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FULL PAPER

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Sonochemical synthesis of library benzodiazepines using highly efficient molecular ionic liquid supported on Fe-MCM-41 nanocomposites as a recyclable catalyst

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In this study, library substituted benzodiazepines was synthesized using molecular ionic liquid supported on Fe-MCM-41 nanocomposites (Fe-MCM-41-IL). This protocol using ultrasound provided advantages such as rapid, clean conversion and simplicity in experimental setup that led to rapid generation of benzodiazepines under mild condition. The catalyst can be easily isolated by using an external magnetic field and reused in the next reaction up to six cycles without obvious activity decreasing.

KEYWORDS
benzodiazepines, catalyst, Fe-MCM-41-IL nanocomposites, synthesis, ultrasound

1 | INTRODUCTION

MCM-41 structures have hexagonal arrays of uniform channels, high surface area and pore volume and hydrothermal stability that make them as potential heterogeneous nanocatalysts to a larger variety of organic reactions.[1–7] Also, the introduction of metal ingredient to MCM-41 leads to catalyst properties enhancement, which is beneficial to organic reaction. In comparison to other metals, impregnation of iron species into MCM-41 is significant benefits for the use of this metal in catalysis because of Lewis acidity, cheap, low in toxicity, easily accessible, and stability of Fe (III) metal (Fe-MCM-41).[8–12] On the other hands, various organic groups of functionalizing the surfaces of MCM-41 have been investigated recently because surface modification provides rising of the surface properties for many potential applications including catalysis.[13–16] The latest developments in supported ionic liquid systems have mainly focused on catalytic applications by functionalized ionic liquid onto the surface of MCM-41 framework (MCM-41-IL).[17–19]

MCRs combine from three up to eight reactants to furnish products containing structure or substructure of all starting materials in one pot, that offers significant advantages in normal linear synthesis because of its convergent, flexible, atom efficient nature and reducing the number of purification steps.[20–23] Over the past decade, considerable attention has been focused on the development of new methodologies to MCRs, especially applicability of nanocatalysts in MCRs.[24–27] Among the wide varieties of MCRs, the synthesis of benzodiazepine is a reaction of three component that is considered a privileged scaffold in medicinal chemistry, bioactive natural products and many biologically active compounds bear this core.[28–31]

Benzodiazepine molecules are important substructures in a number of molecules which exhibit an array of both pharmaceutical and biological activities.[32] The various members of the benzodiazepine family have been used as commercially available in clinical practice for the management of panxiolytic,[33] antianxiety,[34] anticonvulsant,[35] antidepressive sedative, antileishmanial,[36] and antitumor activity[37,38] as well as inhibitor of

mitochondrial F1F0 ATP hydrolase.[39] In recent years, three-component synthesis of benzodiazepines have been developed under different condition such as; thermal,[40] electroactive[41] and microwave[42] in the presence of variety heterogeneous catalysts e.g., $Pd_2(dba)_3$,[43] CsF catalyst,[44] $PdCl_2(MeCN)_2$.[45]

The ultrasound-synthesized has been increasingly applied as an efficient tool in promoting chemical transformations and for the rapid generation of combinatorial chemicals.[46] The reactions carried out under ultrasonic procedure have been attained with short reaction times, higher yields, cleaner conversion, improved selectivity, and mild reaction conditions as compared to the conventional methods.[47–57] It should be noted that although a number of methods have been reported for the synthesis of benzodiazepines most of the procedures involve thermal condensation that require high temperature, long reaction times, and purification steps and tedious workups such as column chromatography.

The present study has been developed the Fe-MCM-41-IL as a nanocatalyst and recyclable catalyst for synthesis of benzodiazepine products in higher yields under mild conditions and ultrasound irradiation.

2 | EXPERIMENTAL

2.1 | Materials and apparatus

All chemicals were purchased from Fluka, Merck and Aldrich chemical companies. FT-IR spectra were obtained as KBr pellets on a Perkin-Elmer 781 spectrophotometer and on an impact 400 Nicolet FT-IR spectrophotometer. ^1H NMR and ^{13}C NMR were recorded in $CDCl_3$ and DMSO-d_6 solvents on a Bruker DRX-400 spectrometer with tetramethylsilane as internal reference. The XRD patterns were recorded on an X-ray diffractometer (Bruker, D8 ADV ANCE, Germany) using a Cu-Ka radiation (λ = 0.154056 nm) in the range 2θ = 0.5–5°. The N_2 adsorption/desorption analysis (BET) was performed at −196 °C using an automated gas adsorption analyzer (Tristar 3000, Micromeritics). The surface morphology of the supported catalyst was studied by transmission electron microscopy (TEM), with an accelerating voltage of 300 kV (CM30 300 kV). Elemental analysis were carried out using a Joel SEM instrument (model- VEGA/TESCAN) combined with an INCA instrument for energy dispersive X-ray spectroscopy scanning electron microscopy (EDS), with scanning electron electrode at 15 kV. The magnetic property of the catalyst was studied by vibrating sample magnetometer (VSM, Meghnatis Daghigh Kavir Company, Kashan, Iran). Melting points are determined in open capillaries using an Electrothermal Mk3 apparatus and are uncorrected. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica-gel poly gram SILG/UV 254 plates (from Merck Company).

2.2 | Preparation of Fe-MCM-41

The Fe-MCM-41 was prepared through in situ coprecipitation of Fe (III) on MCM-41. The experimental details were as follows: 2.24 g of $FeCl_3.6H_2O$ was added to a mixture of 1.0 g of CTAB, 3.5 ml of 2 M NaOH aqueous solution and 480 ml of deionized water. Then 5 ml of tetraethyl orthosilicate (TEOS) was subsequently dropped into the homogeneous solution under stirring. After stirring for 2 hr at ambient temperature, the product was separated by filtration, washed with deionized water, and dried at 100 °C for 6 hr. The solid product was calcined at 550 °C for 6 hr to obtain Fe-MCM-41 structure.

2.3 | Preparation of ionic liquid

To prepare the ionic liquid, the β-hydroxy-1,2,3-triazole was prepared according to the literature procedures.[58] Briefly, 3-chloropropyltrimethoxysilane (12.0 ml, 50 mmol) was added to a solution of β-hydroxy-1,2,3-triazole (3.4 g, 50 mmol) in dry toluene (50 ml), and the mixture was refluxed overnight under a nitrogen atmosphere. Then, the 1,4-butanesultone was added to the reaction mixture and stirred at room temperature for 8 hr to produce the zwitter ionic triazolene ammonium salt. Conc. H_2SO_4 (0.54 ml, 10 mmol) was added drop wise into the solution of the above residue in ethanol (30 ml) over 30 min and the final mixture was stirred at 50 °C for another 8 hr. The final mixture was evaporated under reduced pressure to give the ionic liquid as a viscous yellow liquid.

2.4 | Modification of Fe-MCM-41 with ionic liquid

For immobilization of IL onto Fe-MCM-41 nanoparticles, the solution IL (0.3 g) was diluted with dry $CHCl_3$ and was then added slowly to a suspension of 1 g hydrated Fe-MCM-41 nanoparticles in dry $CHCl_3$ (180 mL), under argon atmosphere. The resulting mixture was refluxed for 24 hr. After cooling, the solid materials were filtered off and the residue was washed with $CHCl_3$ and then dried in oven at 90 °C overnight to give IL matrix immobilized on Fe-MCM-41 named as Fe-MCM-41-IL.

2.5 | Typical procedure for synthesis of benzodiazepines

The *o*-phenylenediamine (1 mmol), tetronic acid (1 mmol), aldehydes (1 mmol) and 15 mg of Fe-MCM-41-IL in H_2O (5 ml) were irradiated at 40 W in an ultrasonic probe. After sonication at ambient temperature until completion of the reaction (5–10 min), the catalyst was separated magnetically from the product solution and used for subsequent cycles after washing and drying under vacuum. Then the products were further recrystallized by 50% EtOH to give pure product (FT-IR, ^{1}H NMR and ^{13}C NMR of products see the Supporting Information).

2.6 | 4-(1-Oxo-3,4,9,10-tetrahydro-1H-2-oxa-4,9-diazabenzo[f]azulen-10-yl)-benzonitrile (4a)

Pale white solid, mp: 280–282 °C; IR (KBr): 3419, 3060, 2926, 1730, 1626, 1530, 1394, 1334, 1280, 1161, 1039, 745 cm^{-1},^{1}H NMR(400 MHz, DMSO-d$_6$) (σ, ppm): 9.84 (s, 1H, NH),7.28–7.09 (m, 5H, ArH), 6.72 (d, J¼ 8.0 Hz, 1H, ArH), 6.70–6.68 (m, 2H, ArH), 6.57 (d, J¼ 7.9 Hz, 1H, ArH), 6.07 (d, 1H, NH), 5.06 (d, J¼ 4 Hz, 1H, CH), 5.01 (dd, J¼ 5.2 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, DMSO-d$_6$) (σ, ppm): 172.7, 158.6, 143.7, 137.2, 127.8, 127.0, 126.4, 122.7, 120.5, 120.2, 119.4, 96.6, 65.9, 57.2.

3 | RESULTS AND DISCUSSION

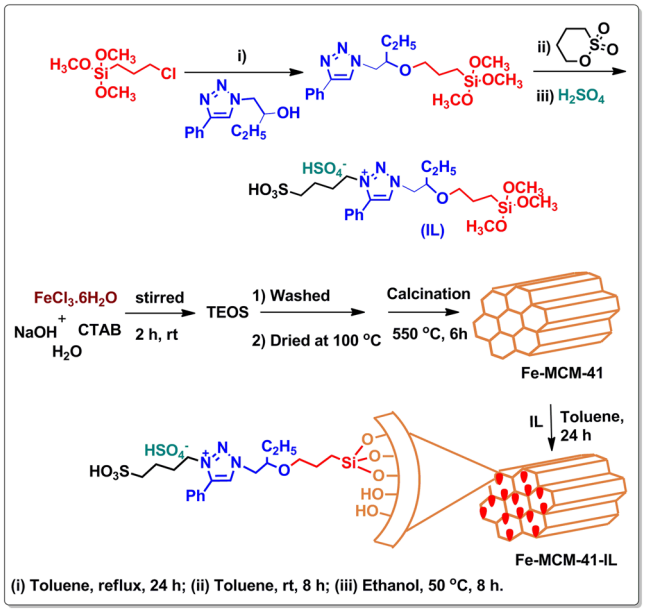
3.1 | Synthesis and characterization

The preparation procedures adopted for obtaining Fe-MCM-41-IL with its structural formulation is given in Scheme 1.

The N_2 adsorption–desorption isotherms are necessary to ascertain the manner in which the pore parameters (namely, diameter, pore volume, surface area, etc.) change in Fe-MCM-41 matrixes containing loadings of the Fe-MCM-41-IL. The N_2 adsorption and desorption isotherms are given in Figure 1.

From Figure 1, it could be seen that the N_2 sorption isotherms exhibited a type-II-like behavior and capillary condensation at relative pressures of 0.3 < P/P0 < 0.5, which was the characteristic of mesoporous materials.[59] The total pore volumes, sizes and surface areas of Fe-MCM-41 and Fe-MCM-41-IL are given in Table 1.

It could be concluded from Table 1, that introduction of ionic liquid significantly affected the surface area and pore volume of the support and there was a negligible change in pore size and volume after grafting process.



SCHEME 1 Different steps for synthesis of Fe-MCM-41-IL.

As shown in Figure 2, from the TEM images, the well-ordered pore arrangements and the incorporation of iron in the mesoporous silicate framework were visible. Meanwhile the long-rang order and mesoporous structure arrays were not disturbed significantly after Fe doping.

The Fe and Si contents in Fe-MCM-41 were determined using X-ray fluorescence analysis (XRF) and their results was shown that the weight percentages of Si and Fe were 33.63 wt.%, 9.03 wt.%, respectively. The supported ionic liquid Fe-MCM-41-IL was further confirmed by energy dispersive spectrometer (EDS) (Figure 3). The obtained results by EDS were as follows (%): C, 5.40; N, 5.25; Si, 17.38; O, 61.32; S, 6.92; Fe, 3.72.

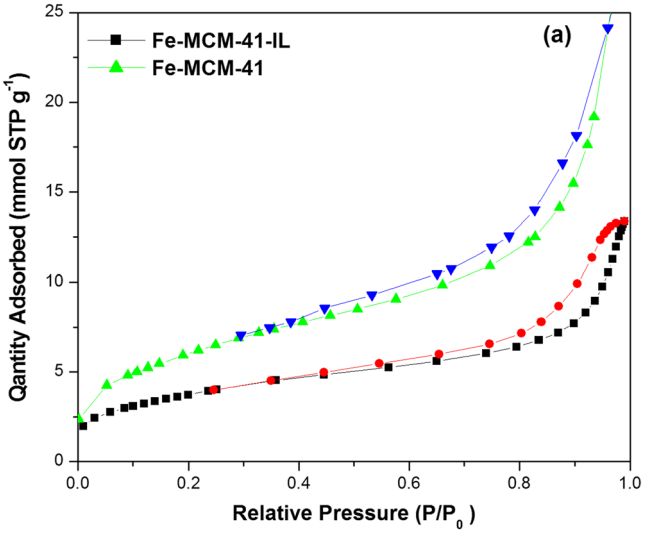


FIGURE 1 N_2 adsorption–desorption isotherms of Fe-MCM-41 and Fe-MCM-41-IL

TABLE 1 Pore volume, surface area, and average pore diameter of Fe-MCM-41 and Fe-MCM-41-IL

Sample	Surface area[a] ($m^2\ g^{-1}$)	Pore Size[b] (nm)	Pore Volume[c] ($cm^3\ g^{-1}$)
Fe-MCM-41	307.98	8.42	0.42
Fe-MCM-41-IL	225	8.25	0.38

[a]Calculated by the BET model.

[b]Calculated by the BJH model from the desorption isotherm.

[c]Total pore volume at $P/P_0 = 0.99$.

The thermal stability of the Fe-MCM-41-IL was investigated through TGA, shown in Figure 4a. The TGA thermogram of Fe-MCM-41-IL show two peaks, namely, (i) 25–130 °C corresponding to adsorbed water (1.6%), (ii) neat IL started to decompose at 140 °C and completely decomposed at 550 °C (7.5%) (iii). The results obtained from TGA analysis confirmed presence of IL supporting onto MCM-41-IL.

The FT-IR spectra, XRD and VSM curve of Fe-MCM-41 matrix and IL were provided and reported in Supporting Information.

3.2 | Optimization of the reaction

Initially, we studied the optimization of the reaction conditions using o-phenyldiamine (1 mmol), tetronic acid (1 mmol), and aldehydes (1 mmol) as model substrates. However different set of reaction conditions were screened under ultrasonic irradiation, amount of Fe-MCM-41-IL catalyst and different catalysts in various solvents, according to Table 2.

When changing the amount of catalyst, the reaction proceeded rapidly (within 5 min) to give the desired product in 93% under neat conditions.

In order to evaluate the efficiency of sonochemical synthetic method and also catalytic activity of Fe-MCM-41-IL, the model reaction was checked in the presence of different amounts of Fe-MCM-41-IL at various ultrasound times and solvents (Table 1, entries 2–8). Also, in a control experiment where a similar model reaction was carried out under ultrasound irradiation without catalyst (entry 1) and stirring at room temperature (entry 9), the desired product was isolated in lower yield and higher reaction time and this study confirmed that the reaction was accelerated significantly under ultrasonic

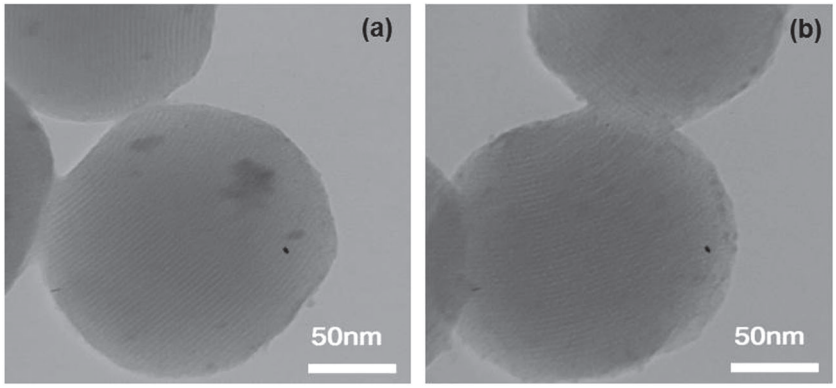


FIGURE 2 Typical TEM images of a) Fe-MCM-41 and b) Fe-MCM-41-IL

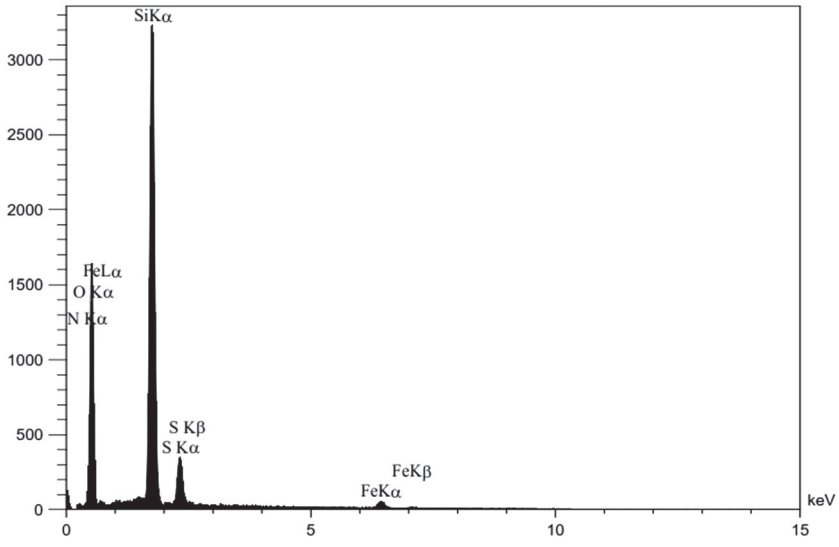


FIGURE 3 EDS pattern of Fe-MCM-41-IL

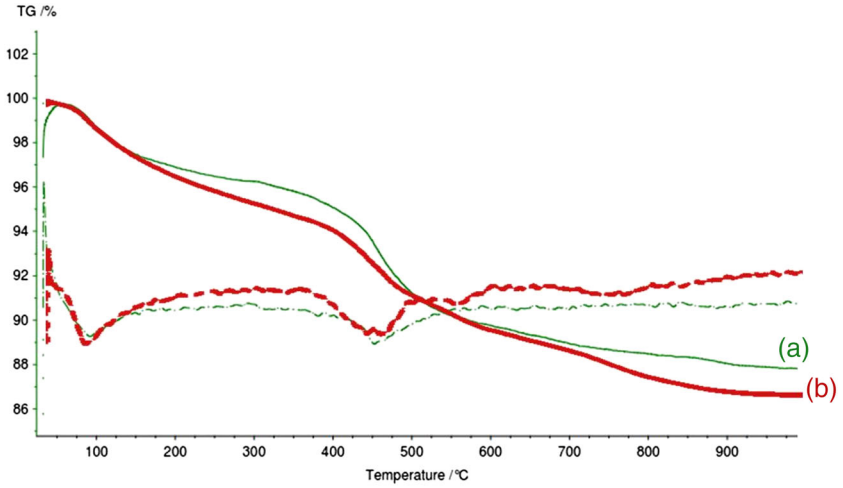
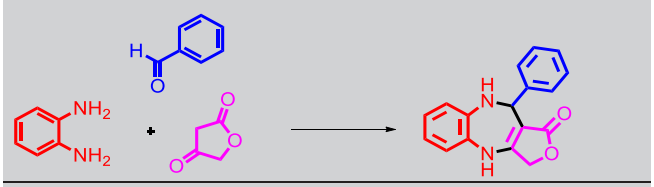


FIGURE 4 TGA curves of the Fe-MCM-41-IL and recycled Fe-MCM-41-IL

TABLE 2 Effect of catalyst amount on the reaction[a]



Entry	Catalyst (amount, mg)	Solvent	Method (time, min)	yield
1	-	H_2O	sonication (30)	50
2	Fe-MCM-41-IL (5)	H_2O	sonication (10)	68
3	Fe-MCM-41-IL (10)	H_2O	sonication (7)	82
4	Fe-MCM-41-IL (15)	H_2O	sonication (5)	93
5	Fe-MCM-41-IL (20)	H_2O	sonication (5)	93
6	Fe-MCM-41-IL (15)	THF	sonication (5)	55
7	Fe-MCM-41-IL (15)	CH_3N	sonication (5)	75
8	Fe-MCM-41-IL (15)	EtOH	sonication (5)	80
9	Fe-MCM-41-IL (15)	H_2O	stirring (60)	45
10	Fe-MCM-41 (15)	H_2O	sonication (5)	61
11	MCM-41 (15)	H_2O	sonication (5)	40

[a]Reaction condition: o-phenyldiamine (1 mmol), tetronic acid (1 mmol), benzaldehyde (1 mmol), catalyst (Fe-MCM-41-IL), solvent (5 ml).

method. This can be due to an increase the dispersion of nanocomposite (catalyst) into the bulk of sample that cause increasing mass transfer between the immiscible reactants during ultrasound irradiation.

Also for more understanding the catalytic performance of Fe-MCM-41-IL, the Fe-MCM-41 and MCM-41 were tested as catalyst in this reaction model (entries 10 and 11). These results confirmed that the IL supported onto Fe-MCM-41 provided a proton source in all steps of the synthesis of benzodiazepines. Also, the incorporation of iron into MCM-41 generated acid sites[60] that led to improving in the synthesis of benzodiazepines using Fe-MCM-41 to MCM-41 catalyst. On the other hand, the incorporation of iron in the MCM-41 provided magnetic properties for the catalyst. Therefore, the Fe-MCM-41 catalyst was able to be recycled simply via attaching an external magnet after completion of the reaction.

These results demonstrated a significant improvement of the reaction outcome through the effect of ultrasound and catalyst. Thus the best yields were observed when the reaction was carried out using 15 mg of the catalyst in H_2O under ultrasonic irradiation. However, the combination of the prepared Fe-MCM-41-IL nanocomposite with an ultrasonic probe was supportive for enhancing the sonocatalytic synthesis efficiency.

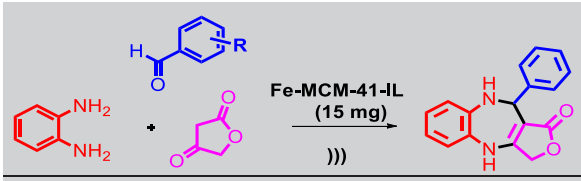
With the obtained optimal conditions, a synthesis of a small library of substituted benzodiazepines was then carried out using 1:1:1 molar ratio of o-phenyldiamine tetronic acid and aldehyde derivatives containing electron-donating as well as electron-withdrawing groups, Fe-MCM-41-IL catalyst under ultrasound irradiation (Table 3).

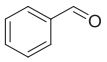
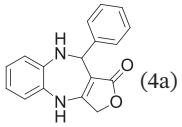
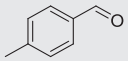
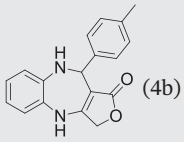
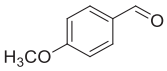
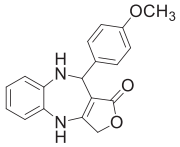
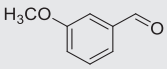
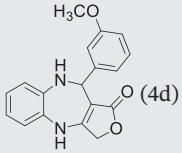
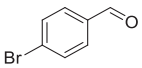
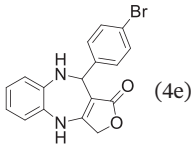
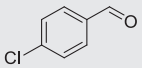
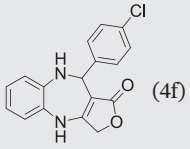
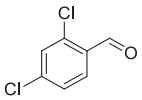
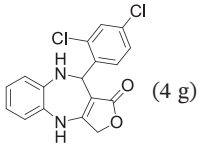
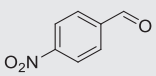
The electron-deficient aldehydes were found to be more effective substrate relative to the electron-rich aldehydes. The reaction times of aldehydes with electron-rich groups were longer than those of with electron withdrawing groups, thus these groups gave the benzodiazepine products in lower yields.

The proposed mechanism of benzodiazepines synthesis by Fe-MCM-41-IL is depicted in Scheme 2.

After the protonation of tetronic acid by Fe-MCM-41-IL catalyst, an amino group of o-phenylenediamine would be added and affording enaminone intermediate (I). In a subsequent step, the condensation of aldehyde and intermediate (I) would give intermediate (II), which after condensation would obtain main product through intramolecular cyclization.

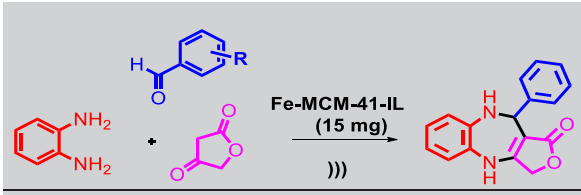
TABLE 3 Sonosynthesis of benzodiazepines[a]

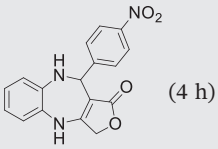
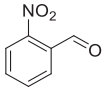
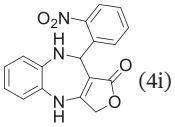
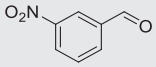
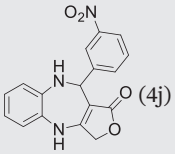
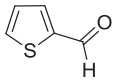
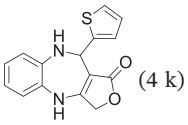


Entry	Aldehydes	Products	Time (min)	Yield [b]
1		 (4a)	5	93
2		 (4b)	10	91
3		 (4c)	10	89
4		 (4d)	10	90
5		 (4e)	5	89
6		 (4f)	5	90
7		 (4 g)	5	92
8			5	97

(Continues)

TABLE 3 (Continued)



Entry	Aldehydes	Products	Time (min)	Yield [b]
		 (4 h) (4h)		
9		 (4i) (4i)	5	95
10		 (4j) (4j)	5	90
11		 (4 k) (4k)	10	90

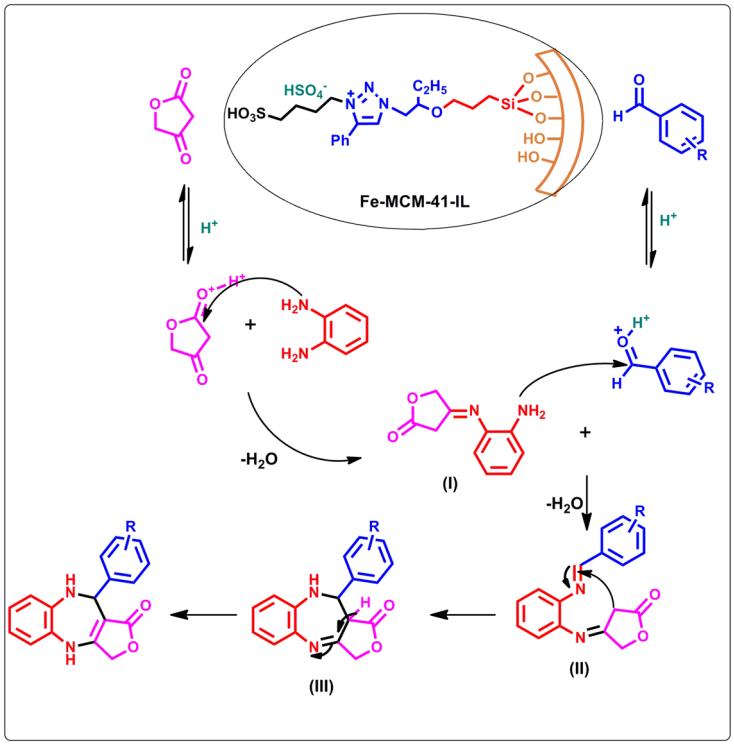
[a]Reaction condition: *o*-phenyldiamine (1 mmol) tetronic acid (1 mmol), aldehydes (1 mmol), catalyst (Fe-MCM-41-IL, 15 mg), water (5 ml), 5–10 min sonication.

[b]Isolated yields.

Nevertheless, these yields with the improvement induced by ultrasound were greater than those obtained using other reported methods where the reactions were performed at high temperatures using significantly longer times.[41,42]

3.2.1 | Heterogeneity test

Any leaching of the active species from the support makes the catalyst unattractive, and hence, it is worthwhile to understand the stability of the Fe-MCM-41-IL, the leaching of IL from the MCM-41 surface was studied. Heterogeneity experiment was carried out by filtering the catalyst and the reaction mixture under ultrasound irradiation after 2.5 min the solid product was obtained as product **4a** in 47% yield. Then, the filtrate was allowed to react up to 5 min in absence of catalyst. After up to 5 min, the solid product was obtained with low yield (20%) that can be due to existence ultrasound irradiation. Also, to confirm stability of Fe-MCM-41-IL catalyst, the IL leaching was studied. The IL content after catalyst recycling was determined by TGA and FT-IR analysis. In TGA analysis, the IL amount of recyclable catalyst was with negligible decrease approximately 0.34% to fresh catalyst (7.5% reducing to 7.16%, Figure 4b). On the basis of these results, it can be concluded that there is slight leaching of IL species from the support MCM-41. The FT-IR spectrum of recycled Fe-MCM-41-IL catalyst is shown in the Figure S1c. The FT-IR spectrum of recycled Fe-MCM-41-IL is similar to Fe-MCM-41-IL. So the presence of IL in the framework after reuse of the catalyst and stability of catalyst was confirmed.



SCHEME 2 Proposed mechanism for sono-synthesis of benzodiazepines using Fe-MCM-41-IL catalyst.

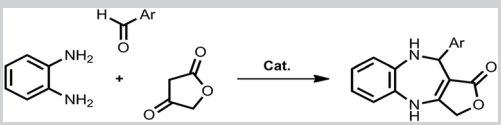
3.2.2 | Comparative with other reported methods

A comparative study for the reaction of *o*-phenylendiamine, tetronic acid and aldehydes with other reported methods was summarized in Table 4. The results exhibited the significant improvements in the reaction condition of present work with previous studies. It was noteworthy that higher yield of benzodiazepines using Fe-MCM-41-IL catalyst along with other parameters such as short reaction time, lower catalyst dosage and usage recyclable and heterogeneous catalyst made it more suitable method than the other reported methods for synthesis of benzodiazepines. In addition to, ultrasound-assisted is a highly efficient tool for modifying the affinity between reactants and catalyst compared to conventional synthetic techniques.

3.2.3 | Recycling of catalyst

Due to the additional advantage of solid catalyst, the recovering of catalyst Fe-MCM-41-IL was explored. Therefore, the catalyst could be magnetically recovered by employing an external magnet after completion the reaction and washed with water, dried under vacuum and reused in a subsequent reaction. The reaction scale was amplified 6 cycles to ensure that the catalyst of good quality was available for us to perform several recycling reactions. The recycling results of Fe-MCM-41-IL are reflected in Figure 5.

TABLE 4 Synthesis of benzodiazepines under different conditions[a]



Entry	Catalyst	Catalyst amount	Solvent	t (°C)	T (min)	Yield (%)	Ref.
1	HOAc	0.1	H_2O	150/MW	15	85	42
2	CF_3COOH	2 Drops	EtOH	78/Reflux	360	73	41
3	Fe-MCM-41-IL	60 mg	EtOH	r.t	35	95	61
4	Fe-MCM-41-IL	15 mg	H_2O	r.t/U.S	5	97	this work

[a]Reaction condition: *o*-phenyldiamine, tetronic acid, aldehydes.

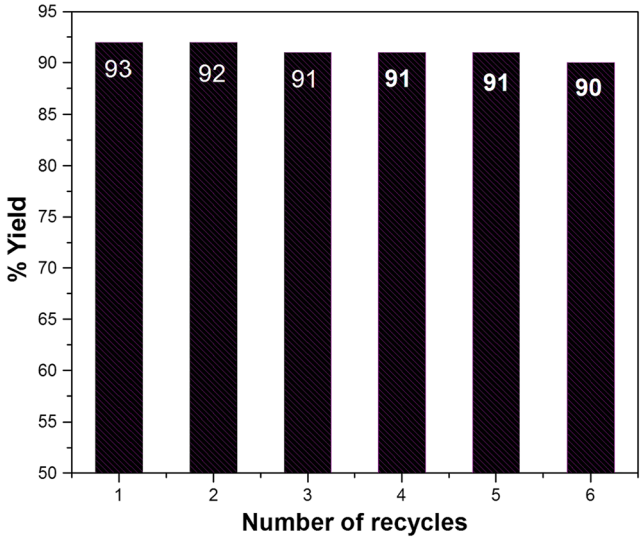


FIGURE 5 The recyclability test of Fe-MCM-41-IL catalyst

It is worthy to note the magnetic field-assisted separation is considered a "green" separation approach because can be easy, fast and clean separation and avoid the centrifugation and filtration that required extra energy and catalyst loss, and save the time in achieving catalyst recovery.

4 | CONCLUSION

In summary, we have developed preparation and effect of confinement of a molecular ionic liquid in Fe-MCM-41 framework. Then a facile ultrasonic method was studied for synthesis of a library of bnzodiazepines using Fe-MCM-41-IL as nanocatalyst. The use of this method compared to heating method was found to extremely simplify and green both the experimental setup and the workup which enabled speedy synthesis of benzodiazepines in high yields and short reaction times under mild conditions.

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Additional supporting information may be found online in the Supporting Information section at the end of the article.

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