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Supporting Information

Kinetics and enthalpies of methane adsorption in microporous materials AX-21, MIL-101 (Cr) and TE7

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Materials

AX-21 is a high-surface area activated carbon powder synthesised from a precursor derived from coconut shells that is treated with KOH [1]. The material was commercialised in the past by the Anderson Development Company (Michigan, USA). The process was further refined by the Kansai Coke and Chemicals Company of Japan, which produced highly activated carbons using KOH treatment of petroleum coke, coal and coconut shells char, and renamed the material MAXSORB. MIL-101 (Cr) is a metal-organic framework first reported by Férey et al. [2]. The material is crystalline, has a high surface area, good thermal and mechanical stability, and is predominantly mesoporous, with the crystal structure showing pore sizes of 0.7, 2.9 and 3.1 nm. The TE7 carbon beads are high surface area activated carbons derived from phenolic resins which were commercialised by MAST Carbon International (now CarbonTex, Woking, UK), and have been used as a model adsorbent for gas uptake studies [3].

Kinetic data

The HTP-1 doses the required pressure of gas onto the sample in the reactor and calculates the uptake based on the pressure difference (volumetric or manometric method). The HTP-1 records the real-time uptake, pressure and temperature of the sample at irregular intervals over time, and once the uptake equilibrates (i.e., does not change over a period of time) it records the value as the equilibrium adsorption point. The minimum and maximum equilibrium times were set at 20 and 45 minutes, with the first pressure point in each isotherm having a minimum equilibration time of 30 and maximum time of 60 mins to allow for thermal equilibration. The HTP-1 has adjustable parameters in its software and uses the linear driving force (LDF) model for the kinetic analysis of the real-time data. It continuously fits the data points and once the uptake reaches 99.9% of the equilibrium value predicted by the LDF model within the equilibration

times, the software records the point as equilibrated and advances to the next isotherm point. The temperature control was achieved using an integral cryofurnace that works with recirculating liquid nitrogen.

Fits to kinetic data

AX-21, 325 K

Figure S1 – Kinetic data for the AX-21 at 325 K with an equilibration pressure of (A) 0.35 MPa, (B) 0.50 MPa, (C) 0.68 MPa and (D) 0.87 MPa. Solid black dots are the experimental methane uptake points, the red line is the LDF fit and the blue line is the temperature (in K) in the sample cell.

MIL-101 (Cr), 300 K

Figure S2 – Kinetic data for the MIL-101 (Cr) at 300 K with an equilibration pressure of (A) 0.37 MPa, (B) 0.52 MPa, (C) 0.70 MPa and (D) 0.89 MPa. Solid black dots are the experimental methane uptake points, the red line is the LDF fit and the blue line is the temperature (in K) in the sample cell.

MIL-101 (Cr), 325 K

Figure S3 – Kinetic data for the MIL-101 (Cr) at 325 K with an equilibration pressure of (A) 0.37 MPa, (B) 0.53 MPa, (C) 0.71 MPa and (D) 0.90 MPa. Solid black dots are the experimental methane uptake points, the red line is the LDF fit and the blue line is the temperature (in K) in the sample cell.

TE7, 300 K

Figure S4 – Kinetic data for the TE7 at 300 K with an equilibration pressure of (A) 0.34 MPa, (B) 0.50 MPa, (C) 0.68 MPa and (D) 0.87 MPa. Solid black dots are the experimental methane uptake points, the red line is the LDF fit and the blue line is the temperature (in K) in the sample cell.

TE7, 325 K

Figure S5 - Kinetic data for the TE7 at 325 K with an equilibration pressure of (A) 0.35 MPa, (B) 0.51 MPa, (C) 0.69 MPa and (D) 0.89 MPa. Solid black dots are the experimental methane uptake points, the red line is the LDF fit and the blue line is the temperature (in K) in the sample cell.

Differential Scanning Calorimetry experiments

Differential scanning calorimetry (DSC) was performed on a Setaram μ DSC7 Evo module equipped with high-pressure sample holder. The DSC was connected to a Setaram Hy-Energy PCTPro-2000, which had stepwise increases in pressure. The methane from the PCTPro-2000 was supplied to the DSC, which was then allowed to equilibrate and the pressure was measured. Data was collected and analysed using Setaram's Calisto and Origin 2018b software (OriginLab Corporation, Northampton, MA, USA). The data was acquired at 300 K.

To calculate the zero-coverage enthalpy from the DSC, the first exothermic peak in Figure S6 were integrated and divided by the mass of the sample (54.04 mg of MIL-101(Cr)). The integrated peak is equal to 11.96 J per gram of MIL-101 (Cr). The equilibrium pressure that corresponded to the exothermic peak was 0.213 MPa and this pressure had to be correlated with uptake, to calculate heat per mol of methane. Using the absolute uptake formula for the same temperature that was modelled previously [1], the corresponding uptake was calculated. After converting to moles, the integrated peak value was divided by the uptake in mol methane per g of adsorbent to yield J per mol of CH₄ (19.6 kJ mol⁻¹).

Figure S6 - Differential Scanning Calorimetry for methane on the MIL-101 (Cr) done at 300 K using a high-pressure calorimeter coupled to a high-pressure volumetric apparatus. The black line is the heat flow of the DSC and the blue line corresponds to the equilibrium pressure in the chamber.

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