

Supporting information

Opposite particle size effect on the adsorption kinetics of ZIF-8 for gaseous and solution adsorbates

Xinxin Fan, Junwen Zhou, Teng Wang, Jie Zheng*, Xingguo Li*

Beijing National Laboratory for Molecular Sciences (BNLMS), (The State Key Laboratory of Rare Earth Materials Chemistry and Applications), College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China

1. Materials and characterization techniques

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, 99%) and 2-methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$, 99%) were purchased from J&K Scientific Ltd. Span80, Tween80 and N,N-dimethylformamide (DMF, 99.5%) were purchased from Shantou Xilong Chemicals Corporation. Ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.7%) and methanol (CH_3OH , 99.7%) were purchased from Beijing Chemical Works. All chemicals were used as received without further purification.

The structure and morphology of the samples were studied by X-ray diffraction (XRD, Rigaku D/max 200 diffractometer, $\text{Cu K}\alpha$), high-resolution transmission electron microscopy (HRTEM, JEM 2100, 200 kV), and scanning electron microscopy (SEM, Hitachi S4800). N_2 and H_2 adsorption isotherms and kinetic measurements at 77 K were carried out by using an Autosorb IQ gas sorption analyzer (Quantachrome), samples were outgassed under vacuum at 180 °C for 12 hours before test. The surface area of the sample is determined by a Brunauer–Emmett–Teller (BET) method. The pore size distribution is obtained by Non Local Density Functional Theory (NLDFT) method implanted in the software package AsiQwin assuming a slit/cylinder pores model. The relative concentration of I_3^- was characterized by a UV-Vis recording spectrophotometer (Shimadzu UV-2401PC) with a dual beam measurement system.

2. Sample preparation

2.1 Synthesis of 70 nm ZIF-8 (ZIF-8_water)

ZIF-8_water was prepared by a surfactants mediated method in aqueous solution according to our previous report.¹ Typically, mixed surfactant 0.75 g (Span 80 and Tween 80 in molar ratio 1:1.2) was dissolved in 60 mL deionized water and was ultrasonicated for 10 minutes to give a homogeneous emulsion. 2-methylimidazole (2-MeIM, 0.90 g, 10.96 mmol) was added to the emulsion followed by another 10 min sonication. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1.60 g, 5.38 mmol) was dissolved in 80 mL water. Both solutions are adjusted to 60 °C. The zinc solution was poured into the emulsion containing surfactants and 2-methylimidazole under moderate stirring. After 1 h, the milky solution was centrifuged at 15000 rpm to separate the ZIF-8 nanocrystals. The obtained solid was redispersed in ethanol and refluxed for 24 h to remove the surfactants and unreacted reactants. The products are separated by centrifugation and dried at 85 °C.

2.2 Synthesis of 100 nm ZIF-8 (ZIF-8_methanol)

ZIF-8_methanol was prepared in methanol solution. Typically, zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2.98 g, 10 mmol) was dissolved in 100 mL methanol. A second solution was prepared by dissolving 2-methylimidazole (2-MeIM, 3.28 g, 40 mmol) in 100 mL methanol. The

two solutions were mixed under moderate stirring, and the stirrer was stopped after 1 min. After being kept at room temperature for 12 h, the white products were centrifuged at 15000 rpm and washed with methanol for several times.² After centrifugation, the products were dried at 85 °C.

2.3 Synthesis of 3 µm ZIF-8 (ZIF-8_ethanol)

ZIF-8_ethanol was prepared in ethanol solution. Typically, zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2.98 g, 10 mmol) was dissolved in 100 mL ethanol. A second solution was prepared by dissolving 2-methylimidazole (2-MeIm, 3.28 g, 40 mmol) in 100 mL ethanol. The two solutions were mixed under moderate stirring, and the stirrer was stopped after 1 min. After being kept at room temperature for 12 h, the white products were centrifuged at 15000 rpm and washed with ethanol for several times.³ After centrifugation, the products were dried at 85 °C.

3. Measurement of the adsorption kinetics

3.1 Measurement of I_3^- adsorption kinetics by ZIF-8 in liquid phase

All samples were outgassed under vacuum at 180 °C for 12 h before measurement. In a typical measurement, 20 mg activated ZIF-8 samples were dispersed in 200 mL 0.4 mM KI/I_2 solution under stirring. At certain time point, a small amount of mixture was drawn by a syringe and filtered through a 0.45 µm porous membrane into a quartz cuvette for UV-Vis measurement. The absorption peak at 287 nm is used to calculate the relative concentration.¹

3.2 Measurement of H_2 adsorption kinetics by ZIF-8 at 77 K

The H_2 adsorption kinetics was measured on an Autosorb IQ gas sorption analyzer (Quantachrome). In a typical measurement, 100 mg sample was loaded into a glass cell and was outgassed under vacuum at 180 °C for 12 hours before measurement. The measurement is carried out in the vector dosing mode which is implanted in the setup. Briefly, certain amount of H_2 was first introduced into the gas dosing manifold with calibrated volume which is separated from the sample cell. The pressure of the manifold is measured so that the exact amount of H_2 in the manifold can be obtained. Before H_2 dosing, the sample was kept in liquid nitrogen at H_2 partial pressure of 0 bar. The manifold was then connected to the sample cell by opening the dosing valve. The equalized pressure of the manifold and the sample cell versus time is automatically recorded. The pressure drop due to the volume expansion and also the non-uniform temperature is first calibrated by helium expansion before the measurement and is represented by the term effective free volume (V_f). After correction for V_f , the pressure is converted to the amount of adsorption, which is presented in the form of amount of gas uptake per ZIF-8 cage. The calibration, measurement and data processing are automatically controlled by the software AsiQwin. The amount of introduced H_2 into the manifold is controlled to give the final equilibrium H_2 partial pressure to be about 0.06 bar.

Figures and Tables

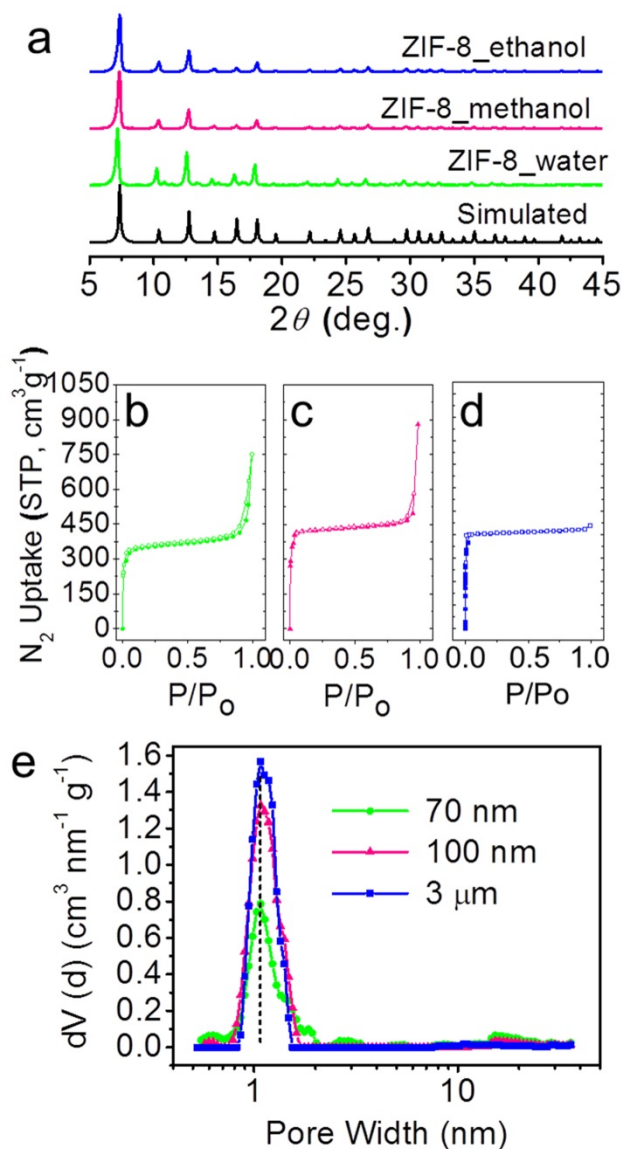


Figure S1. Characterization of structure and porosity of ZIF-8 samples. (a) PXRD patterns of ZIF-8 samples in comparison with simulated curve. (b-d) Nitrogen adsorption isotherms of ZIF-8_water (b), ZIF-8_methanol (c) and ZIF-8_ethanol (d). (e) Pore size distribution of ZIF-8 samples.

Table S1. Particle size and pore characterization results given by nitrogen adsorption measurements at 77 K for ZIF-8 samples.

	<i>Particle size</i>	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)
ZIF-8_water	$70 \pm 13 \text{ nm}$	1360	0.49
ZIF-8_methanol	$100 \pm 7 \text{ nm}$	1769	0.60
ZIF-8_ethanol	$3 \pm 0.3 \mu\text{m}$	1846	0.59

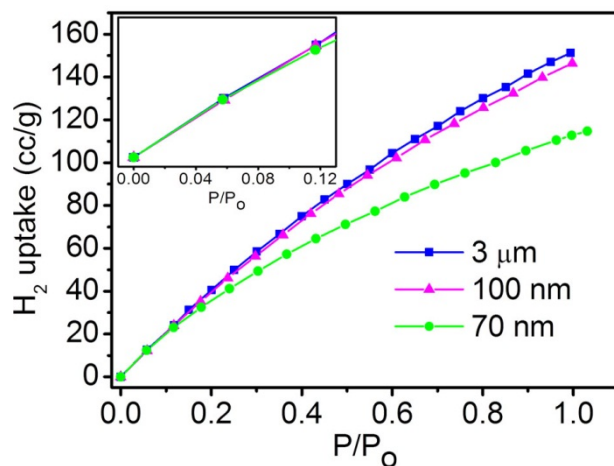


Figure S2. Hydrogen sorption isotherms at 77K for ZIF-8 samples. The inset shows the isotherms for pressure increment 0-0.13bar, in which region the adsorption isotherms are linear and the adsorption capacity is similar for the three samples.

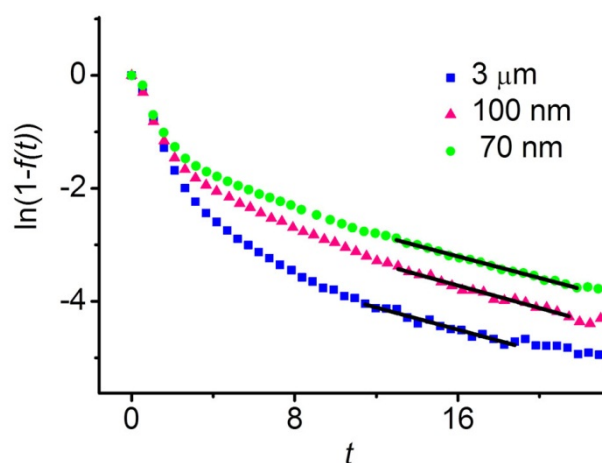


Figure S3. Plot of $\ln(1-f(t))$ versus t for H_2 adsorption kinetics by three ZIF-8 samples, which show non-uniform slopes within the entire time region. The adsorption kinetics, therefore, cannot be described by a single exponent. The three samples with different particle size show similar slope after sufficiently long time (the solid lines), indicating that the rate parameter for the slow component k_2 in the double exponential decay function is similar for the three samples.

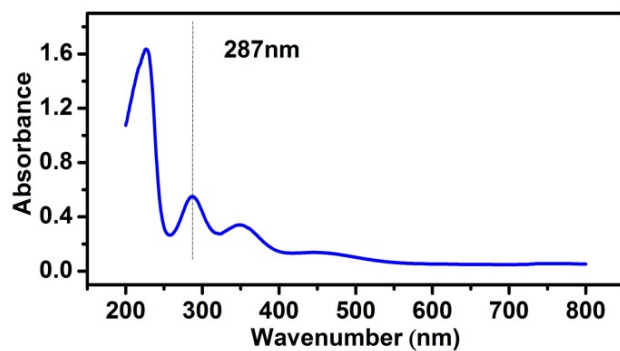


Figure S4. The UV-Vis spectrum of I₃⁻

References:

1. X. Fan, W. Wang, W. Li, J. Zhou, B. Wang, J. Zheng and X. Li, *ACS Appl. Mat. Interfaces*, 2014, **6**, 14994-14999.
2. J. Cravillon, S. Münzer, S.-J. Lohmeier, A. Feldhoff, K. Huber and M. Wiebcke, *Chem. Mater.*, 2009, **21**, 1410-1412.
3. J. Zhou, X. Yu, X. Fan, X. Wang, H. Li, Y. Zhang, W. Li, J. Zheng, B. Wang and X. Li, *J. Mater. Chem. A*, 2015, **3**, 8272-8275.