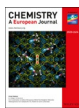


## Porous Catalysts

Iron Coordination to Hollow Microporous Metal-Free Disalphen Networks: Heterogeneous Iron Catalysts for CO<sub>2</sub> Fixation to Cyclic Carbonates\*\*Kyoungil Cho,<sup>[a]</sup> Sang Moon Lee,<sup>[b]</sup> Hae Jin Kim,<sup>[b]</sup> Yoon-Joo Ko,<sup>[c]</sup> Eun Joo Kang,<sup>\*,[d]</sup> and Seung Uk Son<sup>\*,[a]</sup>

**Abstract:** This work shows that a hollow and microporous metal-free *N,N'*-phenylenebis(salicylideneimine) (salphen) network (H-MSN) can be engineered by Sonogashira coupling of [tetraiodo{di(Zn-salphen)}] building blocks with 1,4-diethynylbenzene in the presence of silica templates and by successive Zn and silica etching. Iron(III) ions could be incorporated into the H-MSN to form hollow and microporous Fe-disalphen networks (H-MFeSN) with enhanced microporosity and surface area. The H-MFeSN showed efficient catalytic performance and recyclability in the CO<sub>2</sub> conversion to cyclic carbonates.

Iron is the fourth most abundant element in the Earth's crust.<sup>[1]</sup> In the past, there were catalytic applications of iron, such as the Haber process.<sup>[2]</sup> During the last several decades, various transition metals and ligands have been developed and applied to catalytic reactions. Recently, based on the accumulated knowledge in the transition metal catalysis, there has been renewed interest in iron catalysis.<sup>[3]</sup>

Chemical fixation of CO<sub>2</sub> is an important research subject.<sup>[4]</sup> For example, cyclic carbonates have been prepared by the reaction of CO<sub>2</sub> with epoxides.<sup>[5]</sup> The cyclic carbonates have been used for the synthesis of polymers and the electrolytes of batteries.<sup>[5]</sup> Although numerous catalytic systems,<sup>[5]</sup> including iron catalysts,<sup>[6]</sup> have been developed for this conversion, heterogeneous iron catalysts are relatively rare.<sup>[7]</sup> Recently, we reported

efficient and homogeneous iron catalysts for CO<sub>2</sub> conversion to cyclic carbonates.<sup>[8]</sup> However, the system suffered from the mixing of catalysts with the resultant cyclic carbonates. Thus, more studies on the efficient heterogeneous iron catalysts are required.

Recently, various microporous organic network (MON) materials have been prepared by the coupling of building blocks, showing chemical stability and high surface areas.<sup>[9]</sup> Thus, the MON can be a good platform of catalytic systems. There have been reports on the development of catalysts based on MONs.<sup>[10]</sup> However, iron-based MON catalysts have been relatively less explored.<sup>[11]</sup>

Our research group has studied the morphological engineering of MONs.<sup>[12]</sup> For example, by using various hard templates, we have engineered hollow MON materials.<sup>[13]</sup> The hollow morphologies show benefits, such as shortened diffusion pathways of substrates, enhancing the catalytic function of MON materials.<sup>[14]</sup> If a hollow MON material with metal-free coordination sites is prepared, it can be a versatile platform to develop heterogeneous transition metal catalysts. In this work, we report the synthesis of a hollow and microporous metal-free *N,N'*-phenylenebis(salicylideneimine) (salphen) network (H-MSN) and the complexation of irons to form the hollow and microporous Fe-disalphen catalyst (H-MFeSN). The catalytic performance in the CO<sub>2</sub> conversion to cyclic carbonates is also investigated.

Figure 1 shows the synthetic schemes of H-MSN and H-MFeSN. First, we designed the [tetraiodo{di(Zn-salphen)}] building block (denoted as A in Figure 1), which is a new compound and characterizable by NMR and HR-MS. When we used the [tetraiodo{di(metal-free salphen)}] building block for the synthesis of H-MSN, the Pd and Cu catalysts were trapped in the disalphen ligands, resulting in the failure of catalytic networking for the MON. When we used the [tetraiodo{di(Fe-salphen)}] building block for the synthesis of H-MFeSN, the Fe ions were etched through a silica etching process. In addition, the chemical structure of the [tetraiodo{di(Fe-salphen)}] building block could not be characterized by NMR studies due to the paramagnetic nature. Thus, we conducted the Sonogashira coupling of the [tetraiodo{di(Zn-salphen)}] building block with 1,4-diethynylbenzene in the presence of silica spheres (an average diameter of 255 nm). After silica etching with a HF solution, H-MSN was obtained. The reaction of H-MSN with FeCl<sub>3</sub> in methanol resulted in H-MFeSN.

The morphologies of H-MSN and H-MFeSN were investigated by scanning (SEM) and transmission electron microscopy

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[\*\*] salphen = *N,N'*-phenylenebis(salicylideneimine).

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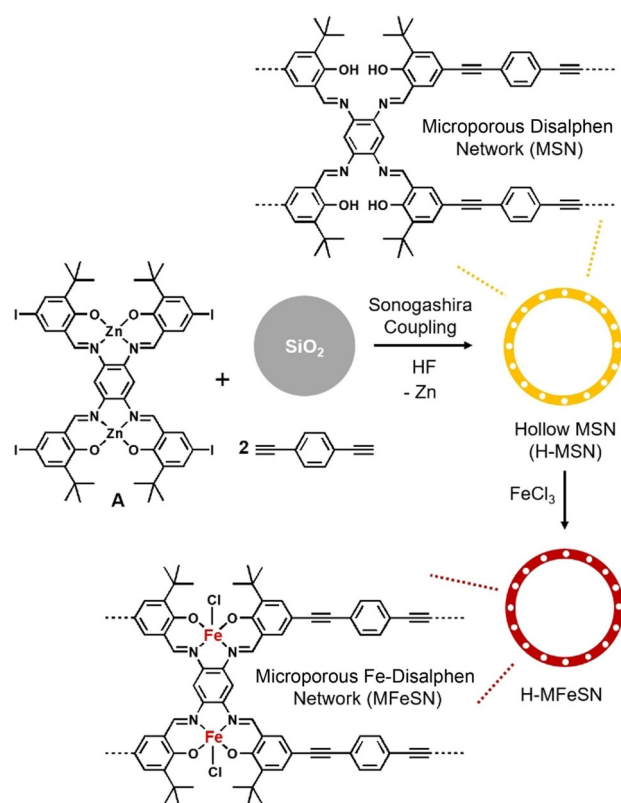


Figure 1. Synthesis of H-MSN and H-MFeSN.

(TEM; Figure 2a–f). The SEM and TEM images of H-MSN showed its hollow morphology with a diameter of 352 nm and a shell thickness of 48 nm (Figure 2a–c). After Fe complexation to H-MSN, the resultant H-MFeSN showed no change from the original hollow morphology (Figure 2d–f). The chemical surroundings of elements were investigated by X-ray photoelectron spectroscopy (XPS). While the N 1s orbital peak of H-MSN that appeared at 399.2 eV shifted slightly to 399.1 eV in the XPS spectrum of H-MFeSN, the O 1s peak of H-MSN at 532.6 eV shifted significantly to 531.3 eV (H-MFeSN) through Fe complexation, matching well with the conventional observations of metal–phenolate species (Figure 2g).<sup>[15]</sup> The Zn 2p orbital peaks were not observed in the range of approximately 1010–1060 eV in the XPS spectra of H-MSN and H-MFeSN, supporting the assumption that the Zn ions were completely etched. The Fe 2p<sub>1/2</sub> and Fe 2p<sub>3/2</sub> orbital peaks of H-MFeSN were observed at 724.8 and 711.2 eV, respectively, matching well with those of the Fe<sup>III</sup>–salen complexes reported in the literature.<sup>[16]</sup> In the elemental analysis of H-MSN by energy dispersive X-ray spectroscopy (EDS), Zn was not detected (Figure 2h). In contrast, the EDS analysis of H-MFeSN indicated that Fe was successfully incorporated into H-MSN.

According to the analysis of N<sub>2</sub> adsorption–desorption isotherm curves, surprisingly, the H-MFeSN showed a higher surface area of 469 m<sup>2</sup> g<sup>−1</sup> and a greater micropore volume of 0.13 cm<sup>3</sup> g<sup>−1</sup> than H-MSN which showed a surface area of 290 m<sup>2</sup> g<sup>−1</sup> and a micropore volume of 0.06 cm<sup>3</sup> g<sup>−1</sup> (Figure 3a,b).

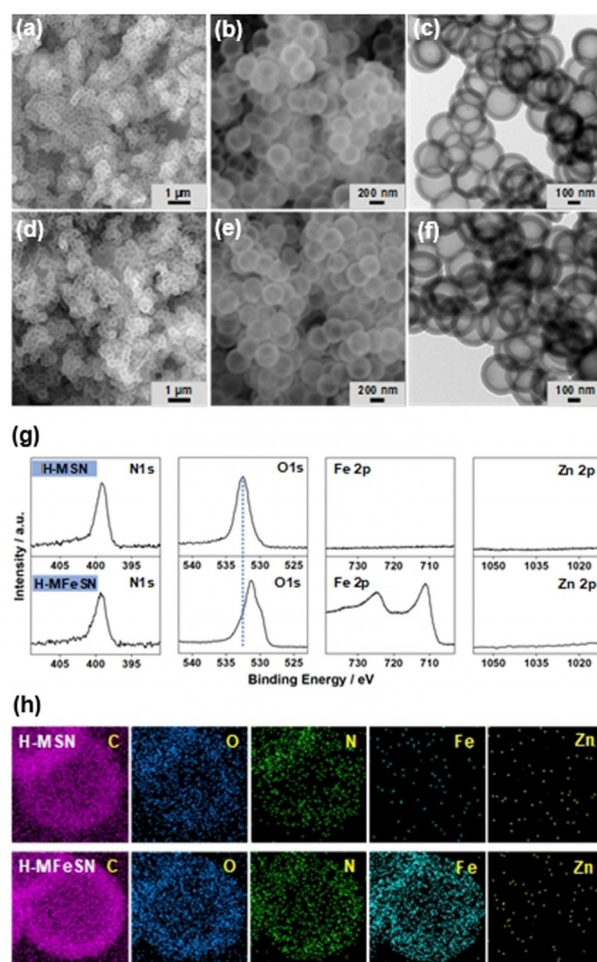
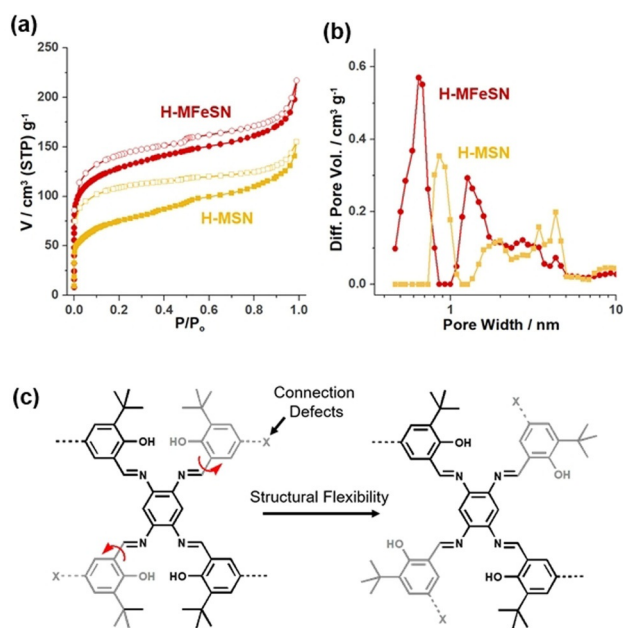


Figure 2. SEM images of H-MSN (a,b) and H-MFeSN (d,e). TEM images of H-MSN (c) and H-MFeSN (f). XPS spectra (g) and EDS elemental mapping images (h) of H-MSN and H-MFeSN.

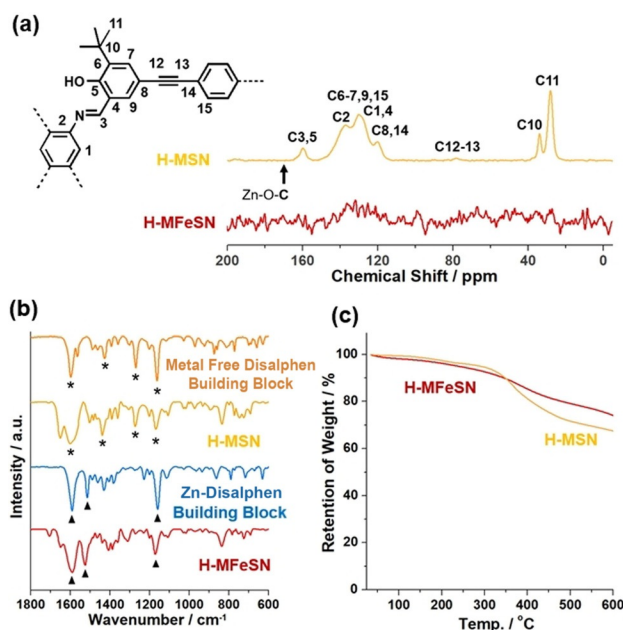
Below, we elaborate on the reasons for this. In the conventional synthesis of MON by Sonogashira coupling of building blocks, the building block should be sufficiently rigid to form microporous networks. If the building blocks have rotational flexibility, the microporosity of MON can be reduced through the stacking of chemical moieties in the MON. While Fe–disalphen moieties in H-MFeSN can form a relatively rigid geometry, the metal-free disalphen in the H-MSN can have structural flexibility between imine bonds and aromatic substituents, which can be a reason for the reduced microporosity and surface area of H-MSN (Figure 3c). The MON materials prepared by Sonogashira coupling are rich in connection defects; this can facilitate the structural flexibility. We suggest that the multiple adsorption processes in the adsorption isotherm of H-MSN and the different desorption process in the desorption isotherm with a big hysteresis may originate from structural flexibility. In contrast, through Fe complexation to disalphen molecules, the structure of H-MFeSN becomes more rigid and the microporosity enhanced.

The chemical structures of H-MSN and H-MFeSN were further characterized by solid-state <sup>13</sup>C NMR and IR absorption



**Figure 3.** N<sub>2</sub> adsorption-desorption isotherm curves at 77 K (a) and pore size distribution diagrams (b; based on the DFT method) of H-MSN and H-MFeSN. The suggested structural flexibility of H-MSN (c).

studies (Figure 4a,b). The solid-state <sup>13</sup>C NMR spectrum of H-MSN showed <sup>13</sup>C peaks at 28.1, 33.6, 80, and ca. 114.4–145.7 ppm, corresponding to methyl groups, tertiary aliphatic carbons, alkynes, and aromatic groups, respectively (Figure 4a). The <sup>13</sup>C peaks of the imine carbon and phenolic carbon (aromatic carbon neighboring to OH group) of H-MSN were observed at 159.6 ppm. It is noteworthy that the <sup>13</sup>C peaks of Zn-



**Figure 4.** Solid-state <sup>13</sup>C NMR spectra (a) of H-MSN and H-MFeSN. IR spectra (b) of metal-free disalphen building block, H-MSN, Zn-disalphen building block, and H-MFeSN. TGA curves (c) of H-MSN and H-MFeSN.

O-C in the Zn-salphen are known to appear at about 170 ppm.<sup>[17]</sup> No <sup>13</sup>C peak was detected in this region in the <sup>13</sup>C NMR spectrum of H-MSN, supporting the theory of metal-free disalphen moieties in H-MSN. A solid-state <sup>13</sup>C NMR study to H-MFeSN, did not provide a meaningful spectrum, due to the paramagnetic nature of the Fe<sup>3+</sup> ions (Figure 4a).

In the IR spectrum, the tetraiodo metal-free disalphen building blocks show four main vibration peaks at 1600 (C=N), 1427, 1269 (C–O), and 1164 cm<sup>-1</sup> (indicated by asterisks in Figure 4b). In comparison, the tetraiodo Zn-disalphen building block shows three main vibration peaks at 1594 (C=N), 1513, and 1158 cm<sup>-1</sup> (indicated by triangles in Figure 4b), due to the shift of the C–O vibration through metal coordination.<sup>[18]</sup> As expected, the IR spectrum of H-MSN shows four main vibration peaks at 1600 (C=N), 1435, 1270 (C–O), and 1165 cm<sup>-1</sup>, resembling that of the tetraiodo metal-free disalphen compound. The IR spectrum of H-MFeSN shows three main vibration peaks at 1594 (C=N), 1524, and 1168 cm<sup>-1</sup>, resembling that of the tetraiodo Zn-disalphen building block. According to combustion elemental analysis, the N contents in the H-MSN and H-MFeSN were analyzed to be 3.37 and 2.79 wt%, respectively, corresponding to a salphen content of 1.20 and 0.996 mmol g<sup>-1</sup>. Powder X-ray diffraction studies revealed that H-MSN and H-MFeSN are amorphous, which is a conventional feature of MON materials prepared by Sonogashira coupling<sup>[19]</sup> (Figure S1 in the Supporting Information). Thermogravimetric analysis (TGA) showed that H-MSN and H-MFeSN are stable up to about 230 and 220 °C, respectively (Figure 4c).

Iron-salen complexes have shown promising performance as a Lewis acid catalyst in various organic transformations.<sup>[20]</sup> Considering the microporosity and the thermal stability of H-MFeSN, we studied its catalytic performance in the CO<sub>2</sub> conversion to cyclic carbonates. Table 1 and Figure 5 summarize the results.

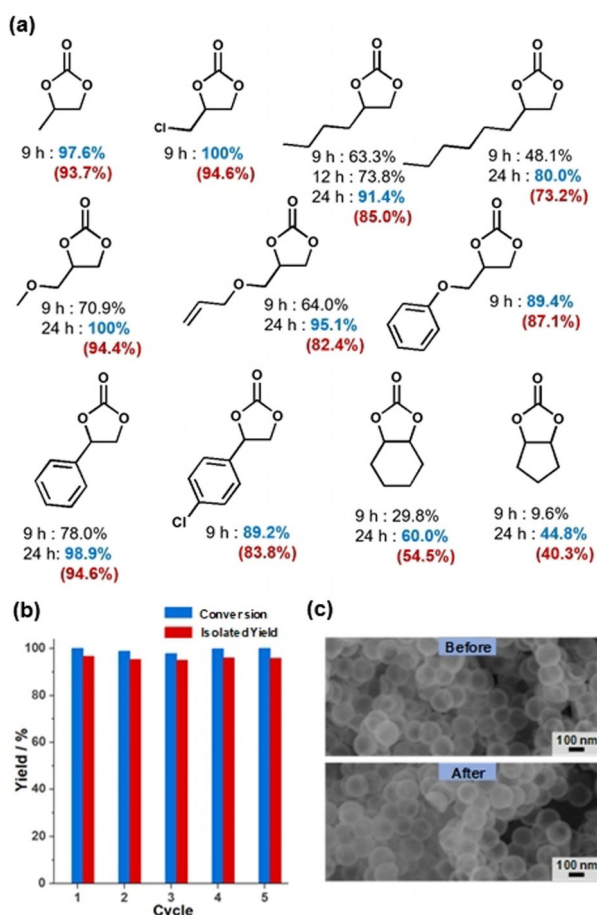
Through a literature survey, we figured out that most reactions of CO<sub>2</sub> conversion to cyclic carbonates by iron catalysts were conducted at 100 °C under 20 bar CO<sub>2</sub>.<sup>[6–8]</sup> In this regard,

**Table 1.** Catalytic performance of H-MFeSN in the CO<sub>2</sub> conversion with propylene oxide (PO) to cyclic carbonates.<sup>[a]</sup>

| Entry | [Mol %] | T [°C] | Time [h] | Yield [%] <sup>[b]</sup> | TON  | TOF [h <sup>-1</sup> ] |
|-------|---------|--------|----------|--------------------------|------|------------------------|
| 1     | 0.0250  | 100    | 3        | 26.5                     | 1060 | 353                    |
| 2     | 0.0250  | 100    | 6        | 45.1                     | 1800 | 301                    |
| 3     | 0.0250  | 100    | 9        | 57.5                     | 2300 | 256                    |
| 4     | 0.0250  | 100    | 12       | 67.8                     | 2710 | 226                    |
| 5     | 0.0250  | 100    | 24       | 78.9                     | 3160 | 132                    |
| 6     | 0.0500  | 100    | 1.5      | 50.8                     | 1020 | 677                    |
| 7     | 0.0500  | 100    | 3        | 82.1                     | 1640 | 547                    |
| 8     | 0.0500  | 100    | 6        | 94.1                     | 1880 | 314                    |
| 9     | 0.0500  | 100    | 9        | 97.6                     | 1950 | 217                    |
| 10    | 0.0500  | 100    | 12       | 100                      | 2000 | 166                    |
| 11    | 0.0500  | 40     | 12       | 25.8                     | 516  | 43                     |
| 12    | 0.0500  | 60     | 12       | 52.8                     | 1060 | 88                     |
| 13    | 0.0500  | 80     | 12       | 76.4                     | 1530 | 127                    |

[a] Reaction conditions: CO<sub>2</sub> (20 bar), H-MFeSN (10.8 mg for 0.0250 mol %, 21.5 mg for 0.0500 mol %), tetrabutylammonium bromide (TBABr, 13.8 mg for 0.100 mol %, 27.6 mg for 0.200 mol %), PO (42.9 mmol), neat. [b] Conversion yield based on <sup>1</sup>H NMR studies.





**Figure 5.** The yields (a) of cyclic carbonates (reaction conditions: 20 bar CO<sub>2</sub>, 0.0500 mol% H-MFeSN, 0.200 mol% TBABr, 42.9 mmol epoxides, 100 °C, neat. Blue numbers: conversion yields; red numbers: isolated yields by column chromatography). Recyclability (b) of 0.0500 mol% H-MFeSN (reaction conditions: 100 °C, 42.9 mmol PO, 20 bar CO<sub>2</sub>, 0.200 mol% TBABr, 12 h, blue: conversion yields, red: isolated yields of products). SEM images (c) of H-MFeSN before and after five successive catalytic reactions.

we scanned the experimental conditions of the catalytic reactions at 100 °C under 20 bar CO<sub>2</sub> (Entries 1–10 in Table 1). When we used 0.0250 mol% H-MFeSN and 0.100 mol% tetrabutylammonium bromide (TBABr) with propylene oxide (PO) at 100 °C, the yields of cyclic carbonate gradually increased to 67.8 and 78.9% after 12 and 24 h, respectively, corresponding to TONs of 2710 (TOF: 226 h<sup>-1</sup>) and 3160 (TOF: 132 h<sup>-1</sup>; entries 1–5 in Table 1). When we increased the amount of H-MFeSN to 0.0500 mol%, with 0.200 mol% TBABr and PO at 100 °C, the yield of cyclic carbonate reached 82.1 and 94.1% after 3 and 6 h, respectively, corresponding to TONs of 1640 (TOF: 547 h<sup>-1</sup>) and 1880 (TOF: 314 h<sup>-1</sup>; entries 6–8 in Table 1). After 9 and 12 h, the yields further increased to 97.6 and 100%, respectively, corresponding to TONs of 1950 (TOF: 217 h<sup>-1</sup>) and 2000 (TOF: 166 h<sup>-1</sup>; entries 9–10 in Table 1).

When the reaction temperatures were decreased to 80, 60, and 40 °C, the yields of cyclic carbonates after 12 h were 76.4, 52.8, and 25.8%, respectively, corresponding to TONs of 1528 (TOF: 127 h<sup>-1</sup>), 1056 (TOF: 88 h<sup>-1</sup>), and 516 (TOF: 43 h<sup>-1</sup>; entries 11–13 in Table 1). When we used 0.200 mol% TBABr,

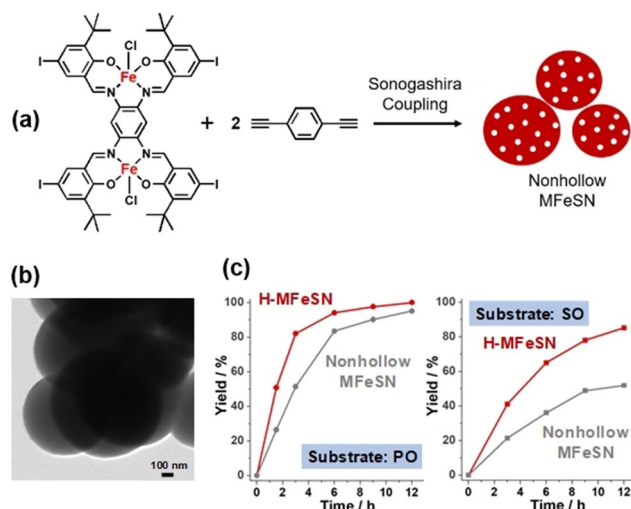
20 bar CO<sub>2</sub>, and PO at 100 °C in the absence of H-MFeSN, the yields of cyclic carbonates were 33.1 and 36.3% after 9 and 12 h, respectively, supporting the catalytic action of H-MFeSN (Figure S2 in the Supporting Information).

Next, we scanned the range of epoxide substrates and Figure 5a summarizes the results. For the longer alkyl substituents of the epoxides, the reaction times need for > 80% yields increase. When we used PO, 2-butyl-oxirane, and 2-hexyl-oxirane, the yields of cyclic carbonates after 9 h at 100 °C were 97.6, 63.3, and 48.1%, respectively. After 24 h, the yields of cyclic carbonates obtained from 2-butyl-oxirane and 2-hexyl-oxirane reached 91.4 and 80.0%, respectively. The epoxides with ether substituents also resulted in good conversions to cyclic carbonates. When we used 2-methoxymethyl-oxirane and 2-allyloxymethyl-oxirane, the yields of cyclic carbonates after 9 h at 100 °C were 70.9 and 64.0%, respectively. After 24 h, the yields of cyclic carbonates obtained from 2-methoxymethyl-oxirane and 2-allyloxymethyl-oxirane reached 100 and 95.1%, respectively. The epoxides with aromatic substituents showed good conversions to cyclic carbonates. When we used 2-phenyl-oxirane (styrene oxide, SO), 2-(4-chlorophenyl)-oxirane, and 2-phenoxy-methyl-oxirane, the yields of corresponding cyclic carbonates obtained after 9 h at 100 °C were 78.0, 89.2, and 89.4%, respectively. After 24 h, the cyclic carbonate of SO showed a yield of 98.9% (an isolated yield of 94.6%). In contrast, cyclohexene oxide and cyclopentene oxide were relatively poor substrates, yielding 60.0 and 44.8% of cyclic carbonates after 24 h at 100 °C.

Considering the thermal stability of H-MFeSN (Figure 4c), we tested the recyclability. H-MFeSN could be recovered by centrifugation and reused after simple washing. As shown in Figure 5b, the H-MFeSN maintained the catalytic performance in the five successive reactions of CO<sub>2</sub> with PO, yielding 100, 98.8, 97.8, 99.8, and 100% of cyclic carbonates. According to the SEM and IR studies, the H-MFeSN recovered after five successive reactions shows complete retention of the original hollow morphology and chemical structure (Figure 5c and S3 in the Supporting Information).

In our recent report, homogenous iron catalysts showed TONs of 184–380 with TOFs of 15–32 h<sup>-1</sup> for the SO conversion to cyclic carbonates (yields of 92–95%) at 100 °C.<sup>[8]</sup> Also, it is noteworthy that a recently reported heterogeneous iron catalyst showed a TON of 57.2 with a TOF of 5.72 h<sup>-1</sup> for the SO conversion to cyclic carbonate (a yield of 92%) at 100 °C.<sup>[7]</sup> In comparison, the H-MFeSN showed a TON of 1980 with a TOF of 82.4 h<sup>-1</sup> for the SO conversion to cyclic carbonate (a yield of 98.9%) at 100 °C. According to a recent review<sup>[21]</sup> and our literature survey,<sup>[6]</sup> homogeneous iron catalysts show TONs of 80–3480 with TOFs of 40–2733 h<sup>-1</sup> for the PO conversion to cyclic carbonates (yields ≥ 74%) at 100 °C (Table S1 in the Supporting Information). In comparison, the heterogeneous H-MFeSN catalyst shows TONs of 1640–3160 with TOFs of 132–547 h<sup>-1</sup> for the PO conversion to cyclic carbonates (yields ≥ 78.9%) at 100 °C. In this regard, H-MFeSN is a promising heterogeneous iron catalyst for the CO<sub>2</sub> conversion to cyclic carbonates and its excellent performance is attributable to the hollow morphology and microporosity.

To investigate the morphology effect of H-MFeSN, we prepared nonhollow MFeSN as a control system without using silica templates (Figure 6a).



**Figure 6.** Synthetic scheme (a) and TEM image (b) of nonhollow MFeSN (for SEM images of nonhollow MFeSN, see Figure S3 in the Supporting Information). Catalytic performance (c) of H-MFeSN and nonhollow MFeSN in the CO<sub>2</sub> conversion to cyclic carbonates (reaction conditions: 0.0500 mol% catalysts, 20 bar CO<sub>2</sub>, 0.200 mol% TBABr, 42.9 mmol epoxides, 100 °C, neat).

SEM and TEM analysis showed that the nonhollow MFeSN has irregular morphologies with a broad size range of 200 nm to about 1  $\mu$ m (Figures 6b and S3 in the Supporting Information). The surface area of nonhollow MFeSN was measured to be 450 m<sup>2</sup>g<sup>-1</sup> (c.f. H-MFeSN: 469 m<sup>2</sup>g<sup>-1</sup>). The N content of the nonhollow MFeSN was analyzed to be 3.56 wt% (salphen content = 1.28 mmol g<sup>-1</sup>). Whereas 0.0500 mol% H-MFeSN produced cyclic carbonates from PO with 50.8 and 82.1% yields after 1.5 and 3 h at 100 °C, respectively; 0.0500 mol% nonhollow MFeSN produced the cyclic carbonates with 26.4 and 51.4% yields, respectively (Figure 6c). In the cases of SO, whereas H-MFeSN produced cyclic carbonates with 78.0 and 85.2% yields after 9 and 12 h at 100 °C, respectively, the nonhollow MFeSN produced cyclic carbonates with 48.9 and 51.9% yields, respectively. (Figure 6c) These results indicate that the hollow morphology of H-MFeSN is beneficial in the catalytic performance due to the reduced diffusion pathways of substrates.

In conclusion, the formation of MONs using new [tetraiodo{di(Zn-salphen)}] building blocks in the presence of silica templates and successive silica etching resulted in H-MSN bearing metal-free disalphen moieties. Fe<sup>III</sup> complexation resulted in a microporous iron catalysts (H-MFeSN), which showed excellent catalytic performance for CO<sub>2</sub> conversion to cyclic carbonates with TONs of 2960–3800 (TOFs of 135–213 h<sup>-1</sup>) for PO (yields  $\geq$  74%) and a TON of 1980 (TOF of 165 h<sup>-1</sup>) for SO (a yield of 98.9%) at 100 °C. We believe that various metals can be coordinated to H-MSN to give new catalysts.

## Experimental Section

### General information

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on 400 MHz and 500 MHz Varian spectrometers. HR-MS spectra were obtained on a JEOL JMS 700. SEM, TEM, and EDS-elemental mapping were obtained by a JSM6700F and a JEOL 2100F. XPS spectra were obtained on a Thermo VG spectrometer. N<sub>2</sub> isotherm curves were obtained at 77 K by a Micromeritics ASAP2020. Pore size distributions were analyzed by DFT. Solid-state <sup>13</sup>C NMR spectra were obtained at the CP/TOSS mode on a 500 MHz Bruker ADVANCE II NMR spectrometer. IR spectra were obtained on a Bruker VERTEX 70 FT-IR spectrometer. TGA curves were obtained on a Seiko Exstar 7300. Elemental analysis was conducted on a CE EA1110 analyzer. Powder X-ray diffraction studies were conducted on a Rigaku MAX-2200.

### Synthesis of [tetraiodo{di(Zn-salphen)}] building block

3-(*tert*-Butyl)-2-hydroxy-5-iodobenzaldehyde was prepared by synthetic procedures reported in the literature.<sup>[22]</sup> For the preparation of [tetraiodo{di(metal-free salphen)}], 1,2,4,5-benzenetetraamine tetrahydrochloride (1.0 g, 3.5 mmol), 3-(*tert*-butyl)-2-hydroxy-5-iodobenzaldehyde (4.7 g, 16 mmol), and methanol (120 mL) were added to a flame-dried 250 mL Schlenk flask. The reaction mixture was stirred at 90 °C for 2 h. After being cooled to room temperature, an orange solid was separated by filtration, washed with cold methanol, and dried under vacuum. Characterization data of [tetraiodo{di(metal-free salphen)}]: yield: 92%; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 13.56 (s, 4H), 8.66 (s, 4H), 7.62 (s, 4H), 7.60 (s, 4H), 7.16 (s, 2H), 1.41 ppm (s, 36H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 163.2, 160.6, 158.2, 139.6, 138.9, 121.1, 111.1, 80.0, 35.2, 29.2 ppm; HR-MS: *m/z* calcd. for C<sub>50</sub>H<sub>55</sub>N<sub>4</sub>O<sub>4</sub>I<sub>4</sub> [M+H]<sup>+</sup>: 1283.0402; found: 1283.0398.

For the preparation of the [tetraiodo{di(Zn-salphen)}] building block, [tetraiodo{di(metal-free salphen)}] (1.0 g, 0.78 mmol) and chloroform (70 mL) were added to a flame-dried 250 mL Schlenk flask. Anhydrous zinc acetate (0.32 g, 1.7 g) in ethanol (70 mL) was added, the reaction mixture was stirred at 80 °C for 2 h and the color changed to a transparent deep red. The solvent was evaporated. A red solid was separated by recrystallization in chloroform. Characterization data of the [tetraiodo{di(Zn-salphen)}] building block: yield: 80%; <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 9.12 (s, 4H), 8.36 (s, 2H), 7.70 (s, 4H), 7.35 (s, 4H), 1.46 ppm (s, 36H); <sup>13</sup>C NMR (125 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 171.8, 162.2, 145.7, 142.3, 139.0, 122.8, 73.1, 35.7, 29.7 ppm; HR-MS: *m/z* calcd for C<sub>50</sub>H<sub>51</sub>N<sub>4</sub>O<sub>4</sub>I<sub>4</sub>Zn<sub>2</sub> [M+H]<sup>+</sup>: 1406.8672; found: 1406.8679.

### Synthesis of H-MSN, H-MFeSN, and nonhollow MFeSN

Silica templates with a diameter of 255 nm were prepared by the Stöber method.<sup>[12b,14,22]</sup> For the synthesis of H-MSN, silica spheres (0.30 g), [(PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub>] (8.4 mg, 12  $\mu$ mol), CuI (2.3 mg, 12  $\mu$ mol), triethylamine (20 mL), and THF (10 mL) were added to a flame-dried 50 mL Schlenk flask and the reaction mixture was sonicated for 1 h at room temperature. The [tetraiodo{di(Zn-salphen)}] building block (0.17 g, 0.12 mmol) and 1,4-diethynylbenzene (30 mg, 0.24 mmol) were added, the reaction mixture was stirred at 80 °C for 2 days. After being cooled to room temperature, the solid was separated by centrifugation, washed with acetone (40 mL) thrice, methanol (40 mL) thrice, and methylene chloride (40 mL) thrice, and dried under vacuum. The dried solid was added to a mixture of aqueous HF solution (48–51%, 5 mL), methanol (10 mL), and water (15 mL) in a 50 mL Falcon tube, the reaction mixture was stirred for 2 h at room temperature. Caution: The HF solution is ex-

tremely toxic and should be handled with specific gloves in a hood. The excess HF solution should be treated with NaOH solution. The solid (H-MSN) was separated by centrifugation, washed with a mixture of methanol (10 mL) and water (30 mL) four times, methanol (40 mL) twice, and acetone (40 mL) twice, and dried under vacuum.

For the preparation of H-MFeSN, H-MSN (0.52 g), FeCl<sub>3</sub> (0.19 g, 1.2 mmol), methanol (120 mL), and triethylamine (0.27 mL, 1.9 mmol) were added to a flame-dried 250 mL Schlenk flask. The reaction mixture was heated at 60 °C for 10 h. After being cooled to room temperature, the solid (H-MFeSN) was separated by centrifugation, washed with acetone (40 mL) thrice, methanol (40 mL) thrice, methylene chloride (40 mL) thrice, and dried under vacuum.

For the preparation of nonhollow MFeSN (Also, refer to Figure S3 in the Supporting Information), [tetraiodo(di(Fe-salphen))] building block was prepared as follows. In a flame-dried 250 mL Schlenk flask, [tetraiodo(di(metal-free salphen))] (1.0 g, 0.78 mmol) and chloroform (70 mL) were added. FeCl<sub>3</sub> (0.28 g, 1.7 mmol) in ethanol (70 mL) and triethylamine (0.48 mL) were added, and the reaction mixture was stirred at 80 °C for 2 h. After being cooled to room temperature, the reaction mixture was stirred for 2 h. After solvent evaporation, the [tetraiodo(di(Fe-salphen))] (deep violet solid) was separated through recrystallization in chloroform. Characterization data of the [tetraiodo(di(Fe-salphen))] building block: yield: 75%; HR-MS: *m/z* calcd for C<sub>50</sub>H<sub>50</sub>N<sub>4</sub>O<sub>4</sub>Cl<sub>2</sub>Fe<sub>2</sub> [M]<sup>+</sup>: 1459.8087; found: 1459.8075. NMR spectra could not be obtained due to the paramagnetic nature of the compound. For the preparation of nonhollow MFeSN, [(PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub>] (8.4 mg, 12 μmol), CuI (2.3 mg, 12 μmol), triethylamine (20 mL), and THF (10 mL) were added to a flame-dried 50 mL Schlenk flask and the reaction mixture was sonicated for 1 h at room temperature. The [tetraiodo(di(Fe-salphen))] building block (0.18 g, 0.12 mmol) and 1,4-diethynylbenzene (30 mg, 0.24 mmol) were added, and the reaction mixture was stirred at 80 °C for 2 days. After being cooled to room temperature, the solid was separated by centrifugation, washed with acetone (40 mL) thrice, methanol (40 mL) thrice, and methylene chloride (40 mL) thrice, and dried under vacuum.

### Procedures for catalytic reactions

H-MFeSN (salphen content = 0.996 mmol g<sup>-1</sup>, 10.8 mg for 0.0250 mol%, 21.5 mg for 0.0500 mol%), tetrabutylammonium bromide (TBABr, 13.8 mg for 0.0250 mol% H-MFeSN, 27.6 mg for 0.0500 mol% H-MFeSN), and epoxide (42.9 mmol) were added to an autoclave, and CO<sub>2</sub> (20 bar) was charged at room temperature. The autoclave was heated at the given temperature for the given reaction time. After being cooled to room temperature, excess CO<sub>2</sub> was discharged. The reaction mixture was transferred to a 50 mL Falcon tube using methylene chloride. The catalyst was recovered by centrifugation. After solvent evaporation, cyclic carbonates were isolated by column chromatograph and characterized by <sup>1</sup>H and <sup>13</sup>C NMR studies<sup>[6–8]</sup> (Figure S4 in the Supporting Information). For the recyclability tests, H-MFeSN (21.5 mg, 0.0500 mol%), TBABr (27.6 mg), and PO (3.00 mL, 42.9 mmol) were added to an autoclave. After being charged with CO<sub>2</sub> (20 bar), the autoclave was heated at 100 °C for 12 h. After being cooled to room temperature, excess CO<sub>2</sub> was discharged. The mixture was transferred to a 50 mL Falcon tube using methylene chloride. The catalyst was recovered by centrifugation, washed with methylene chloride, acetone, and methanol, dried under vacuum, and used for the next run.

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### Conflict of interest

The authors declare no conflict of interest.

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