Microporous organic polymers as CO₂ adsorbents: advances and challenges

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Abstract

Microporous organic polymers (MOPs) with internal pores less than 2 nm have potential use in gas separation, sensing, and storage, in the form of membranes, monoliths, fibers, or adsorbent granules. These covalently bonded polymers are being formed by reacting with rigid organic monomers, and MOPs have lately been studied for capturing CO₂ from gas mixtures in the form of membranes and adsorbents. Especially, the potential of MOPs in the processes of carbon capture and storage has been in the focus and small pore MOPs are preferred for regular separation processes but larger pores could be suitable if cryogenic processes would be used. Recent studies (2014 – mid 2019) on the potential use of MOPs as CO₂ adsorbents and, to some degree, CO₂-selective membranes are reviewed.

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1. Introduction

The global emissions of greenhouse gases (GHGs) are increasing and with those the risks for irreversible changes to the environment. Numerous approaches are needed to decrease the emissions of GHGs, and among these carbon capture and storage (CCS) is commonly judged to be important [1]. CCS comprises processes for capture, transport, and storage of CO₂ and its principles are straightforward. However, it has not yet been commercially implemented because of the lack of global policies, negative public perception of CO₂ storage, association to the fossil-fuel industry, and the costly capture step of CCS.

The potential of using microporous (pores < 2 nm) organic polymers (MOPs) in CCS should first be analyzed in relation to processes for capturing CO₂ at existing point sources by retrofitting separation processes to large power plants, cement and steel factories, and pulp mills. The industry standard for CO₂ capture is the use of costly amine scrubbers that could entail environmental concerns with respect to amine emissions [2–4]. Using MOPs as advanced functional materials in the adsorption- or membrane-based capture of CO₂ instead of amine scrubbers could lower down the critically high operational costs for the CO₂ capture by being more energy efficient [5–7]. More energy-efficient processes make investment decisions less risky and also the global energy balances of the power plants or industrial processes more attractive.

Alternative processes for CO₂ capture at point sources include those based on adsorption, partitioning over polymer membranes, and combinations thereof. The cost reduction prospects for membrane-based separation processes are in principle advantageous, as they would not necessarily involve a phase change in the membrane. The prospects of using hollow fibers, such as the Matrimid® 5218, to capture CO₂ from gas mixtures in combination with cryogenic separation are promising. It seems that the capital expenses associated with the recovery of CO₂ can be lowered using cryogenic conditions [8,9]. Irrespective of the temperature used, the properties of the MOPs in the form of hollow fibers, granules, and so on are critical to the cost of the CO₂ separation. In general, the MOPs should have high CO₂-over-N₂ selectivities, low costs, small environmental footprints and allow for high fluxes of flue gas and good mechanical and chemical resistances. In light of our expertise, this review is mainly focused on the prospects of using MOPs as CO₂ adsorbents but instances of the potential use of MOPs in CO₂ separation membranes are also being highlighted.

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2. Advances and challenges for MOPs as adsorbents for CO2

The composition and temperature of emitted gases at large point sources of CO2 vary but they consist of dilute CO2 in mainly N2 at ambient pressure with a temperature of typically 323 K. Upon contact with such gas mixtures, CO2 will preferably adsorb over N2 on the internal surfaces of the MOPs. In general, the adsorption of CO2 occurs via physisorption or chemisorption. Under physisorption, the gas-solid interactions are dominantly weak with contributions from, for example, electric field gradient (efg) - electric quadrupole moment interactions and van der Waals interactions. Chemisorption of CO2 involves electronic reconfiguration of CO2 during the interaction with the solid surface or porous polymer backbone.

The heat of adsorption (Q_\text{st}) of CO2 and CO2-over-N2 selectivity is higher for the MOPs that operate on chemisorption than on physisorption and such MOPs are typically regenerated thermally in temperature swing adsorption (TSA) processes. In turn, TSA is applicable when the CO2 concentration is low. Relevant gas mixtures with low concentrations of CO2 are found in natural gas, flue gas of natural gas power plants, and indoor air. MOP-based chemisorbents typically contain aliphatic amines and operate in analogy with CO2—amine scrubbing systems. With the assistance of solid-state 13C NMR and in situ infrared spectroscopy, recent studies have revealed that CO2 chemisorbs on amine-modified sorbents as carbamic acid, bicarbonates, and ammonium-carbamate ion pairs depending on the amine density, presence of water, amine-amine distance, and so on. Since the seminal study of Lu et al. [13] on amine-tethered porous polymer networks, several synthetic strategies (i.e., chemical modification, physical impregnation) have been adopted to introduce alkyl amine species into MOPs aiming to increase their CO2 capture performance (Table 1) [12,14-21]. It should be noted that although the amine-modified MOPs have high CO2 adsorption capacities and high CO2-over-N2 selectivities, the high Q_\text{st} (up to 80 kJ/mol) would result in a large energy use during the regeneration of the sorbents. In addition, the adsorption kinetics and the cyclic adsorption performance are other concerns. In this context, it would be desirable to balance the effects of chemisorption and physisorption of CO2 by, for instance, tuning the amine densities and introducing amines with appropriate basicity in the MOPs to achieve both high separation and energy efficiencies [18].

MOPs that operate on physisorption of CO2 can be used in vacuum swing adsorption (VSA) and pressure swing adsorption (PSA) processes, and the processes put different requirements on the adsorbents. In VSA processes, the CO2 capacity at a pressure of 0.05–0.15 bar at a temperature of about 323 K is of large importance [26,27]. In PSA processes, it will be the effective CO2 capacity over the pressure swing range (typically several bars) that is of large importance. One argument against the applicability of PSA processes for the CO2 capture at low pressure sources relates to the compression of large volumes of gas containing mainly N2. The flow rate of the flue gas from a normal sized coal-fired power plant is very large, around 200–500 m3/s [28,29]. Many of the CO2 adsorption studies of MOPs have, hence, been focused on their capacity to capture CO2 at low pressures with a VSA process since in mind. It is worth noticing that most studies have been conducted at a standard temperature of 273 K. This choice may be relevant for the sake of comparison; however, the real temperature is higher which drastically reduces the actual CO2 adsorption capacity. In the linear regime of the CO2 adsorption isotherm, the uptake of CO2 will only be about 13% for a MOP at an industrially relevant temperature of 323 K as compared with 273 K when assuming a Q_\text{st} of 30 kJ/mol, which is typical for physisorption. For MOPs with very small pores [22,30-33], the loss in capacity at 323 K would be smaller as the corresponding CO2 adsorption isotherm will curve in the pressure regime of 0–0.15 bar of CO2 at a temperature of 273 K. In general, MOPs with very small pores could be suitable for the VSA-driven CO2 capture and the CO2 capacity may be quite significant even though they do not have ultrahigh surface areas [34-37]. The CO2-over-N2 selectivity of MOPs with very small pores can be enhanced kinetically as N2 is expected to diffuse slower in the MOPs than CO2. Kinetically enhanced selectivity of adsorbents is used in the production of N2 from air by using carbon molecular sieves [38], however, its applicability for high flow rates is not yet established. To use the effect of kinetics for the removal of CO2 from CH4 in the low-flow upgrading of raw biogas seems uncomplicated with a suitable sorbent. For high flow applications such as flue gas capture of CO2, it is critical to assure that the intraparticle diffusion rate of CO2 is high for the kinetically active sorbent and that the adsorbed CH4 that might eventually build up in the sorbent can be recovered by intermittent regeneration. Several of the MOPs that contain small micropores have been shown to display relatively high and kinetically enhanced CO2-over-N2 selectivity with values of about 100 [39-47]. Zhang et al. [48] prepared a set of benzoazolate-based MOPs with tunable micropore sizes. The CO2-over-N2 selectivity for the MOPs increased from 69 to 97 by decreasing the average pore size from 1.4 to 1.0 nm. On the other hand, the MSN-14 and COX-10.N (linear regime) is dependent on the Q_\text{st} of CO2 and N2 and the shapes of the isotherms, and the Q_\text{st} (CO2) is roughly 20–40 kJ/mol. The values for Q_\text{st} (N2) have not been determined for MOPs to our best knowledge. They are expected to be low and maybe about 12 kJ/mol that has been reported for porous carbons [49]. Yassin et al. [50] synthesized a family of cyanovinyl-based MOPs and observed that the values of Q_\text{st} (CO2) were proportional to the density of the cyanovinyl groups. By increasing the cyanovinyl content from 0 to 50.4%, the Q_\text{st} increased from 20.9 to 40.3 kJ/mol. As indicated by theoretical calculations, the sharp efgs induced by the cyanovinyl groups in the MOPs served as high-energy sites for the adsorption of CO2. Consequently, the CO2-over-N2 selectivity was significantly increased (from 14 to 96) when the cyanovinyl content was increased as aforementioned. The revealed structure–thermodynamic–property relationships for MOPs provided a consistent description.

Also the combination of kinetic and thermodynamic effects can enhance the CO2 capture performance of MOPs, and they are not always easy to separate. For example, the studies by Arab et al. [23], Abdelmoaty et al. [51], Rabbani et al. [52], Sekizkardes et al. [53], and Islamoglu et al. [54] developed a range of MOPs consisting of N-rich building units (i.e., aminal, imidazole, thiazole, oxazole, triazine, aniline, azo). Both small pores and N-containing species in these MOPs seemed to have enhanced the efgs in the MOPs, which in turn promoted a strong interaction with CO2. The MOPs had high CO2 adsorption capacities at 0.05–0.15 bar and high CO2-over-N2 selectivity of up to 95, here, the small pores could have enhanced the selectivity also by kinetics. By introducing N- and O-containing moieties as efg-enhancing (CO2–philic) sites in hexazatetraphenyleno-based conjugated triazine frameworks, relatively high CO2 adsorption capacities of up to 2.0 mmol/g at 0.15 bar were observed at a temperature of 297 K [24]. Huang et al. [25,55] also varied the efgs of covalent organic frameworks (COFs; a type of crystalline MOPs with atomically ordered frameworks and porous channels) by elaborated chemical manners. The enhanced Q_\text{st} with values up to 43.5 kJ/mol resulted in significantly enhanced CO2-over-N2 selectivity of up to 323, which was comparable with those of high performing CO2 sorbents (i.e., CuBTC, Mg-MOF-74, NaX zeolite). The studies mentioned previously have demonstrated that pore surface engineering in MOPs through, for instance, predesign of the monomers, selection of appropriate polymerization reactions, postmodification, is a powerful approach to exploit high
Table 1
Selected microporous organic polymers and their CO₂ capture performances.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>( S_{\text{BET}} ) (m²/g)</th>
<th>Pore size (nm)</th>
<th>( \text{CO}_2 ) uptake at 273 K (mmol/g)</th>
<th>( \text{CO}_2/\text{N}_2 ) selectivity</th>
<th>( Q_{st} ) (kJ/mol)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amine-modified MOPs (chemisorbents)</td>
<td></td>
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</tr>
<tr>
<td>435</td>
<td>0.56</td>
<td>0.76</td>
<td>1.36</td>
<td>3.0</td>
<td>97&lt;sup&gt;a&lt;/sup&gt;</td>
<td>68</td>
</tr>
<tr>
<td>72</td>
<td>1.7</td>
<td>1.13</td>
<td>1.43</td>
<td>2.30</td>
<td>1040&lt;sup&gt;b&lt;/sup&gt;</td>
<td>80</td>
</tr>
<tr>
<td>100&lt;sup&gt;d&lt;/sup&gt;</td>
<td>–</td>
<td>0.91</td>
<td>1.16</td>
<td>1.80</td>
<td>10140&lt;sup&gt;c&lt;/sup&gt;</td>
<td>75</td>
</tr>
<tr>
<td>555</td>
<td>1</td>
<td>2.60&lt;sup&gt;e&lt;/sup&gt;</td>
<td>3.0&lt;sup&gt;e&lt;/sup&gt;</td>
<td>4.3&lt;sup&gt;e&lt;/sup&gt;</td>
<td>555&lt;sup&gt;b&lt;/sup&gt;</td>
<td>55</td>
</tr>
<tr>
<td>Ultramicroporous/functionalized MOPs (physisorbents)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1108</td>
<td>0.6</td>
<td>0.73</td>
<td>1.79</td>
<td>5.40</td>
<td>40&lt;sup&gt;c&lt;/sup&gt; (35&lt;sup&gt;c&lt;/sup&gt;)</td>
<td>33</td>
</tr>
<tr>
<td>1235</td>
<td>1.0</td>
<td>0.86</td>
<td>1.84</td>
<td>5.36</td>
<td>35&lt;sup&gt;c&lt;/sup&gt; (40&lt;sup&gt;c&lt;/sup&gt;)</td>
<td>29</td>
</tr>
<tr>
<td>1090</td>
<td>0.35–0.90</td>
<td>1.60</td>
<td>3.0</td>
<td>6.30</td>
<td>183&lt;sup&gt;c&lt;/sup&gt;</td>
<td>27</td>
</tr>
<tr>
<td>364</td>
<td>1.40</td>
<td>0.63</td>
<td>1.46</td>
<td>3.95</td>
<td>323&lt;sup&gt;c&lt;/sup&gt;</td>
<td>44</td>
</tr>
</tbody>
</table>

MOPs, microporous organic polymers.

<sup>a</sup> Initial slope selectivity.
<sup>b</sup> Simplified ideal adsorbed solution theory (IAST) selectivity.
<sup>c</sup> IAST selectivity.
<sup>d</sup> Calculated from CO₂ adsorption isotherm at 273 K.
<sup>e</sup> Recorded at 295 K.
performance CO₂ sorbents by increasing the efgs or by inducing 
sites with a specific tendency to interact with CO₂.

If the flue gas can be compressed, or integrate with cryogenic 
cooling, economically in a similar manner as for membrane-based 
CO₂ separation \[8,9\], then the properties of the optimal MOPs 
would be quite different as compared with those suitable for VSA-
based separation at 323 K. For PSA or cryogenic VSA/PSA processes, 
it would be the effective CO₂ capacity at high pressures or low 
temperatures that would be the most defining parameters of the 
MOPs. A high-pressure CO₂ adsorption capacity can be assured by a 
high specific surface area of the MOP. It has been shown that 
using rigid and tetrahedrally shaped monomers one can prepare 
MOPs with ultrahigh surface areas of over 6000 m²/g with associ-
ated very high CO₂ adsorption capacities of up to 48.2 mmol/g at 
295 K and 50 bar \[56\]. Alternatively, by introducing flexible skel-
etons into the MOPs one could effectively increase the CO₂ 
adsorption capacity at high pressures by physical swelling \[57,58\]. 
In addition, it is important to note that MOPs with a very high 
volumetric capacity (the volume of the sorbate adsorbed per vol-
ume of the sorbent) are ideal in processes as they can contribute to 
reduce the size of the columns \[59\].

3. Classification and synthesis of MOPs as CO₂ sorbents

There are numerous ways of categorizing the MOPs, and no 
standard has been agreed on; however, a first natural division is to 
single out the linear MOPs from network-based ones. The micro-
porosity in linear MOPs emerges from the high free volume stem-
mencing from the contorted building blocks leaving the polymers 
porous. Since Budd et al. \[60\] developed the first polymer of 
intrinsic microporosity (PIM); PIM-1, several PIMs linked by amide 
\[61\], imide \[62\], Tröger’s base \[63\], aromatic units \[64\] and their 
modified versions \[65–67\] have been reported. Although most of 
the PIMs do not show outstanding CO₂ adsorption capacities, their 
typically good solubility in organic solvents makes them process-
able into membranes for the separation of CO₂ from mixed gases 
\[68,69\]. Recently, several studies of mixed matrix membranes 
(MMMs) based on PIMs and CO₂-phlic fillers (i.e., metal organic 
frameworks (MOFs) \[70,71\], silica nanoparticles \[72\], polymers 
\[73\], porous carbons \[74\]) have aimed to break the Robeson upper 
bounds for CO₂/N₂ and CO₂/CH₄ separation, assuring both high 
permeability and selectivity. In addition, it has been demonstrated 
that by introducing functional polar groups in either the PIMs or 
fillers, the intermolecular interactions between the components 
were enhanced and thus the rigidity of the membranes \[70,75,76\]. 
As a result, the rigidified membranes showed a significantly 
enhanced aging and operation stability as compared with the PIM-
1 membranes. Enhanced stability is of great importance for prac-
tical applications.

Another group of MOPs that have been studied since along time 
are the hyper-cross-linked polymers (HCPs) \[77\]. They have already 
been commercialized for applications such as solvent cleanup and 
so on. Friedel-Crafts alkylation and Scholl coupling reaction are 
common and powerful approaches for the synthesis of HCPs 
\[78,79\]. Owing to the general applicability of the reaction, almost 
all of the aromatic compounds and heterocycles can be used as 
monomers to construct the HCPs. The advantages of HCPs over 
other porous materials are in their synthetic diversity and potential 
low cost. Recently, Börnmayr and Hedin synthesized a class of 
HCPs from biobased molecules in sulfolane \[80\]. The resultant HCPs 
showed tunable pore structures with surface areas of 
610–1440 m²/g and large CO₂ uptakes of 2.6–4.0 mmol/g (273 K, 
1 bar). The economical and environmentally friendly synthesis of 
biobased HCPs provides a sustainable approach for the develop-
ment of MOPs.

Covalent triazine frameworks (CTFs) are a new type of MOPs 
linked by triazine units \[81\]. Because of their high stability, rich 
microporosity, and abundant nitrogen content, CTFs are being 
considered as promising candidates for CO₂ capture \[26,82,83\]. 
Since Kuhn et al. \[84\] synthesized a family of CTFs by trimerization 
of aromatic nitrile monomers under ionothermal conditions, 
several groups have dedicated significant efforts in developing new 
CTF materials for various applications. Apart from ionothermal 
trimerization reactions taking place under harsh conditions, a 
range of mild synthesis strategies including supracritical catalyzed 
reactions \[85,86\], Friedel-Crafts reactions \[87\], polycoupling 
reactions \[88\] have been recently developed for the synthesis of 
CTFs. For example, Wang et al. \[89\] synthesized a new family of 
CTFs (CTF-Huazhong University of Science and Technologies via 
polycondensation of aldehyde and amidine dihydrochloride 
monomers at relatively low temperature (120 °C) and ambient 
pressure and atmosphere. The resultant CTFs showed high CO₂ 
adsorption capacities up to 3.16 mmol/g at 273 K and 1 bar. More 
significantly, the synthesis procedures can be easily scaled up to 
prepare CTFs in gram quantities, which is beneficial to practical 
applications.

Condensation reactions are most common in the synthesis of 
MOFs and can be performed with and without the use of catalysis. 
For example, the condensation reactions between amines and al-
dehydes have been used to synthesize MOPs being linked by imine 
\[36\], aminal \[90,91\], and benzimidazole \[52\] units. The N-cont-
aining species and the ultramicropores in these MOPs could enable 
strong interaction with CO₂, which is as mentioned of great 
advantage in the CO₂ capture at low pressures. Notably, conden-
sation reactions that are reversible and under kinetic control allow 
construction of crystalline COFs possible. In this context, COFs with 
predesigned architectures, tunable porosities, and optimized CO₂ 
separation performances can be synthesized in terms of reticular 
chemistry and crystal engineering \[92\].

The catalytic coupling chemistries are well developed within 
organic chemistry and have also been used extensively for the 
synthesis of MOPs. A class of conjugated microporous polymers 
and porous aromatic frameworks has been synthesized by Yamamoto, 
Sonogashira, and Suzuki coupling reactions, and so on. \[93,94\] 
These polymers usually possess high specific surface areas because 
of their high degree of polymerization and rigid 2D or 3D networks. 
Apart from these porous polymers with C–C linkages, recent 
studies have used other coupling reactions (i.e., Buchwald–Hartwig 
coupling, oxidation coupling, diazocoupling reaction) to enable the 
synthesis of MOPs with azo \[95–97\], secondary amine \[98,99\], and 
polyacarbazole \[100,101\] linkages (Table 2).

An alternative way to enhance the efgs in MOPs is to decorate 
them with ionic moieties. The corresponding ionic microporous 
organic polymers (IMOPs) have attracted a growing interest in the 
field of CO₂ capture. The incorporated ion pairs are either covalently 
bonded to the pore wall or attached to it with either cations or 
anions as pendant units. As such, their physicochemical properties, 
functionalities, and active sites for CO₂ binding, can be regulated 
through pore surface engineering, that is, the screening of building 
units to backbones, pendant groups, and ionic tectonism. Several 
key design requirements are generally being considered for the 
IMOPs, which include the pore parameters, host-guest interactions, 
and charge effects. The high surface area and large pore volume of 
the IMOPs assure many accessible binding sites for CO₂ and suffi-
cient accommodating space, which are considered crucial to a high 
CO₂ uptake capacity \[105–107\]. Generally, also for IMOPs, the 
introduction of rigid and contortive building blocks into the poly-
mer backbone is the most frequently used approach to achieve high 
porosity. However, synthesizing IMOPs with high surface areas and 
small pores is far more challenging than for neutral MOPs because
Table 2

Selected reactions for the synthesis of microporous organic polymers.

<table>
<thead>
<tr>
<th>Chemical equations</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>[63]</td>
<td></td>
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<tr>
<td>[102]</td>
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<td>[52,103]</td>
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<td>[104]</td>
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<td>[23]</td>
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<td>[98]</td>
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</table>
of the strong electrostatic repulsion that emerges in the micropores. Small pores can be introduced by using hard or soft templates, which have been popular to use from a synthetic point of view, however, their uses are time and energy intensive. It is of our opinion that a template-free approach is more favorable, such as the postmodification of presynthesized nonionic MOPs. For this purpose, various synthetic strategies including coupling reactions (i.e., Sonogashira reaction [108,109], Suzuki-Miyaura cross-coupling reaction [110], Yamamoto reaction [111,112], and Eglinton coupling [113], Friedel-Crafts reaction [114], free-radical polymerization [115], trimerization reaction [116], and Schiff-base reaction [117]) can be used.

IMOPs with polar pore surfaces have strong efgs, which enhance the efg-quadrupole interactions between the frameworks and guest CO2 molecules [118]. As for the other MOPs, the incorporation of heteroatoms (i.e., N, O, P, S, and B) or CO2-philic ionic moieties into the framework/pore surface through direct polymerization or postsynthesis modification would be beneficial for the CO2 capture. The charges themselves enhance the efgs as well [119]. It seems that tetraalkylammonium cations have a stronger interaction with CO2 than imidazoliums as the latter have a delocalized positive charge [120]. Similarly, the adsorption ability of CO2 also can be affected by the nature of the anion. All in all, the ions in the IMOPs can promote the CO2 adsorption, and a proper design of the IMOPs is especially important [55].

The IMOPs have both covalent and ionic bonds, which allow the pores and interaction potentials with CO2 to be controlled and enhanced. Till now, a series of IMOPs have been studied for achieving a high CO2 uptake and selectivity and their pore-surface functionalities have been moderated by backbone modification, adjustment of the pendant groups, and counter-ion exchange. Both direct polymerization and postsynthetic modification have been used. With direct polymerization, several types of IMOPs with backbone building units including cationic [121], anionic [122], and zwitterionic moieties [123] have been studied. Note that the CO2 adsorption performance would be readily tuned by controlling the ionic moieties of the backbone. For instance, IMOPs synthesized from vinyl-functionalized quaternary phosphonium salts through free-radical polymerization reaction (Table 3) have exhibited high surface areas (up to 758 m$^2$/g) and high CO2 adsorption capacity (2.23 mmol/g at 273 K) [124]. Luo et al. reported on a series of IMOPs being synthesized via a one-pot free-radical copolymerization of ionic vinylimidazolium-based metallosalen moieties with divinylbenzene as a cross-linker under solvothermal polymerization conditions [125]. The obtained polypolyvinylimidazolium-based metallosalen IMOPs (DVB@ISA) had a surface area of 590 m$^2$/g, pore volume of 0.55 cm$^3$/g, and high CO2/N2 adsorptive selectivity. Liu and Landskron [126] synthesized anionic IMOPs with cova-

The ability to alter the counter ions of IMOPs is a distinctive advantage that allows the properties of CO2 capture and selectivity without changing the polymer backbone to be engineered. Direct polymerization via ionic monomers containing different anions is one strategy to alter the counter ions of IMOPs. Xie et al. [128] prepared a series of sponge-like IMOPs with different anions (BF$_4$, PF$_6$, and Cl), which were synthesized by quaternary ammonium-based monomers via a free-radical polymerization reaction. The CO2 sorption capacity of the IMOPs was reduced in the order of BF$_4 >$ PF$_6 >$ Cl. Ion exchange of already prepared IMOPs is another approach to tune the CO2 adsorption performance. Fischer et al. [112] synthesized two IMOPs (CPN-1-Br and CPN-2-Br) with tetra-
rakis (4-bromophenyl) methane using the Yamamoto coupling and Sonogashira-Hagihara reaction. The initial prepared polymers CPN-1-Br and CPN-2-Br exhibited high surface areas of 1455 and 540 m$^2$/
g and good CO2 uptakes of 2.49 and 1.55 mmol/g at 273 K and 1 bar, respectively. The CPN-1-Br was anion exchanged into the CPN-1-Cl, which had an enhanced CO2 uptake (2.85 mmol/g), being consistent with the properties of the smaller anion (Cl). Rukmani et al. [129] studied the CO2 adsorption and selectivity of the ionic and functionalized PIM-1 (fonomIM-1) with counter ions being Li$^+$, Na$^+$, K$^+$, Rb$^+$, or Mg$^{2+}$. The counter ion type enabled the CO2 adsorption capacity and selectivity for CO2/CH4 and CO2/N2 gas mixtures to be tuned. Overall, it is clear that the type of counter ion influences the CO2 adsorption performance of the IMOPs.

In short, IMOPs are promising adsorbents for CCS. Generally, they feature a higher CO2 capture ability than their neutral analogs of similar surface areas owing to the enhanced efgs, and we summarized important strategies to the design and methods to engineer the pore surfaces. Challenges, important to overcome in the future, are that IMOPs typically have low surface areas, broad pore size distributions, and are difficult to obtain directly by using coupling reactions.

4. Processing and shaping of MOPs

Processing of powders of network polymer–based MOPs into functional forms is critical to their applications in gas separation processes. Except for a few soluble MOPs such as PIMs with linear structures, they are usually insoluble in common solvents and have no observable glass transition temperatures because of the rigid, conjugated, or highly cross-linked structures. Therefore, solution and melt processing used for conventional polymers are not suitable for the processing of MOPs. The weak processability of MOPs has largely hampered their practical applications. Only recently, this issue has been started to be addressed by researchers. A number of MOP aerogels have been successfully synthesized from the corresponding organogels via freeze-drying, subcritical, or supercritical drying [130–132], which are powerful methods to prepare low-density materials. Certain polymerization reactions that have been performed without stirring or agitation have been shown successful to form directly MOPs as aerogels and monoliths [133,134]. In addition, flexible and freestanding MOP membranes have also been recently developed [135,136]. Noteworthy, 3D-printing techniques have been shown to hold great potential for the structuring and processing of MOPs [137,138]. Such structured MOP materials can not only be used as sorbents for CO2 capture but also have a great potential for applications in nanofiltration, heterogeneous catalysis, oil cleanup, solar steam generation, artificial muscles, and so on.

5. Summary

The fully organic backbone of MOPs and the possibilities of the detailed control achieved by polymer and organic chemistry render
the MOPs with certain advantages over zeolites, activated carbons, and MOF compositions, as adsorbents for CO₂. Their relatively low hydrophilicity, high surface area, and low densities are of great advantage when the MOPs are used to support amines for chemisorption of CO₂. Decorating the internal pores of the MOPs by efg-enhancing groups such as the ionic species of the IMOPs enhances the physisorption abilities of the MOPs. The recent progress made in the processing and shaping of MOPs could potentially boost their practical applications in the CO₂ capture and other fields. The high cost of the MOPs is still a big obstacle for their large-scale preparation and the road to industrialization. In addition, most reported MOPs have been synthesized in organic solvents at elevated temperatures with catalysts (e.g., noble metal catalysts, organic catalysts), followed by procedures of filtration, purification, and drying. Obviously, the current synthesis technologies for MOPs are not economically and environmentally friendly. In this regard, further exploration of inexpensive and more sustainable monomers and facile and green synthesis routes are greatly being desired.

In contrast to crystalline porous materials such as MOFs and zeolites, most MOPs have been obtained in amorphous forms. Except for a few examples of COFs and CTFs synthesized under delicate conditions, it is still challenging to create ordered structures in MOPs, which has hampered the design of MOPs with predetermined pore structures. It would be highly advantageous to develop advanced simulation models allowing precise prediction of the pore size and the pore geometry in MOPs at the molecular level, which could guide the design of MOPs with high performances in CO₂ capture.

Table 3
Selected reactions for the synthesis of microporous organic polymers.

<table>
<thead>
<tr>
<th>Chemical equations</th>
<th>Ref.</th>
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<tbody>
<tr>
<td><img src="image1.png" alt="Chemical equation" /></td>
<td>[124]</td>
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<tr>
<td><img src="image2.png" alt="Chemical equation" /></td>
<td>[126]</td>
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<td><img src="image3.png" alt="Chemical equation" /></td>
<td>[127]</td>
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<tr>
<td><img src="image4.png" alt="Chemical equation" /></td>
<td>[112]</td>
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* a CO₂ adsorption capacity at 273 K and 1 bar.
At the moment, it is still unclear if the MOPs are most promising as gas separation membranes for CO₂ separation, adsorbents for VSA-based capture, or adsorbents for cryogenic swing adsorption processes. The ideal properties of the MOPs are very different for these three applications. Hence, it is crucial that the engineering and chemistry communities stay in close contact when further developing the MOPs for CO₂ separation purposes.

Decloration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

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