Electronic supplementary information (ESI)

Nitrogen-doped porous carbon monolith as a highly efficient catalyst for CO₂ Conversion

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Figure S1. Photograph of the precursor before pyrolysis.



Figure S2. PSDs of the N-doped carbon porous monoliths activated at different temperatures.



Figure S3. SEM images of the samples by different feedstocks in the Teflon-lined stainless-steel autoclave at 180 °C and 24 h a) alginic acid (AA) and ethylenediamine, b) alginic acid (AA), ethylenediamine and glutaraldehyde, c) alginic acid (AA), ethylenediamine, glutaraldehyde and pyrrole.



Figure S4. FT-IR spectra of the obtained carbon monoliths pyrolyzed at 750, 850, 950 and 1000 °C, respectively.

With an increase in the carbonization temperature, the bands in general become broader and overlap due to the strong absorption of the carbon materials. The weak bands at ca. 3417 cm⁻¹ (3000-3700 cm⁻¹) can be assigned to the presence of the N-H and/or O-H stretching vibration.^[S5-S7] The peaks around ca. 1599 cm⁻¹ are attributed to N-H in-plane deformation vibrations or C=C stretching vibration, which shows the presence of aromatic rings or the presence of both species.^[S8] The peaks at 1355–800 cm⁻¹ which are attributed to C–N stretching vibrations, in-plane C–H and N–H deformations and out-of-plane C–H and N–H deformations.^[S9-S11] These results suggest that N–H and C–N species are present in the resultant monolith and activated samples, and that they are gradually removed with the increase of activation temperature.

Table S1. Textural properties and chemical compositions of the N-doped porous carbon monoliths.

| | Textural proper | ties | Chemical composition[wt%] | | | |
|---------|-------------------------|------------------------|---------------------------|------|-------|------|
| Sample | $S_{BET}[m^{2} g^{-1}]$ | $V_t[cm^3g^{-1}]^{a)}$ | С | Н | 0 | Ν |
| AA-750 | 628 | 0.259 | 74.4 | 2.05 | 16.2 | 7.35 |
| AA-850 | 1225 | 0.569 | 86.59 | 0.42 | 10.58 | 2.41 |
| AA-950 | 2241 | 1.526 | 90.38 | 0.30 | 7.94 | 1.38 |
| AA-1000 | 2486 | 1.899 | 93.67 | 0.35 | 5.37 | 0.61 |

| | AA-750 | | AA-850 | | AA-950 | | AA-1000 | |
|---------------|-------------------------|------|-------------------------|------|-------------------------|------|-------------------------|------|
| N species | Peak position/ eV | N% | Peak position/ eV | N% | Peak position/ eV | N% | Peak position/ eV | N% |
| Pyridinic | 397.4 | 33.9 | 397.4 | 14.1 | 398.6 | 27.6 | | |
| Pyrrolic | 400.0 | 61.5 | 400.4 | 74.7 | | | | |
| Quaternary | | | | | 401.3 | 62.8 | 400.9 | 80.7 |
| Pyidine oxide | 402.0 | 4.6 | 403.5 | 11.2 | 404.1 | 9.6 | 403.5 | 19.3 |

Table S2. Detailed breakdown of N1s spectra from four samples under different activation temperatures from XPS analysis, indicating peak position and the contents of the four types of nitrogen atoms.



Figure S5. Yields of chloropropene carbonate at different CO_2 pressures with AA-950 as the catalyst.

Scheme S1. Two proposal mechanisms of cycloaddition of CO_2 to epichlorohydrin catalysed by N-doped porous carbon monoliths, a) major pathway. b) minor pathway.





Figure S6. Optimized structures of stationary points along with the reaction pathway. The abbreviations used here are consistent with those in the text. Distances are in angstrom (Å).

Computational methods

All calculations were performed using density functional theory (DFT) with the hybrid functional B3LYP^[S12] as implemented in Gaussian 09 package.^[S13] With dispersion interaction included, geometry optimizations were carried out with the 6-311+G(d,p) basis set, which includes diffuse basis set. The dispersion effects were considered using an empirical formula by Grimme.^[S14] On the basis of optimized geometries, more accurate energies were obtained by performing single point calculations with a larger basis set, 6-311+G(2d,2p). Frequency calculations were performed to obtain zero-point energies (ZPE) and to confirm the nature of stationary points. It is a common experience that entropy effects can be very big for a free CO₂ molecule. However, as described in the part of experiments above, the present investigated reactions essentially happened in liquid phase since the reacting CO₂ was actually dissolved in liquid epoxide with a very high pressure (4 MPa). Therefore, entropy effects were safely omitted in the present calculations. The energies reported in the present paper are all corrected for both ZPE and dispersion effects.

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