Design and synthesis of multifunctional porous N-rich polymer containing s-triazine and Tröger’s base for CO₂ adsorption, catalysis and sensing

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Experimental Details

Synthesis of 2,4,6-tris(4-aminophenyl)-s-triazine (TAPT)

TAPT was synthesized according to the literature. In a typical synthesis, 10 mL trifluoromethanesulfonic acid was added into a three-necked round bottom flask maintained at 0 °C under N₂ atmosphere. The solution was stirred for 0.5 h. Separately, 4-aminobenzonitrile (590.0 mg, 5 mmol) was added to the trifluoromethanesulfonic acid solution at 0 °C under N₂ atmosphere. The reaction mixture was warmed up to room temperature and was allowed to stir under N₂ for 24 h. The contents were neutralized by adding about 250 mL of 2 M NaOH solution. Upon neutralization, a pale-yellow precipitate (487.3 mg) was obtained, which was filtered and washed with copious amounts of distilled water. Yield: 82.6%. ¹H NMR (300 MHz, DMSO-δ6) δ (ppm): 8.4-8.3 (d, 6H, Ar–H), 6.71-6.67 (d, 6H, Ar–H), 5.92 (s, 6H, Ar–NH₂). ¹³C NMR (75 MHz, DMSO-δ6) δ (ppm): 169.6, 152.9, 130.1, 123.0, 113.1.
Characterization

Fig. S1 TG analysis of porous N-rich polymer.

Fig. S2 Experimental powder X-ray diffraction PXRD pattern of porous N-rich polymer.
**Fig. S3** Size distribution of porous N-rich polymer in EtOH (0.1 mg/mL) determined by DLS Analysis.

**Fig. S4** SEM images of porous N-rich polymer.
Heat of CO$_2$/CH$_4$ Adsorption Calculation

The isosteric heats ($Q_{st}$) of adsorption for porous N-rich polymer were calculated by fitting the CO$_2$ adsorption isotherms measured at 273 K, 283 K and 298 K to the Virial equation.

The isosteric heats ($Q_{st}$) of adsorption for porous N-rich polymer were calculated by fitting the CH$_4$ adsorption isotherms measured at 273 K and 298 K to the Virial equation.

\[
\ln P = \ln N + \frac{1}{T} \sum_{i=0}^{m} a_i N_i + \sum_{i=0}^{n} b_i N_i
\]

\[
Q_{st} = - R \sum_{i=0}^{m} a_i N_i
\]

$N$: amount adsorbed (mg/g);
$P$: pressure (mmHg);
$T$: temperature (K);
$a_i$, $b_i$: constants;
$R$: 8.314 J·mol$^{-1}$·K$^{-1}$
Fig. S6 Virial fitting for CO₂ isotherms of porous N-rich polymer.

Fig. S7 The isosteric heat of adsorption for CO₂.
**Fig. S8** CH₄ adsorption isotherms at 273 K and 298 K for porous N-rich polymer.

**Fig. S9** Virial fitting for CH₄ isotherms of porous N-rich polymer.
Prediction of adsorption of binary mixture by IAST theory

In order to perform the IAST calculations, the single-component isotherm was fitted by the single-site Langmuir-Freundlich (SSLF) adsorption model to correlate the pure-component equilibrium data and further predict the adsorption of mixtures. The SSLF model is described as:

\[ N_0(f) = \frac{N_1 k_1 f}{1 + k_1 f} \]

Where \( f \) is the fugacity of bulk gas at equilibrium with adsorbed phase, \( N \) is the model parameter of the maximum adsorption amount, and \( k \) is the affinity constant.

Based on the above model parameters of pure gas adsorption, we used the IAST model, which was proposed by Myer and Prausnitz in 1965 to predict the multi-component adsorption. Analogous to Raoults’s law for vapor-liquid equilibrium, the IAST assumes that the adsorbed solutions are ideal and all activity coefficients in the adsorbed phase are unity. Thus, the adsorption equilibrium between adsorbed and gas phases will lead to the following equation.
\[ P y_i \phi_i = x_i f_0^i(\pi) \]

Where \( f_0^i \) is the fugacity of the equilibrium gas phase corresponding to the spreading pressure \( \pi \) for the adsorption of pure gas \( i \), \( \phi_i \) is the gas fugacity coefficient of component \( i \) calculated by PR equation of state, and \( x_i \) and \( y_i \) are the molar fraction of component \( i \) at the adsorbed and bulk phases, respectively. The binary gas mixing process is carried out at constant spreading pressure \( \pi \) and indicated by

\[
\int_0^{f_1^0} N_1(f_1) d\ln(f_1) = \int_0^{f_2^0} N_2(f_2) d\ln(f_2)
\]

Where the single-component adsorption amount and selectivity are further obtained from the above equation by numerical integration and root exploration. To investigate the separation of binary mixtures, the adsorption selectivity is defined by

\[
S_{ij} = \frac{x_i}{x_j} \frac{y_i}{y_j}
\]

Where the selectivity refers to the first component over the second one, and the \( x_i, x_j \) and \( y_i, y_j \) denote the molar fractions of species \( i, j \) in the adsorbed and bulk phases, respectively.
Fig. S11 CO$_2$ adsorption isotherms at 273 K and 298 K for porous N-rich polymer.

Fig. S12 Nitrogen adsorption isotherms at 273 K of porous N-rich polymer.
**Fig. S13** CH₄ adsorption isotherms at 273 K and 298 K for porous N-rich polymer.

**Fig. S14** IAST selectivities for CO₂/CH₄ at 273 K and 298 K for 50:50 mixtures of porous N-rich polymer.
**Fig. S15** IAST selectivities for CO$_2$/CH$_4$ at 273 K and 298 K for 5:95 mixtures of porous N-rich polymer.

**Fig. S16** IAST selectivities for CO$_2$/N$_2$ at 273 K for 15:85 mixtures of porous N-rich polymer.
Fig. S17 IAST selectivities for CO$_2$/N$_2$ at 273 K for 50:50 mixtures of porous N-rich polymer.

The concentration of hydrochloric acid vapor was determined according to the following definitions:

$$ppm = \frac{c \times V_{HCl} \times V_m}{V}$$

Where $c$ is the molar concentration of the hydrochloric acid, $V_{HCl}$ is the volume of the hydrochloric acid, $V_m$ is the molar volume of gas, and $V$ is the volume of the glass solution bottle.
**Fig. S18** UV-Vis diffusive reflectance spectra of the polymer by hydrochloric acid vapor at different concentrations within 10 s.

**Fig. S19** UV-Vis diffusive reflectance spectra of the polymer by hydrochloric acid vapor (1345 ppm) at different times.
**Fig. S20** UV-Vis diffusive reflectance spectra of the polymer in several hydrochloric acid/ammonia cycles within 15 s.

**Fig. S21** Reusability of the porous N-rich polymer catalysts in the syntheses between benzaldehyde and malononitrile.
**Fig. S22** Reusability of the porous N-rich polymer catalysts in the syntheses between 4-bromobenzaldehyde and malononitrile.

**Fig. S23** $^1$H NMR spectrum of benzylidenemalononitrile.
**Fig. S24** $^1$H NMR spectrum of 4-bromobenzylidenemalononitrile.

**Fig. S25** $^1$H NMR spectrum of 4-methylbenzylidenemalononitrile.
**Fig. S26** $^1$H NMR spectrum of 4-chlorobenzylidenemalonodinitrile.

**Fig. S27** $^1$H NMR spectrum of 4-cyanobenzylidenemalononitrile.
Fig. S28 ¹H NMR spectrum of 4-nitrobenzylidenemalononitrile.

Table S1. Elemental analysis of porous N-rich polymer.

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<tr>
<th>Element</th>
<th>N-rich Polymer</th>
<th>Calculated</th>
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<tr>
<td>C [%]</td>
<td>67.71</td>
<td>74.98</td>
</tr>
<tr>
<td>H [%]</td>
<td>4.973</td>
<td>4.44</td>
</tr>
<tr>
<td>N [%]</td>
<td>18.44</td>
<td>20.58</td>
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<td>C/N ratio</td>
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<td>3.64</td>
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Table S2. The values of selectivity calculated by the IAST method

<table>
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<tr>
<th>CO₂/N₂</th>
<th>CO₂/CH₄</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>Selectivity</td>
</tr>
<tr>
<td>-------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>this porous polymer</td>
<td>55.3</td>
</tr>
<tr>
<td>MOPI-1</td>
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<tr>
<td>ALP-3</td>
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<tr>
<td>TNP3</td>
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REFERENCES


6. S. Dey, A. Bhunia, D. Esquivel and C. Janiak, *J. Mater. Chem. A*, 2016, **4**, 6259-
6263.