Supporting Information

Study on the Desorption Process of *n*-Heptane and Methyl Cyclohexane Using UiO-66 with Hierarchical Pores

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Content

1. Methods

On the basis of downstream alkane concentration changes as a function of time after feed flow starts, we can get the breakthrough curves of UiO-66. The breakthrough adsorbtion capacity of UiO-66 on fixed bed can be calculated through equation (1).

$$q_b = \frac{MC_0}{m}\int_0^{t_b}(1-\frac{C}{C_0})dt \times 100 \quad (1)$$

Where M is mass flow rate of feed side (g/min), C_0 and C are content of adsorbate in feed and outlet-gas side (wt %), respectively; m is packing quality (dry basis) of bed adsorbent (g), t_b is breakthrough time (C/C_0=0.05, min); q_b is breakthrough adsorbed capacity (g/100g).

Concentration vibration of adsorbate can be calculated using equation (2) through GC-external standard method:

$$c_i = \frac{A_i}{A_s} \times c_{s,i} \quad (2)$$

Desorption capacity of specific component on UiO-66 fixed bed can be calculated using equation (3):

$$q_d = \left(\frac{M_{ads} \times \int_0^t V_d \times c_i dt}{V_m} - m_{dead} \right) \div m \times 100 \quad (3)$$

Desorption rate of specific component on UiO-66 fixed bed can be calculated using equation (4):

$$\theta = \frac{q_d}{q_e} \times 100\% \tag{4}$$

Where $c_{s,i}$ is molar concentration of adsorbate in standard gas (%), c_i is molar concentration of adsorbate in outlet-gas (%), A_s and A_i is peak area of adsorbate in standard gas and outlet-gas, respectively; M_{ads} is molar mass of adsorbate (g/mol), V_d is gas flow (mL/min), V_m is molar volume of gas in standard condition (L/mol), m_{dead} is mass of adsorbate in dead volume (g), q_d is desorption mass (g/100g) and θ is desorption rate (%).

Adsorption selectivity (α) for analysis *n*HEP and MCH on UiO-66 fixed bed can be calculated using equation (5):

$$\alpha = (\frac{q_i}{c_{i0}}) \Big/ (\frac{q_j}{c_{j0}}) \tag{5}$$

Where q_i and q_j is breakthrough adsorbed capacity of component i and j (g/100g), c_{i0} and c_{j0} is content of component in raw materials (wt %).

Based on the temperature of desorption peak and Polanyi-Wigner equation [1], and assuming that desorption reaction follows first-order kinetic equation, we can deduce equation (6) [2]:

$$\ln\left(\frac{\beta_H}{RT_p^{\,2}}\right) = -\left(\frac{E_d}{RT_p}\right) - \ln\left(\frac{E_d}{k_0}\right) \tag{6}$$

Where β_H is heating rate (K/min), T_p is the temperature of desorption peak (K), E_d is activated energy of desorption (kJ/mol), R is the perfect gas constant (8.314 J/mol·K).

2. Potentiometric Acid-base Titration

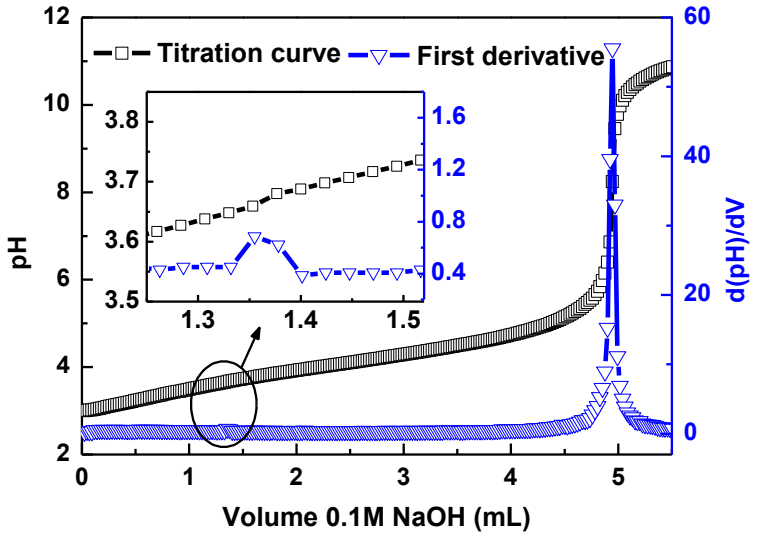

Figure S1. Acid–base titration curve (black) and first-derivative curve (blue) for benzoic acid (insert showed the partial enlarged view).

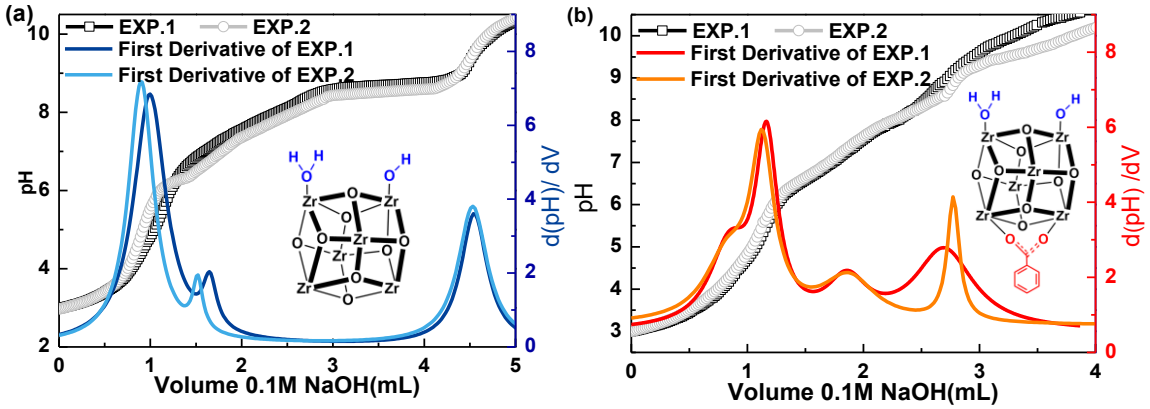

Figure S2. Acid–base titration curves and first-derivative curves for (a) UiO-66 and (b) H-UiO-66 (insert showed the structural formula).

3. Elemental Analysis

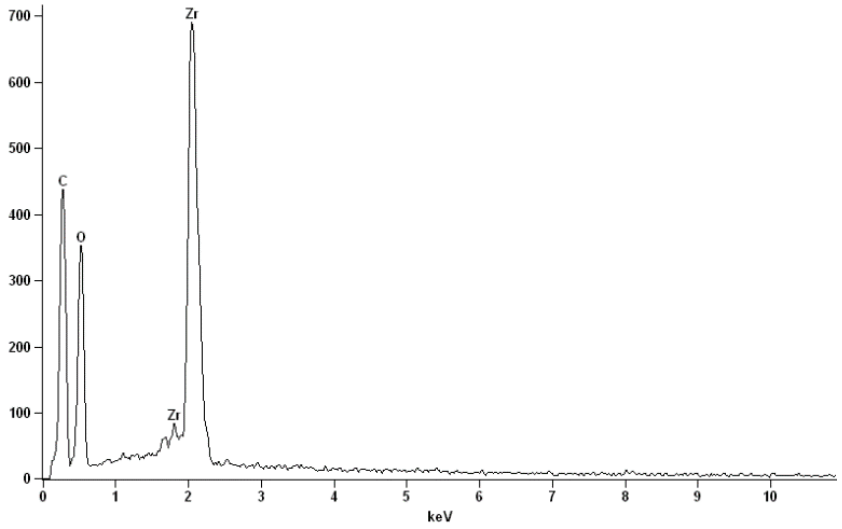

Figure S3. EDS elemental analysis of H-UiO-66.

4. Temperature Program Desorption

Table S1. Peaks Area Percentage Integrated from TPD Plots.

adsorbate	adsorbent	heating rate (K/min)	peak area percentage (%)			R^2
			peak 1	peak 2	peak 3	
*n*HEP	UiO-66	5	57.96	29.79	12.24	0.99995
		7	58.16	30.30	11.54	0.99999
		10	57.86	32.46	9.67	0.99999
		13	59.35	31.34	9.31	0.99999
		Mean	58.33	30.98	10.69	-
	H-UiO-66	5	62.08	26.78	11.14	0.99999
		7	63.31	26.38	10.31	0.99999
		10	63.84	25.38	10.78	0.99999
		13	63.88	27.51	8.61	0.99999
		Mean	63.28	26.51	10.21	-
MCH	UiO-66	5	24.37	67.43	8.20	0.99995
		7	25.66	64.77	9.57	1.00000
		10	27.34	64.30	8.36	0.99998
		13	25.78	65.83	8.39	1.00000
		Mean	25.79	65.58	8.63	-
	H-UiO-66	5	30.12	64.77	5.11	0.99996
		7	28.73	65.93	5.33	0.99995
		10	29.62	62.38	8.00	0.99987
		13	29.27	63.58	7.15	0.99984
		Mean	29.44	64.16	6.40	-

5. Adsorption Performance

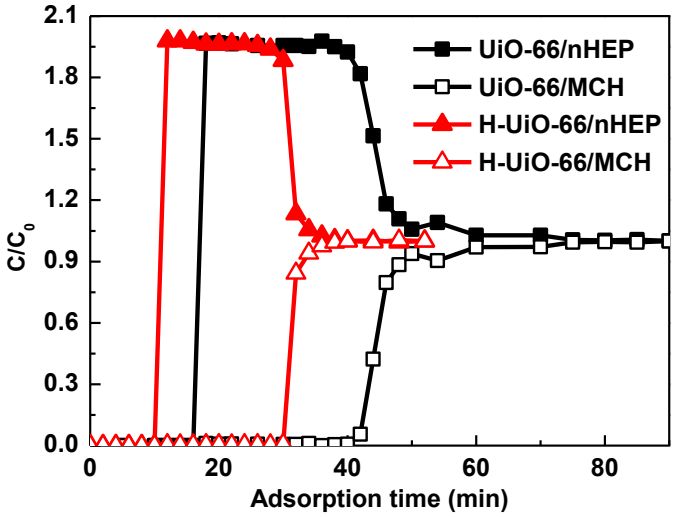

Figure S4. The breakthrough curves for adsorption of *n*HEP/MCH on UiO-66 and H-UiO-66 at 473 K.

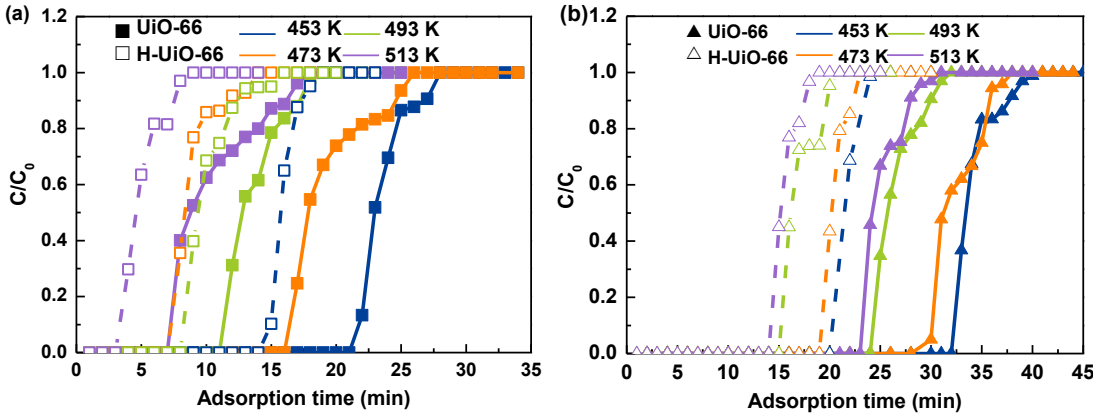

Figure S5. The breakthrough curves for adsorption of (a) *n*HEP and (b) MCH on UiO-66 (solid) and H-UiO-66 (hollow) under varied temperature.

Reference

(1) Cvetanović R. J.; Amenomiya Y. A Temperature Programmed Desorption Technique for Investigation of Practical Catalysts. *Cat. Re*v. **1972**, *1* (6), 21–48.

(2) Huang W.; Zhou X.; Xia Q.; Peng J.; Wang H.; Li Z. Preparation and Adsorption Performance of GrO@Cu-BTC for Separation of CO_2/CH_4. *Ind. Eng. Chem. Res.* **2014**, *53* (27), 11176–11184.