

Electronic Supplementary Information

Synthesis of 1,3,5,7-tetrakis(4-cyanatophenyl)adamantane and its microporous polycyanurate network for adsorptions of organic vapors, hydrogen and carbon dioxide

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Experimental Section

Materials and measurement

Cyanogen bromide, cuprous bromide, boron tribromide (BBr_3), sodium methoxide and liquid bromine were purchased from J&K Chemical Co., Ltd. Nonylphenol, diphenyl sulfone, acetone, dichloromethane, chloroform, iron powder, ethyl acetate, *N,N*-dimethylformamide (DMF), methanol and triethylamine were provided by Shanghai Chemical Reagent Co. Dichloromethane and acetone were purified by refluxing over phosphorus pentoxide and distilled prior to use. Triethylamine was purified by distillation over calcium hydride. Other chemical reagent were of reagent grade and used as received. All chromatographic separations were carried out on silica gel (400 mesh) purchased from Qingdao Make Silica Gel Drier Co., Ltd. 1,3,5,7-Tetraphenyladamantane (TPAD) was synthesized according to a published method.⁷²

Fourier transform infrared spectra (FTIR) were recorded using a Nicolet 20DXB FT-IR spectrophotometer in the 400-4000 cm^{-1} region. ^1H NMR and ^{13}C NMR spectra were measured on a 400 MHz Varian INOVA NMR spectrometer, using tetramethylsilane as an internal reference. Melting points were performed using an X-4 melting-point apparatus with microscope. Solid-state ^{13}C CP/MAS (cross-polarization with magic angle spinning) spectrum was recorded on a Varian Infinity-Plus 400 spectrometer at 100.61 MHz. Elemental analyses were determined with an Elementar Vario EL III elemental analyzer. X-ray diffractions (XRD) from 5° to 60° were performed on Rigaku D/max-2400 X-ray diffractometer (40 kV, 200 mA) with a copper target at a scanning rate of $2^\circ/\text{min}$. Thermogravimetry measurement (TG) was performed in the nitrogen atmosphere on a NETZSCH TG 209 thermal analyzer at a heating rate of $10^\circ\text{C min}^{-1}$. Field-emission scanning electron microscopy (FE-SEM) experiments were carried on a Nova NanoSEM 450. High-resolution Transmission Electron Microscopy (HR-TEM) images were obtained on a Hitachi HT-7700 operated at 100 kV. Adsorption and desorption measurements for all the gases were conducted on an Autosorb iQ (Quantachrome) analyzer. Before sorption measurements, the samples were degassed at 120°C under high vacuum for 24 h. Adsorption and desorption isotherms of nitrogen were measured at 77 K. The surface areas was calculated

according to the Brunauer-Emmett-Teller (BET) model in the relative pressure (P/P_0) range from 0.075 to 0.175. The total porous volumes was obtained from the N_2 isotherms at $P/P_0 = 0.90$. Carbon dioxide sorption isotherms were measured at 273 K and 298 K up to 1.0 bar. N_2 and CH_4 sorption isotherms at 273 K were measured. Water, benzene and cyclohexane vapors adsorption isotherms were measure with the pressure up to the saturated vapor pressure at 298 K.

Synthesis of 1,3,5,7-tetrakis(4-bromophenyl)adamantane (TBAD). Iron powder (0.2 g, 3.58 mmol) and TPAD (10 g, 22.7 mmol) were suspended in chloroform (100 mL). Liquid bromine (4.66 mL, 91.5 mmol) in chloroform (20 mL) was dropwise added to the mixture under vigorous stirring at room temperature. After complete addition, the mixture was continuously stirred at 70 °C for 7 h. After cooling to room temperature, the precipitate was filtered and washed with ethanol. Crystallization gave 6.12 g white needle crystals with a yield of 35.9%. m. p.: >300 °C. 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.481 (d, 8H, $J = 8.8$ Hz), 7.327 (d, 8H, $J = 8.8$ Hz), 2.086 (s, 12H). FTIR (KBr, cm^{-1}): 3028, 2932, 2899, 2853, 1489, 1077, 1007, 822, 780.

Synthesis of 1,3,5,7-tetrakis(4-methoxyphenyl)adamantane (TMAD). TBAD (2.26 g, 3 mmol) and sodium methoxide (1.94 g, 36 mmol) were suspended in a mixture of methanol (8.5 mL) and DMF (20 mL). The mixture was stirred and heated 110 °C for 1 h, and CuBr (1.72 g, 12.0 mmol) was added in one portion. After 6 h, the reaction was stopped. The crude product was purified through silica gel column chromatography to obtain 0.78 g white solid with a yield of 51.7%. m. p.: 265-269 °C. 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.392 (d, 8H, $J = 8.8$ Hz), 6.885 (d, 8H, $J = 8.8$ Hz), 3.800 (s, 12H), 2.084 (s, 12H). FTIR (KBr, cm^{-1}): 2927, 2847, 1610, 1513, 1248, 1035, 833, 802.

Synthesis of 1,3,5,7-tetrakis(4-hydroxyphenyl)adamantane (THAD). A solution of TMAD (2.21 g, 3.94 mmol) in anhydrous dichloromethane (80 mL) was added BBr_3 (18 mL of 2.64 mol L^{-1} dichloromethane solution) dropwise at -78 °C under nitrogen atmosphere. The resulting mixture was stirred overnight. The reaction mixture was poured into ice water (150 mL) and stirred vigorously for 30 min. The precipitate was filtered and washed with water. Drying the precipitate under vacuum gave 1.91 g white product with a yield of 96.0%. m. p.: >300 °C. 1H

NMR (400 MHz, *d*-DMSO): δ (ppm) 9.126 (s, 4H), 7.288 (d, 8H, $J = 8.8$ Hz), 6.706 (d, 8H, $J = 8.8$ Hz), 1.909 (s, 12H). FTIR (KBr, cm^{-1}): 3383, 2926, 2850, 1613, 1514, 1255, 825.

Synthesis of 1,3,5,7-tetrakis(4-cyanatophenyl)adamantane (TCAD). A solution of cyanogen bromide (2.8 g, 26.5 mmol) in anhydrous acetone (40 mL) was stirred at -30 °C and added simultaneously dropwise with a solution of THAD (2.87 g, 5.7 mmol) in acetone (60 mL) and a solution of triethylamine (3.2 mL, 22.8 mmol) in acetone (20 mL). After complete addition, the mixture was stirred at -30 °C for 1 h, -10 °C for 1 h and room temperature for 1 h. The resulting mixture was evaporated to remove acetone, then filtered and washed with water. The residue went through silica gel column with dichloromethane as an eluent afford 2.59 g white solid with a yield of 75.1%. m. p.: 229-231 °C. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.546 (d, 8H, $J = 8.8$ Hz), 7.314 (d, 8H, $J = 8.8$ Hz), 2.143 (s, 12H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 151.34, 147.37, 127.22, 115.41, 108.85, 49.96, 39.24. FTIR (KBr, cm^{-1}): 3067, 2932, 2902, 2852, 2270, 2238, 1598, 1503, 1194, 1168, 831, 797.

Preparation of porous cyanate ester framework (PCN-AD). To a mixture of TCAD (1.3 g) and diphenyl sulfone (15 g) was added nonylphenol (0.013 g). The resulting mixture was heated under nitrogen atmosphere at 150 °C for 2h, 180 °C for 4 h, 250 °C for 4 h, 300 °C for 2 h and 330 °C for 2 h. The gel obtained was rushed and extracted with THF in a Soxhlet apparatus for 24 h. The yellow solid was then dried under vacuum at 150 °C for 2 days with quantitative yield. Elemental anal. calcd for $\text{C}_{38}\text{H}_{28}\text{N}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$: C 71.29, H 4.72, N 8.75, O 15.24; found: C 71.63, H 5.78, N 8.96, O 13.63%.

Table S1. A_0 , A_1 , K_H and Q_0 values for H_2 and CO_2 adsorptions in PCN-AD.

| | T (K) | K_H (mol g ⁻¹ Pa ⁻¹) | A_0 (mol g ⁻¹ Pa ⁻¹) | Q_0 (kJ mol ⁻¹) |
|--------|---------|---|---|-------------------------------|
| H_2 | 77 | 1.649E-06 | -13.315 | 8.19 |
| | 87 | 3.790E-07 | -14.786 | |
| CO_2 | 273 | 1.420E-07 | -15.767 | 32.4 |
| | 298 | 4.287E-08 | -16.965 | |

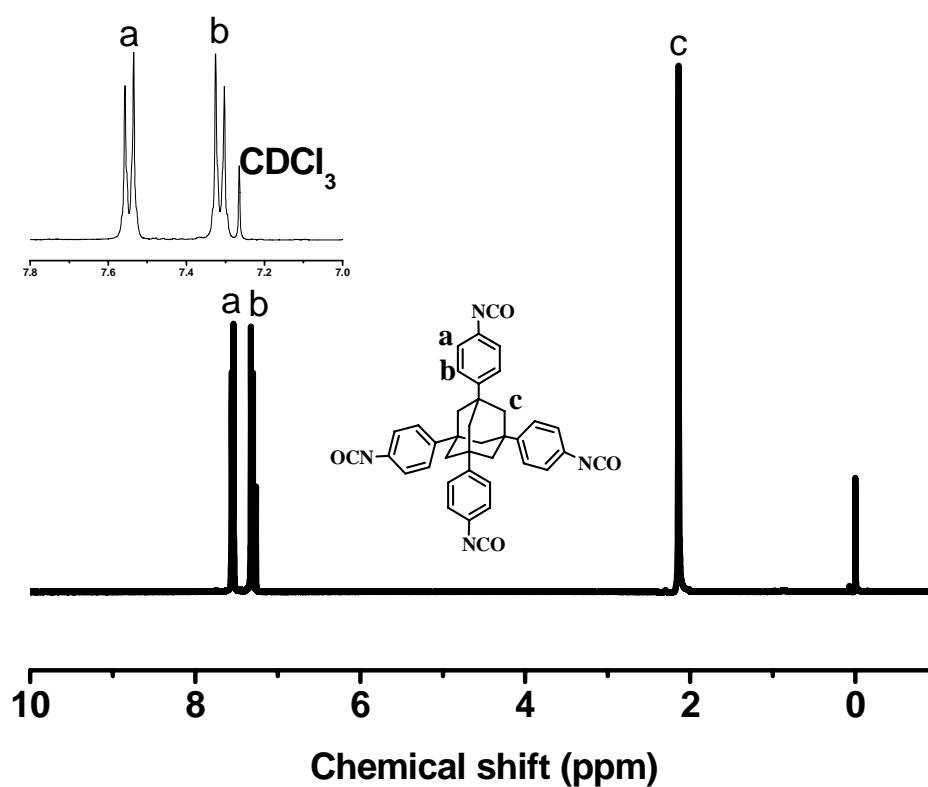


Fig. S1. ¹H NMR spectrum of 1,3,5,7-tetrakis(4-cyanatophenyl)adamantane (TCAD).

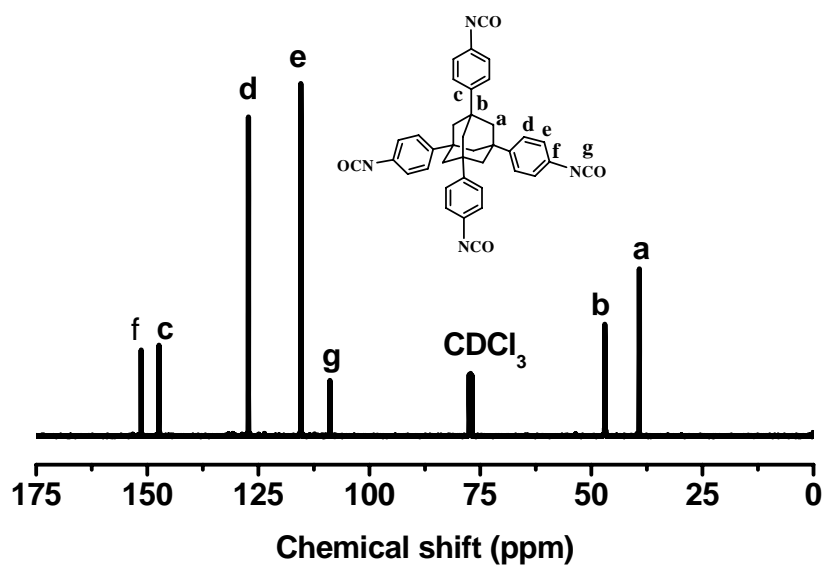


Fig. S2. ^{13}C NMR spectrum of 1,3,5,7-tetrakis(4-cyanatophenyl)adamantane (TCAD).

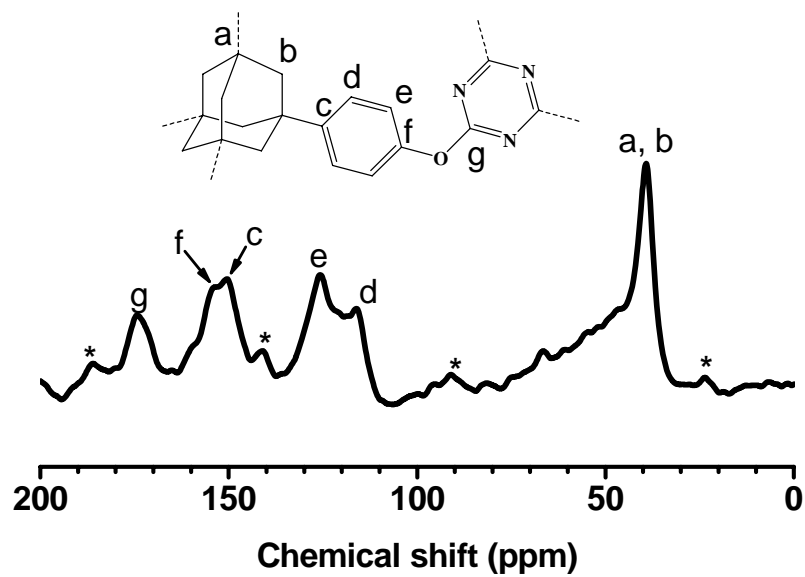


Fig. S3. Solid-state ^{13}C CP/MAS NMR spectrum for PCN-AD. Asterisks (*) indicate peaks arising from spinning side bands.

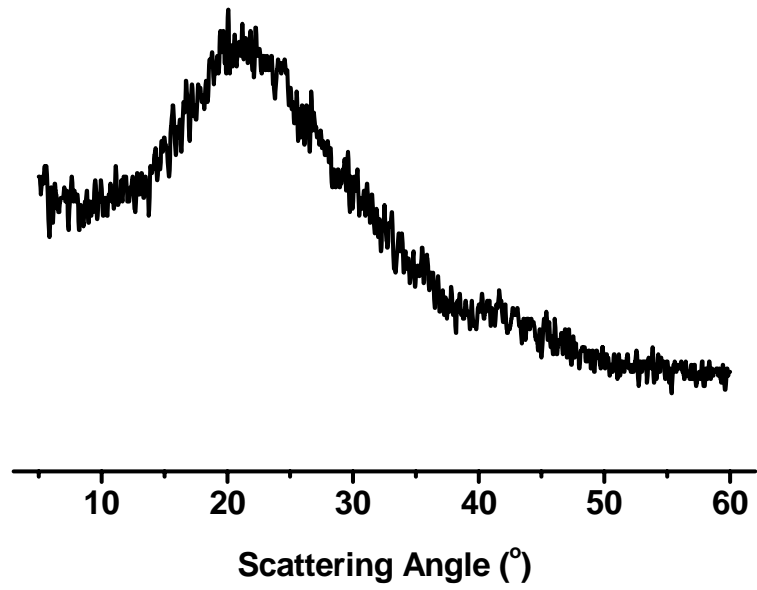


Fig. S4. X-ray diffraction pattern of PCN-AD.

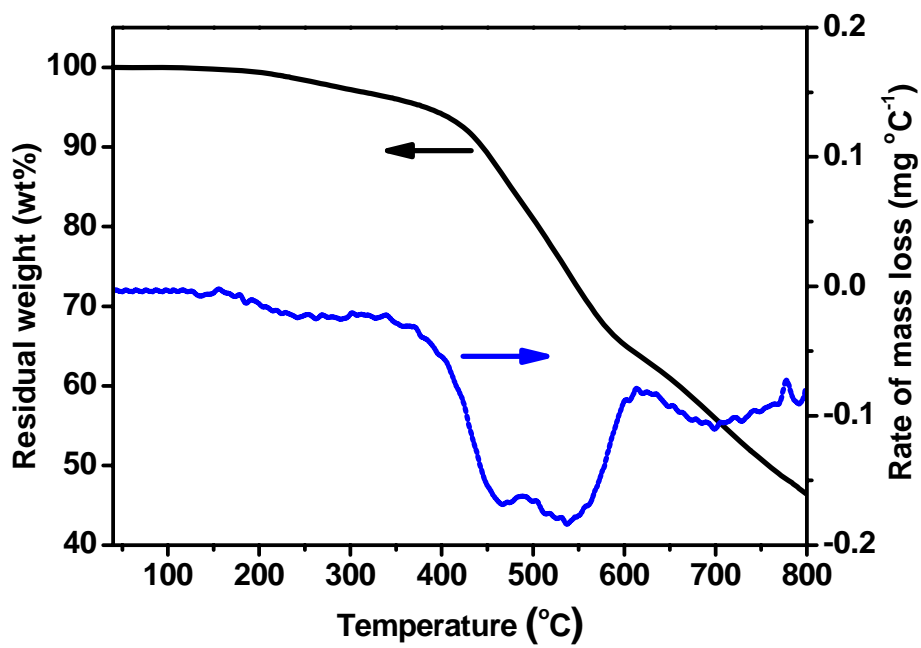


Fig. S5. TG and DTG curves of PCN-AD.

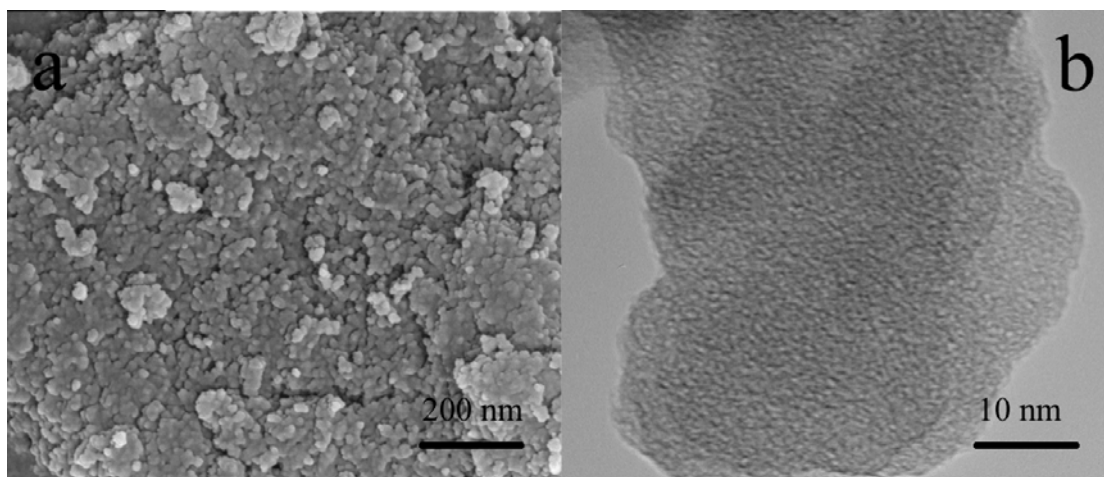


Fig. S6. FE-SEM (a) and HR-TEM (b) images of PCN-AD.

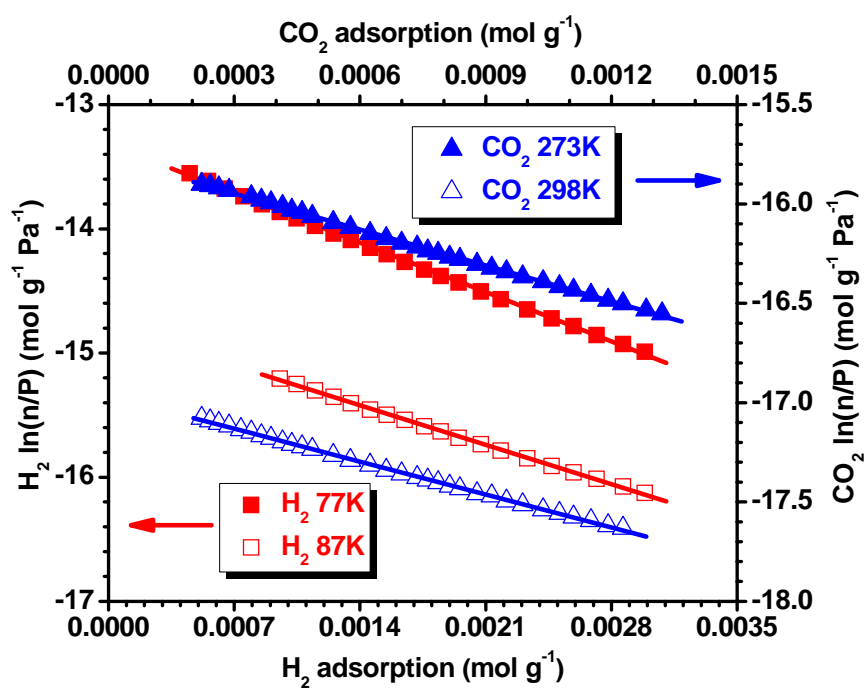


Fig. S7. Virial plots of H_2 and CO_2 adsorptions for PCN-AD.

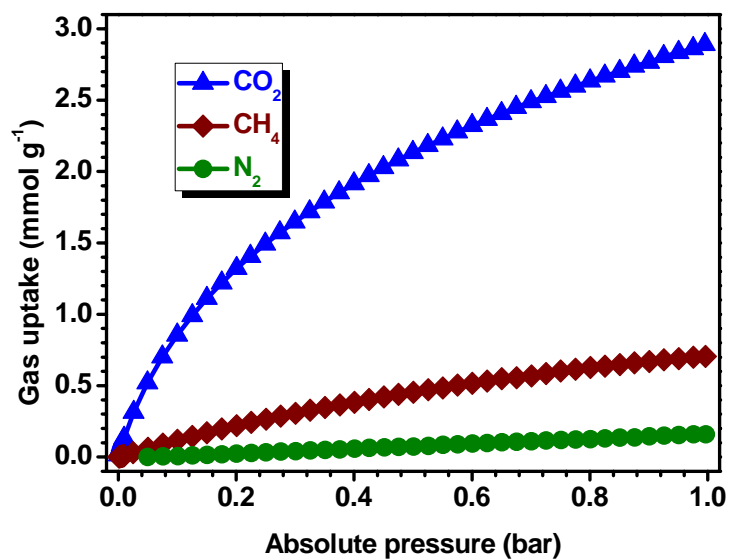


Fig. S8. Adsorption isotherms of CO₂, CH₄ and N₂ gases at 273 K for PCN-AD.

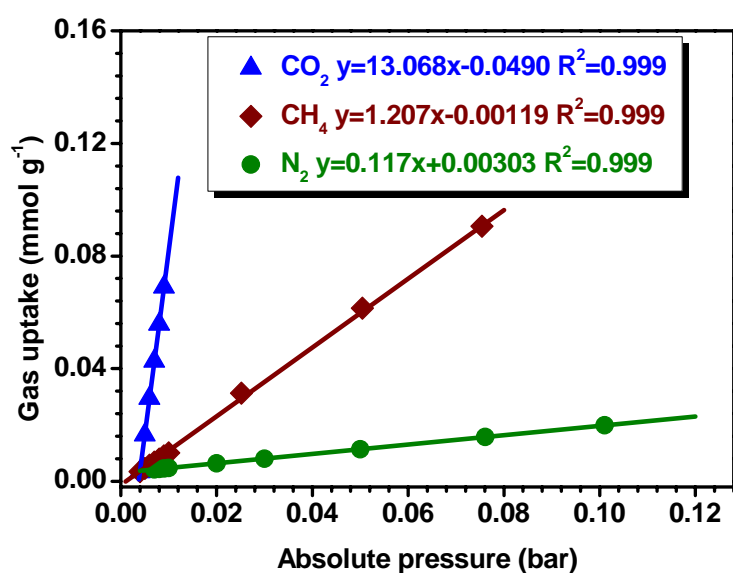


Fig. S9. Adsorption selectivities of CO₂ over N₂ and CH₄ for PCN-AD derived from the initial slope method at 273 K.