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ARTICLE TYPE

Target Synthesis of a Novel Porous Organic Framework and Its Application in CO₂/CH₄ separation

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A novel porous organic framework based on Tetra-(4-anilyl)-methane and cyanuric chloride has been designed and synthesized successfully, which possesses permanent porosity, selective gas adsorption, and high selectivity of CO₂ towards CH₄.

As a new class of adsorbent materials, porous organic frameworks (POFs) have attracted attentions in sustainable energy and environment research. POFs are produced via coupling rigid organic building blocks via strong covalent bonds, which are light frameworks and display permanent porosity, large surface area, enhanced pore stability and improved stability toward environmental condition such as moisture. **Error! Reference source not found.** Additionally, mature organic-based synthesis strategies offer control and diversity over both structure and properties at the molecular level. To name a few, COFs by Yaghi et al. **Error! Reference source not found.**, MOPs **Error! Reference source not found.**, HCPs **Error! Reference source not found.** and CMPs **Error! Reference source not found.** by Cooper et al., PIMs **Error! Reference source not found.** by Budd and McKeown et al., CTFs **Error! Reference source not found.** by Antonietti and Thomas et al., PAFs **Error! Reference source not found.** by Zhu et al., PPNs **Error! Reference source not found.** by Zhou et al.

Carbon dioxide, being one of the predominant greenhouse gases, is always considered as a disadvantageous composition in fuel gas such as methane. In natural gas for example, the presence of certain percent CO₂ will cause the corrosion of the relevant pipeline and equipment. Thus, separation of CO₂ from CH₄ is crucial in the industrial application. Among currently accessible CO₂ capture technologies, adsorption using porous solids is regarded as the most promising technology. To date, various porous solids, such as activated carbons **Error! Reference source not found.**, MOFs **Error! Reference source not found.** and POFs have been utilized as adsorbents. Enhanced CO₂ adsorption has been observed in various classes of nitrogen-functionalized framework, due to dispersion and electrostatic forces generated between CO₂ and N heteroatom or acid-base type interactions or amine group. **Error! Reference source not found.** Comparing to most other gases (except H₂, He, Ne, H₂O, and NH₃), CO₂ has a smaller kinetic diameter of 3.30 Å, so the other highly efficient way of achieving high CO₂ selectivity is to control the pore size.

Herein we present a novel porous organic framework, named as

PAF-36, by coupling tetrahedral building units and N-rich unit cyanuric chloride interconnected via -NH- group. Combining with the selective adsorption behavior and an enhanced interaction between CO₂ and framework surface, PAF-36 shows the CO₂/CH₄ selectivity as high as 63.2 for an equimolar CO₂/CH₄ mixture at 10 bar and 298K, thus have promising potential in CO₂ separation from methane.

Tetraphenylmethane and its derivatives have a tetrahedron molecule conformation and are proved to be effective building units to construct POFs with desired three-dimensional structures. **Error! Reference source not found.** Cyanuric chloride is an important industrial chemical of low-cost but high reaction activity towards amine and alcohol. Furthermore, triazines of cyanuric chloride offer high nitrogen content, which is a desirable feature for CO₂-specific gas operations. **Error! Reference source not found.** Tetra-(4-anilyl)-methane and cyanuric chloride can be easily condensed into polymers, PAF-36, in dimethylacetamide in presence of N, N-diisopropylethylamine without any use of expensive catalysts. (Fig.1)

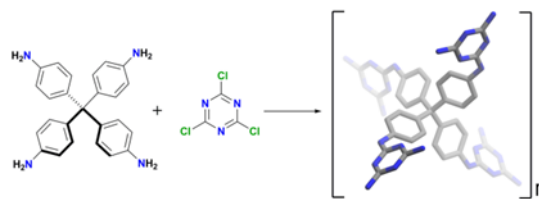


Fig. 1 Scheme of PAF-36 synthesis reaction

The connectivity of the PAF-36 obtained so and the presence of derivatives of both building units were confirmed by Fourier Transform Infrared Spectroscopy (FTIR) and solid-state ¹³C NMR (see ESI, Fig.s1 and Fig.s2). The disappearance of N-H bands of primary amines at 1625 cm⁻¹ clearly indicated the substitution of amine group in tetra-(4-anilyl)-methane building unit. The peaks at 1411 and 1569 cm⁻¹, which are assigned to the C=N stretching vibration, proved the existence of triazine rings in framework. The C-Cl stretching bands at 850 cm⁻¹ were diminished to an undetected level, suggesting essentially complete reaction of starting cyanuric chloride. ¹³C solid-state NMR (CP/MAS) spectroscopy (see ESI, Fig.s2) clearly indicated a peak at 67.9 ppm, which is assigned to the sp³ C and a series close peaks in a range of 100-200 ppm, which is assigned to the

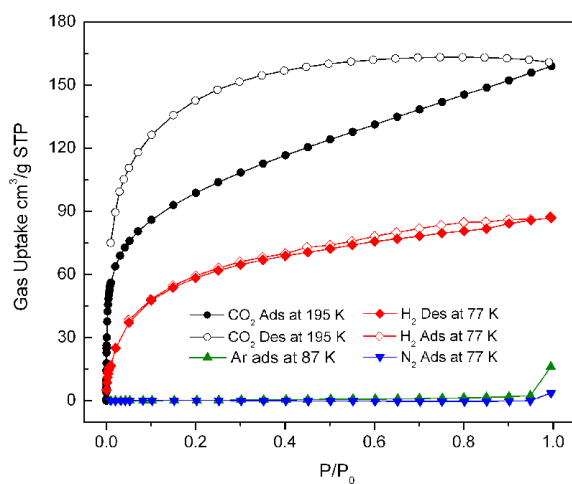
sp² C in the benzene rings and triazine rings. The powder X-ray diffraction (see ESI, Fig. s3 and Fig. s4) demonstrated only three broad diffraction signals at around 2θ of 8, 15, 22 degree. It implied PAF-36 is mainly amorphous, of much lower crystallization degrees comparing with the PAF-6^{Error! Reference source not found.} which synthesized through the analogous building unit and method. Scanning electron microscopy (SEM) imaging revealed PAF-36 powders are composed of the agglomerates of micro- and nanoparticles (See ESI, Fig. s6). Thermal gravimetric analysis (TGA) of the PAF-36 showed a slight mass lost before 350 °C under air. (See ESI, Fig. s5)

To investigate the porosity of PAF-36, we performed gas sorption experiments for various probe molecules, including N₂, Ar, H₂, CO₂, and CH₄. The resulting isotherms are shown in Fig. 2. Despite only relatively small differences in the kinetic diameters of probe gases, such as H₂ (2.89 Å), CO₂ (3.30 Å), Ar (3.54 Å), N₂ (3.64 Å), and CH₄ (3.76 Å),^{Error! Reference source not found.} a very large difference in the adsorption isotherms was observed for PAF-36. N₂ and Ar adsorption isotherms for PAF-36 revealed very low uptakes at 77 K and 87 K. This result indicates that these gases are barely adsorbed in the PAF-36 pores at low temperature and that adsorption mainly occurs on the external surface. In contrast, the significant amounts of CO₂ and H₂ are adsorbed. Both H₂ and CO₂ adsorption isotherms exhibit a sharp uptake in the low pressure region (10⁻⁵~10⁻³ atm), which is a signature feature of microporosity. This behaviour is analogous to the molecular sieving effect observed in zeolite 4A, which shows O₂ adsorption but no N₂ uptake at 123 K. In view of the kinetic diameters of 3.30 Å for CO₂ and 3.54 Å for Ar, it can be inferred that the pore openings in PAF-36 are between 3.30 and 3.54 Å in diameter assuming that the framework structure does not change upon gas adsorption. By fitting the CO₂ isotherm based on Langmuir equation at 195 K, PAF-36 has an estimated surface area of 989 m² g⁻¹, corresponding to a BET surface area of 540 m² g⁻¹. The value is significantly higher than other MOFs^{Error! Reference source not found.} and microporous polymers^{Error! Reference source not found.} performing analogous selective gas adsorption. Similar to many polymer networks, PAF-36 also shows a hysteresis loop in CO₂ adsorption. The large hysteresis suggests that the framework exhibits a swelling behavior in CO₂.

Fig. 2 Gas sorption isotherms of PAF-36 at low temperature

The isosteric heats of adsorption were calculated from the CO₂ adsorption isotherms at 273 K and 298 K (Fig.s7). As expected, at zero-loading, PAF-36 showed the heat of adsorption (Q_{st}) of 36.9 kJ mol⁻¹, substantially higher than that of acid-functionalized porous polymer, PPN-6-SO₃H and PPN-6-SO₃Li (30.4 and 35.7 kJ mol⁻¹)^{Error! Reference source not found.}, CMP-1-COOH(32.6 kJ mol⁻¹)^{Error! Reference source not found.}. The high Q_{st} value in PAF-36 can be attributed to the cooperation of the high polar framework and the small pore size effect. The large dipole moment arising from the high content of N atoms in the framework should facilitate strong dipole-quadrupole interactions between the pore surface and CO₂. Besides, small pore sizes have been reported to increase the heat of adsorption. In the narrow-pore structures, CO₂ molecules can interact with multiple pore surfaces simultaneously. For H₂ adsorption, the small pore also tends to a high adsorption enthalpies. PAF-36 features a Q_{st} of hydrogen adsorption as high as 19.6 kJ mol⁻¹ (Fig. s8). There is only a few organic nanoporous materials^{Error! Reference source not found.} that exhibit a Q_{st} of adsorption in the range of 15 to 20 kJ mol⁻¹, which is highly desired for hydrogen storage at room temperature^{Error! Reference source not found.}.

The selective adsorption behavior, demonstrated by the isotherms depicted in Fig. 2, indicates that PAF-36 can be used for CO₂ separations. Furthermore, the nature of size exclusion of CH₄ and the high adsorption enthalpy of CO₂ of PAF-36 prompted us to study the separation of CO₂ from CH₄, the major component in such as natural gas and landfill gas. Nowadays, separation of CO₂ from natural gas carried out on a scale of billions of tons per year in the United States alone. The single component CO₂ and CH₄ adsorption results obtained on PAF-36 at 298 K are shown in Fig.s9a. It is clearly evidenced that CO₂ is adsorbed in a significantly larger amount comparing with CH₄. We applied the ideal adsorption solution theory (IAST) proposed by Myers and Prausnitz in 1965^{Error! Reference source not found.} to predict the adsorption amount of each component of the mixture. As suggested in previous studies, the dual-site Langmuir–Freundlich (DSLf) adsorption model-based IAST theory was explored the adsorption selectivity of porous materials^{Error! Reference source not found.}. The selectivity of PAF-36 for CO₂/CH₄ was calculated under the typical feed composition for natural gas purification (5% CO₂ and 95% CH₄) and general feed composition of landfill gas (50% CO₂ and 50% CH₄) at 298 K and 10 bar as shown in Fig. s9. Extremely high CO₂/CH₄ selectivity in a range of 24.3-63.2 is obtained for the landfill gas. For natural gas separation, PAF-36 shows very high CO₂/CH₄ selectivity (24.3-30.2) and little pressure dependence in the wide pressure region (0-10 bar).



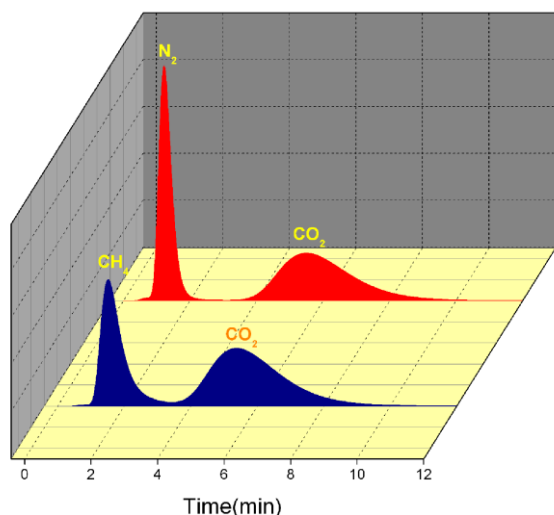


Fig. 3 GC chromatograms on a PAF-36-packed open tubular column D (20 cm long \times 2mm i.d.) for separation of N_2/CO_2 and CH_4/CO_2 mixtures, respectively.

This selectivity is comparable to or even better than the highest value (30) reported from $Li_{0.55}$ -reduced diimide based porous polymer^{Error! Reference source not found.} and much better than that of other reported porous solids at the same or similar conditions (0.89 for MOF-177^{Error! Reference source not found.}, 2.28 for Cu-BTC^{Error! Reference source not found.}, 1.32 for ZIF-8^{Error! Reference source not found.}, 2.30 for MIL-53(Al)^{Error! Reference source not found.}, 7.89 for PAF-1-450^{Error! Reference source not found.}, 3.7 for activated carbon^{Error! Reference source not found.} for equimolar CO_2/CH_4 binary mixtures at $T = 298$ K and $p = 1$ bar; 15 for $Li_{0.35}$ -reduced diimide based porous polymer^{Error! Reference source not found.} at $T = 298$ K and $P = 2$ bar). The high selectivity for CO_2 should be ascribed to the synergy of the size exclusion and the strong adsorbate-surface interactions of PAF-36 as well as the higher critical point of CO_2 than those of other gases. These results suggest that PAF-36 is a promising candidate for natural gas purification and landfill gas separation, particularly at low pressures (< 100 kPa), such as vacuum PAS unit.

Different from the thermodynamic separation in equilibrium state, kinetic separation is accomplished as a result of the difference in the diffusion rates of different components, which is valued more importance in industrial applications. For characterization of the kinetic separation of the CO_2/CH_4 and CO_2/N_2 mixtures, PAF-36 was packed in a column and evaluated by means of gas chromatography (GC). As shown in Fig 3, a baseline separation of CO_2 from CH_4 and N_2 is achieved on the PAF-36 packed column. The result clearly endorses the promising application of PAF-36 for selective adsorption of CO_2 .

Conclusion

We have successfully synthesized a novel porous organic framework, PAF-36, based on a catalyst-free condensation of cyanuric chloride and tetra-(4-anilyl)-methane. PAF-36 exhibited a selective gas adsorption cryogenic temperature and an enhanced

isosteric heat of adsorption. IAST prediction indicates that the CO_2 adsorption selectivity of PAF-36 is in the range of 24.3-63.2 for landfill gas (an equimolar CO_2/CH_4 mixture), and in the range of 4-30 for natural gas with the CO_2 to CH_4 volume ratio of to 5:95 at 10 bar and 298 K. For its low-cost nature and the superior performance of CO_2 separation, PAF-36 should be the promising candidate as selective adsorption and separation of CO_2 .

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Notes and references

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