Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Competitive Adsorption of water vapor with VOCs Dichloroethane, Ethyl Acetate and Benzene on MIL-101(Cr) in humid atmosphere

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CONTENTS

TEXT：

S1. Synthesis of MIL-101. Firstly, $Cr(NO_3)_3 .9H_2O$ (2.00 g, 5.0mmol) and 1,4-benzene dicarboxylic acid (0.82 g, 5.0mmol) were added and dissolved in deionized water (24.0ml). The mixture solution was stirred for approximately 15 min at 313 K, and then hydrofluoric acid (0.25 ml) was added drop wise into the solution. Next, this mixture solution was heated at 493K for 8h plus a cooling ramp down to room temperature for 12 h. After that, the solution was filtered and the product was washed with DMF (25 ml× 3 times) to remove residual non-reacted reactants. To ensure the removal of the unreacted 1,4-benzenedicarboxylic acid completely, the resulting product was dissolved in ethanol for 20 h at 373 K, and then NH_4F solution (30 mmol/L) for 10 h at 333 K. Finally, the resulting sample was dried at 150 °C for 10 h under vacuum for removal of the residual solvent, and thus the green porous MIL-101 sample used in this work was obtained.

S2. Measurement of Adsorption Isotherms of DCE, EA, benzene and water Vapor.

Adsorption isotherms of DCE, EA and benzene vapor on MIL-101 sample were measured by using a standard gravimetric technique (intelligent gravimetric analyzer, IGA-003, Hiden). The IGA-003 is equipped with an ultra-sensitive balance of resolution 0.2 μg mounted in the thermostated heat sink with high precision temperature control. About 60-70 mg samples was weighted for each run. Prior to the measurements, the sample in the vessel of the IGA-003 was vacuumed up to 3-5 Pa and outgassed at 423 K for 5 h to remove any residual guests, adsorbed water and gases. After that, isotherms of DCE, EA and benzene on the sample were carried out from 0 to 9 mbar at 298-318 K. To get more exact isotherm data, buoyancy correction experiment was also employed.

Adsorption isotherms of water vapor on MIL-101 sample were measured by means of a commercial dynamic vapor sorption system (DVS, Quantachrome) equipped with a microbalance with an accuracy of 1μg. Details of measurement procedure are as follows:

Before measurement, the samples are activated at 150 ℃ for 10 h. The dry nitrogen gas and the wet gas are mixed together, and then heated to the setting temperature. The relative humidity (RH) is precisely controlled and monitored by a humidity probe. The real-time weight change of the samples is measured by a microbalance with a accuracy of 1μg. Adsorption is considered to reach the kinetic equilibrium when the change of sample mass is lower than 0.002 mass%/min. After a series of equilibrium water vapor uptake at different relative humidities have been measured, to plot water vapor uptakes versus relative humidities yields an isotherm of water vapor on the sample.

S3. Temperature Programmed Desorption Experiments.

In this work, TPD experiment was performed on a gas chromatography workstation (GC-9560, Huaai, Shanghai) as we previously reported [1]. MIL-101 sample was pre-activated at 150 ºC under vacuum for 12 h, and then was quickly transferred into a desiccator which contained a given dehydrated VOCs (EA, DCE, and benzene) and water vapour. Adsorption was conducted at room temperature (about 298 K) and ambient pressure for 30 min. The organic/water-laden MIL-101 samples (about 350-400 mg) were quickly packed in a copper tube between two silica wool plugs. The heating programme immediately started from 313 to 443 K under the atmosphere of high-purity N_2 (for benzene)/H_2 (for water vapour) with a flow rate of 30 ml/min. The heating rates varied from 5 to 13 K/min and the tube effluents were detected by using a gas chromatograph with hydrogen flame ionization (FID) and temperature coefficients of delay (TCD) detectors. According to the experimental TPD curves, the activation energy for desorption of VOC on the sample can be estimated.

Polanyi-Wigner equation was employed to describe the TPD curves[2-4]:

$$r_\mathrm{d} = -\frac{\mathrm{d}\theta_\mathrm{A}}{\mathrm{d}t} = k_0 \theta_\mathrm{A}{}^n \exp\left(-\frac{E_\mathrm{d}}{\mathrm{R}T}\right) \tag{1}$$

Where is the desorption rate (mol/s), k_0 is a constant that depends on the desorption kinetics (s^{-1}), θ_A is the fractional coverage of adsorbent surface, n is the order of the desorption process, E_d is desorption activation energy of adsorbate (kJ/mol), and R is the gas constant (8.314 J/ K•mol). Assume the desorption process follow first-order kinetics (n=1) and the desorption activation energy of the adsorbate can be calculated by:

$$\ln\left(\frac{\mathrm{R}T_\mathrm{p}{}^2}{\beta_\mathrm{H}}\right) = \frac{E_\mathrm{d}}{\mathrm{R}T_\mathrm{p}} + \ln\left(\frac{E_\mathrm{d}}{k_0}\right) \tag{2}$$

Where β_H is the heating rate (K /min), T_p is the peak temperature of TPD curves.

S4. Breakthrough experiment.

Fig. 1 shows the experiment setup for determination of breakthrough curves. It consists of three sections: (a) preparation of gas mixture, (b) adsorption chamber, and (c) online analysis system of effluent gas. The gas flow line of nitrogen was divided into three branches: one was for pure nitrogen gas, one was connected to bubble tube for production of VOCs gas, and the third one was connected to water saturator for humidity adjustment. The relative humidity (R.H.) of the gas was controlled or adjusted to desired value with an accuracy of ± 3.0% through the control of three branches of gases. The gas mixture of solvent vapors, water vapor, and pure nitrogen were delivered to a gas mixer, and then delivered to the adsorption column whose temperature could be controlled to an accuracy of±0.5°C. The VOC concentration, relative humidity, and flow rate of gas mixture through the adsorption column were controlled by mass flow controllers. In the experiment, the flow-rate of gas mixture through the adsorption column was 70 ml/min. 25.0 mg MIL-101 sample was filled in a iron packed bed. The packed bed was about 0.5 cm in length and the inner diameter was 3.0mm.The temperature of the packed bed was kept at 308 K. The composition of exit gas stream from the adsorption column was continuously determined by using an online gas chromatography (GC9560, Shanghai, China) equipped with a hydrogen flame ionization detector (FID) and with work station HW-2000 (Nanjing Qianpu Company). The breakthrough curves of DCE, EA and benzene on MIL-101 can be obtained at 308K at relative humidities of 5%, 40%, and 80%, separately.

On the basis of experimental breakthrough curves, working adsorption capacity of an adsorbent in fixed bed for VOC can be found out using following equation (3) [6, 7].

$$q_w = \int_0^{t_b} \left(C_0 - C_{exit}\right)\frac{Q}{W}dt \qquad (3)$$

Where, q_w is working adsorption capacity, mmol/g; Q is the flow rate of the feed containing VOC, ml/min; W is the weight of adsorbent, g; t_b is breakthrough time, min;

C_o and C_{exit} are separately the concentrations of VOC inlet and outlet, mmol/ml. In this work, C_{exit} is defined or chosen as 5% of the inlet concentration C_o.

S5. Sample Characteristics.

Figure S2 shows the SEM image of MIL-101 sample synthesized by using microwave irradiation method. The SEM image exhibited a clear octahedral morphology of MIL-101 crystallized product. Its crystal sizes of MIL-101 were more uniform, and were in the range of 100-200 nm.

Figure S3 gives the powder X-ray single-diffraction pattern of MIL-101 synthesized in this work. It showed that the main diffraction peaks appeared separately at 2θ=3.29°, 5.88º, 8.44°, 9.06°, 10.34°, 16.53° and 16.92°. These peak positions in the diffraction pattern were in good agreement with those of MIL-101(Cr) reported in the literature[5].

FIGURES

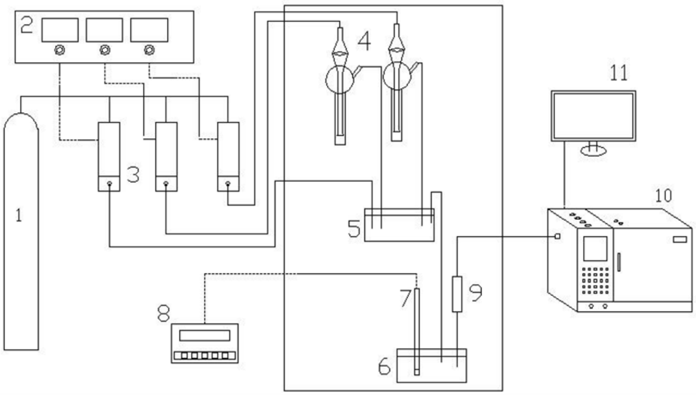

Fig. S1. Self-assembly equipment for dynamic adsorption experiment (1. N_2 cylinder;2, 3. Massflow controller; 4. Bubble tubes; 5,6. Gas mixer; 7. Humidity sensor; 8. Hygrometer; 9.

Adsorption column; 10. Furnace; 11. Gas chromatograph workstation; 12. Display device.)**.**

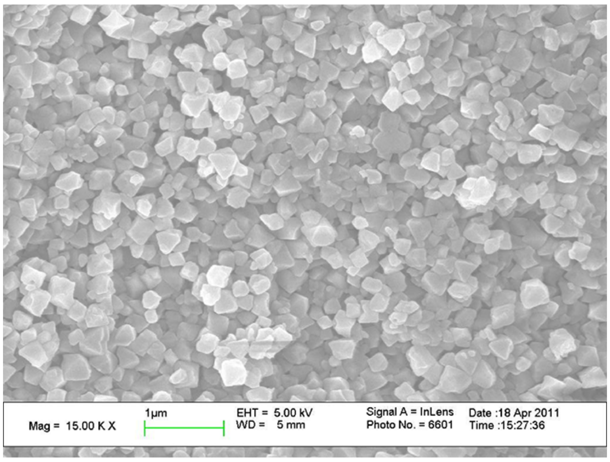

Figure S2. SEM image of the MIL-101.

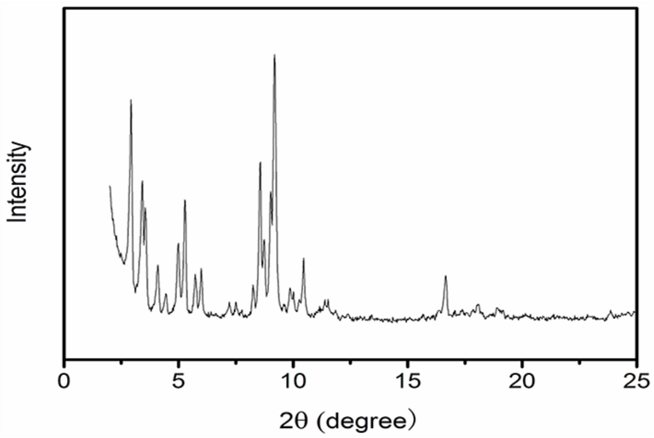

Figure S3. Powder XRD pattern of the synthesized MIL-101.

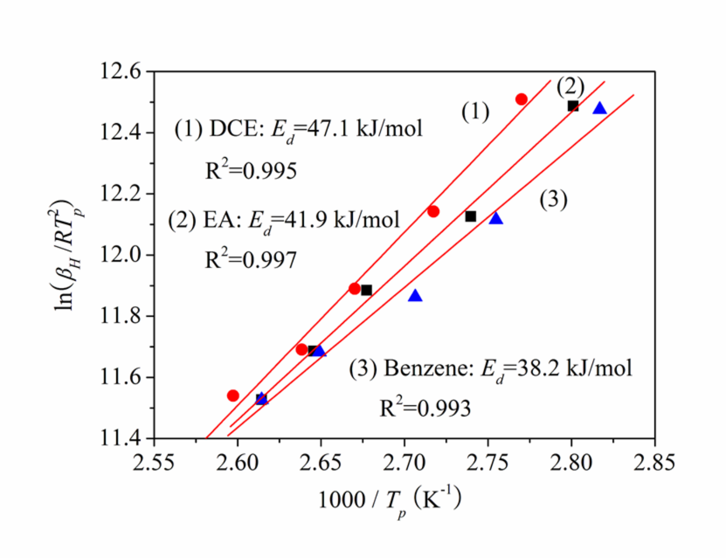

Figure S4. Linear dependence between $\ln\left({T_P^2R}/{\beta_H}\right)$ and ${1}/{T_P}$ of EA, DCE and bezene on the MIL-101 on the basis of equation (2).

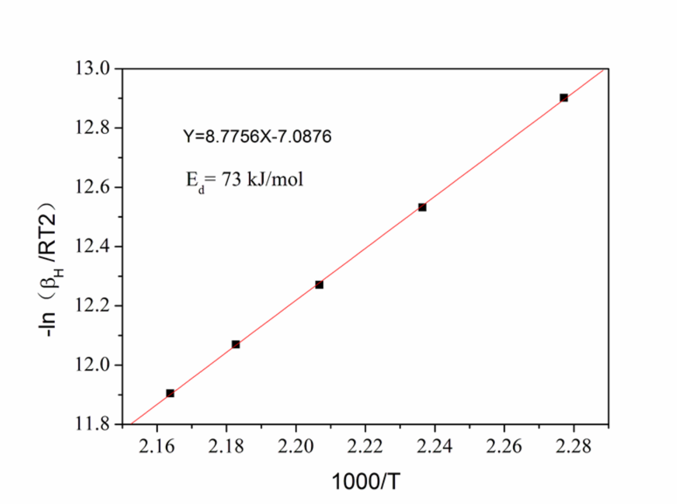

Figure S5. Linear dependence between $\ln\left({T_P^2R}/{\beta_H}\right)$ and ${1}/{T_P}$ for TPD of H_2O vapor on the MIL-101 on the basis of equation (2).

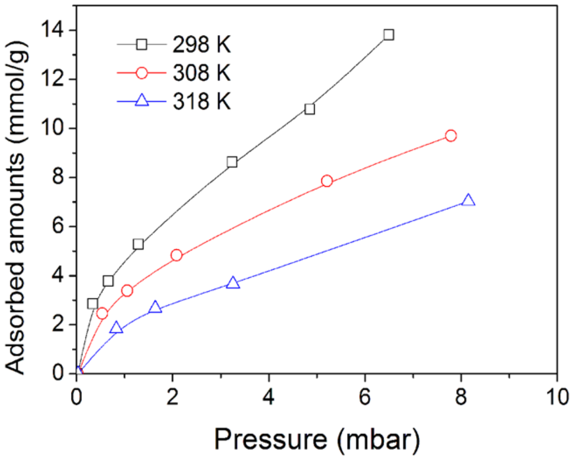

Figure S6a. Isotherms of DCE on MIL-101 at 298-318 K.

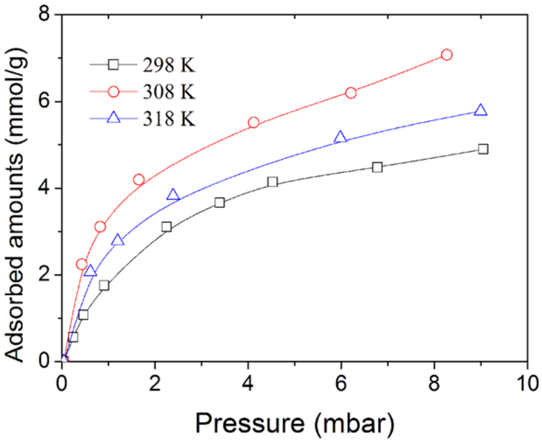

Figure S6b. Isotherms of EA on MIL-101 at 298-318 K.

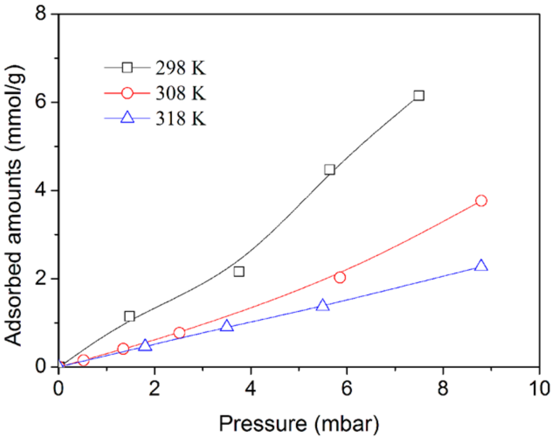

Figure S6c. Isotherms of benzene on MIL-101 at 298-318 K.

TABLES

Table S1. Fitting Parameters and Linear Correlation Coefficient of Langmuir and Freundlich Models for the Isotherms of the DCE, EA and Benzene on MIL-101.

VOC	Model	q_m	K_L	R^2
DCE	Langmuir	13.3	0.31	0.99
EA	Langmuir	6.67	0.62	0.99
Benzene	Freundlich	K_F	n	R^2
		0.21	0.76	0.99

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