Accepted Article

Title: New Meets Old: Accelerating Membrane-based CO2 Separation by Soluble Nanoporous Polymer Networks Produced Via Mechanochemical Oxidative Coupling

Authors: Xiang Zhu, Yinying Hua, Chengcheng Tian, Carter W. Abney, Peng Zhang, Tian Jin, gongping Liu, Katie L. Browning, Robert L. Sacci, Gabriel M. Veith, Hong-Cai Zhou, Wanqin Jin, and Sheng Dai

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201710420
Angew. Chem. 10.1002/ange.201710420

Link to VoR: http://dx.doi.org/10.1002/anie.201710420
http://dx.doi.org/10.1002/ange.201710420
New Meets Old: Accelerating Membrane-based CO₂ Separation by Soluble Nanoporous Polymer Networks Produced Via Mechanochemical Oxidative Coupling

Xiang Zhu, Yinying Hua, Chengcheng Tian,* Carter W. Abney, Peng Zhang, Tian Jin, Gongping Liu,* Katie L. Browning, Robert L. Sacci, Gabriel M. Veith, Hong-Cai Zhou, Wanqin Jin* and Sheng Dai*

Abstract: Achieving homogeneous dispersion of nanoporous fillers within membrane architectures remains a great challenge for mixed-matrix membrane (MMMs) technology. Imparting solution processability of nanoporous materials would help advance the development of MMMs for membrane-based gas separations. For the first time, we report a novel mechanochemical-assisted oxidative coupling polymerization strategy to create a new family of soluble nanoporous polymer networks. The solid-state ball-milling methodology affords inherent molecular weight control over polymer growth and therefore provides unexpected solubility for the resulting nanoporous frameworks. MMM-based CO₂/CH₄ separation performance was significantly accelerated by these new soluble fillers. We anticipate this facile protocol will facilitate new possibilities for the rational design and synthesis of soluble nanoporous polymer networks and promote their applications in membrane-based gas separations.

The interest in curtailing greenhouse gas emissions through capture of CO₂ from flue gas and removal of CO₂ from synthesis gas (mainly CH₄ and H₂) has inspired an extensive search for novel methodologies capable of efficient separation of CO₂.[1] Membrane-based CO₂ separation technology has gained significant attention as a promising solution, due to its lower energy costs and reduced environmental impact.[2] Among the various types of CO₂-selective membranes, polymeric membranes have been the most widely studied, whereas they suffer from a well-known compromise between the permeability and selectivity as shown in the upper bound Robeson curves.[3] Coupling polymer matrices with nanoporous filler particles, for example nanoporous organic networks (NPNs), could lead to synergistic improvements in membrane-based CO₂ separation performance, but difficulties are encountered in achieving homogeneous dispersion of these nanoporous fillers within MMMs.[4]

Although significant progresses have been made in the synthesis of NPNs by linking multidentate organic scaffolds towards a wide variety of potential applications,[5] it remains a great challenge to fabricate soluble nanoporous organic networks (SNPNs) through a rapid and straightforward method, mainly because it is very difficult to control the growth of polymeric architectures.[6] Ladder-like “polymers of intrinsic microporosities” (PIMs) with contorted sites have been reported as a family of soluble porous polymers and successfully utilized in membrane-based gas separations.[7] Recently, Cooper et al. pioneered another successful synthesis of soluble porous polymer using a hyperbranching-based approach based on Suzuki-catalyzed aryl-aryl coupling copolymerization.[8] The obvious downside is the use of the costly Pd-containing catalyst and necessity of complicated organic synthetic processes, significantly limiting the potential for practical implementation. In this regard, the search for novel techniques that are capable of efficient and facile synthesis of SNPNs is of great interest, importance, and urgency. Imparting solution processability would help advance development of NPNs and enable the combination of unique features such as intrinsically high porosity towards MMM-based CO₂ separations.

Scheme 1. The synthesis route of soluble NPNs based on the oxidative coupling polymerization (OCP).

In this work, we report a novel strategy for the rationally-designed synthesis of a novel family of SNPNs. The key to our approach lies in the use of a mechanochemical (MC)-assisted FeCl₃-mediated oxidative coupling polymerization (OCP).[9] MC synthesis strategy has been demonstrated as a versatile alternative technique that enables the preparation of nanoporous materials through sustainable solid-state assembly pathways. By using mechanochemistry to promote the oxidative polymerization, the molecular weight of the resulting materials can be controlled. Their homogeneous dispersion within membrane architectures were facilely realized, and MMM-based CO₂/CH₄ separation performance was significantly accelerated. A high CO₂ permeability of 675 barrer together with a CO₂/CH₄ selectivity of...
COMMUNICATION

25 was achieved. This innovative solvent-free assemble approach not only provides a means to achieve SNPNs in a rapid and straightforward fashion, but also enables us to achieve high-performance MMMs for CO₂ separation.

Our synthetic strategy is shown in Scheme 1. We first started by pursuing a NPN prepared by a novel solvent-mediated FeCl₃-initiated oxidative coupling reaction[9] (method A, details can be found in the Supporting Information). We reasoned that a ladder-like scaffold plays a crucial role in achieving high porosity, as have been extensively studied in the context of PIM chemistry.[76] Accordingly, 3,3',3'-tetramethyl-2,2',3,3'-tetrahydro-1,1'-piro[indenyl]-6,6'-dial (BPSPI-OH) was selected and prepared for use due to possessing the desired ladder-like structure. Following reflux overnight, a brown solid (OCP-NPN-1) was obtained possessing a high Brunauer-Emmett-Teller (BET) surface area (~ 834 m² g⁻¹), evaluated by nitrogen adsorption-desorption isotherms (Figure S1). The BET surface area is comparable to that of many previously-reported porous organic polymers, for example crystalline covalent-triazine-framework-1[9] (CTF-1, SA_BET = 791 m² g⁻¹) and amorphous conjugated microporous polymer-1[10] (CMP-1, SA_BET = 834 m² g⁻¹), thus confirming the feasibility of our OCP methodology for the construction of nanoporous polymers.

The molecular structure of the resultant sphere-like polymer was characterized using ¹H-¹³C cross-polarization magic-angle spinning (CP-MAS) ¹³C NMR (Figure S2). The aliphatic carbons in the backbone were clearly revealed by the resolved resonance at ~ 30, 43 and 58 ppm, respectively, while the signal peak at ~ 157 ppm corresponded to vibrational ball milling state (Figure S2). The aliphatic carbons were clearly revealed by the resolved resonance at ~ 30, 43 and 58 ppm, respectively, while the signal peak at ~ 157 ppm corresponded to vibrational ball milling state (Figure S2). The aliphatic carbons were clearly revealed by the resolved resonance at ~ 30, 43 and 58 ppm, respectively, while the signal peak at ~ 157 ppm corresponded to the oxygen atom (Figure S2b). High thermal stability was observed for the resultant network (Figure S3). However, the amorphous network OCP-NPN-1 (Figure S4) was insoluble in common organic solvents, like tetrahydrofuran (THF, Figure S5) and dichloromethane (CH₂Cl₂).

Motivated by the aforementioned results, we subsequently initiated a novel mecha-nocchemical (MC)-assisted solid-state OCP of BPSPI-OH to attempt the fabrication of soluble nanoporous networks (method B, Scheme 1). Recent work has demonstrated mecha-nocchemical methods efficiently enable facile generation of soluble porous coordination polymers[11] and hold great promise for the synthesis of nanoporous organic frameworks.[22] However, the direct synthesis of SNPNs using the mecha-nocchemistry is rarely reported. We anticipated that this innovative methodology could enable a rapid growth of polymer networks and therefore provide solution processability for the resultant materials through limiting the inherent molecular weight.

In our initial attempt at solid-state OCP promoted by ball-milling, the white BPSPI-OH moiety (150 mg, 0.49 mmol) and two mass equivalents of FeCl₃ (300 mg, 1.85 mmol) were mixed in a zirconium oxide milling jar with a stainless steel ball and subjected to vibrational ball-milling in a Retsch mixer mill 400 at 30 Hz for 0.5 h (Figure S6). The obtained black solid was carefully washed with a mixed solution of ethanol and dilute HCl to remove the FeCl₃. According to the x-ray photoelectron spectroscopy (XPS) result, only 0.1 at.% content of Fe was detected, where a high O-doping content of 26.4 at.% was achieved. The binding energy of O₁s at 532.0 eV (Figure S7) was assigned to O-C (80.3 %) and at 530.5 eV to O=C (19.7 %). These active sites could facilitate CO₂ binding inside the framework. The BET surface area of the resulting material (MC-OCP-NPN-1) (Figure S8) is lower than that of solvent-mediated OCP-NPN-1 (470 vs 834 m² g⁻¹). Nevertheless, this value is comparable to that of the soluble CMP (SCMP1) reported by Cooper et al. (SA_BET = 505 m² g⁻¹).[6a] The pore size distribution (PSD), calculated from the CO₂ isotherm at 273 K, indicates the intrinsic microporous nature (Figure S9).[6a] More importantly, MC-OCP-NPN-1 can be dissolved in many common organic solvents, like THF, ethanol acetate and dimethylformamide (Figure 1), which may give a rise to homogeneously disperse these nanoporous particles within a membrane architecture. No Tyndall effect was observed for the dichloromethane (CH₂Cl₂) solution of MC-OCP-NPN-1, further confirming the formation of a homogeneous solution (Figure S10). Interestingly, when dissolving and re-precipitating the polymer from CH₂Cl₂, a significant decrease in BET surface area was observed (205 vs 470 m² g⁻¹, Figure S8). Nonetheless, this value can be further enhanced to be 319 m² g⁻¹ when we repeated the dissolution and re-precipitating process using CH₂Cl₂/EtOH (volume ratio: 1 to 4) instead. We reasoned that the swelling of MC-OCP-NPN-1 in different solvents may account for this BET difference.[13] In addition, upon lamination under UV irradiation, the dissolved MC-OCP-NPN-1 affords a bright blue-luminescent solution (Figure 1). As shown in the photoluminescence spectrum, MC-OCP-NPN-1 exhibits a maximum emission at ~ 470 nm (Figure 1c), suggesting an inherently conjugated architecture.[6a] This is rarely observed for conventional soluble PIMs. Additionally, the ¹³C NMR spectra matches well with that of OCP-NPN-1 (Figure S11).

Table 1. Effects of amounts of FeCl₃ and grinding time on N₂ adsorption property and molecular weight of OCP-CNP.

<table>
<thead>
<tr>
<th>Sample</th>
<th>FeCl₃ (mass eq.)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>S_BET (m² g⁻¹)</th>
<th>M_w (kDa)</th>
<th>M_z (kDa)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCP-NPN-1</td>
<td>2</td>
<td>12</td>
<td>95</td>
<td>834</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>MC-OCP- NPN-1</td>
<td>2</td>
<td>0.5</td>
<td>35</td>
<td>470</td>
<td>3.7</td>
<td>6.9</td>
<td>1.85</td>
</tr>
<tr>
<td>MC-OCP- NPN-2</td>
<td>2</td>
<td>0.5</td>
<td>16</td>
<td>430</td>
<td>3.0</td>
<td>5.8</td>
<td>1.94</td>
</tr>
<tr>
<td>MC-OCP- NPN-3</td>
<td>4</td>
<td>0.5</td>
<td>65</td>
<td>733</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>MC-OCP- NPN-4</td>
<td>2</td>
<td>0.25</td>
<td>36</td>
<td>448</td>
<td>3.0</td>
<td>6.1</td>
<td>2.03</td>
</tr>
</tbody>
</table>

Figure 1. (a) Photographs of soluble performance of MC-OCP-NPN-1 in various solvents; (b) THF solution of MC-OCP-NPN-1 shows bright luminescence under UV irradiation (λ=365 nm); (c) Photoluminescence spectrum of MC-OCP-NPN-1.
Gel permeation chromatography (GPC) analysis with a polystyrene standard was then performed to study the molecular weight of MC-OCP-NPN-1 (Figure S12).[6a] The weight-averaged molecular weight (Mw) was determined to be ~ 6.9 kDa and was larger than that of SCMP1 (5316 g mol⁻¹, ~ 5.3 kDa). Likewise, the material also shows a good molecular weight distribution with polydispersity index (PDI) of 1.85. Additionally, the ¹H NMR spectrum of MC-OCP-NPN-1 was measured (Figure S13), which may further support the proposed polymeric structure. Clearly, these promising results confirm the MC-assisted solid-state OCP approach affords a nanoporous network with exceptional solution processability, which has never been observed in previously-reported methods.

Inspired by this success, we speculated that the quantity of FeCl₃ during the ball-milling process could play a significant effect on the porosity and solution processability for the resulting materials. We performed a detailed investigation into the synthetic parameter space governing solid-state OCP preparation. With the same milling time (0.5 h), a significant improvement in isolated yield as a function of FeCl₃ amount is observed (Table 1); i.e., the use of 1 mass eq. of FeCl₃ affords a low 16% yield, whereas a much higher 65% isolated yield was obtained at 4 mass eq. of FeCl₃. Moreover, the BET surface area of the latter material (MC-OCP-NPN-3) also increased to 733 m² g⁻¹, close to that of OCP-NPN-1. In contrast, MC-OCP-NPN-3 shows very poor solubility in common organic solvents, such as THF (Figure S5). Accordingly, the quantity of FeCl₃ is a key to the successful development of soluble architectures. Furthermore, we tried to decrease the milling time from 0.5 h to 0.25 h to improve the reaction efficiency. By this revised protocol, the new network MC-OCP-NPN-4 was obtained with similar isolated yield, BET surface area, and molecular weight as MC-OCP-NPN-1. This result suggests that MC-assisted OCP is a much more efficient and facile pathway toward the rapid synthesis of soluble nanoporous polymer networks than Cooper’s “hyperbranching method”. [6a] Moreover, this innovative approach also constitutes a new direction for the development of novel nanoporous polymers through solid-state assembly methods.

As a proof of concept, soluble MC-OCP-NPN-1 was then employed as a nanoporous filler for the fabrication of mixed-matrix membranes. 2,2-bis(3,4-carboxyphenyhexafluorobenzene (6FDA)-diaminomethylhexyl) (DAM), was selected as the polymer matrix. As anticipated, homogeneous MMMs can be facilely prepared, even with an extremely high filler containing of 60 wt% (details can be found in the supporting information). As shown in Figure 2b and c, sphere-like MC-OCP-NPN-1 nanoparticles were uniformly incorporated within polyimide matrices and the membrane surfaces were dense and defect free. The cross-section views at lower magnification also indicate integrated morphologies, with the thickness is ~ 30 - 40 µm (Figure 2). The difference between the observed surface morphologies of the membranes originates from the solvent evaporation during the membrane preparation process and the containment of polymer fillers. The uniformity of the hybrid membrane was improved as the loading of the polymer fillers was increased, which may be due to the complex phase separation behavior of mixtures of MC-OCP-NPN-1/polyimide/chloroform. Furthermore, excellent bending abilities were clearly observed (Figure S14), even with the highest MC-OCP-NPN-1 loading of 60 wt%, suggesting good mechanical properties for these new membrane materials.

We then carried out the membrane-based separation of CO₂ from CH₄ to study the permeation properties of these promising MMMs. The pure gas permeation properties were measured by a “constant-pressure” system with feed pressure of 3 bar and temperature of 30 °C.[2a] The CO₂ permeability of the polyimide membrane was significantly enhanced by incorporating...
nanoporous MC-OCP-NPN-1, and gradually improved as the increase of filler containing within the membrane. Interestingly, when 60 wt% MC-OCP-NPN-1 was loaded, the resultant MMM exhibits 2-fold higher CO2 permeability than that of pure polyimide membrane (675 vs 322 barrer, Figure 3a). To our delight, the obtained CO2/CH4 selectivity maintained very well and was slightly decreased from 29 to 25. It should be noted that all the measured permeabilities and selectivities of MMMs agree well with the predicted values based on the Maxwell model, suggesting an ideal mixed-matrix morphology was formed (Figure 3a). As a result, the permeation performance of pure MC-OCP-NPN-1-based membrane could be predicted (CO2 permeability of 1995 barrer and CO2/CH4 selectivity of ~ 23), which is very promising for CO2/CH4 separation.[26,27] We reasoned that the intrinsic adsorption affinity of CO2 over CH4 on MC-OCP-NPN-1 may account for this efficient membrane-based separation performance. As such, the CO2 and CH4 adsorption isotherm was recorded at 25 °C and 1 bar, respectively, to get a better understanding. As shown in Figure 3b, MC-OCP-NPN-1 can adsorb 20.9 cm3 g−1 of CO2 whereas only 5.8 cm3 g−1 of CH4 uptake was obtained. Clearly, MC-OCP-NPN-1 exhibits a much higher CO2 binding affinity and high-performance membrane-based CO2/CH4 separation could be expected for MC-OCP-NPN-1-based MMMs.

In summary, a mechanochemical-assisted oxidative coupling polymerization strategy has been implemented for the first time to create a novel family of soluble fluorocarbon nanoporous polymer networks. The uniqueness of the solid-state ball-milling methodology accommodates facile polymer growth and therefore gives rise to unexpected solubilities for the resulting nanoporous frameworks. This innovative protocol not only provides a means to achieve soluble porous polymers in a rapid and straightforward fashion, but also enables us to achieve a homogeneous dispersion of porous polymers within membrane architectures. The resulting mixed-matrix membrane exhibits an efficient membrane-based CO2/CH4 separation with a high CO2 permeability of 675 barrer and a CO2/CH4 selectivity of 25. In general, the concept presented here can provide new opportunities for the synthesis of more soluble nanoporous organic frameworks and promote the membrane-based applications of these new nanoporous materials.

Acknowledgements

The research was supported financially by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, US Department of Energy, W.J. G. L and Y. H thank the support from National Natural Science Foundation of China (Nos. 21476107, 21776125).

Keywords: mechanochemical • oxidative coupling polymerization • soluble nanoporous polymer networks • mixed-matrix membranes • CO2/CH4 separation


A novel mechanochemical-assisted oxidative coupling polymerization strategy has been developed for the first time to create a novel family of soluble nanoporous polymer networks. The solid-state ball-milling methodology affords inherent molecular weight control over polymer growth and therefore provides unexpected solubility in the resulting nanoporous frameworks. Mixed-matrix membrane-based CO₂/CH₄ separation performance was significantly accelerated by these new soluble fillers.

Xiang Zhu, Yinying Hua, Chengcheng Tian,* Carter W. Abney, Peng Zhang, Tian Jin, Gongping Liu,* Katie L. Browning, Robert L. Sacci, Gabriel M. Veith, Hong-Cai Zhou, Wanqin Jin*, Sheng Dai*