

Hydroboration of Hollow Microporous Organic Polymers: A Promising Postsynthetic Modification Method for Functional Materials

Sohee Bang,[§] June Young Jang,[§] Yoon-Joo Ko, Sang Moon Lee, Hae Jin Kim, and Seung Uk Son*



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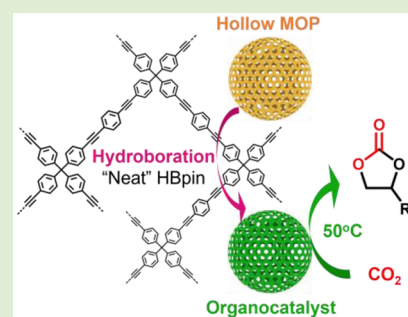


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ABSTRACT: This work shows that hydroboration can be efficiently applied to the postsynthetic modification (PSM) of the Sonogashira–Hagihara coupling-based microporous organic polymers (MOPs). Hollow MOPs (H-MOPs) were prepared by template synthesis through the Sonogashira–Hagihara coupling of tetra(4-ethynylphenyl)methane with 1,4-diiodobenzene. The H-MOPs were used as platforms in the PSM-based functionalization. The heat-treatment of H-MOPs in the presence of a neat pinacolborane reagent resulted in the successful addition of pinacolborane groups to the internal alkynes of H-MOPs, generating H-MOPs with pinacolboranes (H-MOP-BPs). The pinacolborane moieties in the H-MOP-BP were further converted to boronic acid groups. The resultant H-MOP-BAs were used as heterogeneous organocatalysts in the CO₂ fixation with epoxides to cyclic carbonates at ambient temperature (50 °C). Moreover, H-MOP-BAs could be recycled with retention of the catalytic performance in five successive reactions.



Microporous organic polymers (MOPs) are versatile materials that have been applied to various purposes including adsorbent, catalysis, and energy storage.^{1–4} Over the past decade, the functionalization methods of MOPs have been continually developed.⁵ Especially, the so-called postsynthetic modification (PSM) has been regarded as an efficient method for the functionalization of MOPs, because the MOPs prepared with relatively simple organic building blocks can be used for tailored functionalization.^{6–9}

In 2007, Cooper et al. showed that MOPs can be prepared by the Sonogashira–Hagihara coupling of multihaloarenes with multiethynylarenes.¹⁰ Since then, various MOPs have been prepared by the Sonogashira–Hagihara coupling of organic building blocks.^{11–13} The Sonogashira–Hagihara coupling-based MOPs are rich in alkyne moieties in their chemical structures. In 2012, Weber et al. showed that the thiol–yne click reaction can be applied for the PSM of the Sonogashira–Hagihara coupling-based MOPs.¹⁴ However, unfortunately, other examples of the PSM-based functionalization of the alkyne moieties in the Sonogashira–Hagihara coupling-based MOPs are quite limited.^{15–19} Thus, further explorations of PSM-based functionalization methods are required.

At present, boron is a very versatile element in organic syntheses.^{20,21} For example, organoboron compounds have been utilized not only as organocatalysts,^{22–29} but also as coupling partners of aryl halides in the Suzuki–Miyaura coupling reactions.³⁰ The Brown hydroboration of alkenes or alkynes is a powerful method of generating organoboron compounds.³¹ Thus, the hydroboration of the Sonogashira–

Hagihara coupling-based MOPs can be a very attractive approach for the preparation of functional MOPs. However, as far as we are aware, the hydroboration of the Sonogashira–Hagihara coupling-based MOPs has not been reported.

Recently, the chemical conversion of CO₂ to useful compounds has become a more and more important subject.³² For example, the CO₂ fixation with epoxides to cyclic carbonates has been extensively studied.³³ The cyclic carbonates have been used not only as electrolytes of batteries, but also as precursors of polymers.³³ From the aspect of energy, CO₂ conversion at ambient temperature is important to reduce the consumption of fossil fuels.

To accelerate the CO₂ conversions to cyclic carbonates, various metal-based heterogeneous catalysts have been developed.³⁴ On the other hand, heterogeneous organocatalysts have recently been studied for the CO₂ fixation with epoxides.^{35,36} However, most heterogeneous organocatalytic systems required high reaction temperatures (>100 °C) or long reaction times at ambient temperature (Tables S1 and S2 in the SI). Recently, Zhang and a co-worker reported that CO₂ can be converted to cyclic carbonates at 50 °C with molecular boronic acids.³⁷ However, as far as we are aware, boron molecule-based heterogeneous organocatalysts for the

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CO₂ conversion to cyclic carbonates have not been reported. In this work, we report the hydroboration of the Sonogashira–Hagihara coupling-based MOPs and the development of heterogeneous organocatalysts bearing boronic acids for the mild CO₂ fixation to cyclic carbonates.

Figure 1 shows the hydroboration of hollow MOPs (H-MOPs) to form H-MOPs bearing pinacolborane moieties (H-

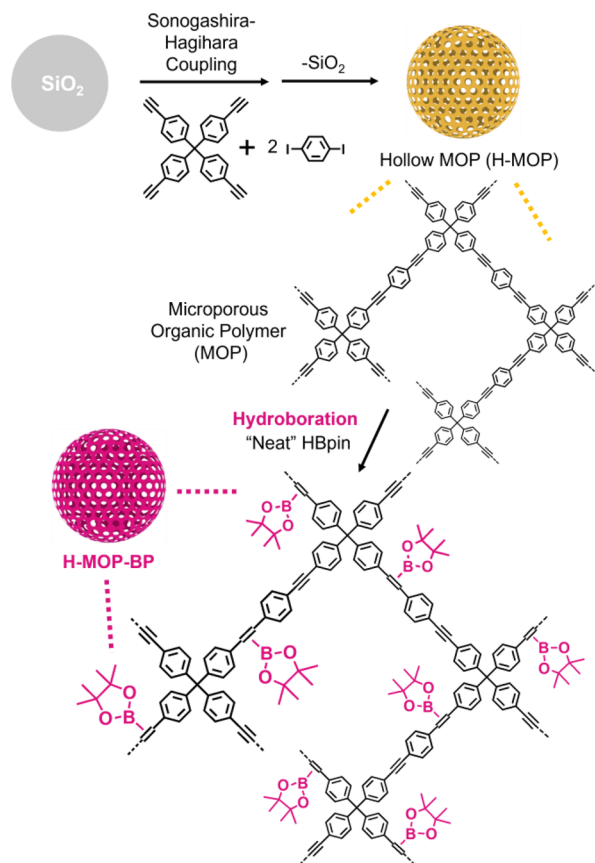


Figure 1. Postsynthetic modification of hollow MOPs (H-MOPs) by hydroboration with neat pinacolboranes (HBPin) to generate H-MOPs bearing pinacolboranes (H-MOP-BPs).

MOP-BPs). The H-MOPs were prepared using silica spheres as templates.³⁸ The Sonogashira–Hagihara coupling of tetra(4-ethynylphenyl)methane with 1,4-diiodobenzene in the presence of silica spheres resulted in the formation of SiO₂@MOPs. The silica etching from the SiO₂@MOPs generated the H-MOPs.

It was reported that pinacolborane groups can be added to diphenylacetylene (DPA) at 120 °C using a neat pinacolborane (HBPin) reagent.³⁹ According to the analysis of N₂ adsorption–desorption isotherm curves based on the Brunauer–Emmett–Teller (BET) theory, the H-MOPs showed a high surface area of 817 m²/g and a pore volume of 0.54 cm³/g. Considering the porosity of H-MOPs, the H-MOPs were heated with neat HBPin at 120 °C for 48 h to form H-MOP-BPs. With a fixed amount (50 mg) of H-MOPs, the amount of HBPin was increased gradually from 0.50 to 1.0 and 2.0 mL to form H-MOP-BP1, H-MOP-BP2, and H-MOP-BP3, respectively.

The addition of pinacolboranes to H-MOPs was characterized by solid state ¹³C NMR and infrared (IR) absorption spectroscopy (Figure 2a,b). The ¹³C NMR spectrum of H-

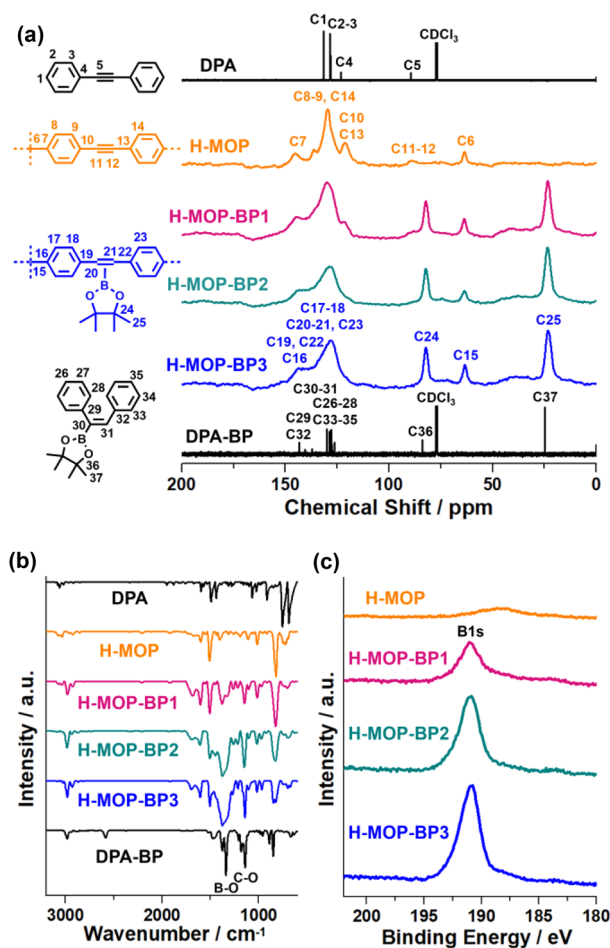


Figure 2. (a) Solid and solution state ¹³C NMR and (b) IR spectra of H-MOP, H-MOP-BPs, DPA, and DPA-BP. (c) XPS B 1s orbital spectra of H-MOP and H-MOP-BPs.

MOPs showed the ¹³C peaks of benzyl carbon and internal alkyne at 64 and 89 ppm, respectively. The aromatic ¹³C peaks of H-MOPs were observed at 121–146 ppm, matching well with those of MOPs prepared by the tetra(4-ethynylphenyl)methane and 1,4-diiodobenzene in the literature.⁹ In the ¹³C NMR spectra of H-MOP-BPs, the ¹³C peaks of the aliphatic groups of pinacol moieties appeared at 23 and 82 ppm, matching with the model pinacolborane adduct of DPA (Figure 2a).³⁹ As the amounts of a pinacolborane reagent increased, the ¹³C peaks of pinacolborane moieties gradually increased with a decrease of the ¹³C peaks of internal alkynes at 89 ppm, indicating that the amounts of pinacolborane moieties in H-MOP-BPs increased. The IR spectra of H-MOP-BPs showed the B–O and C–O vibration peaks at 1342 and 1141 cm⁻¹, respectively, indicating that the pinacol borane moieties were successfully added to H-MOPs (Figure 2b). In the X-ray photoelectron spectra (XPS) of H-MOP-BPs, the B 1s orbital peaks were observed at 191 eV, and their intensities gradually increased with an increase in the amounts of pinacolborane moieties (Figure 2c).

According to the inductively coupled plasma-optical emission spectrometry (ICP-OES), the amounts of pinacolborane moieties in H-MOP-BP1, H-MOP-BP2, and H-MOP-BP3 were analyzed to be 1.81, 3.22, and 3.46 mmol/g, respectively (Table S3 in the SI). The surface areas and the porosity of H-MOP-BPs were investigated through the analysis

of N_2 adsorption–desorption isotherm curves based on the BET theory. As the amounts of pinacolborane moieties in H-MOP-BPs increased, the surface areas gradually decreased from 817 (H-MOP) to 454 (H-MOP-BP1), 148 (H-MOP-BP2), and 137 m^2/g (H-MOP-BP3), respectively (Figure S1 and Table S3 in the SI). In addition, the pore volumes decreased from 0.54 cm^3/g (H-MOP) to 0.33 (H-MOP-BP1), 0.18 (H-MOP-BP2), and 0.17 cm^3/g (H-MOP-BP3), respectively.

Considering the retained high surface area and porosity of H-MOP-BP1, we studied its further modification to H-MOPs bearing boronic acids (H-MOP-BA) by the treatment with KHF_2 and $FeCl_3$ (Figure 3d). It was reported that the molecular DPA-BP can be converted to 1,2-diphenylvinylboronic acid by the treatment of KHF_2 and $FeCl_3$.⁴⁰ According to

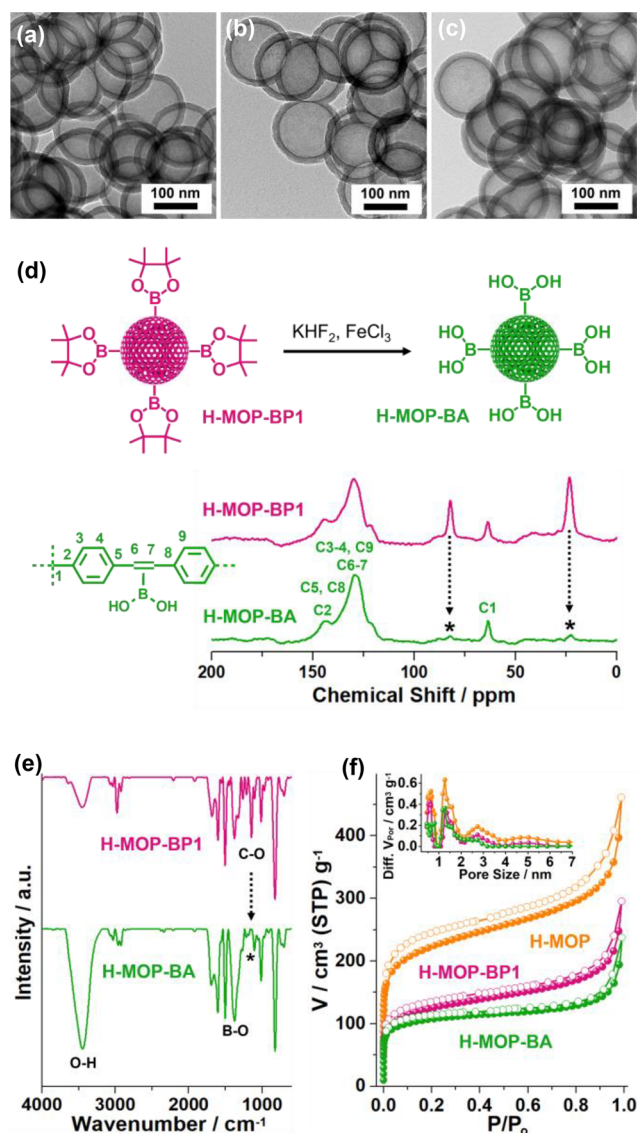


Figure 3. TEM images of (a) H-MOP, (b) H-MOP-BP1, and (c) H-MOP-BA. (d) A scheme of the H-MOP-BP1 conversion to H-MOP-BA and the corresponding solid state ^{13}C NMR spectra. (e) IR spectra of H-MOP-BP1 and H-MOP-BA. (f) N_2 adsorption–desorption isotherm curves obtained at 77 K and pore size distribution diagrams based on the DFT method of H-MOP, H-MOP-BP1, and H-MOP-BA.

the transmission electron microscopy (TEM), the H-MOPs showed a hollow shape with an average diameter of 162 nm and an average shell thickness of 15 nm (Figure 3a). The H-MOP-BP1 and H-MOP-BA completely retained the original hollow structure of H-MOP (Figure 3b,c). The conversion of H-MOP-BP1 to H-MOP-BA was characterized by the solid state ^{13}C NMR and IR spectroscopy (Figures 3d,e).

In the ^{13}C NMR spectrum of H-MOP-BA, the aliphatic ^{13}C peaks of pinacolboranes disappeared, indicating the successful conversion of pinacolboranes to boronic acids (Figure 3d). In the IR spectrum of H-MOP-BA, the C–O vibration peak of H-MOP-BP1 disappeared at 1141 cm^{-1} with an appearance of the O–H vibration peak at 3455 cm^{-1} (Figure 3e). The surface area and pore volume of H-MOP-BA were significantly retained with 399 m^2/g and 0.25 cm^3/g , respectively (Figure 3f and Table S3 in the SI). The content of boronic acids in H-MOP-BA was analyzed to be 1.25 mmol/g by ICP-OES. H-MOP, H-MOP-BPs, and H-MOP-BA were amorphous, matching with the features of MOPs in the literature (Figure S2 in the SI).¹ Thermogravimetric analysis showed that H-MOP-BA was stable up to 285 $^{\circ}C$ (Figure S3 in the SI).

Considering the existence of boronic acids, a high surface area, and porosity of H-MOP-BA, we studied its organocatalytic performance for mild CO_2 fixation to cyclic carbonates. Figures 4 and S4 and S5 in the SI and Table 1 summarize the results. As shown in Figure 4a and entries 1–4 in Table 1, the CO_2 fixation with epichlorohydrin to cyclic carbonates at 50 $^{\circ}C$ was much enhanced by H-MOP-BA (0.50

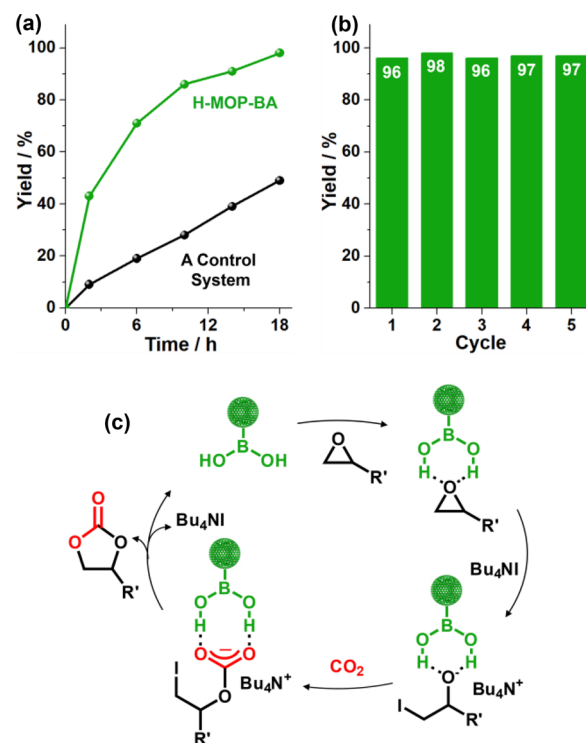
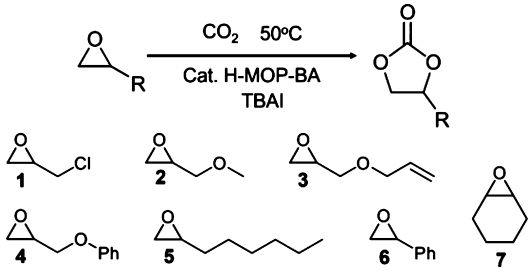


Figure 4. (a) CO_2 fixation (10 bar) with epichlorohydrin (4 mmol) to cyclic carbonates at 50 $^{\circ}C$ by H-MOP-BA (0.50 mol % boronic acid) and 1.0 mol % TBAI or 1.0 mol % TBAI (a control system). (b) Recyclability tests CO_2 fixation (10 bar) with 2-methoxymethylloxirane (4 mmol) to cyclic carbonates at 50 $^{\circ}C$ for 24 h by H-MOP-BA (0.50 mol % boronic acid) and 1.0 mol % TBAI. (c) A proposed catalytic cycle of the CO_2 fixation with epoxides to cyclic carbonates by a H-MOP-BA and TBAI.

Table 1. Catalytic CO₂ Fixation with Epoxides to Cyclic Carbonates at 50 °C by H-MOP-BA^a


entry	cat. (mol %)	cocat. (mol %)	epoxide	time (h)	yield ^b (%)
1		0.50	1	18	27
2	0.50	0.50	1	18	76
3		1.0	1	18	49
4	0.50	1.0	1	18	98 (88)
5	0.25	1.0	1	18	76
6	0.50	1.0	1	14	91
7	0.50	1.0	1	10	86
8	0.50	1.0	1	6	71
9	0.50	1.0	1	2	43
10	0.50	1.0	2	18	84
11	0.50	1.0	2	24	96 (81)
12	0.50	1.0	3	18	54
13	0.50	1.0	3	36	72
14	0.50	1.0	3	48	88 (80)
15	0.50	1.0	4	18	50
16	0.50	1.0	4	36	68
17	0.50	1.0	4	48	81 (80)
18	0.50	1.0	5	48	38 (32)
19	0.50	1.0	6	48	56 (49)
20	0.50	1.0	7	48	23 (12)
21 ^c	0.50	1.0	2	24	98
22 ^d	0.50	1.0	2	24	96
23 ^e	0.50	1.0	2	24	97
24 ^f	0.50	1.0	2	24	97

^aReaction conditions: CO₂ (10 bar), epoxide (4 mmol), H-MOP-BA (1.25 mmol boronic acids per cat. g), TBAI, 50 °C. ^bNMR yields (isolated yields are given in parentheses). ^cThe catalyst recovered from entry 11 was used. ^dThe catalyst recovered from entry 21 was used. ^eThe catalyst recovered from entry 22 was used. ^fThe catalyst recovered from entry 23 was used.

mol % boronic acids). While H-MOP-BA (0.50 mol % boronic acids), tetrabutylammonium iodide (TBAI, 1.0 mol %), and epichlorohydrin showed a 86% yield of cyclic carbonate at 50 °C for 10 h, the 1.0 mol % TBAI showed a 28% yield of cyclic carbonate (Figure 4a).

When the amount of H-MOP-BA decreased to 0.25 mol %, the yield of cyclic carbonate decreased to 76% (entry 5 in Table 1). When the reaction times were reduced to 14, 10, 6, and 2 h, the yields of cyclic carbonates gradually decreased to 91, 86, 71, and 43%, respectively (entries 6–9 in Table 1).

In control tests, H-MOP-BP1 (0.50 mol % pinacolborane) with 1.0 mol % TBAI showed a 56% yield of cyclic carbonate from epichlorohydrin at 50 °C for 18 h, which is similar to the case of 1.0 mol % TBAI. H-MOP-BA (0.50 mol % boronic acid) without TBAI showed no conversion of epichlorohydrin. These results indicate that both H-MOP-BA and TBAI are critical for the efficient CO₂ fixation to cyclic carbonates. When the reaction was conducted under 1 bar CO₂, H-MOP-BA (0.50 mol % boronic acid) and 1.0 mol % TBAI showed a 71%

yield of cyclic carbonate from epichlorohydrin at 50 °C for 18 h.

According to the XPS analysis, H-MOP, H-MOP-BP1, and H-MOP-BA showed residual Pd, Cu, and I, which has been well-known in the Pd catalyst-based MOP materials in the literature.⁴¹ The combination of H-MOP with TBAI showed the nearly same conversion of epichlorohydrin as the case of TBAI, indicating that the contributions of residual Pd, Cu, and I are minor in the CO₂ fixation to cyclic carbonates.

Next, various epoxides were investigated as the reaction partners of CO₂ (entries 10–20 in Table 1). While various epoxides with one substituent showed good conversions to cyclic carbonates, those with longer substituents required more reaction times. While the 2-(methoxymethyl)oxirane showed a 96% yield of cyclic carbonate at 50 °C after 24 h, 2-(allyloxymethyl)oxirane, 2-(phenoxymethyl)oxirane, and 2-hexyloxirane showed yields of 88, 81, and 38% at 50 °C after 48 h, indicating that the sizes of epoxides are a critical factor in the catalytic action of boronic acids in the micropores (entries 10–18 in Table 1). When the reaction temperature was increased to 100 °C, the yield of cyclic carbonate from 2-hexyloxirane increased to 97% after 48 h. The styrene oxide and cyclohexene oxide showed the low yields of 56 and 23% yields, respectively, due to the reduced reactivities of epoxides (entries 19–20 in Table 1). When the reaction temperature was increased to 100 °C, the yields of cyclic carbonates from styrene oxide and cyclohexene oxide increased to 97 and 57%, respectively.

The recyclability of H-MOP-BA was investigated. In the five successive recycled reactions, the catalytic performance of H-MOP-BA was retained with the yields in the range of 96–98% (Figure 4b and entries 11 and 21–24 in Table 1). According to TEM and XPS analysis, the recovered H-MOP-BA after the five successive reactions showed retention of the original hollow structure and the chemical surrounding of boronic acid species (Figure S5 in the SI). The reaction mechanism can be suggested as follows (Figure 4c).^{37,42} First, the boronic acid groups of H-MOP-BA activate epoxides through the formation of hydrogen bonding. Second, the activated epoxides are attacked by iodides of TBAI. The generated oxide moieties can form hydrogen bonding with the boronic acid. Third, carbon dioxide can be inserted to form carboxylate moieties, which form hydrogen bonding with the boronic acids of H-MOP-BA. Finally, the formation of cyclic carbonates induces the regeneration of TBAI and H-MOP-BAs.

The catalytic performance of H-MOP-BA was superior to those of heterogeneous organocatalytic systems working at ambient temperature in the literature (Table S2 in the SI).^{43–51} The heterogeneous organocatalysts in the literature showed CO₂ conversion with epichlorohydrin to cyclic carbonates at 40–60 °C with TONs of 26–61 and TOFs of 0.45–5 h^{−1}.^{43–51} Under similar reaction conditions, H-MOP-BA in this work showed CO₂ conversion with epichlorohydrin to cyclic carbonates at 50 °C with a TON of 196 and a TOF of 11 h^{−1}. In our control tests, H-MOP-BA showed enhanced catalytic performance, compared with the corresponding nonhollow MOP-BA catalyst (Figures S6–S7 in the SI). It is noteworthy that the hollow structures of heterogeneous catalysts are beneficial in the catalytic performance due to the facilitated mass transfer of substrates and the efficient utilization of catalytic sites.^{1,52}

In addition, H-MOP-BA showed superior catalytic performance to the boronic acid-based homogeneous catalysts (Figure

S7 in the SI).³⁷ Recently, Zhang et al. showed that various aromatic boronic acids can catalyze CO₂ conversions with epoxides to cyclic carbonates through the formation of hydrogen bonding.³⁷ When epichlorohydrin was used as a substrate in the presence of 10 mol % 2,6-dimethylphenylboronic acid and 5 mol % TBAI, the reaction with 10 bar CO₂ showed a 96% yield of a cyclic carbonate at 50 °C for 7 h, corresponding to a TON of 9.6 and a TOF of 1.4 h⁻¹, respectively. In comparison, the heterogeneous H-MOP-BA catalyst (0.50 mol % boronic acid) in this work showed the 98% yield of a cyclic carbonate with epichlorohydrin, 10 bar CO₂, and 1.0 mol % TBAI at 50 °C for 18 h, corresponding to a TON of 196 and a TOF of 11 h⁻¹, respectively. In our own comparison studies, 1,2-diphenylvinylboronic acid (DPA-BA, 0.50 mol %) showed the 72% yield of a cyclic carbonate with epichlorohydrin, 10 bar CO₂, and 1.0 mol % TBAI at 50 °C for 18 h. We suggest that while aromatic boronic acids can form aggregates such as dimers or trimers, the microporous network of H-MOP-BA can serve as an efficient platform to distribute the boronic acid groups, which can be a reason for the good catalytic performance.

In conclusion, this work shows that H-MOPs can be successfully postfunctionalized by hydroboration. The appropriate addition of pinacolboranes to the internal alkynes in H-MOPs resulted in the retention of a high surface area (454 m²/g) and porosity. Even after the further conversion of pinacolboranes of H-MOP-BP1 to H-MOP-BA, a high surface area of 399 m²/g and a pore volume of 0.25 cm³/g were retained. Through the formation of hydrogen bonding between the boronic acids of H-MOP-BA and oxygens in epoxides, the epoxides could be activated. The H-MOP-BA showed good performance as a heterogeneous organocatalyst in the CO₂ fixation at 50 °C with epoxides to cyclic carbonates. We believe that the PSM method in this work can be applied to the various tailored functionalization of MOPs.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmacrolett.2c00385>.

Experimental procedures, additional characterization data of MOP materials, and a comparison table of catalytic performance (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Seung Uk Son – Department of Chemistry, Sungkyunkwan University, Suwon 16419, Korea; orcid.org/0000-0002-4779-9302; Email: sson@skku.edu

Authors

Sohee Bang – Department of Chemistry, Sungkyunkwan University, Suwon 16419, Korea

June Young Jang – Department of Chemistry, Sungkyunkwan University, Suwon 16419, Korea

Yoon-Joo Ko – Laboratory of Nuclear Magnetic Resonance, NCIRF, Seoul National University, Seoul 08826, Korea

Sang Moon Lee – Korea Basic Science Institute, Daejeon 34133, Korea

Hae Jin Kim – Korea Basic Science Institute, Daejeon 34133, Korea; orcid.org/0000-0002-1960-0650

Complete contact information is available at:

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Author Contributions

[§]These authors contributed equally to this work. CRediT: Seung Uk Son conceptualization (lead), formal analysis (lead), project administration (lead), supervision (lead), writing-original draft (lead), writing-review & editing (lead); Sohee Bang formal analysis (equal), investigation (equal), methodology (equal); June Young Jang formal analysis (equal), investigation (equal), methodology (equal); Yoon-Joo Ko investigation (supporting), methodology (supporting); Sang Moon Lee investigation (supporting), methodology (supporting); Hae Jin Kim formal analysis (equal), supervision (supporting).

Notes

The authors declare no competing financial interest.

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