Electronic Supplementary Materials *Mendeleev Commun.,* 2023, **33**, 817–820

Adsorption of methane and ethane on HKUST-1 metal–organic framework and mesoporous silica composites

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I. Experimental setup

The following reagents were used in the work: copper nitrate trihydrate (Fisher Chemical, 99%), 1,3,5-benzenetricarboxylic acid (Acros, 99%), tetraethoxysilane (Acros, 99%), cetyltrimethylammonium bromide (Acros, 99%). *N,N*-dimethylformamide (DMF) was purified by vacuum distillation.

The reference HKUST-1 sample was synthesized according to the procedure[S1] from copper nitrate trihydrate and benzene-1,3,5-tricarboxylic acid in a mixture of DMF, water, and ethanol. Other HKUST-1 sample was obtained using the same synthesis variables, but *via* preliminary reagent grinding before solvothermal reaction.

Mesoporous silica MCM-41 was synthesized according to the procedure[S2] by hydrolysis of tetraethoxysilane in the presence of NaOH and cetyltrimethylammonium bromide.

Biporous Silica (BPS) has been synthesized in the Laboratory headed by Prof. I. I. Ivanova (Department of Chemistry, Lomonosov Moscow State University).[S3]

In the synthesis of the HKUST-1@silica composites, a mixture of 1.035 g (3.4 mmol) of copper nitrate trihydrate, 0.500 g (2.4 mmol) of benzene-1,3,5-tricarboxylic acid and 2.0 g of silica (BPS or MCM-41) was carefully ground in a mortar and transferred to a flask with a mixture of 10 ml DMF and 10 ml deionized water. Then the resulting mixture was heated at 100°C for 24 h with vigorous stirring. The produced composite was separated by centrifugation, washed successively with DMF (3×20 ml) and methanol (3×20 ml), then dried in a vacuum of $\sim 10^{-2}$ Torr at 150°C. The yields were 2.608 g (HKUST-1@MCM-41) and 2.654 g (HKUST-1@BPS), respectively.

The specific surface area of the materials (BET) was calculated from nitrogen adsorption data in the relative pressure p/p^0 range from 0.05 to 0.20. The total pore volume (V_Σ) was estimated at $p/p^0 = 0.95$ taking into account the asymptotic behavior of the isotherm at relative pressures approaching 1. The cumulative volume corresponding to $p/p^0 > 0.95$ according to the BJH method was taken as the mesopore volume (V_{meso}).

The microstructure of the materials was studied by field emission scanning electron microscopy (FE-SEM) using a Hitachi SU8000 electron microscope. The images were acquired in the secondary electron mode at an accelerating voltage of 10 kV. The target-oriented approach was utilized for the optimization of the analytical measurements.[S4] The samples were mounted on a 3 mm copper grid with a carbon film and fixed in a grid holder. Images were acquired in the bright-field STEM mode at a 30 kV accelerating voltage. The morphology of the samples was studied taking into account the correction for the surface effects of deposition of the conductive layer.

X-ray diffraction measurements were performed with an EMPYREAN instrument (PANanalytical, UK) using non-monochromated Cu$K\alpha$ radiation (λ = 1.5418 Å) and tube voltage/current 40 kV/35 mA, in the 2θ angle range of 3-30°.

The content of C, H in all materials was determined using express-gravimetry method,[S5] whereas Si was determined via spectrophotometry using Cary-100 apparatus.[S5]

Methane and ethane adsorption were measured using a setup based on the classical Sieverts method.[S6] The setup is described in detail in our previous work[S1]. The adsorption values were calculated from the results of pressure measurements at 12-16 points using high-precision empirical equations of state for each gas. Before measurements, the samples were evacuated directly in the setup at 140°C at a residual pressure of less than $3\cdot10^{-4}$ Torr. The sample volume was determined via gas pycnometry using helium. Adsorption equilibrium was attained at each point after 2–3 h. The total measurement error determined in blank experiments with an empty reactor and with the same number of measurement points was 0.1 mmol for ethane and 0.05 mmol for methane (at 30 atm).

The IAST selectivities for the ethane/methane pair were calculated using the ideal adsorbed solution theory according to literature.[7,8] The selectivity for a pair of gases was calculated as the ratio:

$$S = \frac{x_{C_2H_6}/x_{CH_4}}{y_{C_2H_6}/y_{CH_4}}$$

where x is the mole fraction of the respective gas in the adsorbed phase and y is the mole fraction of the respective gas in the gas phase. To numerically solve the integral equation of the IAST theory, the experimental isotherms were approximated by sets of B-splines. The selectivity was calculated for the pressure ranges at which $P^*(CH_4)$ and $P^*(C_2H_6)$ were within the experimental pressure ranges.

The ideal selectivity was calculated from the experimental data by dividing the interpolated C_2H_6 and CH_4 adsorption values at the equal pressure.

II. The composition of the HKUST-1@BPS and HKUST-1@MCM-41 materials

Table S1. Elemental analysis data for the HKUST-1@BPS and HKUST-1@MCM-41 composites

Material	*w*(C), %	w(H), %	w(Si), %	w(SiO_2), %
HKUST-1@BPS	8.775	1.115	32.095	73.7
HKUST-1@MCM-41	5.765	1.09	32.585	81.2

III. N_2 low temperature adsorption measurements for the synthesized composites

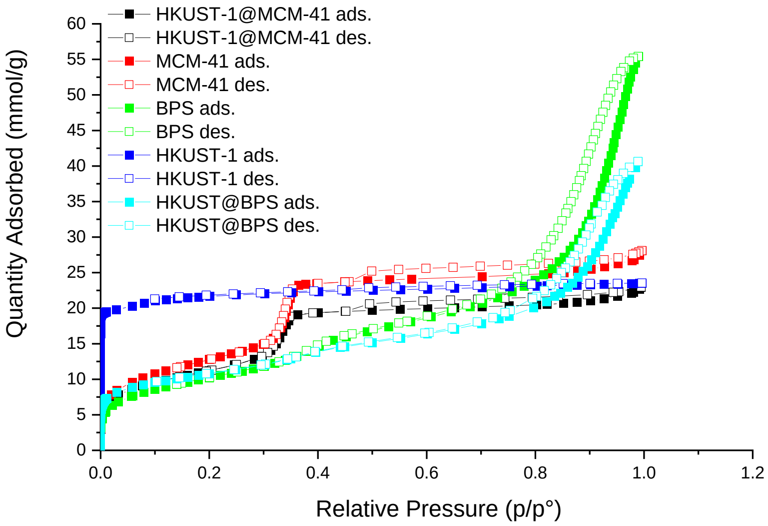

Figure S1. Adsorption isotherms of N_2 at 77 K.

Table S2. Textural characteristics of the synthesized materials.

Material	HKUST-1, %	S_{BET}, m^2/g	V_{total}, cm^3/g	V_{micro}, cm^3/g	V_{meso}, cm^3/g	D_{pore}, nm
HKUST-1	100%	1648	0.816	0.714	0.102	0.6-1.2
MCM-41	-	1043	0.974	-	0.974	2.9-5
BPS	-	831	1.921	-	1.921	3.1, 7-40
HKUST-1@MCM-41	18.8	909	0.793	0.024	0.769	0.6-1.2; 2-5
HKUST-1@BPS	26.3	414	0.44	0.2	0.24	1.74; 7-30

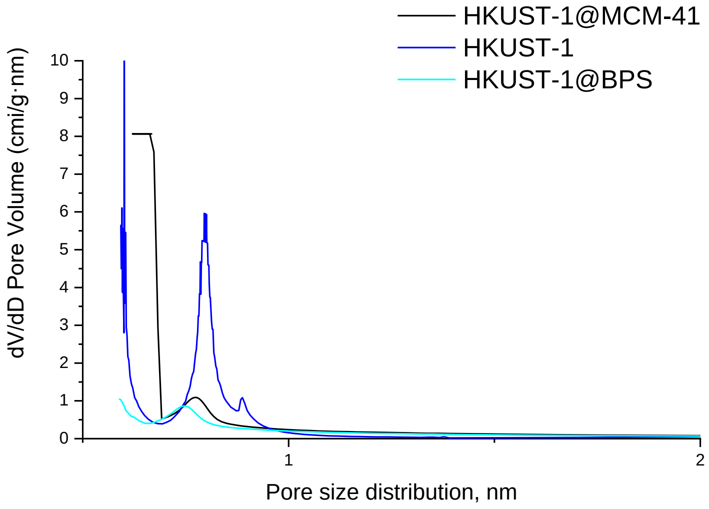

Figure S2. Micropore size distribution (Horvath-Kawazoe method).

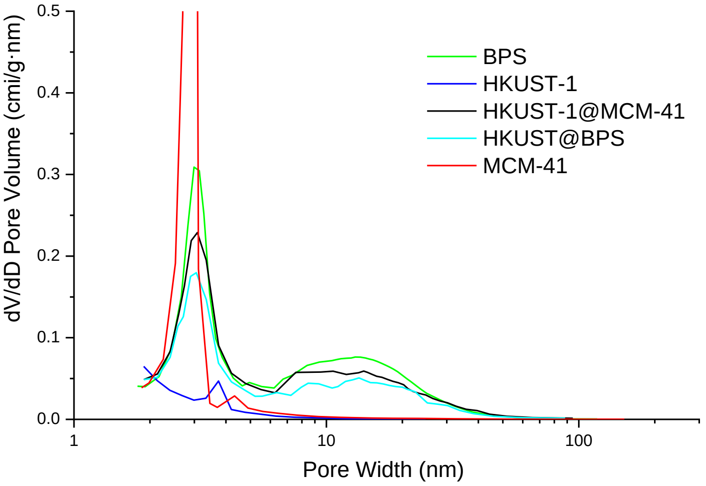

Figure S3. Mesopore size distribution (Harkins and Jura method).

IV. SEM study of the HKUST-1 sample synthesized through preliminary reagent grinding

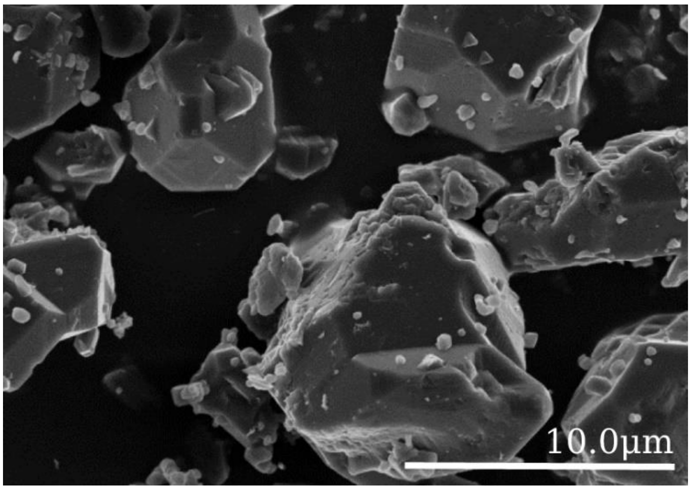

Figure S4. SEM micrograph of the HKUST-1 sample synthesized through preliminary reagent grinding.

V. Capacities and selectivities of obtained adsorbents in respect of ethane/methane pair

Table S3. Adsorption capacities of synthesized materials on methane and ethane at 298 K.

Adsorbent	a(C_2H_6, 1 atm), mmol/g	a(CH_4, 1 atm), mmol/g	a(C_2H_6, 5 atm), mmol/g	a(CH_4, 5 atm), mmol/g	a(C_2H_6, 20 atm), mmol/g	a(CH_4, 20 atm), mmol/g
HKUST-1	5.65	0.74	8.15	2.73	9.11	7.03
MCM-41	0.52	0.12	2.10	0.51	6.13	1.70
BPS	0.53	0.11	1.76	0.5	4.80	1.51
HKUST-1@MCM-41	1.15	0.22	2.28	0.83	5.01	1.96
HKUST-1@BPS	1.08	0.23	2.35	0.85	5.05	1.99

Table S4. Selectivity values of the obtained adsorbents.

Adsorbent	Ideal selectivity		IAST selectivity at $y(CH_4)$=0.9	
	$C_2H_6:CH_4$ at p = 1 atm	$C_2H_6:CH_4$ at p = 5 atm	$C_2H_6:CH_4$ at p = 1 atm	$C_2H_6:CH_4$ at p = 5 atm
HKUST-1	7.76	2.95	16.13	16.05
MCM-41	5.01	4.0	5.0	5.09
BPS	4.76	3.49	2.54	4.29
HKUST-1@MCM-41	4.47	2.67	10.08	11.1
HKUST-1@BPS	4.91	2.73	9.51	10.9

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