

Supporting Information

Polymer Coating Assisted Shaping of Metal-Organic Framework Particles into Pellets with Enhanced Methane Uptake

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Section S1. Materials

Copper(II) nitrate hydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, Tokyo Chemical Industry, 98%), 1,3,5-benzenetricarboxylic acid (H_3BTC , Alfa Aesar, 98%), triethylamine (TEA, Aladdin, 99%), oleic acid (OA, Aladdin, 85%), acetic anhydride (Ac_2O , SCRC, 98.5%), sodium hydroxide (NaOH, Aladdin, 96%), n-hexane (SCRC, 97%), dichloromethane (DCM, Greagent, 99.5%), cyclohexane (Adamas, 99%), petroleum ether (PE, Greagent, 60-90 °C), 1-methyl-2-pyrrolidinone (NMP, Aladdin, 99%), anhydrous ethanol (Greagent, 99.7%), and anhydrous methanol (Greagent, 99.5%) were purchased from the mentioned sources and used without further purification. 4,4'-Oxydiphthalic anhydride (ODPA, Aladdin, 97%) was purified by recrystallization in acetic anhydride. 2,4,6-trimethyl-1,3-phenylenediamine (DAM, Adamas, 98%) was purified by recrystallization in ethanol.

Section S2. Synthesis

Synthesis of ODPA-DAM

ODPA-DAM was obtained by following a previous method.¹ 2.152 g (14.33 mmol) DAM was dissolved in 15 mL NMP under a nitrogen atmosphere. Then, the reaction vessels were immersed in an ice-bath. 4.445 g (14.33 mmol) ODPA and additional 15 mL NMP was added into the reaction solution. Then the mixture was stirred for 24 hours to form a viscous poly (amic acid) (PAA) solution. For the imidization, a solution of 2 mL triethylamine (TEA) and 5.4 mL of Ac_2O dissolved in 6 mL NMP was added. The mixture was stirred at room temperature for another 24 hours. The obtained mixture was added slowly into methanol to obtain white polyimide fibers.

The as-synthesized polyimide was washed several times by anhydrous methanol before drying in a vacuum oven at 150 °C for 24 h.

Synthesis of HKUST-1

HKUST-1 was synthesized following a previously reported method with slight modification.² First, 2.5 mL of NaOH aqueous solution (1 M) was added to a mixed solution of deionized water (17.5 mL), ethanol (30 mL), OA (10 mL) and n-hexane (4.25 mL) under stirring at 50 °C to obtain a thermostable microemulsion system. Then, 250 mg of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ dissolved in 5 mL of deionized water. After stirring for 10 minutes, 250 mg of H_3BTC dissolved in a mixed solution of deionized water (3.25 mL) and ethanol (4.25 mL) was added to the above solution. The mixture was heated to 70 °C for 2 hours with continuous stirring. The product was collected by centrifugation and washed by a mixture of cyclohexane and anhydrous ethanol for three times.

Synthesis of HKUST-1@ODPA-DAM

HKUST-1@ODPA-DAM was obtained following a previous method.³ Firstly, the above synthesized 5 mg HKUST-1 was dispersed in 2.5 mL DCM, then add 0.5 mg above synthesized ODPA-DAM into the solution. After ultrasound for 10 min, 5 mL of petroleum ether was quickly poured into the mixture under stirring (600 rpm), the MOF and polymer quickly precipitate to form HKUST-1@ODPA-DAM in a matter of seconds. The product was collected by centrifugation and washed 3 times with petroleum ether. This synthesis can be scaled up to form the same product.

Compression procedure

Universal testing machines (INSTRON 5960) were used to compact the powder. A cylindrical die of 6 mm in diameter and close-fitting compression punch were used for this purpose. 30 mg powder were added into the die for compaction, and the speed of the punch is set at 1 mm/min during the compression until the targeted force is reached. The punch finally raises at 10 mm/min during the ascent. Finally, the tablets were taken down and stored at N₂ atmosphere.

Section S3. Characterization

Transmission electron microscope (TEM) images were acquired on a JEM 1400 field-emission transmission electron microscope with voltage set at 120 kV. Scanning electron microscope (SEM) images were acquired on a JEOL JSM 7800F Prime SEM. Powder X-ray diffraction patterns (PXRD) were acquired on a Bruker D8 Advance diffractometer with Cu K α radiation. TGA experiments were performed on a PerkinElmer TGA 8000. Samples were firstly heated to 150 °C and retained at that temperature for 30 minutes under N₂ atmosphere to remove residual solvent and then heated to 700 °C at a rate of 20 °C/min under oxygen (O₂) atmosphere, and then kept 700 °C for 10 min, and finally raised the temperature to 750 °C with rate of 20 °C/min at O₂. Gas adsorption analysis was performed on MicrotracBEL-Belsorp-MAXII volumetric gas adsorption analyzer. All samples were activated at 120 °C under vacuum for 6 h before measurement.

High-pressure adsorption

High-pressure adsorption isotherms of 80 bar (298 K) were measured on an iSorbTMHP1 instruments from Quantachrome. The experimental data of high-pressure gas adsorption obtained

from instrument was as excess gravimetric adsorption capacity (N_{excess}). Then, the N_{excess} was transformed into total uptakes (N_{total}) by using equation: ⁴

$$N_{total} = N_{excess} + \rho * V_{pore} \quad (1)$$

where ρ is the density of the gas at the given adsorption pressure and temperature, obtained from NIST, and V_{pore} is the pore volume of the adsorbent, obtained from N₂ adsorption isotherms at 77 K of sample. The total gravimetric uptake can be transferred to volumetric capacity by multiplying the bulk density of the adsorbent.

Bulk density measurement

The bulk density of hand packing HKUST-1 followed a previously reported method. ⁵ We filled a 1 mL syringe with MOF powder and pressed hard (by hand) while loading in glove box. We could pack about 365 mg into a 0.9 mL volume, yielding a so-called “tapped density” of 0.40 g/cm³. The bulk density of HKUST-1(3) and HKUST-1@ODPA(3) were obtained by weighing the mass of the pellet in glove box filled with nitrogen and measuring the height of the pellet to calculate the volume.

Section S4. Supplemental figures and tables

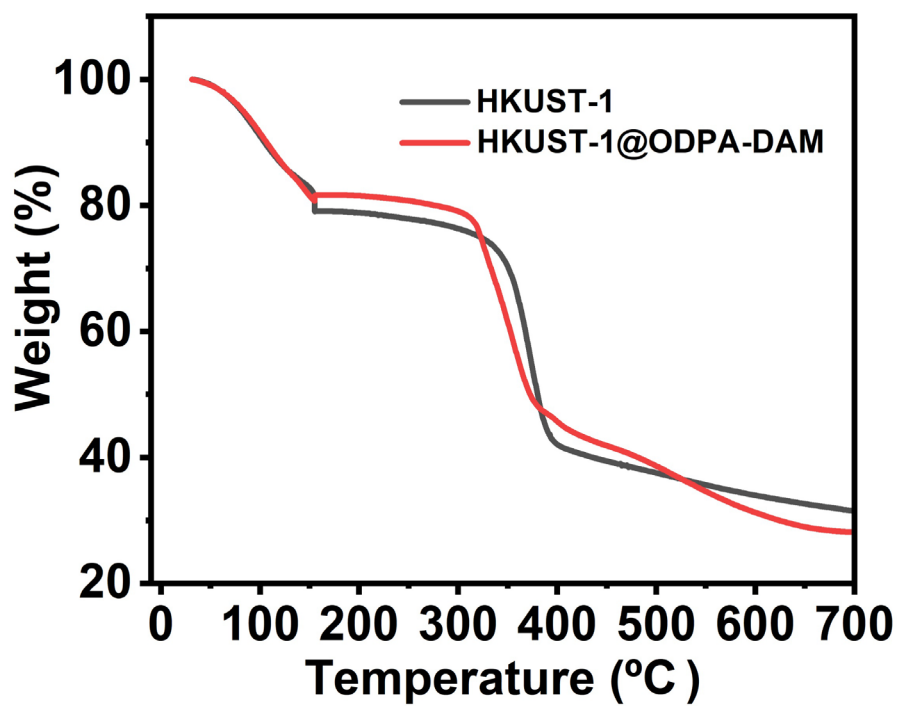


Figure S1. TGA profiles of HKUST-1 and HKUST-1@ODPA-DAM.

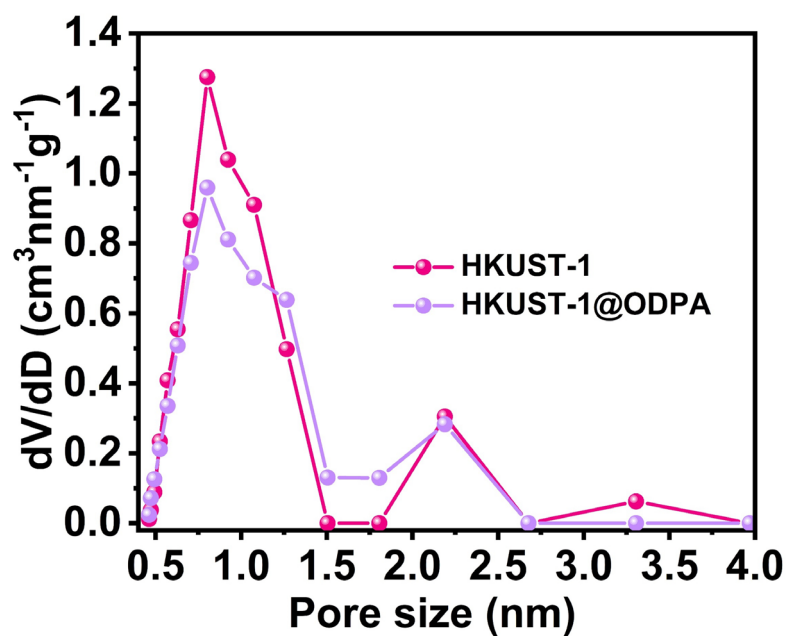


Figure S2. Pore size distribution of HKUST-1 and HKUST-1@ODPA.

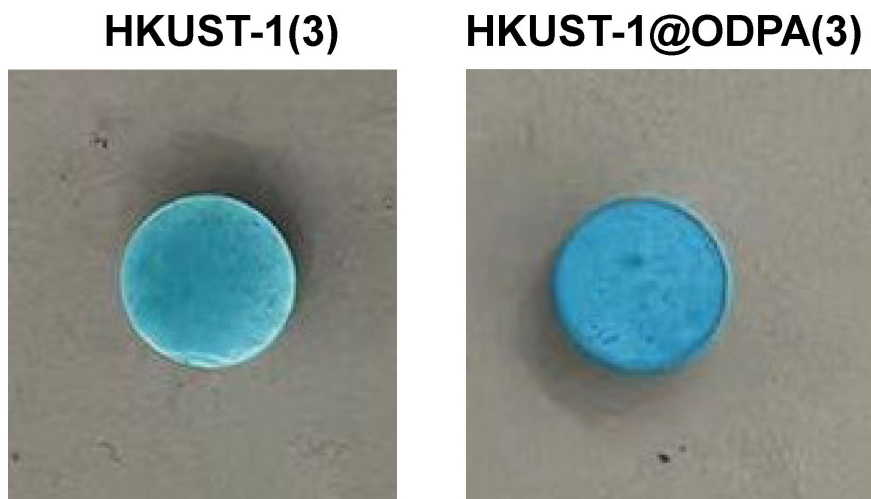


Figure S3. Photographs of HKUST-1(3) and HKUST-1@ODPA(3) pellets.

Table S1. The relationship between compaction force and pressure during shaping.

Compaction force (KN)	Pressure (MPa)
0.1	3.54
0.5	17.70
1	35.39
3	106.16
5	176.93

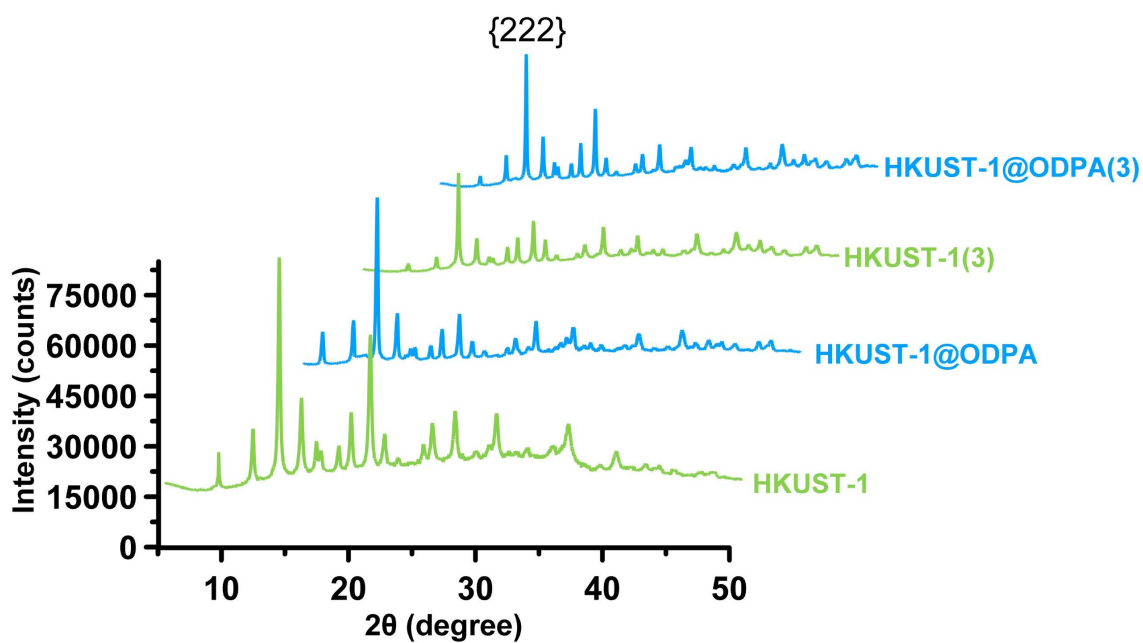


Figure S4. PXRD patterns of HKUST-1, HKUST-1@ODPA, HKUST-1(3) and HKUST-1@ODPA (3).

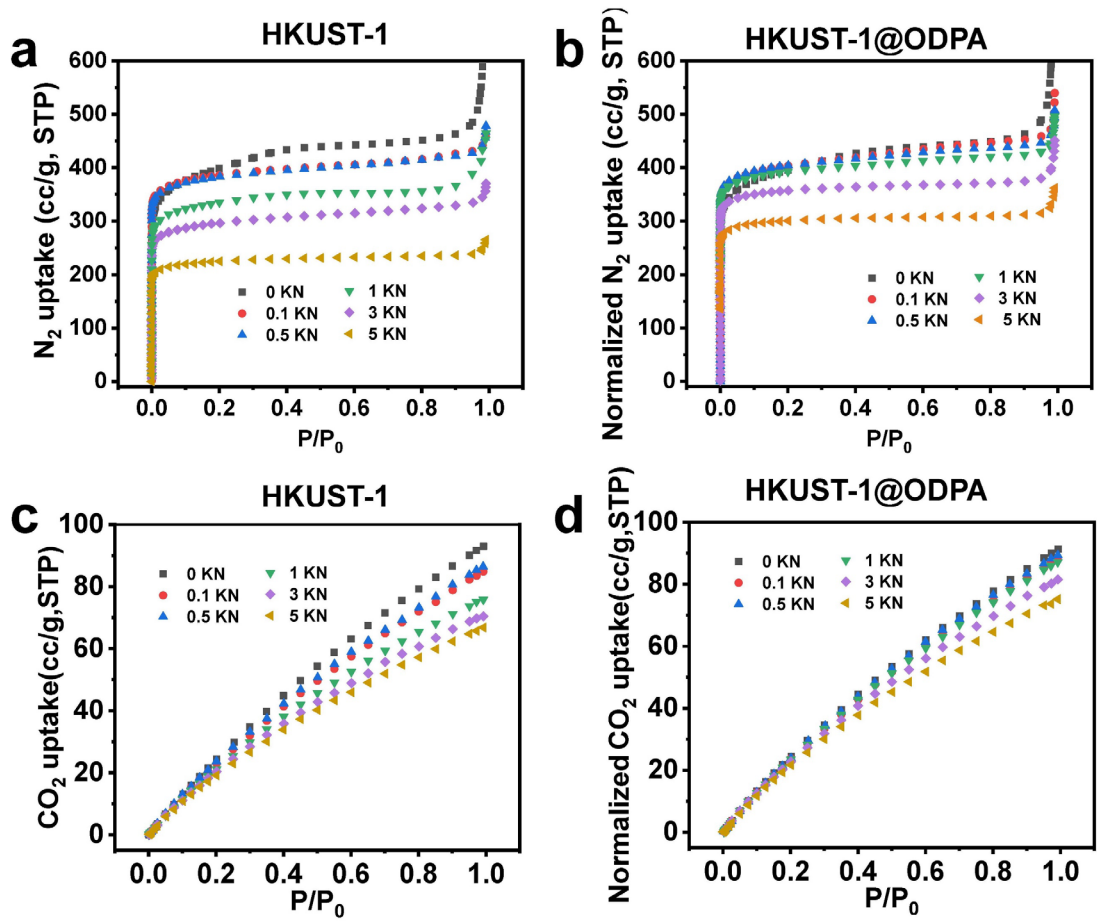


Figure S5. N₂ adsorption isotherms (77 K) of HKUST-1 (a) and HKUST-1@ODPA pellets (b) obtained under various compaction force. CO₂ adsorption isotherms (298 K) of HKUST-1 (c) and HKUST-1@ODPA pellets (d) obtained under various compaction force.

Table S2. The normalized BET surface area, N₂ uptake capacity (0.95 P/P₀, 77 K) and CO₂ uptake capacity (1 bar, 298 K) of HKUST-1 and HKUST-1@ODPA pellets obtained under various compaction force.

Sample	Normalized BET surface area (m ² /g)	Normalized N ₂ uptake capacity (0.95 P/P ₀ , 77 K) (cc/g)	Normalized CO ₂ uptake capacity (1 bar, 298 K) (cc/g)
HKUST-1	1499	485	93.0
HKUST-1(0.1)	1480	431	84.6
HKUST-1(0.5)	1462	427	86.5
HKUST-1(1)	1300	388	75.8
HKUST-1(3)	1161	334	70.4
HKUST-1(5)	895.5	239	66.8
HKUST-1@ODPA	1501	489.536	91.3
HKUST-1@ODPA(0.1)	1513	458.56	88.0
HKUST-1@ODPA(0.5)	1526	446.55	89.3
HKUST-1@ODPA(1)	1495	430.102	87.1
HKUST-1@ODPA(3)	1431	379.853	81.5
HKUST-1@ODPA(5)	1208	314.66	75.1

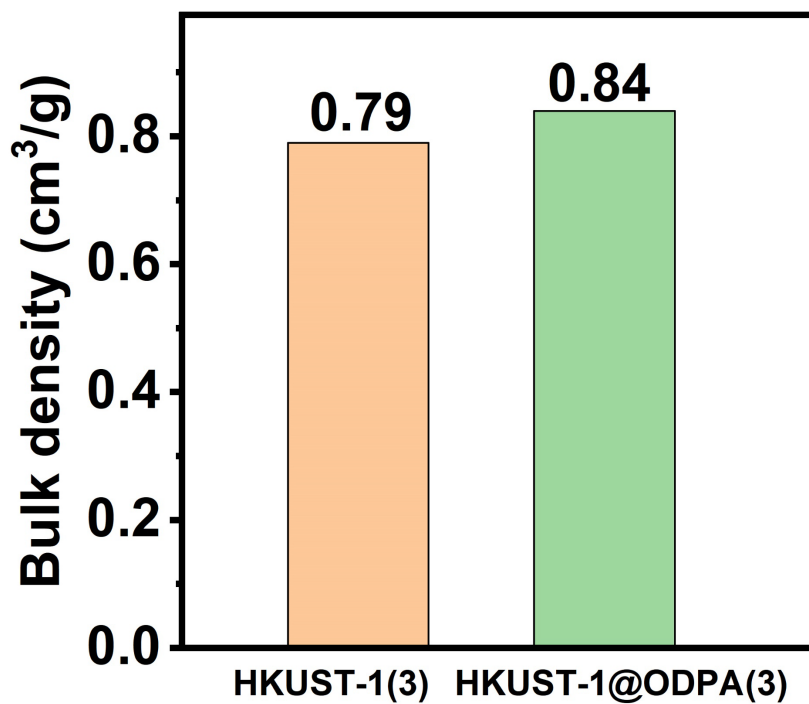


Figure S6. The bulk density of HKUST-1(3) and HKUST-1@ODPA(3).

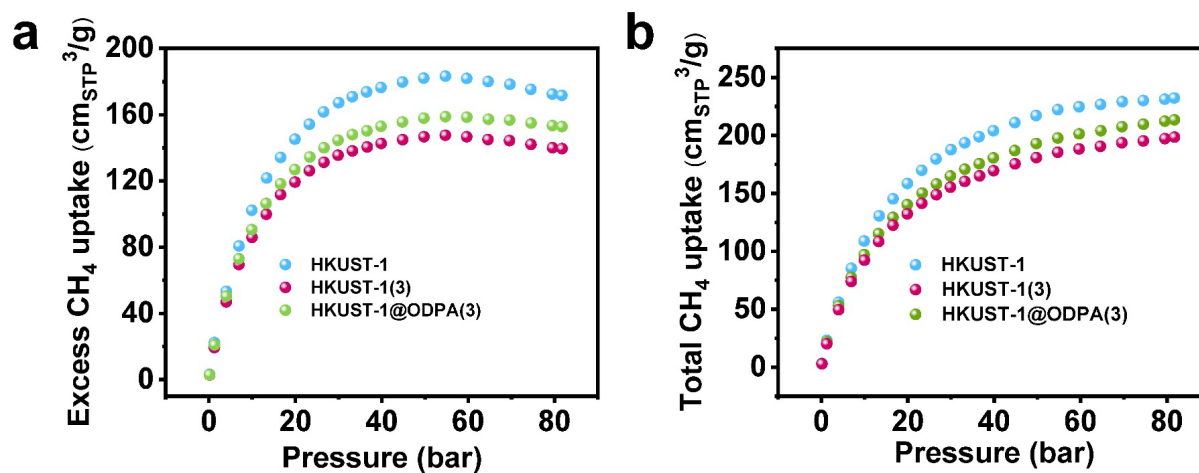


Figure S7. Excess gravimetric CH₄ adsorption (a) and total gravimetric CH₄ adsorption (b) isotherms at 298 K of HKUST-1, HKUST-1(3) and HKUST-1@ODPA(3).

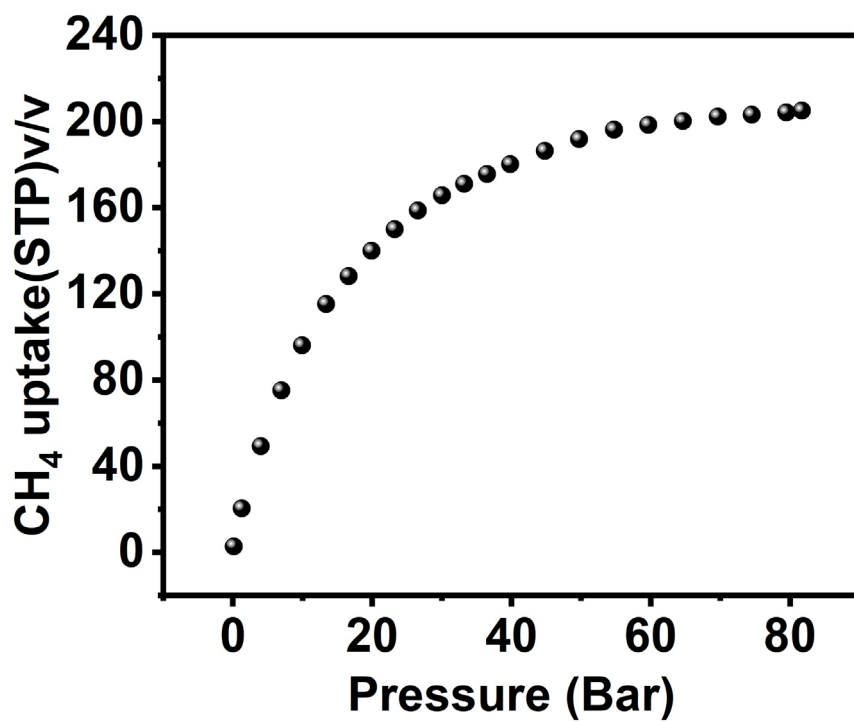


Figure S8. Total volumetric CH₄ adsorption isotherms (298 K) of HKUST-1 based on the crystal density (0.883 cm³/g).

References

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