RESEARCH ARTICLE



Chemistry

Ship-in-bottle preparation of multi-SO₃H functionalized ionic liquid@MIL-100(Fe) for acid-catalyzed ring-opening of epoxides

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Abstract

The fact that the homogeneous acid catalysts are usually separated difficulty than heterogeneous catalysts from the reaction media, the opportunity to combine the advantages of both homogeneous and heterogeneous catalytic systems by immobilizing ILs within the pores of a porous solid support host is an alternative method. In this research, a multi-SO₃H functionalized ionic liquid derived from hexamethylenetetramine (HMTA) and 1,3-propane sultone was entrapped inside the pores of MIL-100(Fe) through the ship-in-bottle method and utilized for heterogeneous acid-catalyzed ring-opening of epoxides under solvent-free conditions. The physicochemical properties of prepared catalyst were fully elucidated by various methods. FT-IR spectroscopy and elemental analysis approved the successful incorporation of modified groups within the MIL-100(Fe) cavities. The concentration of acid sites was measured via the acid-base titration which exhibited the 0.9 mmol/g H⁺ in the catalyst structure. Also, thermogravimetric analysis (TGA) profile showed the loosing of modified groups at 300-600°C. Moreover, X-ray diffraction (XRD) analysis showed that the MIL-100(Fe) structure was retained after modification and nitrogen adsorption-desorption analysis (BET method) manifested the decrease in surface area caused by incorporation of ionic liquid. The fabricated catalyst exhibited high catalytic efficiency in methanolysis of styrene oxide (99% conversion in 3 h) under ambient conditions and used without a substantial drop in product yield in further rounds.

KEYWORDS

Brønsted acid, epoxide ring-opening, heterogeneous catalyst, metal-organic framework, ship-in-bottle

INTRODUCTION 1

Metal-organic frameworks (MOFs) are 3D porous materials obtained from the coordination bond between metal ions or clusters and multidentate organic linkers. The unique properties of these materials including high surface area, ultrahigh porosity, adjustable pore dimensions,

and surface functionalization possibilities make them as promising candidates for potential applications in the field of heterogeneous catalysis.^[1-4] Although various MOFs are directly used as solid catalysts in different organic reactions, most of them require functional active sites within their framework to promote the chemical transformations. Hence, several researches have been

done to insert a broad range of functional species within the nanocages of MOFs through the post-synthetic modification (PSM).^[5–10] In the field of Brønsted acid catalysts, some examples have been focused on the inserting – SO₃H groups in MOFs, for example, post-synthetic sulfonation of organic ligand,^[11,12] sulfonation of aminoligand MOFs,^[13,14] and incorporation of sulfonic groups into the coordination unsaturated sites.^[15,16]

Similar to MOFs, ionic liquids (ILs) comprised from organic cations and inorganic anions have received widespread consideration as novel materials for catalytic processes in recent years.^[17-20] In 2002, Cole et al. published the first report about -SO₃H functionalized ILs and opened a new window to use various Brønsted acid ILs (BAILs) in acid-catalyzed reactions.^[21] Despite the several beneficial properties, for example, low toxicity, less flammability, and thermal stability, the catalytic application of BAILs faces with some limitations like high viscosity and difficult recovery from reaction media when polar substrates such as alcohols are consumed.^[22] To solve these problems, many attempts have been taken for heterogenization of ILs by immobilizing them on a solid support.^[23-29] Because of the structural flexibility and highly designable properties of MOFs, these materials can be used as attractive supports for insertion of ILs.

With this context, the combination of advantages of BAILs and MOFs to form BAILs@MOF can be interesting. For instance, BAIL of quaternary ammonium salt supported on MIL-101(Cr) was constructed by sequential post-modification and exploited for acetalization reaction.^[16] Encapsulation of sulfonic acid functionalized ionic liquids into the MIL-100(Fe) nanocages through ion exchange strategy was investigated to prepare an efficient catalyst for biodiesel production.^[30] Also, the same group entrapped acidic ILs within the nanocages of MIL-100 (Fe) to catalyze the esterification of oleic acid with methanol.^[31] Recently, Xie et al. introduced polyoxometalatebased sulfonated ILs onto the UiO-66-2COOH framework for catalytic biodiesel production in a similar manner.^[32] However, all of these reports involve the BAILs possessing only one -SO₃H groups.

MIL-100(Fe) has been known as water, air, and chemically stable MOF with high surface area and accessible nanocages. The environmentally friendly and nontoxicity of iron as well as the preparation process without using HF or DMF (*N*,*N*-dimethylformamide) make this MOF an attractive and green solid support.^[33,34] It is an Fe(III) containing MOF consisting of two types of nanocages with diameters of 25 and 29 Å and windows of 5.5 and 8.6 Å diameters.^[35] The ship-in-bottle strategy is a proper method to incorporate catalytic active species when they are too large to diffuse into the MOF pores. Therefore, small precursors of active molecules (ship) are

passed through the microporous windows of MOF (bottle), react within the nanocage, and then make larger catalytic active species. As the synthesized active species are larger than the MOF windows, they cannot leave the nanocages of MOF support.

Here, we aim to prepare a new heterogeneous catalyst by entrapping a multi-SO₃H functionalized ILs into the hosting space of MIL-100(Fe) through the ship-in-bottle strategy. For this purpose, hexamethylenetetramine (HMTA) as small precursor entered inside the MIL-100 (Fe) pores, followed by reaction with 1,3-propane sultone, and made the bulky multi-SO₃H functionalized ILs entrapped within the MIL-100(Fe) pores. The resulting BAIL@MIL-100(Fe) provides a sustainable catalyst for the epoxide ring-opening reaction with high catalytic efficiency and high stability.

2 | EXPERIMENTAL

The detail of used chemicals and equipment are available in supporting information.

2.1 | Preparation of MIL-100(Fe)

MIL-100(Fe) was prepared under HF-free conditions according to the Zhang method.^[36] A mixture of 1,3,5-benzene tricarboxylic acid (1.89 g) and Fe (NO₃).9H₂O (4.04 g) in distilled water (6 ml) was heated at 95°C for 12 h under stirring. The orange solid product was purified by Soxhlet extraction with ethanol and dried in 150°C overnight.

2.2 | Ship-in-bottle preparation of Brønsted acidic ionic liquid within MIL-100(Fe)

The Brønsted acidic IL was prepared inside the nanocage of MIL-100(Fe) following the ship-in-bottle method: briefly, HMTA (1 mmol, 0.14 g) was poured into a vial containing absolute methanol (3 ml) and stirred vigorously. After complete dissolution of HMTA, activated MIL-100(Fe) (0.5 g) was added and stirred for 48 h at room temperature. The solid, that is, HMTA-MIL-100 (Fe), was isolated through centrifugation, dried at 100°C, and then dispersed in 3 ml dry toluene. Afterward, 1,3-propane sultone (4 mmol, 350 µl) was added to the mixture and allowed to reflux for 24 h. The resultant solid was collected, Soxhlet washed with ethanol, and dried at 80°C. Then, it was treated by diluted H₂SO₄ (4 mmol in 25 ml of absolute ethanol) for 24 h at 50°C. The final product, that is, BAIL@MIL-100(Fe), was separated, rinsed thoroughly with ethanol, and dried at 100° C.

2.3 | Acid-based titration

The prepared BAIL@MIL-100(Fe) (0.05 g) was suspended in a saturated NaCl solution (10 ml) followed by stirring for 24 h. After filtration, the clear solution was titrated with NaOH solution (0.01 M) in the presence of phenolphthalein indicator to determine the acid content of the prepared catalyst.

2.4 | Catalytic ring-opening of epoxides

Typically, 1 mmol of desired epoxide with 5 ml of alcohol was poured to the 25-ml round-bottom flask. After addition of catalyst (20 mg), the mixture was magnetically stirred at room temperature. The reaction progress was checked by sampling at certain times, and the epoxide

conversion was analyzed employing gas chromatography. The solid catalyst was separated after each cycle and used for another cycle after drying at 80°C to check the reusability.

3 | RESULTS AND DISCUSSION

3.1 | Preparation and characterization of BAIL@MIL-100(Fe)

MIL-100(Fe) has a 3D cage-like structure with pentagonal and hexagonal windows (diameters of 5.5 and 8.6 Å, respectively).^[35] Due to the enough size of the windows, HMTA molecules could be diffused into the nanocages through the larger windows of the framework. First, MIL-100(Fe) was heated under 150°C to remove any solvent trapped in the cavities. Then, HMTA species was entered within the cavities. In the following, nucleophilic reaction of 1,3-propane sultone with HMTA inside the cavities resulted in confining the multi $-SO_3H$ functionalized ILs in the MOF cavities. The overall



SCHEME 1 Schematic shipin-bottle synthesis of BAIL@ MIL-100 (Fe) catalyst

BAIL@MIL-100-Fe

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procedure to prepare the BAIL@MIL-100(Fe) catalyst has been summarized in Scheme 1.

The XRD patterns of the unmodified and SO_3H functionalized MIL-100(Fe) as well as the simulated pattern are presented in Figure 1. The pattern of synthesized MIL-100(Fe) corresponds well with the simulated pattern that approves the successful synthesis of desired material and confirms the crystallinity and phase purity of the sample (Figure 1a,b). As evidenced in BAIL@MIL-100 (Fe) (Figure 1c), the reflections are almost the same as those of the simulated and pure MIL-100(Fe), suggesting that the framework structure has not changed in the functionalization process. On the other hand, the broadness of diffraction peaks in synthesized compounds in comparison with the simulated one is related to the small size of the particles.

Chemical functionalization of solid support was monitored in each step by investigating FT-IR spectra (Figure 2). For HMTA-MIL-100(Fe), the peaks between 3000 and 2800 cm⁻¹ is referred to the aliphatic C–H stretching vibrations of HMTA molecules incorporated within the MIL-100(Fe).^[37] After nucleophilic reaction of propane sultone with HMTA, the new peaks were emerged in the 1000–1300 cm⁻¹ region, owing to the producing of sulfonic acid groups. The vibrational frequencies located at 1033, 1130, and 1220 cm⁻¹ are due to the stretching vibrations of –SO₃H groups.^[31,38–40]

The thermal behavior of pure and post-modified MIL-100(Fe) was carried out using powdered samples under the air flow. As shown in the TGA curve of pure MIL-100 (Fe), two main weight loss could be observed (Figure 3). The initial weight loss, about 30% at 50–250°C, is related to the removal of water and remaining solvent molecules.

The next weight loss, at $300-600^{\circ}$ C, results from complete framework decomposition. For BAIL@MIL-100 (Fe), only 13% weight loss could be seen up to 250°C because of the occupation of nanocages of MIL-100 (Fe) by the BAIL molecules. In the next step, greater weight loss between 300°C and 600°C is arisen from the combustion of multi-SO₃H IL entrapped within the MIL nanocavities.

The N_2 sorption isotherms of MIL-100(Fe) and BAIL@MIL-100(Fe) materials (Figure 4) exhibited a mix of type I/IV isotherms with an H₂-type hysteresis loop, illustrating the solids with microporous windows and



FIGURE 2 FT-IR spectra of (a) MIL-100(Fe), (b) HMTA-MIL-100(Fe), (c) BAIL@MIL-100(Fe), and (d) third recovered catalyst



FIGURE 1 XRD patterns: (a) simulated pattern, (b) MIL-100 (Fe), (c) BAIL@MIL-100(Fe), and (d) third recovered catalyst



FIGURE 3 TGA profiles of prepared materials

mesoporous cages. In addition, such observation approves the maintenance of pore structure upon the functionalization steps. Based on the Brunauer–Emmett–Teller (BET) calculations, a dramatic decrease in surface area from 1142.1 m²/g for MIL-100(Fe) to 320.28 m²/g for BAIL@MIL-100(Fe) indicated that the IL was successfully synthesized within the MOF nanocages (see Table 1).

Further evidence of the presence of BAIL species inside the MIL-100(Fe) framework was collected using elemental analysis (CHNS and EDX-map). Based on CHNS analysis, the nitrogen and sulfur contents of BAIL@MIL-100(Fe) were determined (N: 0.28 mmol/g, S: 0.97 mmol/g) (Table 1).

EDX analysis was employed to further check the elemental composition of BAIL@MIL-100(Fe) catalyst (Figure 5). All the expected elements, that is, Fe, C, N, O, and S, can be seen as significant peaks in the EDX spectrum. Moreover, the corresponding elemental mapping images revealed the uniform distribution of N, O, and S elements in the texture of the catalyst.

Additionally, the amount of incorporated Brønsted acid was achieved 0.9 mmol/g by acid-base titration,



FIGURE 4 N_2 adsorption-desorption isotherms of prepared materials

which is very close to the obtained value from the CHNS analysis.

All of the attained results verified that the BAIL was successfully embedded in the MIL-100 framework.

3.2 | Ring-opening of epoxides in the presence of BAIL@MIL-100(Fe)

The catalytic applicability of BAIL@MIL-100(Fe) was evaluated in the styrene oxide ring opening with methanol, which leads to the formation of 2-methoxy-2-phenylethanol as a major product (Scheme 2). In fact, this valuable product is considered as an important organic intermediate for production of industrial fine chemicals, drugs, and also can be used as organic solvent. Currently, the acid or base-catalyzed ring-opening of epoxide requires higher reaction temperature and longer reaction time, resulting in poor product yield and selectivity. Accordingly, an efficient and easily reusable catalyst is highly desirable to overcome these drawbacks.^[41,42]

As explained in Section 2, 20-mg catalyst was added to the mentioned reactants, and results are illustrated in Figure 6. It was found that, in the presence of BAIL@MIL-100(Fe), epoxide conversion increased over time and reached 99% in 3 h, whereas using MIL-100 (Fe) as catalyst lead to 12.2% of styrene oxide conversion to the product. Moreover, in the absence of the catalyst, no product was formed under the same conditions. It is concluded that the Brønsted acid IL located inside the MOF pores play an important function in the epoxide ring-opening reaction.

In an attempt to clarify the applicability of our solid acid catalyst, reaction of other epoxides and alcohols was examined (Table 2). It was observed that, when 1,2-propylene oxide and 1,2-epoxyhexane was utilized as epoxide in the reaction system, conversions of 46% and 43% was achieved after 24 h, respectively (entries 2 and 3). Also, 1,2-epoxyoctane showed fewer reactivity (38% conversion) at 24 h (entry 4). It is due to the less stability of its formed carbocation in comparison with benzylic

TABLE 1 The elemental analysis and BET surface areas of samples

Sample	N (mmol/g) ^a	S (mmol/g) ^a	Acid amount (mmol/g) ^b	BET surface area (m²/g)	Total pore volume (cm ³ /g)
MIL-100(Fe)	-	-	-	1142.1	0.5774
BAIL@ MIL-100 (Fe)	0.28	0.97	0.9	320.28	0.3628

^aBased on CHNS elemental analysis.

^bBased on acid-base titration.



FIGURE 5 EDX analysis and elemental mapping images of BAIL@MIL-100(Fe)



SCHEME 2 Styrene oxide ring-opening with methanol

carbocation of styrene oxide. Additionally, the employment of ethanol and propanol showed a relation between the styrene oxide conversion and alcohol size, so that ethanol and propanol with longer chain than methanol required a longer reaction time (24 h) to reach 94 and 54% conversion, respectively (entry 1). This variation in reactivity is related to the steric hindrance that increases with alcohol size and hinders to approach the catalytic active sites and activated epoxide within the modified MOF pores.

To ascertain the reusability of the BAIL@MIL-100 (Fe), the solid catalyst was separated from the reaction media, washed several times with ethanol, and reused for additional three cycles (Figure 7). Meanwhile, XRD (Figure 1d) and FT-IR (Figure 2d) analyses of the catalyst after the last test exhibited no noticeable differences compared to fresh catalyst, approving the catalyst stability in the ring-opening reaction.



FIGURE 6 Styrene oxide conversion as a function of time in the ring-opening reaction with methanol. Reaction conditions: styrene oxide (1 mmol), methanol (5 ml), catalyst (20 mg), and room temperature

3.3 | Comparison with other reported catalyst

In order to show the superiority and high efficiency of prepared solid acid catalyst with unique structure and design,

TABLE 2 Alcoholysis of epoxides in the presence of BAIL@MIL-100(Fe)^a





^cEthanol. ^dPropanol.

^eCalculated from GC analysis.



FIGURE 7 Recycling test of BAIL@MIL-100(Fe) catalyst in the methanolysis of styrene oxide. Reaction conditions: styrene oxide (1 mmol), methanol (5 ml), catalyst (20 mg), and room temperature, 3 h

a comprehensive comparison was made between the catalytic activity of BAIL@MIL-100(Fe) catalyst with those reported MOF-based acid catalysts in methanolysis of

styrene oxide, which the data are briefly gathered in Table 3. As indicated, MIL-101(Cr) containing heteropoly acids such as PTA@S1, PTA@S2, Co-POM@MIL-101, and MIL-101(HPW) (entries 2-5) can efficiently produce 2-methoxy-2-phenylethanol at shorter reaction time (20-30 min), but higher catalyst amount or elevated temperature (40°C) are the main reasons for these observations. Although low catalyst dosage similar to our work is used in the case of Fe-BTC and Al₂(BDC)₃ metal organic frameworks (entries 6 and 7), the high reaction temperature is a key factor to achieve high styrene oxide conversion. This is because of the acceleration of substrates and catalyst collisions by increasing the reaction temperature, which leads to more product generation. The other MOF-based acid catalysts (entries 8-14) exhibited very poor catalytic activity at higher reaction time (9-48 h) and temperature (40-60°C) along with using more amount of catalyst dosage. Therefore, according to this comparison, the extraordinary superiority of present work is mostly due to the existence of large amount of sulfonic acid groups incorporated inside the nanocages of MIL-100(Fe) that act as strong Brønsted acidic sites to proceed the conversion of styrene oxide in ambient condition at short reaction time while using a minimum amount of catalyst.

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Entry	Catalyst	Catalyst dosage (wt%)	Temperature (°C)	Time (h)	Conversion (%)	Reference
1	BAIL@MIL-100(Fe)	16.6	R.T.	3	99	This work
2	PTA@S1	33.3	R.T.	0.33	79.3	Zhao et al. ^[43]
3	PTA@S2	133.3	R.T.	0.33	45.1	Zhao et al. ^[43]
4	Co-POM@MIL-101	124.8	R.T.	0.5	100	Marandi et al. ^[44]
5	MIL-101(HPW)	33.3	40	0.33	99.8	Wee et al. ^[41]
6	Fe-BTC	20	40	1	93	Dhakshinamoorthy et al. ^[45]
7	$Al_2(BDC)_3$	20	40	1	67	Dhakshinamoorthy et al. ^[45]
8	Cu ₃ (BTC) ₂	33.3	40	2.5	~ 90	Wee et al. ^[42]
9	Co-BTT	19.05	50	29	67	Biswas et al. ^[46]
10	MIL-101(Cr)-tart	41.7	40	9	100	Berijani and Morsali ^[47]
11	Ln (III)-MOF	~36.45	55	~ 29	80	Silva et al. ^[48]
12	Eu-MOF	34.7	55	48	100	Vilela et al. ^[49]
13	TMU-18	104	60	24	35	Tehrani et al. ^[50]
14	TMU-50S	62.5	60	32	100	Gharib et al. ^[51]

TABLE 3 The comparison of the catalytic efficiency of BAIL@MIL-100(Fe) catalyst with other MOF-based acid catalysts





3.4 | Proposed mechanism

Scheme 3 illustrates the plausible mechanism of epoxides ring-opening in the presence of BAIL@MIL-100(Fe). First, the oxygen atom of the epoxide is protonated with the Brønsted acid sites of the catalyst to form benzylic carbocation (A). Then, the nucleophilic attack of the alcohol to the carbocation and subsequent deprotonation produces the β -alkoxy alcohol (B).

4 | CONCLUSION

Here in, we utilized a ship-in-bottle method to entrap a kind of Brønsted acid ILs (BAIL) with multi-SO₃H groups inside the nanocages of MIL-100(Fe). The data obtained from elemental analysis approved the presence of large amount of sulfonic acid groups (0.97 mmol/g) in catalyst framework, which was almost identical to the number of acid sites evaluated by acid-base titration method

(0.9 mmol/g). These observations along with other physicochemical techniques highly confirmed the accurate synthesis of desired catalyst through this novel synthetic method. The prepared Brønsted acid catalyst was used for the alcoholysis of epoxides under solvent-free conditions and showed superior catalytic activity especially in methanolysis of styrene oxide at room temperature and short reaction time.

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AUTHOR CONTRIBUTIONS

Saeideh sadat Mortazavi: Data curation. Alireza Abbasi: Supervision.

DATA AVAILABILITY STATEMENT

Data sharing not applicable - no new data generated, or the article describes entirely theoretical research.

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