

Facile Approach to Graft Ionic Liquid into MOF for Improving the Efficiency of CO₂ Chemical Fixation

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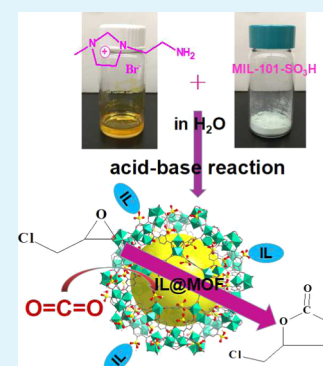
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Supporting Information

ABSTRACT: This work describes a facile approach to modify metal–organic frameworks (MOFs) with ionic liquids (ILs), rendering them as useful heterogeneous catalysts for CO₂ chemical fixation. An amino-functionalized imidazolium-based ionic liquid is firmly grafted into the porous MOF, MIL-101–SO₃H by the acid–base attraction between positively charged ammonium groups on the IL and negatively charged sulfonate groups from the MOF. Analyses by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, ¹H NMR, and N₂ sorption experiments reveal the MOF-supported ionic liquid (denoted as IL@MOF) material remains intact while functioning as a recyclable heterogeneous catalyst that can efficiently convert CO₂ and epichlorohydrin into chloropropene carbonate without the addition of a cocatalyst.



KEYWORDS: Ionic liquid, metal–organic framework, acid–base reaction, cycloaddition, carbon dioxide

INTRODUCTION

Increasing public awareness to sustainability and environmental matters are key issues in society, whereby the problems presented by the escalating amount of carbon dioxide (CO₂) accumulating in our atmosphere is becoming a major priority.¹ To slow or reduce the greenhouse effect caused by its primary component CO₂, its capture and utilization offer an interesting area of research.^{2–7} CO₂ cycloaddition reactions using epoxide precursors to produce cyclic carbonates are a promising environmental and atom economic approach owing to their high reaction yield, nonexistent byproducts, and solventless conditions.^{8–14} Hence, numerous homogeneous catalysts, such as metal halides, metal–salen complexes, ionic liquids (ILs), and other materials,^{15–20} have been developed to perform the cycloaddition reaction. Among these endeavors, ILs continue to be used because of benefits related to their nonflammability, thermal stability, and negligible vapor pressure.^{21,22} Some imidazolium-based ionic liquids have shown a unique ability to enhance the conversion of CO₂ by increasing its adsorption,^{23–25} in addition to their use in other related catalytic reactions.^{26–29} Because of the fact that homogeneous catalytic systems are usually subjected to tougher separation procedures than heterogeneous systems, the opportunity to integrate the advantages of both homogeneous and heterogeneous catalytic

systems by immobilizing ILs within the pores of a porous support host is a promising protocol.³⁰

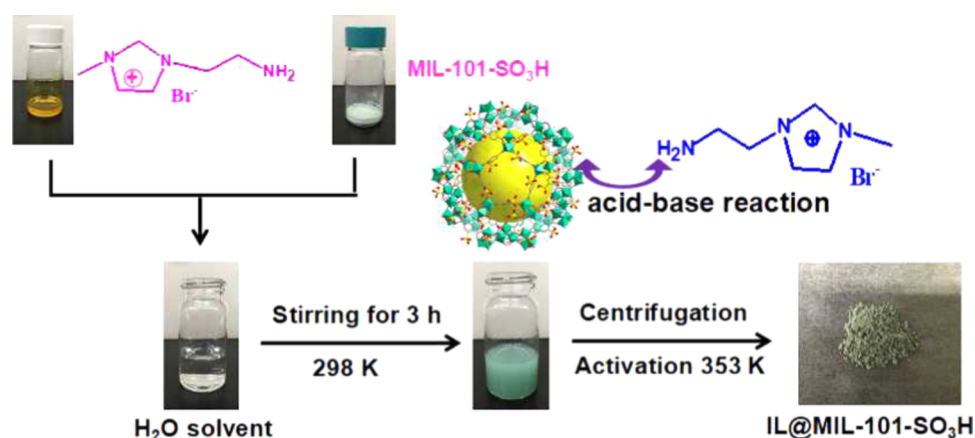
In this study, the porous support comprises a type of metal–organic framework (MOF) also known as porous coordination polymer because it has a high internal surface area, tailorable pores, interesting host–guest interactions, and structural flexibility, in addition to its ability to support ILs, thus enhancing their intrinsic properties.³¹ In this respect, Kitagawa and co-workers have reported the incorporation of IL in such materials and studied the phase behavior of the ILs inside the micropores of zeolitic imidazolate framework (ZIF-8).³² Jhung and co-workers introduced acidic ILs from dichloromethane into dehydrated Materials Institute Lavoisier (MIL-101) by diffusion and demonstrated that the produced material exhibited a remarkable improvement in its ability to adsorb sulfur-containing compounds than that of the parent MOF.³³ The catalytic activities of MOF-supported ILs were recently studied in an effort to overcome some of the drawbacks such as rigorous separation from products or obtaining selective and reusable heterogeneous catalyst with improved catalytic activity.^{34,35} This was demonstrated by Luo et al. that confined

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Scheme 1. Fabrication Procedure of Self-assembled MOF-Supported IL Heterogeneous Catalyst Through the Acid–Base Reaction



a Brønsted acidic IL within the nanocages of MIL-101 by using a tandem postsynthetic strategy. With regard to the acetalization of benzaldehyde with glycol, their hybrid material exhibited superior catalytic performance.³⁶ Similarly, Brønsted acidic IL-modified polyoxometalate (PW₄) was inserted in the MIL-100(Fe) cages and the obtained catalyst exhibited higher catalytic activity for the esterification of oleic acid with ethanol.³⁷ A dual amino-functionalized ionic liquid (DAIL) and polyoxometalate were immobilized into the nanocages of MIL-101(Fe) framework, forming the PW₄/DAIL/MIL-100(Fe) heterogeneous catalyst, which catalyzed the oxidation of benzyl alcohol toward benzaldehyde.³⁴ Although the cycloaddition reaction of CO₂ with epoxides using MOF-supported ionic liquid catalyst has been reported,^{38–41} the fabrication of these catalysts usually have limitations, including multistep fabrication, lengthy reaction time, using co-catalyst, and catalytic procedures requiring high temperature.^{42,43} Therefore, this article explores the design of a highly effective heterogeneous catalyst using a simple single-step method to incorporate ionic liquids within the porous matrix of a MOF and demonstrate its recyclable catalytic performance.

The self-assembly method is a well-established strategy to assemble molecular components into ordered or complex aggregates,⁴⁴ by the attraction between complementary structures, in this case, two oppositely charged species suspended in a fluid. Work demonstrated here provides a rational approach to fabricate a self-assembled heterogeneous catalyst of 1-methyl-3-(2-aminoethyl)imidazolium bromide ionic liquid within MIL-101-SO₃H, which is denoted as IL@MIL-101-SO₃H. The IL is effectively anchored on MIL-101-SO₃H frameworks because of the acid–base reaction between –SO₃H(–SO₃[–]) and –NH₂(NR₃⁺) moieties (Scheme 1). The catalytic performance of the IL@MOF for the cycloaddition of CO₂ with epichlorohydrin was investigated, and it showed that the heterogeneous catalyst is very efficient and stable, with easy separation from the products and ability to be reused multiple times.

EXPERIMENTAL SECTION

Preparation of Catalyst. Synthesis of MIL-101-SO₃H. MIL-101-SO₃H synthesis was carried out according to the previous report.⁴⁵ Monosodium 2-sulfoterephthalic acid (12.5 mmol, >98.0%, TCI), CrO₃ (12.5 mmol, 99.9%, Acros), and concentrated aqueous hydrochloric acid (25 mmol, 12 N, Fisher Chemical) were mixed in a Teflon-lined autoclave. Twenty-five milliliters of water was added, and

the mixture was heated for 6 days at 180 °C. The product obtained was washed with deionized water and methanol three times, followed by air drying at room temperature. The green powder thus obtained was postsynthetically treated in a solution of diluted HCl (0.08 M) in methanol. The resultant green solid was dried overnight at 120 °C under vacuum for further use.

Synthesis of MIL-101-SO₃Na. The MIL-101-SO₃Na was obtained by ion exchange of MIL-101-SO₃H with excess 0.1 M NaCl aqueous solution, according to the previous report.⁴⁶

Preparation of Amino-Functionalized IL. The [2-aemim][Br] (1-methyl-3-(2-amino-ethyl)imidazolium bromide) room-temperature ionic liquid was synthesized according to the published methods with little modification.⁴⁷ A mixture of 1-methylimidazole (0.1 mol, 99%, Acros) and 2-bromoethylamine hydrobromide (0.1 mol, >98%, Alfa Aesar) in 50 mL of ethanol was heated at 80 °C for 12 h. Upon completion, 0.1 mol KOH (85%, Acros) was added to the resulting suspension for neutralization. The main product, imidazolium bromide, was then separated from the KBr by centrifugation, followed by solvent evaporation. Finally, washing the residue with diethyl ether afforded a yellowish ionic liquid.

Synthesis of IL@MIL-101-SO₃H. In a typical synthesis, 50 mg of MIL-101-SO₃H and 21 mg of [2-aemim][Br] IL were dispersed in 10 mL of pure H₂O and were stirred for 3 h at 22 °C. The powder material was then washed with ethanol three times through centrifugation, followed by evacuating at 80 °C for 12 h. The elemental analysis results revealed that nitrogen element content in IL@MIL-101-SO₃H was 3.5 wt %. Furthermore, IL@MIL-101-SO₃H samples with different nitrogen loading contents can be obtained by adjusting the IL concentration dissolved in water with a fixed amount of MIL-101-SO₃H powders. Since one IL molecule has two nitrogen atoms, the IL loading content can be calculated by half the nitrogen value.

Catalytic Performance Evaluation. Cycloaddition of CO₂ with Epichlorohydrin. In a typical experiment, 50 or 80 mg of catalyst, epichlorohydrin (1.0 g, 10.8 mmol, 99%, Alfa Aesar), and a stir bar are loaded into a 25 mL Schlenk tube, which was connected to a CO₂ balloon filled under 1 atm of pressure. The components were stirred at the designated reaction temperature for the listed amount of time. Following the allotted reaction time, all materials were placed in a falcon tube and centrifuged, allowing the liquid component to be extracted and diluted with deuterated solvent for NMR analysis. Reaction yields were calculated by comparing the ratio of epoxide to carbonate. With epichlorohydrin as the model reactant, the effect of reaction times, the catalyst amount, and the temperature were systematically investigated to optimize the conditions for utilization in CO₂ fixation under atmospheric pressure.

Recyclability Investigation of IL@MIL-101-SO₃H Catalyst. The catalyst was separated after the cycloaddition reaction was complete and washed with ethanol three times and dried overnight at 80 °C in vacuum. Afterward, the catalyst was reused for the next catalytic run

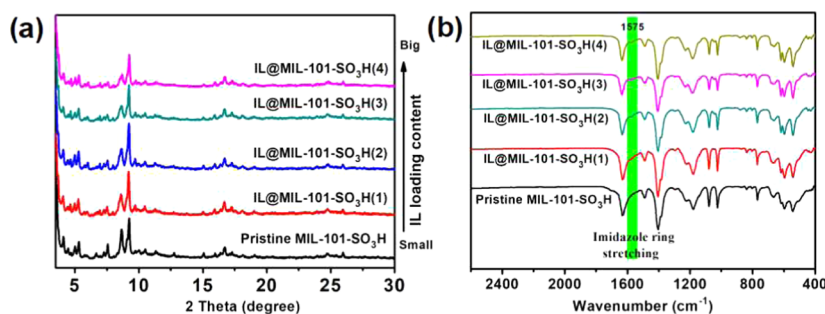


Figure 1. (a) PXRD patterns and (b) FT-IR spectra of IL@MIL-101-SO₃H sample with different ionic liquid loading contents.

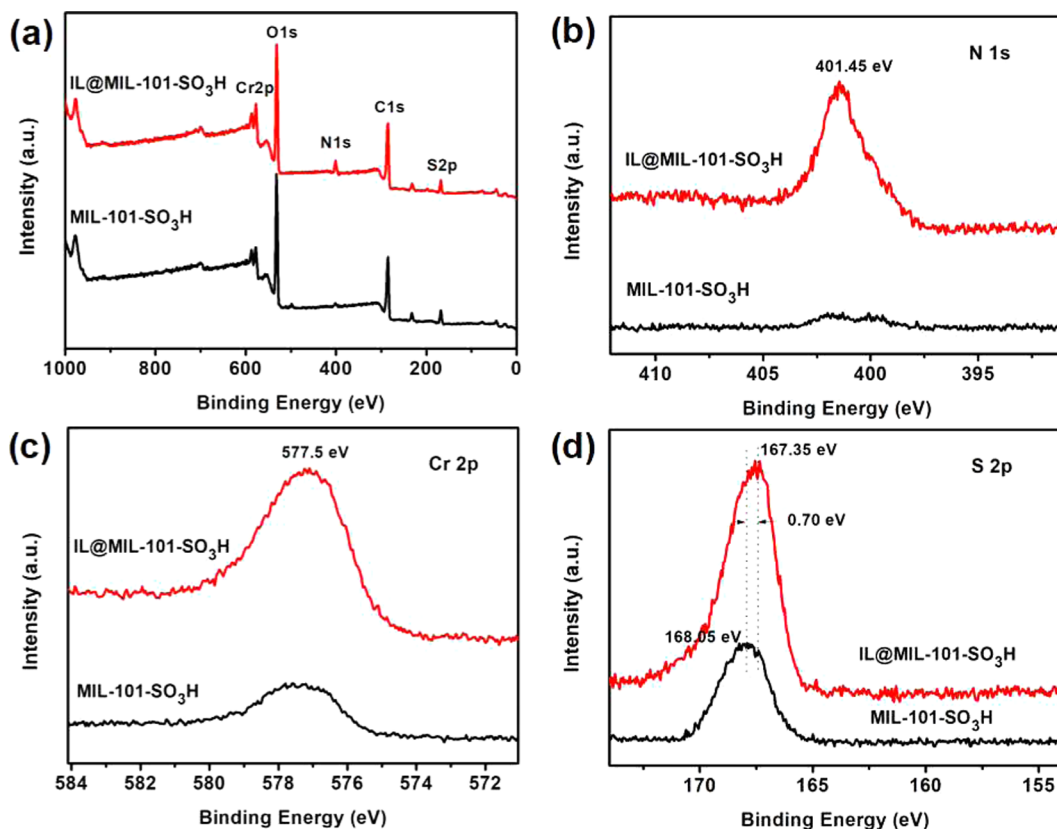


Figure 2. (a) XPS survey spectra for MIL-101-SO₃H and for IL@MIL-101-SO₃H samples and XPS spectra of (b) N 1s, (c) Cr 2p, and (d) S 2p in the MIL-101-SO₃H and IL@MIL-101-SO₃H samples.

under the same reaction conditions. This procedure was repeated at least three times to examine the recyclability of IL@MIL-101-SO₃H catalyst.

RESULTS AND DISCUSSION

Synthesis of Ionic Liquid with Amino Group. For the acid–base reaction, MIL-101-SO₃H bearing –SO₃H group acts as the acidic component. Therefore, the fabrication of an ionic liquid having an amino group located on a terminal side chain would be required to participate as the basic component. 1-Methyl-3-(2-aminoethyl)imidazolium bromide ([2-aemim][Br]) was prepared directly from the equimolar reaction between 1-methylimidazole and 2-bromoethylamine hydrobromide, as previously reported, yielding the desired basic IL.⁴⁷ The corresponding Fourier transform infrared spectroscopy (FT-IR) and ¹H NMR for [2-aemim][Br] are provided in the Supporting Information Figures S1 and S2.

Synthesis and Characterization of IL@MIL-101-SO₃H Catalyst. With amino-functionalized IL in hand, the self-assembly of MIL-101-SO₃H with [2-aemim][Br] IL is carried out at room temperature using water as the solvent. Comparison of the powder X-ray diffraction (PXRD) diffractograms revealed that IL@MIL-101-SO₃H samples with different ionic liquid loading contents retained their high crystallinity and mirrored that of pristine MIL-101-SO₃H (Figure 1a), indicating that the introduced amino-functionalized IL did not alter the structural integrity of the MIL-101-SO₃H framework. Additionally, scanning electronic microscopy (SEM) images revealed that IL@MIL-101-SO₃H sample continued to show regular octahedral-shaped crystals, with an average particle size of ~2 μm, which were similar to that of the parent material (Figure S3). The FT-IR spectra provided more evidence of the IL incorporation in the MOF, as shown in Figure 1b. The imidazole ring stretching vibration at 1575 cm⁻¹ is noticeably present after loading and correlates well

with the spectrum of free [2-aemim][Br] IL (Figure S1) and related reports.⁴⁸ To discern the interactions between IL and MIL-101-SO₃H, the X-ray photoelectron spectroscopy (XPS) survey scans for the Cr, N, and S elements were performed (Figure 2a). In Figure 2b,c, the high-resolution spectra depicted the presence of N element in IL@MIL-101-SO₃H sample and its absence in MIL-101-SO₃H whereas the Cr element in both IL@MIL-101-SO₃H and MIL-101-SO₃H samples showed no peak shift, revealing a negligible change in the electron density of these groups. In addition, the S 2p peak at 168.05 eV in MIL-101-SO₃H sample illustrated a slight shift to lower binding energies of ca. 167.35 eV in IL@MIL-101-SO₃H (shown in Figure 2d), indicating an acid–base reaction between IL and MIL-101-SO₃H has happened between the N and S components.⁴⁹ On the basis of above FT-IR and XPS analyses, the IL with an amino group is part of MIL-101-SO₃H.

Furthermore, thermogravimetric analysis (TGA) was employed to determine the thermal stability of IL@MIL-101-SO₃H. Figure S4 shows that there is no significant difference between both materials before the frameworks begin to decompose around 220 °C. This thermal stability of IL@MIL-101-SO₃H is ideal for its use as a heterogeneous catalyst for CO₂ cycloaddition reactions. To address the placement of the IL, accessible surface area measurements of MIL-101-SO₃H and its IL-modified forms revealed a slight lowering in the surface area from 1458 down to 1049 m²/g, along with smaller calculated pore volumes with an increasing loading of the IL (Figure 3 and Table S1). This result indicates that

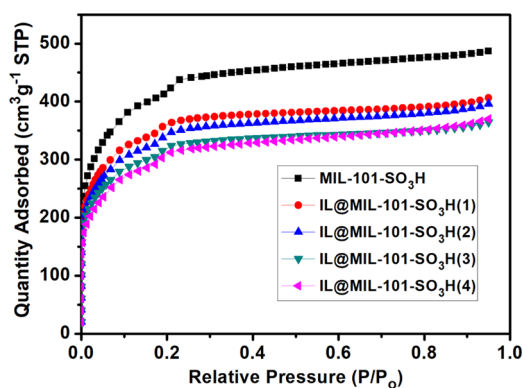


Figure 3. Nitrogen sorption isotherms of MIL-101-SO₃H and IL@MIL-101-SO₃H samples with different ionic liquid loading contents.

imidazolium-based ILs occupy some of the pores of the framework yet do not block the pores access during the N₂ isotherms measurements at 77 K.

Catalytic Activity of IL@MIL-101-SO₃H. Epichlorohydrin was chosen for the cycloaddition with CO₂ to compare the catalytic synthesis of chloropropene carbonate (CC) using the control (no catalyst), MIL-101-SO₃Na, and IL@MIL-101-SO₃H (N, 3.50 wt %) (Table S2). It can be seen that with no catalyst present, there is no significant conversion of epoxide observed and only a small amount of CC was formed using the MIL-101-SO₃Na (Table S2, entry 1–2). However, using IL@MIL-101-SO₃H as a catalyst showed a great increase in activity under the same conditions (Table S2, entry 3).

Given that IL@MIL-101-SO₃H efficiently catalyzed the reaction of epichlorohydrin and CO₂, conditions were then modified to improve the yield of the main product (CC). As illustrated in Figure 4a,b, the optimum reaction parameters that afforded the highest CC yield were evident at 90 °C, 1 atm CO₂, 48 h reaction time, and using 80 mg of catalysts/g of epichlorohydrin. Although the yield of CC product is increased accordingly with the reaction time extended from 24 to 48 h, there was no significant increase in activity when the catalyst amount is increased from 50 to 100 mg.

To further optimize the reaction conditions, IL@MIL-101-SO₃H samples with different IL loadings were evaluated as a catalyst in the CO₂ cycloaddition at 90 °C, and 1 atm CO₂ pressure. The results, summarized in Table 1, showed

Table 1. Catalytic Performance of IL@MIL101-SO₃H with Different IL Loading Contents in the CO₂ Cycloaddition Reaction with Epichlorohydrin^a

entry	catalyst	IL loading (mmol/g)	IL mol % catalysis	yield (%)
1	IL@MIL-101-SO ₃ H(1)	0.4167	0.31	52
2	IL@MIL-101-SO ₃ H(2)	0.4933	0.37	74
3	IL@MIL-101-SO ₃ H(3)	0.5380	0.40	83
4	IL@MIL-101-SO ₃ H(4)	0.5820	0.43	98

^aReaction conditions: epichlorohydrin (10.8 mmol), catalyst (80 mg), time (24 h), CO₂ 1 atm, 90 °C.

improving yields for CC as the IL loading content increased while maintaining the same amount of catalyst at 80 mg. A near linear increase (Figure S5) in product yield was observed with the IL amount, thereby illustrating its crucial role in catalyzing the cycloaddition reaction.

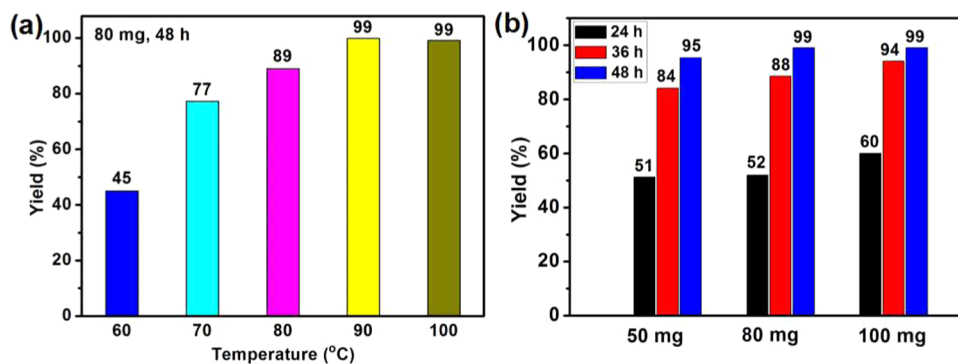


Figure 4. Yield of chloropropene carbonate from the addition of epichlorohydrin with CO₂ by altering the (a) reaction temperature and the (b) catalyst amount and reaction time.

Experiments to further examine the recyclability of the IL@MIL-101-SO₃H catalyst under optimized reaction conditions were subsequently conducted. The results presented in Figure 5 indicated that the IL@MIL-101-SO₃H catalyst could be

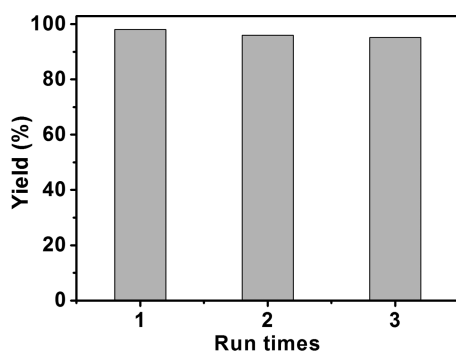


Figure 5. Recycle test of IL@MIL-101-SO₃H catalyst in the CO₂ cycloaddition reaction with epichlorohydrin under optimized conditions. Reaction conditions: epichlorohydrin (10.8 mmol), catalyst (80 mg), $P(\text{CO}_2) = 1 \text{ atm}$, temperature = 90 °C, and time = 24 h.

easily separated through centrifugation and reused in three consecutive runs. Moreover, these cycles did not significantly hinder the product yield (96–98%), reflecting not only the reusability but also the stability of the catalyst. Subsequently, the comparative PXRD analysis of the fresh catalyst and the recovered IL@MIL-101-SO₃H after the third reuse was collected (Figure S6), which demonstrated that the structural integrity of IL@MIL-101-SO₃H was well-preserved after reuse for three catalytic runs. Also, the FT-IR spectrum of the recovered IL@MIL-101-SO₃H sample revealed the imidazole ring stretching vibration (1575 cm⁻¹), indicating the MOF's retention of the IL after three successive runs (shown in Figure S7).

To emphasize the enhanced catalytic performance of our approach in view of the recent progress in MOF-supported IL heterogeneous catalysts for cycloaddition of CO₂ to epichlorohydrin without Bu₄NBr co-catalyst, the results of this work were compared with other reported catalysts.^{38,40,41} As shown in Table S3, the IL@MIL-101-SO₃H exhibits better catalytic activity for this CO₂ cycloaddition system. Thus, the self-assembled IL@MIL-101-SO₃H approach described in this study is a promising strategy for engaging MOF as heterogeneous catalysts for CO₂ cycloaddition with quantitative product yields. On the basis of recent literature results,^{40,48,50} a plausible cycloaddition reaction mechanism catalyzed by the MOF is presented in Scheme S1. In principle, the Lewis acidic center (Cr(III)) of IL@MIL-101-SO₃H activates the epoxide ring via coordination with the oxygen atom (ring activation), followed by nucleophilic attack of the halide anion (Br⁻) of IL@MIL-101-SO₃H on the less sterically hindered β-carbon atom of epichlorohydrin. The latter step leads to formation of an intermediate phase that enables carbon dioxide to react before cyclization and catalyst regeneration.

CONCLUSIONS

In summary, we have adopted an acid–base mediated self-assembly approach for the simple fabrication of a heterogeneous catalyst comprised of MOF-supporting ILs. The obtained IL@MIL-101-SO₃H catalyst exhibits a high catalytic

activity for cyclizing CO₂ with epichlorohydrin under atmospheric pressure without the addition of a cocatalyst such as Bu₄NBr. A noteworthy enhancement of product yield was obtained for IL@MIL-101-SO₃H compared to that of MIL-101-SO₃Na when IL was immobilized within the MOF's porous framework, despite the loading content of IL is minimal (0.4167–0.5820 mmol/g). Importantly, the IL@MIL-101-SO₃H heterogeneous catalyst was separated simply by centrifugation, thus allowing multiple reuse cycles without significant catalytic activity depletion. This facile self-assembly route can be potentially used to support other ILs with acidic or basic groups on functional MOFs to fabricate MOF-supported IL composites, which are expected to immensely broaden their application in various fields.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b08914.

FT-IR spectrum for [2-aemim][Br] ionic liquid (Figure S1); ¹H NMR spectrum of [2-aemim][Br] ionic liquid dissolved in D₂O at ambient conditions (Figure S2); SEM images of MIL-101-SO₃H and IL@MIL-101-SO₃H samples (Figure S3); TGA curves of MIL-101-SO₃H and IL@MIL-101-SO₃H samples (Figure S4); percent yield versus different IL loadings in IL@MIL-101-SO₃H (Figure S5); PXRD patterns of IL@MIL-101-SO₃H catalyst before and after catalytic cycle test (Figure S6); FT-IR spectrum of IL@MIL-101-SO₃H catalyst after catalytic cycle test (Figure S7); plausible mechanism of conversion of epoxide to cyclic carbonates using IL@MIL-101-SO₃H (Scheme S1); structural properties of MIL-101-SO₃H and IL@MIL-101-SO₃H samples with different ionic liquid loading contents (Table S1); performance of different catalysts in the CO₂ cycloaddition of epichlorohydrin (Table S2); summary of the reported cycloaddition of CO₂ to epichlorohydrin catalyzed by MOF-supported IL without adding Bu₄NBr catalytic systems (Table S3) (PDF)

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Notes

The authors declare no competing financial interest.

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