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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 ZnCl_2 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 $\text{m}^2 \text{g}^{-1}$. 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.^{1–3} During the last three decades, extensive studies on the emerging metal-organic frameworks (MOFs)^{4, 5} 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),⁶ and amorphous porous aromatic frameworks (PAFs),⁷ polymers of intrinsic microporosity (PIMs),⁸ porous polymer networks (PPNs),⁹ covalent triazine-based frameworks (CTFs)^{10–19}) are attracting more and more attention because of their great potential for practical applications, for example, gas storage, separation, catalysis, and electronic device.²⁰ Among these materials, CTFs can be obtained by using a cheap catalyst such as ZnCl_2 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^{21–27} by molecular building block (MBB) strategy.^{28–30} 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^{19, 31} of molten ZnCl_2 as the solvent and catalyst because of TCA's rigidity and it can topologically lead to POPs with **ctn** or **bor** topology (Fig. 1)^{6, 32}. 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 (ZnCl_2/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 ZnCl_2 , the BET surface areas of the POPs calculated from the N_2 adsorption isotherm can be altered/enhanced in the range from 760 to 1560 $\text{m}^2 \text{g}^{-1}$. 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. ^{13}C solid 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 ZnCl_2 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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Fig. 1. Schematic showing the expected topology using TCA building blocks (a) case of ctn topology (b) and case of bor topology (c).

The utilization of the monomer (TCA) and ZnCl_2 by ionothermal synthesis gives rise to five POPs under similar experimental conditions except for the amount of molten ZnCl_2 , an ionic liquid used as the solvent and catalyst.^{19, 31} The mass ratio of ZnCl_2 /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 ZnCl_2 /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 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 π - π 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 ZnCl_2 is trapped inside the framework, a feature that is usually observed in such type of materials.¹⁰⁻¹⁹

Fig. 2. N_2 adsorption/desorption isotherms at 77K: black, **KPOP-6a**; red, **KPOP-6b**; green, **KPOP-6c**; blue, **KPOP-6d**; purple, **KPOP-6e**; solid circles, adsorption; open circles, desorption.

Fig. 3. POPs' BET surface areas changing curve versus the mass ratio of ZnCl_2 /monomer (TCA).

Prior to probing the surface of the POPs with 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 $\text{m}^2 \text{g}^{-1}$ 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 $\text{cm}^3 \text{g}^{-1}$ respectively. Interestingly, it is found that the BET surface area increases as the ZnCl_2 mass increases and seems to level off when the ZnCl_2 /TCA ratio is equal to 3 (Fig. 3). The 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

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

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. 6. ^{13}C solid state NMR spectra (black, monomer; red, **KPOP-6a**; blue, **KPOP-6b**; green, **KPOP-6c**; purple, **KPOP-6d**; dark red, **KPOP-6e**).

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 core³⁸, 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 bond³⁹ formed by carbonization of adamantine 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-6a** and **KPOP-6b**, located at 173.4 ppm attributed to the characteristic peak of triazine,^{18, 40} confirmed 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 CO₂ adsorbents^{41,42}, it was further selected to evaluate its CO₂ capture ability (Fig. S7). At 273 K and 298 K, 1 bar, the CO₂ uptake are 3.8 and 2.4 mmol g⁻¹ respectively. The CO₂ 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 CO₂/CH₄ (50:50) and CO₂/N₂ (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 CO₂/N₂ (10:90) and CO₂/CH₄ (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 CO₂/CH₄ selectivity is similar to the reported data but the predicted separation factor of CO₂/N₂ selectivity is quite high among the CTFs materials compared to CTF-1 (20, 298 K),¹² bpim-CTF400 (32, 298 K),⁴⁴ and CTF-FL (48, 273 K),⁴⁵ but lower than few functionalized porous organic polymers like pym-CTF500 (502, 298 K),⁴⁶ and PPN-6-CH₂DETA (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 CO₂ 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 might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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