Carbonization of Covalent Triazine-based Frameworks via Ionic Liquid Induction

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A series of porous organic polymers (POPs) were synthesized using tetrahedral 1,3,5,7-tetracyanoadamantane as the main building block. The POP frameworks in the presence of different amounts of molten ZnCl₂ as an ionic liquid were allowed to alter/enhance the Brunauer–Emmett–Teller (BET) surface areas of the POPs in the range from 760 to 1560 m² g⁻¹. The mechanism of the carbonization was unveiled by IR, EA and solid state NMR which is in situ ionic liquid induced polymerization and carbonization of the POPs.

Since the discovery of zeolites, porous materials have demonstrated practical use in many applications such as catalysis and gas separation. During the last three decades, extensive studies on the emerging metal-organic frameworks (MOFs) showed outstanding properties as compared to traditional porous materials due to their distinguished high degree of structural order and also the plausible alteration/tuning of their cavities. Porous organic polymers (POPs), an inorganic node free version of porous materials (including crystalline covalent organic frameworks (COFs), and amorphous porous aromatic frameworks (PAFs), polymers of intrinsic microporosity (PIMs), porous polymer networks (PPNs), covalent triazine-based frameworks (CTFs) are attracting more and more attention because of their great potential for practical applications, for example, gas storage, separation, catalysis, and electronic device. Among these materials, CTFs can be obtained by using a cheap catalyst such as ZnCl₂ and possess high chemical and thermal stability. These advantages make CTFs a promising candidates for bench and applied studies for a wide range of applications.

We are interested in exploring CTFs with small pore size which is of interest for gas separation application such as carbon capture by molecular building block (MBB) strategy. To be highlighted that applying this concept in POP chemistry is very challenging, as no association-dissociation process occurs during the synthetic process. However, because of the structural characteristic of the monomer, it was compelled to us that this strategy will limit the number of plausible outputs and may allow us to achieve the final awaited structure.

We opted to use 1,3,5,7-tetracyanoadamantane (TCA) as a new tetrahedral building block to construct POPs by ionic liquid of molten ZnCl₂ as the solvent and catalyst because of TCA’s rigidity and it can topologically lead to POPs with ctn topology. This small size monomer can result in the assembly of frameworks with small pore windows of around 0.3-0.6 nm in the predicted structures. Experimentally, we sought at investigating different synthetic conditions, in particular the catalyst/monomer (ZnCl₂/TCA) ratio, to fabricate POPs approaching the envisioned topology. The unveiled POP materials showed larger pore sizes than the predicted/simulated structures, which confirm the high challenge in fabricating ordered POPs.

Interestingly, in the presence of different amounts of molten ZnCl₂, the BET surface areas of the POPs calculated from the N₂ adsorption isotherm can be altered/enhanced in the range from 760 to 1560 m² g⁻¹. Infrared spectroscopy (IR), elemental analysis (EA), powder X-ray diffraction (PXRD), and thermogravimetric analysis (TGA) were used to study the composition of the materials which indicate that the carbonization of the frameworks happens due to the ionic liquid-induction.固体 state NMR clearly shows the carbonization of the adamantane core. Although, it has been reported that microporous and mesoporous CTFs were obtained by tuning the reaction temperature, the associated mechanism has yet to be well understood and demonstrated. Studies on the carbonization of CTFs by the effect of the ZnCl₂ catalyst are still quite rare and our finding tells that when pursuing CTFs with predicted small pores, the effect of the carbonization should be considered.
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![Diagram of TCA building blocks](image)

Fig. 1. Schematic showing the expected topology using TCA building blocks (a) case of \(\text{ctn}\) topology (b) and case of \(\text{bor}\) topology (c).

The utilization of the monomer (TCA) and \(\text{ZnCl}_2\) by ionothermal synthesis gives rise to five POPs under similar experimental conditions except for the amount of molten \(\text{ZnCl}_2\), an ionic liquid used as the solvent and catalyst.\(^{19,31}\) The mass ratio of \(\text{ZnCl}_2/\text{TCA}\) used in KPOP-6a, KPOP-6b, KPOP-6c, KPOP-6d, and KPOP-6e (KPOP = KAUST’s POP) were 0.5, 1, 2, 3 and 5 respectively, resulting in different structures of the POPs as detailed hereafter. To be mentioned that the introduction of a lower ratio of \(\text{ZnCl}_2/\text{TCA}\) (i.e., 0.33-0.25) led to non-porous materials.

PXRD patterns (Fig. S1) show that all the POPs are amorphous, a property common in \(\text{ZnCl}_2\) catalyzed 3D CTFs-type POPs. According to the literatures, there are only a few reports on crystalline CTFs, and all of them display two-dimensional structures with \(\pi-\pi\) stacking interactions between the adjacent layers.\(^ {17,18,34}\) TGA (Fig. S2) was carried out under O\(_2\) atmosphere to study POPs' thermal stability. The results show that the framework total integrity of KPOP-6a and KPOP-6b is intact until 300 °C while KPOP-6c, KPOP-6d, and KPOP-6e start to decompose around 350 °C, which shows a slightly higher thermal stability than the previous two samples. Scanning electron microscope (SEM) images (Fig. S3) show the bulk morphology of all the POPs. Energy-dispersive X-ray spectroscopy (EDS) data of KPOP-6c (Fig. S3f) shows that zinc and chloride exist in the sample, indicating that some of \(\text{ZnCl}_2\) is trapped inside the framework, a feature that is usually observed in such type of materials.\(^ {10-19}\)

Prior to probing the surface of the POPs with \(\text{N}_2\) at 77 K (Fig. 2), all the samples were evacuated overnight under vacuum at 200 °C. The determined BET surface areas are estimated to be 760, 870, 1380, 1560 and 1310 m\(^2\)/g respectively for in KPOP-6a, KPOP-6b, KPOP-6c, KPOP-6d, and KPOP-6e. The corresponding pore volumes calculated at \(P/P_0\) of 0.95 are 0.34, 0.40, 0.70, 0.98 and 0.93 cm\(^3\)/g respectively. Interestingly, it is found that the BET surface area increases as the \(\text{ZnCl}_2\) mass increases and seems to level off when the \(\text{ZnCl}_2/\text{TCA}\) ratio is equal to 3 (Fig. 3). The \(\text{N}_2\) adsorption isotherm at 77 K for KPOP-6e shows a slight hysteresis loop at 0.5 \(P/P_0\), indicative of the presence of mesopores. The pore size distributions were calculated by quenched solid state functional theory (QSDFT) method assuming a cylindrical model (Fig. S4). KPOP-6a and KPOP-6b show uniform micropore size with pore diameters of 1.18 and 1.22 nm, respectively. Micropores and mesopores both exist in KPOP-6c, KPOP-6d, and KPOP-6e. The micropore sizes are 1.50, 1.72 and 1.72 nm, respectively while the mesoporous pore sizes are in the range from 3.2 nm to 4.3 nm for KPOP-6c, KPOP-6d, and KPOP-6e. It was found that the pore sizes and surface areas...
could be tuned by controlling the ratio of ZnCl$_2$ versus monomer (ZnCl$_2$/TCA). It is to mention that the catalytic driven assembly will contribute initially to build uniform micropores when the mass ratios of ZnCl$_2$/TCA is low. When this mass ratio increases, the catalysed fast assembly will contribute in pore disorder and generation of non-uniform pores with different pore sizes. Thus, leading to evident broadening of pore size distribution as shown in Figure S4. EA, IR and solid-state NMR analysis were performed to study/analyse the occurring mechanism.

Fig. 4. Evolution of C/N and C/H molar ratio according to elemental analysis

Elemental analysis (EA) of the POPs (Fig. 4) shows that in KPOP-6a and KPOP-6b, which were prepared with a low amount of ZnCl$_2$, the ratios of C/N and C/H are slightly higher/lower compared with the theoretical ratio derived from the idealized bor and ctn topology. While in KPOP-6c, KPOP-6d, and KPOP-6e made with a higher amount of catalyst, the contents of nitrogen and hydrogen sharply decline which should be due to the carbonization of the framework during the reaction. The IR spectra (Fig. 5) reveal that the intensity of the nitrile peak displayed at 2241 cm$^{-1}$ become weaker in KPOP-6a and KPOP-6b than in the spectra of the monomer and almost disappear in those of KPOP-6c, KPOP-6d, and KPOP-6e. This behavior is attributed to the consumption of the monomer during the reactions. The peaks at 1523 and 1351 cm$^{-1}$ in KPOP-6a and KPOP-6b’s spectra confirm the formation of triazine rings $^{11, 35-37}$ while the very weak intensity of the corresponding peaks in the spectra of KPOP-6c, KPOP-6d, and KPOP-6e is indicative of the triazine decomposition.

Fig. 5. IR spectra of the POPs and monomer.

Solid-state $^{13}$C NMR spectra (Fig. 6) of KPOP-6a and KPOP-6b, reveal two peaks located at 41.2 and 32.2 ppm that are attributed to the two kinds of carbon from adamantane core$^{38}$, confirming the presence of adamantane moieties within the framework of KPOP-6a and KPOP-6b. However, the solid-state $^{13}$C NMR spectra collected on KPOP-6c, KPOP-6d, and KPOP-6e, clearly show that the adamantane units were probably converted to amorphous carbon during the reaction process. The peak located at 123.9 ppm of KPOP-6a and KPOP-6b was attributed to the unreacted nitrile groups while this peak was not present in the case of KPOP-6c, KPOP-6d, and KPOP-6e. The formation of carbon in these last three samples was further confirmed by the presence of a peak located at 127.4 ppm, typical attribution of carbon-carbon double bond formed by carbonization of adamantane indicating that the major components of KPOP-6c, KPOP-6d, and KPOP-6e are amorphous porous carbon. The conclusion obtained from solid-state NMR was also supported by IR and EA. The presence of an extra-peak in both NMR spectra of KPOP-6c, KPOP-6d, and KPOP-6e confirms the presence of triazine moieties.

Based on the EA, IR and solid-state NMR analysis, it was evident that ionic liquid catalyst of molten ZnCl$_2$ promoted the carbonization of the POPs’ frameworks leading to extended pore apertures. When the ZnCl$_2$/TCA ratio is below 3, the surface area increases as a function of the ratio. However, when the ratio reaches 5, the surface area of the POP starts to decrease due to the collapse of the structure after a high degree of carbonization, revealing that the adjustment of the catalyst/organic molecule ratio influenced the porosity of the obtained POPs.
In light of the obtained uniform pores with triazine rings in the frameworks of KPOP-6b, a major metric in the selection of CO$_2$ adsorbents$^{41,42}$, it was further selected to evaluate its CO$_2$ capture ability (Fig. S7). At 273 K and 298 K, 1 bar, the CO$_2$ uptake are 3.8 and 2.4 mmol g$^{-1}$ respectively. The CO$_2$ heat of adsorption for KPOP-6b (Fig. S6) is 31.9 kJ mol$^{-1}$ at low loading (0.027 mmol g$^{-1}$ uptake). Ideal adsorbed solution theory (IAST)$^{43}$ (Fig. S8) was used to qualitatively predict the separation factors of CO$_2$/CH$_4$ (50:50) and CO$_2$/N$_2$ (10:90) mixtures using experimentally obtained single gas adsorption isotherms at 298 K and 273 K. To be noted that IAST selectivity prediction is a valid methodology when the same elaborate model fits matchlessly the experimental data from single gas adsorption isotherms. Consequently, IAST can be confidently used to evaluate gas selectivity in KPOP-6b. The predicted separation factors of CO$_2$/N$_2$ (10:90) and CO$_2$/CH$_4$ (50:50) at 1 bar are 87.9 and 9.2 at 298 K, slightly lower than 101.2 and 11.5 at 273 K. The CO$_2$/CH$_4$ selectivity is similar to the reported data but the predicted separation factor of CO$_2$/N$_2$ selectivity is quite high among the CTFs materials compared to CTF-1 (20, 298 K),$^{12}$ bpm-CTF400 (32, 298 K),$^{44}$ and CTF-FL (48, 273 K),$^{45}$ but lower than few functionalized porous organic polymers like pypm-CTF500 (502, 298 K),$^{46}$ and PNP-6-CH$_2$DETA (442, 298 K).$^{47}$

In conclusion, we report a series of POPs with different pore sizes and surface areas by changing the ratio of the monomer and catalyst, via ionic liquid induced carbonization, a method that is different from the previously reported methodology by changing the reaction temperature. The mechanism was studied by different characterization. From the solid state NMR data, the carbonization was clearly found. This phenomenon may be extended to other monomers and reactions using the same principle. In this study, we illustrated the use of KPOP-6b, which display uniform porosity, as a CO$_2$ adsorbent. Further work is underway to explore the use of these POPs for sensing and adsorption related applications.

Notes and references

Footnotes relating to the main text should appear here. These footnotes should not be numbered.

3. B. Ghanem, Y. Belmabkhout, Y. G. Wang, Y. F. Zhao, Y. Han, M. Eddaoudi and I. Pinnau, Rsc Advances, 2016, 6, 97560-97565.


