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Direct synthesis of ordered imidazolyl-functionalized mesoporous polymers for efficient chemical fixation of CO_2†

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Ordered imidazolyl-functionalized mesoporous polymers (IM-MPs) are directly synthesized by an evaporation-induced self-assembly method, which are further functionalized with bromoethane and employed as highly efficient and recyclable catalysts for the cycloaddition of CO_2 to epoxides.

Nowadays, imidazoles have emerged as key building blocks for many chemicals, especially used as the cations of ionic liquids.[1] Imidazolium-based ionic liquids have received increasing attention because of their unique properties related to the tunable structure as well as potential applications in organic synthesis, catalysis and synthesis of nanostructured materials *etc.*[2] Among various reactions catalyzed by imidazolium-based ionic liquids, the synthesis of cyclic carbonates from epoxides and carbon dioxide (CO_2) is recognized as an effective strategy for the fixation of CO_2 in the viewpoint of atom economy and green chemistry.[3] In order to overcome the intrinsic disadvantages of homogeneous catalysts in catalyst recovery and product purification, great efforts have been made towards the post grafting of the imidazole moiety onto the solid materials including silica, molecular sieves, chitosan and polystyrene resin.[4]

Recently, highly ordered mesoporous phenolic resins have been investigated as innovative solid supports with a wide range of applications. They possess three-dimensionally connected and covalently bonded organic frameworks, which exhibit attractive merits of high surface areas, uniform pore sizes and hydrophobic features.[5] Therefore, we have developed a series of FDU-type mesoporous phenolic resin supported catalysts *via* post-modification, which can be used as active catalysts for various organic reactions.[6] Specifically, the imidazolium-based ionic liquids supported on a FDU-15 mesopolymer are highly active and durable catalysts for the cycloaddition of CO_2 with epoxides. Both the mesoporous organic framework and abundant phenolic hydroxyl groups of the FDU mesopolymer play important roles in the improvement of the catalytic performance.[7] However, the multistep post-modification method mentioned above will inevitably suffer from the low imidazole loading and the inhomogeneous distribution of active species. Besides the post-modification strategy, direct synthesis of the imidazolium-based polymer is an alternative approach.[8] Yuan and co-workers reported a template-free method to synthesize a mesoporous imidazolium-based polymer network.[9] However, the resulting materials have disordered pores. In addition, the fabrication of imidazole polymers with periodically ordered porous architectures through a hard-templating method[10] requires long reaction time and a hazardous chemical etching process.[11] To the best of our knowledge, the direct incorporation of the imidazolyl group into the ordered mesoporous polymer framework with a highly stable content and large surface area is still a great challenge.

Herein, we first report a direct synthesis of ordered imidazolyl-functionalized mesoporous polymers (IM-MPs) with high surface area, large pore volume and tunable ordered mesopores *via* an evaporation-induced self-assembly method (EISA). These materials are readily achieved by a one-step self-assembly of commercial 4-(imidazole-1-yl)phenol (IMP), phenol and formaldehyde as precursors and ampliphilic triblock copolymer F127 as a templating agent. IM-MPs can be easily functionalized by different alkyl substituents and counteranions, providing a broad range of useful properties. As one of the most attractive examples, they were designed as highly efficient and recyclable catalysts for the cycloaddition of CO_2 to epoxides.

According to the schematic illustration shown in Fig. 1A, we synthesized a series of IM-MPs with the calculated amount of imidazole moiety by varying the ratio of IMP to phenol. First, the imidazolyl-functionalized resol was obtained under basic conditions through prepolymerization with IMP, phenol and formaldehyde. Then, the chemically functionalized resol precursor was assembled with the assistance of Pluronic F127 template *via* the EISA method. Followed by a further thermopolymerization at 120 °C and a subsequent vacuum calcination at 350 °C to decompose F127, the porous mesopolymers were obtained, denoted as IM-MPs-*x*, where *x* represents the molar ratio of IMP/(IMP + phenol).

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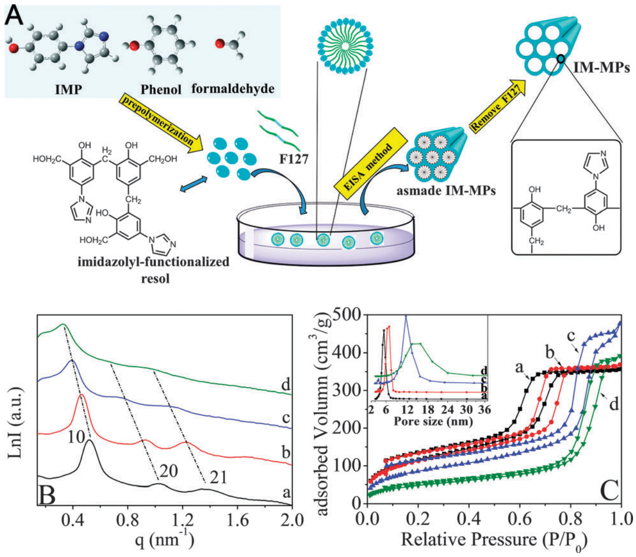

Fig. 1 Schematic illustration of the synthesis procedure for IM-MPs (A). SAXS patterns (B). Nitrogen adsorption–desorption isotherms and BJH pore size distributions (C) of IM-MPs synthesized by regulating the ratio of IMP to phenol: (a) IM-MPs-5%, (b) IM-MPs-20%, (c) IM-MPs-40%, and (d) IM-MPs-60%.

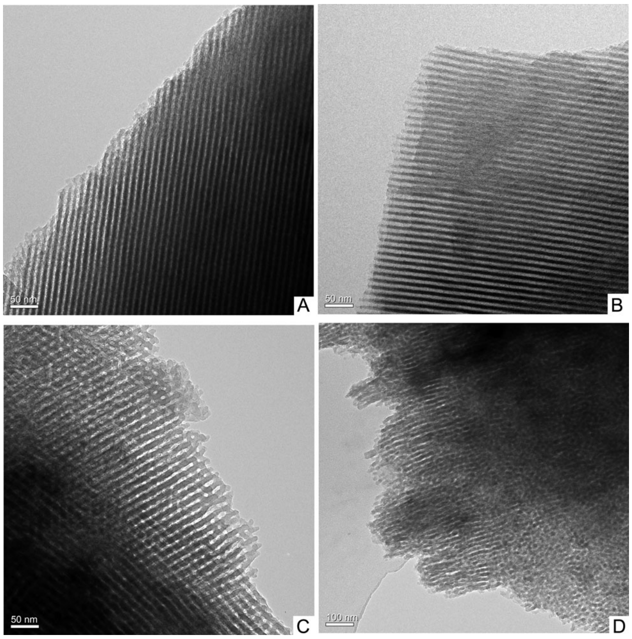

Fig. 2 TEM images taken along the [10] direction of IM-MPs-5% (A), IM-MPs-20% (B), IM-MPs-40% (C) and IM-MPs-60% (D).

The small angle X-ray scattering (SAXS) patterns of IM-MPs different in IMP content are shown in Fig. 1B. The pattern of IM-MPs-5% exhibited three well-resolved peaks at q values of 0.5–1.4 nm^{-1},[5a,c] which could be indexed as the (10), (20) and (21) planes of an ordered 2D hexagonal structure with the *P6mm* space group (Fig. 1B). Upon increasing the molar ratio of IMP/(IMP + phenol) from 5% to 60%, the diffraction peaks shifted distinctly to lower q values and reduced gradually in scattering intensity, implying that the ordering degree of mesostructures in IM-MPs significantly decreased as the IMP content affected the crosslink density of the polymer network.[12] The porosities of IM-MPs were characterized by nitrogen sorption analysis at 77 K (Fig. 1C), all the IM-MP samples displayed a typical IV type isotherm with an apparent H1-type hysteresis loop characteristic of mesoporous structure. With increasing IMP content, the H1-type hysteresis loop with a sharp capillary condensation step shifted dramatically to high relative pressure range, which indicated that the pore size gradually increased in accordance with the pore size distribution.

The corresponding mesopore characteristics are summarized in Table S1 (ESI†). Increasing the IMP content results in the decrease of the BET surface area from 433 to 175 m^2 g^{-1}, the enlargement of pore size from 5.4 to 14.5 nm, presumably because the superfluous IMP degenerated the order of mesostructure and decreased the crosslink degree of the polymer network. The mesostructure of IM-MPs was detected by transmission electron microscopy (TEM). As shown in Fig. 2A, highly ordered cylindrical pores with uniform size were observed clearly along the (10) direction, further confirming the presence of a highly ordered mesostructure in IM-MPs-5%. When the IMP/(IMP + phenol) ratio was increased from 5% to 40% (Fig. 2B and C), the ordered mesostructures were well-maintained. Upon further increasing the ratio to 60%, the TEM image clearly showed a disordered symmetry different from the *P6mm* space group and the rod-like nanotubes with the long-range ordering (Fig. 2D), which was in agreement with the SAXS analysis. The ordering of the mesoporous structure significantly decreased with increasing IMP content, because *para*-substituted IMP may occupy one of the crosslink points of phenol and then disturbed both the condensation of phenol with formaldehyde and the self-assembly of F127 and the resol precursor, leading to a less ordered mesostructure.

According to the TG analysis results (Fig. S1, ESI†), pure IMP was completely lost at 290 °C. By contrast, the as-made IM-MPs-20% showed no significant weight loss at that temperature (Fig. S1c, ESI†), which implies that the highly cross-linked polymer matrix efficiently prevents the IMP from decomposition. And most of the incorporated F127 template could be decomposed and removed at temperature lower than 350 °C (Fig. S1c, ESI†), consistent with the decomposition curve of pure F127 as shown in Fig. S1b (ESI†). It was found that the calcined IM-MPs-20% under vacuum was stable up to 400 °C (Fig. S1d, ESI†). The chemical composition of calcined IM-MP samples was analyzed by CHN analysis (Table S2, ESI†). The nitrogen content for the series of IM-MP samples increased dramatically from 0.77 to 8.4 wt% as the IMP/(IMP + phenol) ratio increases from 5% to 60%. The nitrogen contents of the IM-MPs materials were in good agreement with the theoretical values, indicating that IMP was completely incorporated into the mesoporous polymer frameworks, and the high crosslink density of IM-MPs greatly prevented the decomposition of IMP during the process of template removal. The XPS spectra were measured to identify the surface elemental compositions and the chemical state of nitrogen atoms (Fig. S2, ESI†). The full survey spectra of IM-MPs show similar element species of C, N and O in all samples (Fig. S2A, ESI†). The atom ratio is calculated from the corresponding XPS peak and the data are listed in Table S2 (ESI†). The atom ratio of C/N determined by XPS is closely consistent with the theoretical values and the CHN analysis results. This further revealed that the N content of the IM-MPs could be accurately

Table 1 Catalytic performances of IM-MPs-EtBr in the cycloaddition reaction of CO_2 with propylene oxide[a]

Entry	Catalyst	Yield[b] (%)	Selectivity (%)	TON[c]
1	IM-MPs-5%-EtBr	14	98	249
2	IM-MPs-20%-EtBr	48	99	280
3	IM-MPs-40%-EtBr	54	>99	177
4[d]	IM-MPs-20%-EtBr	99	>99	187

[a] Reaction conditions: cat., 50 mg; PO, 30 mmol; catalyst 50 mg, CO_2 pressure, 1 MPa; temp., 110 °C; time, 3 h. [b] Determined by GC using biphenyl as an internal standard. [c] Turnover number (TON), moles of propylene carbonate per mole of immobilized imidazole ring. [d] Cat., 150 mg.

adjusted, and the IMP species were homogeneously dispersed in the framework of IM-MPs. The shape of the N 1s XPS bands is identical for all IM-MP samples (Fig. S2B, ESI†), which can be deconvoluted into two distinct peaks representing the two nitrogen atoms with different chemical positions derived from the imidazole moiety,[13] attributed to pyridinic nitrogen at ~398.5 eV and pyrrolic nitrogen at ~400.5 eV.[14] The nitrogen environments in the mesoporous polymers are still preserved at low temperature (350 °C), a similar result was observed in the reported literature.[15] Moreover, the successful incorporation of the imidazolyl group into the mesoporous polymer framework has also been confirmed by FT-IR spectra (Fig. S3, ESI†) and solid state ^{13}C MAS NMR spectra (Fig. S4, ESI†).

The cycloaddition reaction of propylene oxide (PO) and CO_2 to propylene carbonate (PC) was used as a model reaction to evaluate the catalytic performance of the IM-MPs based catalyst. In this study, the relatively ordered materials (IM-MPs-5%, IM-MPs-20% and IM-MPs-40%) were further functionalized by bromoethane to obtain target heterogeneous catalysts, designated as IM-MPs-EtBr (Table S3, ESI†). And they showed good catalytic activities (Table 1). We once reported that a pure mesoporous polymer (FDU-15) without addition of IMP and bromoethane could scarcely catalyze the cycloaddition reaction, which indicated that imidazolyl groups of IM-MPs played a critical role in promoting the reaction in cooperation with halide anion Br^- and phenolic hydroxyl groups.[7] Notably, a TON of 280 was achieved on IM-MPs-20%-EtBr which exhibited the highest catalytic activity among the catalysts employed under the identical reaction conditions, which was much higher than that of reported analogous catalysts (Table S4, ESI†).[7,16] The activity of IM-MPs-EtBr was in the order of IM-MPs-20%-EtBr > IM-MPs-5%-EtBr > IM-MPs-40%-EtBr.

With the N content increasing from 0.98 wt% (IM-MPs-5%-EtBr) to 3.0 wt% (IM-MPs-20%-EtBr), more active sites can significantly promote the cycloaddition reaction (entries 1 and 2). However, the TON value was obviously decreased to 177 when the N content of IM-MPs-40%-EtBr increases up to 5.18 wt%. The main reason might ascribe to the fact that part of imidazolyl functionalities was embedded in the polymer matrix during the co-condensation, inaccessible to the substrates. Along with a small surface area, this resulted in a relatively small TON value for the IM-MPs-40%-EtBr sample. Additionally, the PC yield remarkably increased from 48% to 99% when the amount of IM-MPs-20%-EtBr was raised from 50 mg to 150 mg (entries 2 and 4). IM-MPs-20%-EtBr was separated by simple filtration and reused five times without significant loss of activity (Fig. S5, ESI†), which indicated a high stability and reusability of IM-MPs-EtBr.

In conclusion, a one-step synthesis strategy has been successfully employed to prepare an imidazolyl-functionalized ordered mesoporous polymer by direct self-assembly of IMP–phenol–formaldehyde precursors. The synthesized IM-MPs with well-ordered 2D hexagonal structure exhibit high surface areas, large pore volumes and tunable pore size as well as controllable nitrogen content. The flexibility of structural properties and the versatility of the imidazole ring endow IM-MPs with potential applications. Expectedly, the IM-MP materials can be easily functionalized with bromoethane, giving rise to highly efficient and recyclable catalysts for the cycloaddition of CO_2 to epoxides without any use of cocatalysts and organic solvents.

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