 5, entry 7) as well as sterically hindered ortho-substituted aromatic aldehydes (Table 1, entries 6 and 12), both undergo condensation reaction without any difficulty. When fluoro substituted aromatic aldehyde is taken (Table 1, entry 5) the fluoro groups are found to remain inert during the course of condensation reaction. Several sensitive functional groups such as -Cl, -Br, and -NO₂ attached with the aromatic ring are also compatible for this reaction. The turn over number (TON) for different reactions is moderately good, which confirms the high catalytic efficiency of the acid functionalized mesoporous silica materials in these reactions. When the reaction is performed at 313K under identical conditions, the yield of the product (Table 1, entry 11) increases slightly, suggesting that the condensation reaction becomes more facile at higher temperature. When the condensation reaction is performed with thiophene 2,5-dialdehyde (Scheme 5) one of the -CHO group takes part in the reaction, while the other remains intact. 14-(4-Formylphenyl)-14H-dibenzo [a, j] xanthenes, which is obtained via the condensation reaction of terephthaldehyde and 2naphthol under refluxing condition (Scheme 6) is highly useful for the synthesis of different target organic molecules. To confirm the catalytic role of -CO₂H functionalized SBA-15, the condensation reaction between 4-methylbenzaldehyde and 2-naphtol has been carried out in the absence of catalyst (Table 1, entry 10). It is found that even after continuing the reaction for a prolonged time no corresponding xanthene product is observed. We have also carried out the reaction in the presence of pure silica mesoporous SBA-15 (Table 1, entry 13) and -NH₂ functionalized SBA-15 (Table 1, entry 14) for 4-chlorobenzaldehyde. However, no xanthenes derivative was obtained under these conditions too. This data clearly suggests that acid sites present at the catalyst surface are crucial to carry out this condensation reaction.

The condensation reaction between 4-chlorobenzaldehyde and 2-naphthol has been performed using –CO₂H functionalized

Table 1

 CO_2H functionalized SBA-15 catalyzed synthesis of 14-aryl-14*H*-dibenzo [*a*, *j*] xanthenes **3**.^a

Entry	Aldehyde	Time (h)	Yield ^b (%)	Product	TON ^c
1	Сно	6.0	80	3a	8.8
2	Вг-СНО	4.0	75	3b	8.3
3	но-Сно	5.0	80	3с	8.9
4	H₃С—_СНО	5.0	78	3d	8.7
5	Е СНО	5.0	80	Зе	8.8
6	CHO NO 2	4.0	86	3f	9.5
7	Вг	4.0	82	3g	9.1
8	О₂NСНО	4.0	82	3h	9.1
9	сі—Сно	4.5	75	3i	8.3
10 ^d	СІ—СНО	16.0	-	-	-
11 ^e	Н₃С СНО	4.0	84	3d	9.3
12	СНО	4.0	86	3ј	9.5

Table 1 (Continued)



^a Reaction conditions: Ar-CHO: 1.0 equiv., 2-naphthol: 2.0 equiv., solvent: dichloromethane, 5 ml, reaction temperature: 298 K, catalyst: 20 mg.

^b Isolated yield of pure product.

^c Turn over number (TON) = moles of substrate converted per mole of active site.

^d Reaction carried out in the absence of catalyst.

^e Reaction carried out at 313 K.

^f Reaction carried out with mesoporous SBA-15.

^g Reaction carried out with amine functionalized SBA-15.

SBA-15 catalyst in different solvents; the results are given in Table 2. All these condensation reactions are carried out at the same temperature (333 K) and the yield are reported after same reaction time (6 h). The best conversion takes place when dichloromethane is chosen as the solvent, whereas in solvents like tetrahydrofuran or water, the conversion is almost negligible. In case of solvents such as acetonitrile, dimethylformamide, ethanol and toluene, moderate conversion takes place, with yields *ca.* 40–50%. The condensation reaction between 4-chlorobenzaldehyde and 2-naphthol has been taken as a representative case to check the recycling efficiency of the $-CO_2H$ functionalized SBA-15 organocatalyst. The recovered catalyst (as mentioned previously) after each reaction cycle is recycled further for six consecutive times and the results have been plotted in Fig. 5a. It can be seen that the catalyst can be recycled and reused effectively without significant loss of its catalytic activity as well as mesoporous structure (Fig. 1c).

The condensation reaction of aromatic aldehydes (**4a–f**) and 2naphthol (**5**) at 353 K under solvent-free condition to synthesize xanthene derivatives (**6a–f**) (Scheme 6) have been studied in the presence of $-SO_3H$ functionalized MCM-41 as the catalyst. The results (Table 3) suggest that the reactions proceed very smoothly under solvent-free condition and give 14-aryl-14*H*-dibenzo [*a*, *j*] xanthenes in good yield within a short period of time. The TONs for all the reactions are very high, which indicates the high efficiency of the $-SO_3H$ functionalized catalyst. The reactions are not affected by the nature of substituents (electron withdrawing and electron donating) attached with the aromatic ring as well as the



Fig. 6. Proposed catalytic cycle for condensation reaction of aromatic aldehyde and 2-naphthol in the presence of -CO₂H functionalized SBA-15.

position of substitution. The catalyst has been reused for six consecutive cycles for the condensation reaction between 2-naphthol and 4-chlorobenzaldehyde and the results are given in Fig. 5b. A control experiment with the nonporous sulfonic acid functionalized catalyst prepared *via* copolymerization of styrene-divinyl benzene followed by sulphonation with the H_2SO_4 to introduce $-SO_3H$ group was performed (Table 3, entry 8). Internal diffusional is the inherent property for the porous solid catalyst which becomes limited for the nonporous solid catalyst. From the above data it is clear that pores play a decisive role in our mesoporous organocatalyst for the diffusion of organic molecules, which facilitates the condensation reaction and as result rate of the catalytic reaction becomes greater than the nonporous catalyst.

Estimated loading of $-CO_2H$ and $-SO_3H$ groups in AFS-1 and 2 materials are 4.5 and 3.7 mmol g⁻¹, respectively. Although the loading of $-SO_3H$ group and thus total acid strength of the catalyst AFS-2 is less than that of $-CO_2H$ group of AFS-1, the reaction proceeds very smoothly for the $-SO_3H$ functionalized catalyst. This result proves that the acid strength of the $-SO_3H$ group is greater

Table 2

Synthesis of xanthene derivative over — CO_2H functionalized SBA-15 using different solvents.

Entry	Solvent	Yield ^a (%)
1	Dichloromethane	80.0 ^b
2	Tetrahydrofuran	Trace
3	Acetonitrile	45.0
4	Dimethylformamide	50.0
5	Ethanol	30.0
6	Water	Trace
7	Toluene	25.0

^a Reaction carried out at 333 K for 6 h.

 $^{\rm b}$ Reaction carried out at 313 K for 4 h as dichloromethane solvent has boiling point 313 K.

than that of $-CO_2H$ group. Since, in this acid catalyzed condensation reaction is facilitated by the increase of electrophilicity of the aldehyde group, stronger acid site promotes this reaction. Further, the surface areas of AFS-1 and -2 are $250 \text{ m}^2 \text{ g}^{-1}$ and $320 \text{ m}^2 \text{ g}^{-1}$, respectively. Surface area also plays a crucial role in the rate of the

Table 3 SO₃H functionalized MCM-41 catalyzed synthesis of 14-aryl-14*H*-dibenzo [*a*, *i*] xanthenes (**6**) under solvent free conditions.

Entry	Aldehyde	Time (h)	Yield ^b (%)	Product	TON ^c
1	СНО	1	90	3a	12.1
2	Н₃ССНО	2	92	3b	12.4
3	ВгСНО	2	90	3c	12.1
4	Е СНО	2.5	88	3d	11.8
5	СІ—СНО	1.5	95	3e	12.8
6	O ₂ N-CHO	2	88	3f	11.8
7 ^d	СНО	16	-	_	-
8 ^e	СНО	2	30	3a	2.7

^a Reaction conditions: Ar-CHO: 1.0 equiv., 2-naphthol: 2.0 equiv., reaction temperature: 353 K, catalyst: 20 mg.

^b Isolated yield of pure product.

^c Turn over number (TON) = moles of substrate converted per mole of active site.

^d Reaction carried out in the absence of catalyst.

^e In the presence of nonoporous polymer containing —SO₃H group as catalyst.

catalytic reaction, as higher surface area helps favorable diffusion and thus facilitates the reaction. Due to the larger surface area of AFS-2 there is favorable diffusion of organic molecules in the pore channels and as a result the rate of the catalytic reaction is quite high for AFS-2 compared to that of AFS-1. Thus due to higher surface area and stronger acidity the reaction becomes quite facile over $-SO_3H$ functionalized material AFS-2.

It can be observed that the $-SO_3H$ functionalized organocatalyst can be repeatedly used for many reaction cycles without appreciable loss of activity.

Plausible reaction pathway for the condensation reaction over $-CO_2H$ functionalized SBA-15, as a representative case, is shown in Fig. 6. The acid functionalized organocatalyst acts as a protonic acid which increases the electrophilicity of the carbonyl carbon of aromatic aldehyde that undergoes 1,4-addition reaction with 2-naphthol, leading to the formation of the corresponding product, **A**. **A** on further reaction with another molecule of 2-naphthol in the presence of the acid catalyst forms **B**, which undergoes cyclization with the elimination of water molecule to give the xanthene derivative [43,44]. A similar mechanism can be expected to be operating in case of the $-SO_3H$ functionalized AFS-2 catalyst. Since the acid groups present at the surface of the porous materials plays crucial role, so the reaction over $-SO_3H$ functionalized MCM-41 with stronger acidic sites, proceeds more rapidly than $-CO_2H$ functionalized SBA-15.

4. Conclusions

In conclusion, we have developed two metal-free acid catalysts based on mesoporous silica SBA-15 and MCM-41. The -CO₂H functionalized SBA-15 has been prepared via Schiff-base condensation of 3-aminopropyl grafted SBA-15 with 4-formyl benzoic acid, whereas the -SO₃H functionalized catalyst has been synthesized via in situ incorporation of mercaptopropyl group into mesoporous silica, MCM-41, followed by the oxidation of -SH to -SO₃H. Both these materials are highly ordered 2D-hexagonal structure, mesoporosity and retained the organic functionalities at their surfaces. These materials can be used for the condensation reaction of aromatic aldehyde and 2-naphthol for the synthesis of various xanthene derivatives in good yield, under mild conditions in the presence or absence of solvents. These catalytic reactions proceed in the absence of any other external metal co-catalyst and hence they are designated as environmentally benign organocatalytic pathways. Both these organocatalysts can be recovered easily after each catalytic cycle and show high recycling efficiency, which makes them highly attractive for their potential use in large scale synthesis of value added organic fine chemicals.

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- [42] ¹H and ¹³C NMR chemical shifts for different xanthene derivatives reported in Table 1. 14-(Phenyl)-14H-dibenzo [a, j] xanthene (Table 1, entry 1): ¹H NMR (300 MHz, DMSO-*d*₆) δ 8.69 (2H, d, J=9Hz), 7.93 (4H, d, J=9Hz), 7.64 (6H, m), 7.47 (2H, t), 7.16 (2H, t), 6.98 (1H, t), 6.71 (1H, s); ¹³C NMR (300 MHz, DMSO $d_6)\,\delta\,147.9,\,145.4,\,130.8,\,130.6,\,128.9,\,128.5,\,128.3,\,127.9,\,126.8,\,126.1,\,124.4,\,$ 123.4, 117.6, 117.3, 36.5; EIMS, 70 Ev, m/z: 358.32 (M⁺). 14-(4-Bromophenyl)-**14H-dibenzo** [*a*, *j*] xanthene (Table 1, entry 2): ¹H NMR (300 MHz, DMSO-*d*₆) δ 8.65 (2H, d, *J* = 9 Hz), 7.94 (4H, d, *J* = 9 Hz), 7.64–7.53 (6H, m), 7.48 (2H, t), 7.34 $(2H, d, J = 9 Hz), 6.72 (1H, s); {}^{13}C NMR (300 MHz, DMSO-d_6) \delta 147.8, 144.8, 131.2,$ 130.7, 130.6, 130.0, 129.2, 128.5, 126.9, 124.5, 123.3, 119.4, 116.8, 38.6; EIMS, 70 Ev, m/z: 436.79 (M⁺). **14-(4-Hydroxyphenyl)-14H-dibenzo** [*a*, *j*] xanthene (Table 1, entry 3): ¹H NMR (300 MHz, DMSO-d₆) δ 9.69 (1H, s), 8.43 (1H, d, J=9 Hz), 7.57 (1H, d, J=9 Hz), 7.49–7.42 (7H, m), 7.27–7.19 (5H, t), 6.94 (1H, d, J=6 Hz), 6.69 (1H, d, J=9 Hz), 6.45 (1H, s); ¹³C NMR (300 MHz, DMSO- d_6) δ 154.2, 149.2, 137.9, 131.9, 131.4, 129.9, 129.3, 129.2, 127.6, 124.6, 123.3, 118.4, 117.6, 115.8, 37.5; EIMS, 70 Ev, *m/z*: 374.34 (M⁺). **14-(4-Methylphenyl)-14H-dibenzo** [*a*, *j*] xanthene (Table 1, entry 4): ¹H NMR (300 MHz, CDCl₃) δ 8.44 (2H, d, J = 9 Hz), 7.86-7.79 (4H, m), 7.64-7.58 (8H, m), 7.00 (2H, d, J = 9 Hz), 6.48 (1H, s), 2.1 (3H, s); ¹³C NMR (300 MHz, CDCl₃) & 148.7, 142.2, 135.9, 131.5, 131.1, 129.2, 128.8, 128.1, 126.8, 124.2, 122.7, 118.0, 117.5, 37.7, 20.9; EIMS, 70 Ev, $m/z: 372 (M^*). 14-(3-Fluorophenyl)-14H-dibenzo [a, j] xanthene (Table 1, entry 5): ¹H NMR (300 MHz, CDCl₃) <math>\delta$ 6.51(s, 1H), 6.72–8.35 (m, 16H); ¹³C NMR (75 Hz, CDCl₃) δ 38.2, 113.8 and 90, 114.0 (J_{C-F} 21.5 Hz), 115.4 and 115.8 (J_{C-F} 21.5 Hz), 117.2, 118.2, 122.7, 124.31, and 124.32 (J_{C-F} 2.8 Hz) 124.7, 127.3, 129.3, 129.5, 130.1and130.2 (J_{C-F} 8.3 Hz), 131.4, 131.7 (J_{C-F} 19.4 Hz), 147.8, 147.9 (J_{C-F} 6.2 Hz), 149.2, 161.7, 165.1; EIMS, 70 Ev, m/z: 376 (M⁺). 14-(2-Nitrophenyl). **14H-dibenzo** [*a*, *j*] xanthene (Table 1, entry 6): ¹H NMR (300 MHz, DMSO-*d*₆) δ 10.28 (1H, d, *J* = 6 Hz), 9.76 (1H, d, *J* = 9 Hz), 7.97–7.66 (4H, m), 7.40–7.01 (10H, m), 5.75 (1H, s); ¹³C NMR (300 MHz, DMSO-*d*₆) δ 32.7, 118.0, 118.3, 123.2, 124.5, 125.1, 125.3, 127.7, 128.0, 129.3, 129.6, 129.9, 130.6, 132.2, 132.6, 134.4, 141.2 147.5, 149.8; EIMS, 70 Ev, m/z: 425.25 (M⁺) + Na⁺. 14-(3-Bromophenyl)-14Hdibenzo [a, j] xanthene (Table 1, entry 7): ¹H NMR (300 MHz, DMSO- d_6) δ 8.71 (2H, d, J = 9 Hz), 7.94 (4H, d, J = 9 Hz), 7.81 (1H, s), 7.69–7.67 (3H, m), 7.58 (2H, d, J = 9 Hz), 7.48 (2H, t), 7.18–7.10 (2H, m), 6.76 (1H, s); ¹³C NMR (300 MHz, DMSO-d₆) & 155.8, 153.1, 148.6, 148.5, 135.1, 134.6, 131.3, 131.2, 130.9, 129.8, 129.2, 129.1, 128.2,127.6, 125.2, 123.8, 122.3, 120.2, 118.2, 117.3, 109.2, 36.6; EIMS, 70 Ev, m/z: 436 (M⁺). 14-(4-Nitrophenyl)-14H-dibenzo [a, j] xanthene

(Table 1, **entry 8**): ¹H NMR (300 MHz, CDCl₃) δ 8.30–8.46 (4H, m), 7.66–7.72 (4H, m), 7.38–7.50 (6H, m), 7.00 (2H, t), 6.56 (1H, s); ¹³C NMR (300 MHz, CDCl₃) 151.9, 148.7, 131.0, 129.5, 129.0, 128.9, 127.1, 124.5, 123.8, 122.0, 118.0, 115.7, 7.8; EIMS, 70 Ev, *m*/z: 425.2 (M⁺) + Na⁺. **14**-(**4**-**Chlorophenyl**)-**14H-dibenzo** [*a*, **j**] xanthene (Table 1, **entry 9**): ¹H NMR (300 MHz, DMSO-*d*₆) δ 8.66 (2H, d, *J* = 9Hz), 7.94 (4H, d, *J* = 9Hz), 7.75–7.43 (8H, m), 7.23 (2H, d, *J* = 9Hz), 6.73 (1H, s); ¹³C NMR (300 MHz, DMSO-*d*₆) δ 147.9, 144.4, 130.8, 130.7, 130.6, 129.6, 129.2, 128.6, 128.3, 127.0, 124.5, 123.3, 117.6, 116.9, 35.7; EIMS, 70 Ev, *m*/z: **3**92.3 (M⁺). **14-(2-Chlorophenyl)-14H-dibenzo** [*a*, **j**] xanthene (Table 1, **entry 12**): ¹H NMR (400 MHz, CDCl₃) δ 8.69 (2H, d, *J* = 8.53 Hz), 7.78–7.73 (4H, m),

7.58 (2H, t), 7.45–7.33 (5H, m), 7.22 (1H, s), 6.89–6.81 (2H, m), 6.75 (1H, s); 13 C NMR (CDCl₃, 400 MHz) δ 148.8, 143.5, 131.7, 131.7, 130.8, 130.0, 129.5, 129.0, 128.5, 127.8, 127.7, 126.8, 124.3, 123.4, 34.5; EIMS, 70 Ev, *m/z*: 392 (M⁺). **14-(4-Formylphenyl)-14H-dibenzo** [*a*, *j*] xanthene: ¹H NMR (300 MHz, DMSO-d₆) δ 9.76 (1H, s), 8.67 (1H, s), 8.17 (1H, m), 7.76–7.66 (6H, m), 7.27–7.20 (1H, t), 7.13–76.84 (7H, m), 5.75 (1H, s); ¹³C NMR (300 MHz, DMSO-d₆) δ 190.8, 155.8, 153.0, 135.7, 134.2, 130.5, 129.4, 129.2, 128.2, 128.1, 126.6, 124.3, 123.1, 119.4, 109.5, 39.2.; EIMS, 70 Ev, *m/z*: 386 (M⁺).

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