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Mesoporous MCM-41-nPr-NHSO$_3$H as novel and effective nanoreactor catalyst for the synthesis of multi-substituted imidazoles under solvent-free conditions

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Abstract Herein, we report the synthesis and application of mesoporous siliceous MCM-41-nPr-NHSO$_3$H, which was characterized by XRD, IR, TGA and nitrogen physisorption measurements. MCM-41-nPr-NHSO$_3$H was used as an efficient heterogeneous catalyst for the one-pot synthesis of imidazoles derivatives under solvent free conditions with good to excellent yields. The present methodology offers several advantages such as less waste, simplicity of procedure, short reaction time, easy and quick isolation of the products.

Keywords Modified silica MCM-41 · MCM-41-(CH$_2$)$_3$NH$_2$ · MCM-41-nPr-NHSO$_3$H · Imidazole

1 Introduction

The application of silica and silica-based materials to life-science technologies is attracting attention from numerous research fields, including biotechnology, and nanomaterial science. These materials have been assessed as drug or gene delivery systems, bio-separation agents, diagnostic agents, and as sensors due to their high surface areas and straightforward surface modification [1–8].

Mesoporous silicates have attracted much attention in the field of separation, adsorption and catalysis activities due to their remarkable features such as high surface area, high pore volume, regular structure, uniform pore size distribution and high thermal stability [9–12]. They offer the possibility of active site immobilization on their surface. This can be achieved via isomorphous substitution of silicon atoms with transition metals or via surface incorporation of organic functionalities and allows mesoporous materials to be used for heterogeneous catalysis [13]. The importance of the silica-based materials is their robustness and their high specific surface area (200–1500 m^{2}g^{-1}) and a three-dimensional structure made of highly open spaces interconnected to each other. These properties cause the selection of a target analyte with a large number of accessible binding sites, which is a key factor in designing sensor devices with high sensitivity [14]. MCM-41 (Mobil Composition of Matter No. 41) as a meso-porous material consists of a hexagonal array of unidi-rectional pore structures. This material is neutral in charge and exhibits only weak hydrogen-bonding type sites which limit its application in catalysis [15–19]. Therefore, in order to activate its surface an appropriate moiety should be linked.

Imidazoles are a class of heterocyclic compounds that contain nitrogen and are currently under intensive focus due to their wide range of applications, because they have many pharmacological properties and play important roles in biochemical processes [20, 21]. They also serve as useful building blocks for the synthesis of other classes of compounds. Owing to the wide range of pharmacological and biological activities, the synthesis of imidazoles has become an important target in the recent years.

2 Experimental

2.1 Chemicals and instruments

The reagents and solvents used in this work were obtained from Fluka or Merck chemical companies and used without

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further purification. Powder XRD was collected with a Rigaku-Dmax 2500 diffractometer with nickel filtered Cu Ka radiation (λ = 1.5418 Å, 40 kV). FT-IR measurements were performed using KBr disc using a NICOLET impact 410 spectrometer. N_2 adsorption/desorption isotherms were recorded at 196 °C with a Micromeritics ASAP 2020. Before measurements, the samples were out gassed at 120 °C for 12 h. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method and the pore size distributions were measured using Barrett–Joyner–Halenda (BJH) analyze from the desorption branch of the isotherms. The thermogravimetric analysis (TGA) curves were recorded using a Shimadzu DTG-60 instrument. TEM images were recorded using a microscope operating at 200 kV.

2.2 Preparation of MCM-41-nPr-NHSO$_3$H

MCM-41 silica was prepared using the hydrothermal method described by Chen et al. [16]. TEOS and CTAB were used as template. The typical process was followed: 3.64 gr of CTAB and 1.2 gr of NaOH were solved in 108 gr of deionized water and mixed in a stainless steel autoclave, and then 20.41 gr of tetraethyl orthosilicate (TEOS) were added to the solution, which was stirred for 60 min at room temperature. Then, the sol was aged during 1 h and placed in an oven at 110 °C during 96 h. After 96 h, the resulting white precipitate was filtered and washed with deionized water and 50 mL of ethanol. The resulting powder was dried for 2 h at 80 °C. To remove the CTAB template, the resulting powder was mixed with 0.5 ml of HCl (37 wt%) and 20 ml of ethanol. The mixture was stirred at 60 °C for 90 min, washed with deionized water, dried at 70 °C for 6 h, and then calcined at 550 °C for 5 h (heating rate of 2 °C/min). Subsequently, 3-aminopropyltriethoxysilane fabricated on MCM-41 by adding 4.8 gr 3-aminopropyltriethoxysilane to 4.8 gr of MCM-41 in 96 mL n-hexane and the reaction mixture was stirred under reflux condition at 80 °C for 24 h under nitrogen atmosphere. Then the resulting white solid was filtered, washed with n-hexane and dried at room temperature for 24 h to achieve aminofunctionalized-MCM-41 [MCM-41-(CH$_2$)$_3$NH$_2$]. Subsequently 0.5 gr of synthesized MCM-41-(CH$_2$)$_3$NH$_2$ was dissolved in n-hexane and 0.04 mL Et$_3$N was added. The mixture kept at room temperature for 15 min with vigorous stirring. In the next step, chlorosulfonic acid (0.07 mL) was added drop wise over a period of 30 min at room temperature. Hydrogen chloride gas evolved from the reaction vessel immediately. The mixture was stirred for 2 h until HCl gas evolution stopped. The resulting solid was filtered and washed with n-hexane and then with ethanol and water to remove the unreacted chlorosulfonic acid. It was dried under vacuum at room

temperature to give the corresponding solid sulfamic acid-functionalized MCM-41-(CH$_2$)$_3$NH$_2$(MCM-41-nPr-NHSO$_3$H) [Scheme 1].

2.3 General procedure for the synthesis of tri- and tetra-substituted imidazoles

A mixture of benzil (1 mmol), an aromatic aldehyde (1 mmol), ammonium acetate (2.5 mmol), and MCM-41-nPr-NHSO$_3$H (0.1 gr) was heated in the oil bath at 130 °C for the certain period of time. The progress of reaction was monitored by thin-layer chromatography (TLC). Upon completion, the reaction mixture was cooled to room temperature, hot absolute ethanol was added and filtered. The combined filtrate was concentrated by half and allowed to stand at room temperature. The precipitated solid was collected by filtration, dried overnight and recrystallized from absolute ethanol to give substituted imidazole product.

Identical procedure was employed for the synthesis of 1,2,4,5-tera-substituted imidazoles using benzil (1 mmol), aryl aldehyde (1 mmol), a primary amine (1 mmol), ammonium acetate (2.5 mmol) and 0.1 gr of MCM-41-nPr-NHSO$_3$H as catalyst under solvent free condition at 130 °C.

^{1}H and ^{13}C NMR of 4 m: ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.32–7.50 (m, 10 H), 7. 96 (d, J = 7. 2 Hz, 4H), 7.93 (d, J = 8.8 Hz, 2H), 8.02 (d, J = 8. 4 Hz, 2H), 8.50 (s, 1H), 9.87 (br, 1H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 143.6, 131.5, 131.1, 129, 128.6, 128.5, 127.9, 127.5, 126.6, 125.8, 125.4, 125 ppm.

3 Results and discussion

In continuation of our investigation about application of heterogeneous catalysis in organic synthesis [22–26], herein we describe the preparation of a new heterogenised catalyst by functionalization of MCM-41 with 3-amino-propyl triethoxysilane and subsequent immobilization of sulfonic acid group on the synthesized MCM-41-(CH$_2$)$_3$NH$_2$. Resulting MCM-41-nPr-NHSO$_3$H was applied as a new heterogeneous catalyst for the one-pot synthesis of multisubstituted imidazole compounds.

3.1 Catalyst characterization

3.1.1 X-ray diffraction

Figure 1 shows XRD patterns for MCM-41, MCM-41-(CH$_2$)$_3$NH$_2$ and MCM-41-nPr-NHSO$_3$H. XRD patterns illustrate typical peaks corresponding to diffraction at (100), (110) and (200) plane of hexagonal phase. This proves that the framework structure does not deteriorate seriously during treatment with aminopropyltriethoxysilane and
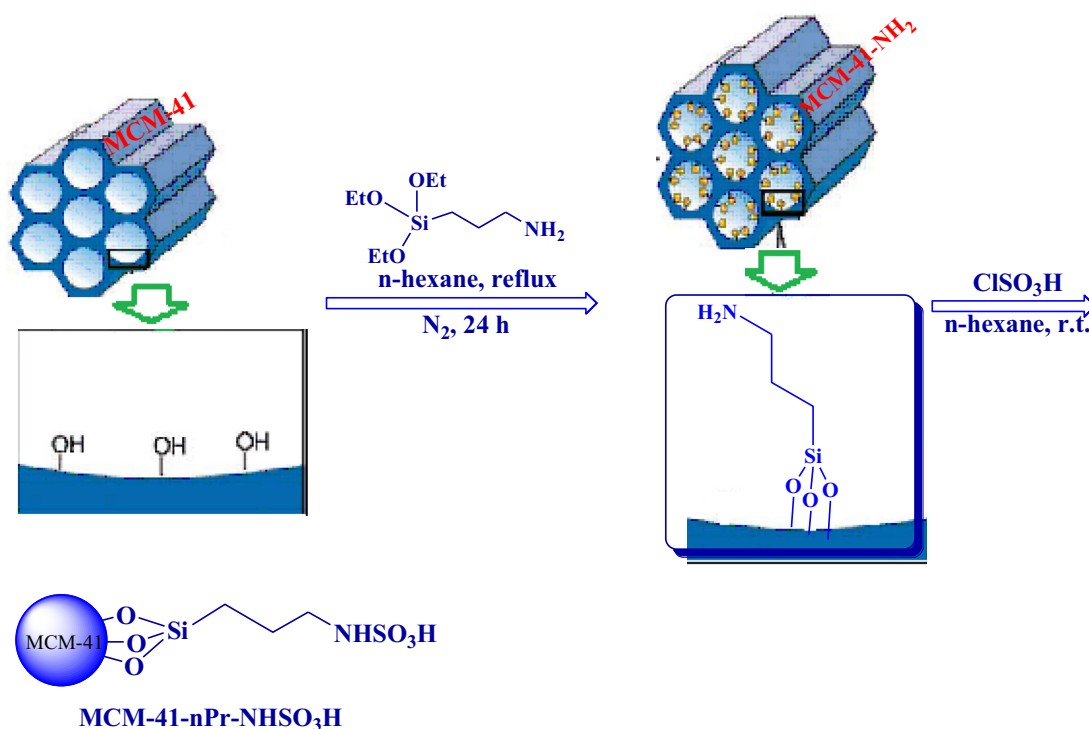
Scheme 1 Synthesis of MCM-41-nPr-NHSO$_3$H

**Fig. 1** XRD patterns of MCM-41; MCM-41-(CH$_2$)$_3$NH$_2$; MCM-41-nPr-NHSO$_3$H
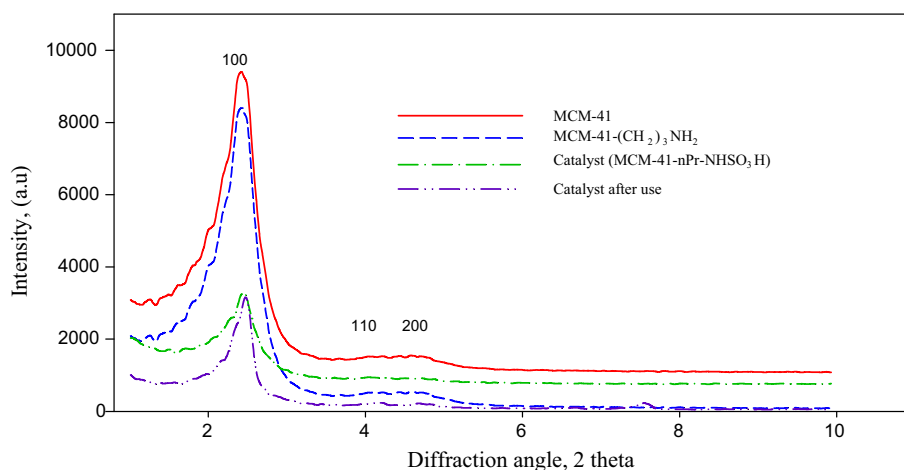
chlorosulfonic acid. Collectively, the XRD pattern of the functionalized MCM-41 also suggest not only a significant degree of short range ordering of the structure and well-formed hexagonal pore arrays of the samples, but also the maintenance of the structural order of the synthesized materials after functionalization.

3.1.2 Thermo gravimetric analysis (TGA)

The thermo gravimetric analysis (TGA) curves of MCM-41, MCM-41-(CH$_2$)$_3$NH$_2$ and MCM-41-nPr-NHSO$_3$H show the mass loss of the organic materials as they decompose upon heating (Fig. 2). The initial weight loss from the MCM-41 (25–120 °C) is due to the removal of physically adsorbed water (the weight loss about 4.25 %). The weight loss (1.6 %) between 120 and 840 °C is attributed mainly to the condensation of silanol groups and removal of chemically adsorbed water. MCM-41-(CH$_2$)$_3$NH$_2$ shows four-step weight loss behavior. Weight loss of MCM-41-(CH$_2$)$_3$NH$_2$ appears about 16.82 % at 120–700 °C, which is contributed to the thermal decomposition of the 3-aminopropyl groups. For MCM-41-nPr-NHSO$_3$H, there is a well-defined mass

Fig. 2 TGA curve of MCM-41, MCM-41-(CH$_2$)$_3$NH$_2$ and MCM-41-nPr-NHSO$_3$H
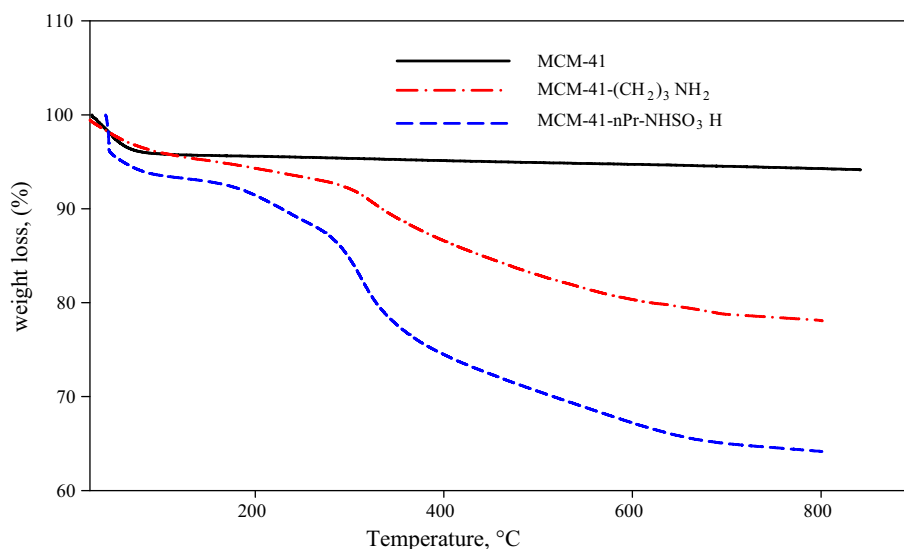
weight loss of 28.16 % between 130 and 700 °C related to the breakdown of the nPr-NHSO$_3$H moieties. Above 700 °C, samples exhibit about (0.7–0.85 %) weight loss due to the dehydroxylation of the silicate networks. On the basis of these results, the well grafting of aminopropyltriethoxysilane and SA groups on the MCM-41 is verified.

3.1.3 N$_2$ Adsorption–desorption isotherm

N$_2$ adsorption isotherm of the samples is recorded. The irreversible type IV adsorption isotherms of MCM-41, MCM-41-(CH$_2$)$_3$NH$_2$ and MCM-41-nPr-NHSO$_3$H with H1 hysteresis loop defined by IUPAC are observed, that is a typical feature of mesoporous materials (Fig. 3a). The Brunauer–Emmett–Teller (BET) specific pore volume and surface area of MCM-41-(CH$_2$)$_3$NH$_2$ and MCM-41-nPr-NHSO$_3$H reduce remarkably compared to calcined MCM-41. The BET surface area of the MCM-41 obtained using N$_2$ adsorption–desorption isotherm was found out to be 986.16 m^2/g and pore volume is 0.711 cm^3/g.

When 3-aminopropyl was modified on the inner surface of MCM-41, its BET pore volume and surface area reduce to 0.340 cm^3/g and 694.98 m^2/g, respectively; also these contents reduce remarkably for MCM-41-nPr-NHSO$_3$H (0.176 cm^3/g and 205.36 m^2/g). The pore size distribution calculated from the adsorption branch of the N$_2$ isotherm by using the BJH method for the MCM-41, MCM-41-(CH$_2$)$_3$NH$_2$ and MCM-41-nPr-NHSO$_3$H are mentioned in Fig. 3b.

As shown in Fig. 3b the BJH pore diameter, BET surface, and pore volume of functionalized MCM-41 decreased with the increasing substances anchored on the surface of MCM-41. These results are attributed to the occupation of organic molecules on the inner surface of the pores.

3.1.4 Transmission electron microscopy (TEM)

Figure 4a shows some representative TEM micrographs of the starting mesoporous calcined MCM-41. Transmission electron microscopy (TEM) image showed the uniform sizes of the pores and channels, which exhibited a hexagonal array of lattice fringes as well as parallel fringes corresponding to the side-on view of the pores. The dimension of the pores estimated by TEM is roughly 3.47 nm that is in agreement with the nitrogen adsorption data, which was discussed above.

3.1.5 Scanning electron microscopy (SEM)

SEM characterization shows that the starting MCM-41 material is composed of particles with size around 5 μm and without regular morphology (Fig. 4b).

3.1.6 Ft-ir

MCM-41, MCM-41-(CH$_2$)$_3$NH$_2$ and MCM-41-nPr-NHSO$_3$H were analyzed by FT-IR in the 4000–400 cm^{-1} region (Fig. 5). The wide bands at 1240–1030 cm^{-1} are typically regarded as Si–O–Si bands of the condensed silica network. The peak 806 cm^{-1} can be assigned to the symmetric stretching vibration of Si–O. When comparing MCM-41 (a spectrum) with MCM-41-(CH$_2$)$_3$NH$_2$ (b spectrum), the peak at 1524 and 1638 cm^{-1} indicates successful incorporation of the amine moiety. This peak (assigned to N–H stretch) is absent in the MCM-41 spectrum that provides evidence for the incorporation of the

Fig. 3 **a** N$_2$ adsorption–desorption isotherm of MCM-41 and MCM-41-(CH$_2$)$_3$NH$_2$. **b** Properties of the functionalized MCM-41
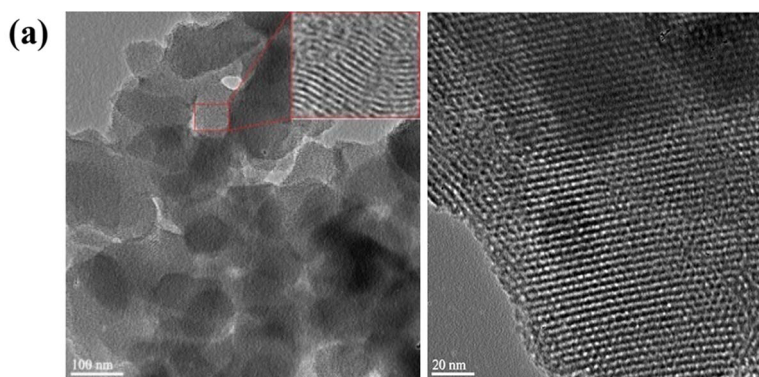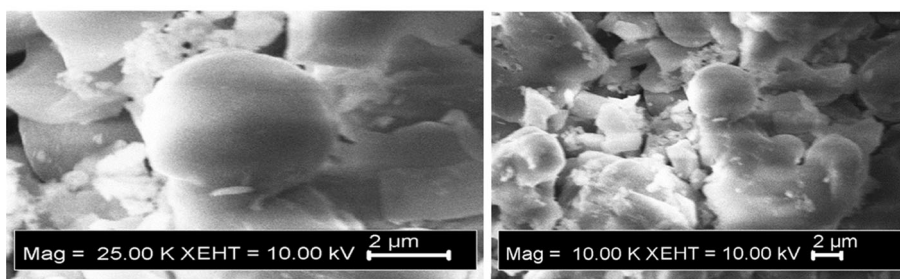

a
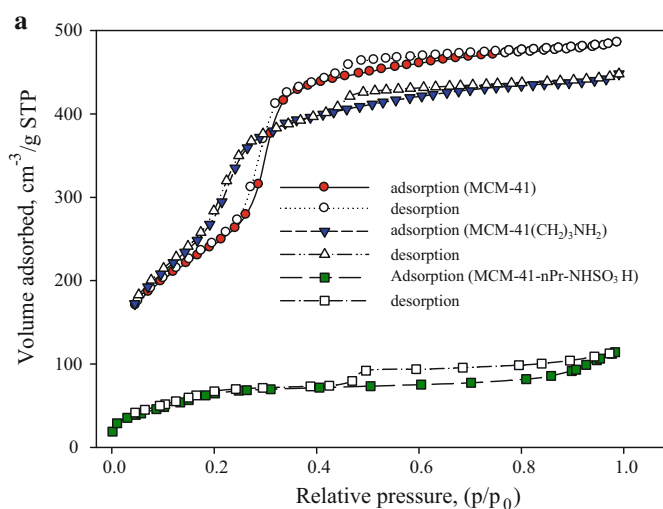
b

Sample	SBET (m^2/g)	Pore diam * (nm)	Pore vol (cm^3/g)	wall diam (nm)
MCM- 41	986.16	3.65	0.711	0.902
MCM-41-(CH$_2$)$_3$NH$_2$	694.98	3.3	0.34	0.906
MCM-41-nPr-NHSO$_3$H	205.36	1.22	0.176	2.93

* Calculated from the adsorption branch of the N$_2$ isotherm by using the BJH method.

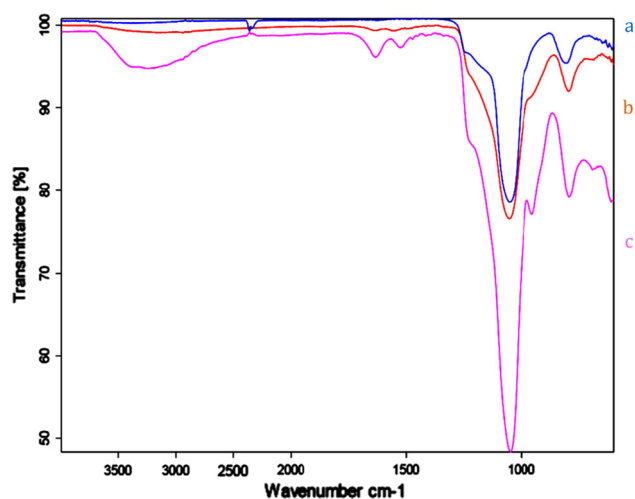Fig. 4 **a** Characterization of MCM-41 by TEM. **b** SEM image of MCM-41 with different magnifications

Fig. 5 FT-IR spectra of (*a spectrum*) MCM-41, (*b spectrum*) MCM-41-(CH$_2$)$_3$NH$_2$, (*c spectrum*) MCM-41-nPr-NHSO$_3$H

Table 1 Effect of the amount of MCM-41-nPr-NHSO$_3$H and ammonium acetate on the synthesis of 2,4,5-trisubstituted imidazoles under solvent-free condition[a]

Entry	NH$_4$OAC (mmol)	Cat. (gr)	Time (min)	Yield (%)[b]
1	2.5	0.04	20	None
2	2.5	0.06	35	None
3	1.25	0.1	–[c]	–
4	2.5	0.1	30	98
5	5	0.1	10	98
6	2.5	None	25	None

[a] Molar ratios of benzil:4-OH-benzaldehyde:1:1 mmol

[b] Isolated yields

[c] Reaction not completed

amine functional group onto the silica surface. Reaction of MCM-41-(CH$_2$)$_3$NH$_2$ with chlorosulfonic acid produces MCM-41-nPr-NHSO$_3$H, which the stretching and out of plane bending of acidic O–H group observed at 2700–3500 (c spectrum).

3.1.7 Evaluation of the catalytic activity of MCM-41-nPr-NHSO$_3$H through the synthesis of 2,4,5-trisubstituted imidazoles

To achieve suitable conditions for the synthesis of 2,4,5-trisubstituted imidazoles, various reaction conditions have been investigated in the reaction of 4-hydroxy benzaldehyde, benzil, and ammonium acetate as a model reaction.

Reactions in various molar ratios of substrates in the presence of MCM-41-nPr-NHSO$_3$H showed that the best conditions were solvent-free at 130 °C and molar ratio of aryl-aldehyde: benzyl :ammonium acetate: of 1:1:2.5 and 0.1 gr of MCM-41-nPr-NHSO$_3$H (entry 4). No product could be detected in the absence of the catalyst (entry 6), it means that the catalyst is absolutely necessary for this condensation. The results are summarized in Table 1.

Using the optimized reaction conditions, this combination was explored by the wide range of substituted and structurally divers aldehydes to synthesize the corresponding products in high to excellent yields (Table 2; Scheme 2).

As shown in Table 2, aldehydes bearing either electron-withdrawing or electron-donating groups perform equally well in the reaction and all imidazoles were obtained in good to excellent yields.

Also same methodology was extended for the synthesis of the tetra-substituted imidazoles in the similar reaction conditions via one-pot, multi-component condensation of

benzil (1 mmol), aldehyde (1 mmol), amine (1 mmol) and ammonium acetate (2.5 mmol) that catalyzed by 0.1 gr of MCM-41-nPr-NHSO$_3$H under solvent-free conditions at 130 °C as depicted in Scheme 2.

As indicated in Table 3, in all cases the reaction gives the products in high yields under solvent-free conditions and prevents problems which many associate with solvent use such as cost, handling, safety and pollution.
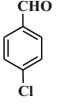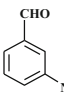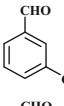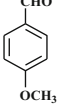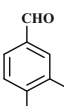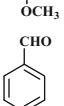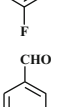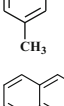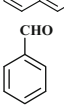
The substrate scope of the reaction was then evaluated using a variety of structurally diverse aldehydes. The obtained results are illustrated in Table 3.

Furthermore, we found that this catalyst demonstrated good recoverability and reusability. The catalyst can be efficiently recovered after completion of reaction by simple filtration. Reusability and recycling of the catalyst (MCM-41-nPr-NHSO$_3$H) was examined through a series of sequential condensations of *p*-Cl-benzaldehyde, benzil and NH$_4$OAC as a model reaction. In a typi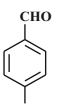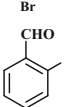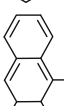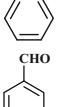cal reaction, the catalyst was recovered by simple filtration from the reaction mixture and reused for five cycles. No observation of any appreciable loss in the catalytic activity of catalyst was observed (Table 2, entry 1). The unchanged nature of the recovered catalyst was demonstrated by XRD after one used (Fig. 1).

4 Conclusions

In conclusion, an efficient and environmentally friendly procedure has been developed for the preparation of imidazoles derivatives in the presence of catalytic amounts of MCM-41-nPr-NHSO$_3$H. This new methodology offers several advantages including high yields, mild reaction conditions, short reaction time, simple work-up procedure and use of non-toxic catalyst. Furthermore, the catalyst

Table 2 One-pot synthesis of 2,4,5-trisubstituted imidazoles catalyzed by MCM-41-nPr-NHSO₃H under solvent free condition at 130 °C

Entry	Aldehyde	Product	Time (min)	Yield (%)[a]	M.p found (°C)	M.p reported (°C)
1	CHO, Cl	**4a**	60	97 (96, 95, 98, 90)[b]	253–254	253–254 [27]
2	CHO, NO₂	**4b**	150	53	306–308	>300 [28]
3	CHO, OH	**4c**	20	98	248–249	258–260 [29]
4	CHO, OCH₃	**4e**	145	83	220–221	226–228 [28]
5	CHO, OCH₃, OCH₃	**4f**	95	86	218–219	217–220 [30]
6	CHO, F	**4g**	90	84	246–249	238 [31]
7	CHO, CH₃	**4h**	45	85	229–231	232–235 [30]
8	CHO (naphthalene)	**4i**	55	69	266–267	273–276 [32]
9	CHO	**4j**	45	82	271–272	271 [28]
10	CHO, Br	**4k**	100	85	253–254	260 [28]
11	CHO, NO₂	**4l**	35	71	219–221	230–231 [33]
12	CHO (anthracene)	**4m**	60	83	220–219	–
13	CHO, OH	**4n**	30	98	255–256	260–261 [28]

Molar ratios of benzil: benzaldehyde: NH₄OAC 1:1:2.5 mmol and 0.1 gr of catalyst

[a] Isolated yield

[b] Yields refers to recycled catalyst

Scheme 2 One-pot synthesis of substituted imidazoles
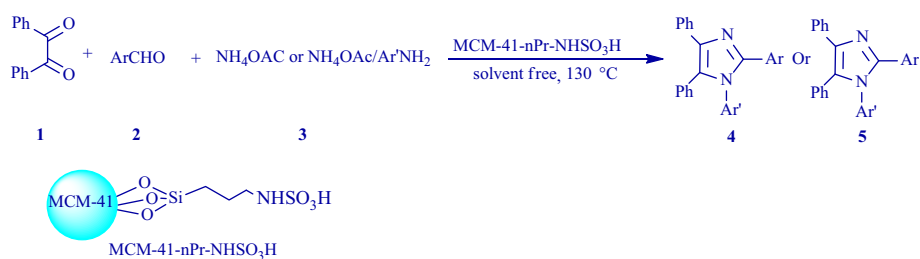
Table 3 Synthesis of 1,2,4,5–tetrasubstituted imidazoles

Entry	Aldehyde	Amine	Product	Time (min)	Yield (%)[a]	M. p found (°C)	M. p found (°C)
1	CHO, OH (3-hydroxybenzaldehyde)	NH₂ (benzylamine)	**5a**	90	94	229–231	232–235 [34]
2	CHO, OCH₃, OCH₃ (dimethoxybenzaldehyde)	NH₂ (benzylamine)	**5b**	110	97	189–192	188–190 [30]
3	CHO, Br (4-bromobenzaldehyde)	NH₂ (benzylamine)	**5c**	60	98	168–169	174–177 [30]
4	CHO, NO₂ (2-nitrobenzaldehyde)	NH₂ (benzylamine)	**5d**	40	96	148–150	152–155 [35]
5	CHO, Cl (4-chlorobenzaldehyde)	NH₂ (benzylamine)	**5e**	80	93	164–166	160–162 [30]
6	CHO, Cl (4-chlorobenzaldehyde)	NH₂, Cl (4-chloroaniline)	**5f**	150	91	186–190	187 [36]
7	CHO, Br (4-bromobenzaldehyde)	NH₂ (aniline)	**5h**	85	97	152–154	152–154 [37]
8	CHO, Me (4-methylbenzaldehyde)	NH₂ (aniline)	**5i**	45	96	181–182	182–184 [38]
9	CHO, OH (4-hydroxybenzaldehyde)	NH₂ (aniline)	**5j**	30	98	182–182	182–184 [38]

Reaction condition: molar ratios of benzil: benzaldehyde: amine: NH₄OAC 1:1:1:2.5 mmol and 0.1 gr of cat. at 130 °C

[a] Isolated yield

could be isolated with simple filtration and the yields achieved above 90 % after reused at five cycles.

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