

# **Remarkable CO<sub>2</sub>/CH<sub>4</sub> selectivity and CO<sub>2</sub> adsorption capacity on the polyamine-decorated metal-organic framework adsorbents**

Qiuju Yan, Yichao Lin, Chunlong Kong\* and Liang Chen\*

Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, China.

## **Electronic Supporting Information:**

Experimental details, scanning electron microscope (SEM), powder X-ray Diffraction patterns (XRD), Fourier Transform Infrared Spectroscopies (IR), Thermogravimetric analysis, N<sub>2</sub> adsorption-desorption isotherms, CO<sub>2</sub>, and CH<sub>4</sub> adsorption isotherms, breakthrough curve experiments, CO<sub>2</sub> selectivity calculations and Henry constant calculation.

## **Table of Contents**

- 1. Experimental**
- 2. Additional Figures**

## 1. Experimental details

### Synthesis of PEI-incorporated amine-MIL-101(Cr) adsorbent

The amine-MIL-101(Cr) was synthesized by a mixture of chromic nitrate hydrate (800 mg, 2 mmol), 2-aminoterephthalic acid (360 mg, 2 mmol), sodium hydroxide (200 mg, 5 mmol) and deionized water (15 ml) in an autoclave at 150 °C for 6~16 h. The as-prepared products were recovered by centrifugation, and washed with DMF at room temperature, and then the products were further washed with hot alcohol at 100 °C for 24 h in an autoclave. Finally, the products were dried at 80 °C in air.

The PEI-incorporated amine-MIL-101(Cr) adsorbent was prepared by an effective wet impregnation method. The detailed process was as follows: first, the amine-MIL-101 (Cr) powders were heated at 160 °C under vacuum condition for 12 h, removing the coordinated water. Second, the desired amount of PEI was dissolved in 1 mL anhydrous methanol under stirring for 30 min, and then desired amount of amine-MIL-101 (Cr) powders were gradually added into the PEI/methanol solution under stirring. The resulting gel was dried over night under room temperature and argon protection, and then the temperature of the sample was increased at programmed rate and held at 110 °C for 12 h under vacuum condition. Finally, a porous, solid PEI-MIL-101 (Cr) adsorbent was obtained. Here amine-MIL-101(Cr) with different PEI loadings, corresponding to 50 wt%, 75 wt% and 100 wt%, were prepared and denoted as **a**, **b** and **c**, respectively. The loaded-PEI was calculated by the following equation:

$$\text{PEI loadings \%} = \frac{\text{Mass}_{PEI}}{\text{Mass}_{MOF}} \times 100\% \quad (1)$$

### Physical measurements of PEI-incorporated amine-MIL-101(Cr) adsorbent

The morphologies of the as-prepared samples were examined using a field emission scanning electron microscope (Hitachi, S-4800). Powder X-ray Diffraction patterns (PXRD) of the samples were collected on a Bruker AXS D8 Advance diffractometer using CuK $\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation at a voltage of 40 kV and 40 mA. The powder

diffraction pattern was scanned over the angular range of 2-25° (2 $\theta$ ) with a step size of 0.02°. Infrared spectra were recorded on KBr/NMOF pellets in a Thermo model Nicolet 6700 spectrometer. Before collecting the spectra, the sample was pretreated under vacuum at a temperature of 150 °C for 12 h. Thermogravimetric analysis was measured using a system provided by Mettler Toledo (model Pyris Diamond TG/DTA) in air at a heat rate of 5 °C / min up to 800 °C. The nitrogen adsorption-desorption isotherm was measured on ASAP 2020M apparatus at 77.3 K. In a general procedure, the dry sample (~200 mg) was loaded into the glass analysis tube. Then we fixed the glass tube to the degas port to be heated and evacuated, including two stages, initially to 90 °C at 10 °C·min<sup>-1</sup> and hold the temperature for 30 min to 110 °C for 8 h. After this, the outgas rate was less than 5  $\mu$ mHg. The sample was then backfilled with N<sub>2</sub> before transferred to the analysis port. Before analysis, the sample was evacuated for 300 min. Finally, N<sub>2</sub> adsorption-desorption isotherm was measured at 77.3 K and the range of relative pressures is between 0 and 1. The BET surface area was calculated over the range of relative pressures between 0.05 and 0.20.

### **CO<sub>2</sub> and CH<sub>4</sub> adsorption measurement**

The single-component adsorption isotherms of the probe gas CO<sub>2</sub> (purity, 99.999%) and CH<sub>4</sub> (purity, 99.99%) were measured separately using volumetric technique by an apparatus from SETARAM France (PCTpro-E&E). Before each measurement, the sample was evacuated at 110 °C for 12 h.

### **Breakthrough measurement**

Breakthrough curve experiments for single-component and mixture gas were carried out using a column with a length of 20 cm and an internal diameter of 0.8 cm. The sample powder was packed in the middle part of the column. Here, the sample mass we used is 0.20 g. Breakthrough allows in situ activation of the sample under argon flow. The experiment methodology is fully described in references [1, 2]. The flow rates of all the pure gases were controlled by mass flow controllers. Before the measurement, the sample was activated at 110 °C for 2 hours. The gas stream from the outlet of the column was analyzed online with a mass spectrometer.

### CO<sub>2</sub> selectivity calculations

The CO<sub>2</sub> selectivities (*S*) of samples were evaluated by the following equation, according to the references [3, 4]:

$$S = \frac{q_{CO_2} / p_{CO_2}}{q_{N_2} / p_{N_2}} \quad (2)$$

where  $q_i$  is the adsorption capacity of *i* component,  $p_i$  is the partial pressure of *i* component. The adsorption capacities of the components are defined to be molar excess adsorption capacities determined without correction for absolute adsorption.

### Regenerability of sample b

To confirm the complete desorption of CO<sub>2</sub>, we measured the mass of activated sample (**b**) before adsorption ( $m_1$ ) and after desorption ( $m_2$ ). The value of  $m_1$  was obtained by measuring the mass of activated sample before adsorption measurement. After the CO<sub>2</sub> adsorption measurement, we placed the sample under vacuum condition at 100 °C for 30 min for desorption, and then we measured the mass ( $m_2$ ) of desorbed sample. Here the values of  $m_1$  and  $m_2$  are  $0.2462 \pm 0.0003$  g and  $0.2465 \pm 0.0003$  g, respectively. Thus, the adsorbed CO<sub>2</sub> can be desorbed at 100 °C under vacuum condition. In addition, the sample exhibits good regenerability for CO<sub>2</sub> capture (see Fig S6).

## 2. Additional Table and Figures

Table S1 The surface areas and pore volumes of amine-MIL-101(Cr), **a**, **b** and **c**.

Samples	BET ( $\text{m}^2 \text{g}^{-1}$ )	Pore Volume ( $\text{cm}^3 \text{g}^{-1}$ )	$\text{N}_2$ saturated adsorption ( $\text{cm}^3 \text{g}^{-1}$ )
Amine-MIL-101(Cr)	2297	2.12	1146.3
<b>a</b>	946.8	0.8	588.8
<b>b</b>	243.3	0.47	322.3
<b>c</b>	96.4	0.37	244.9

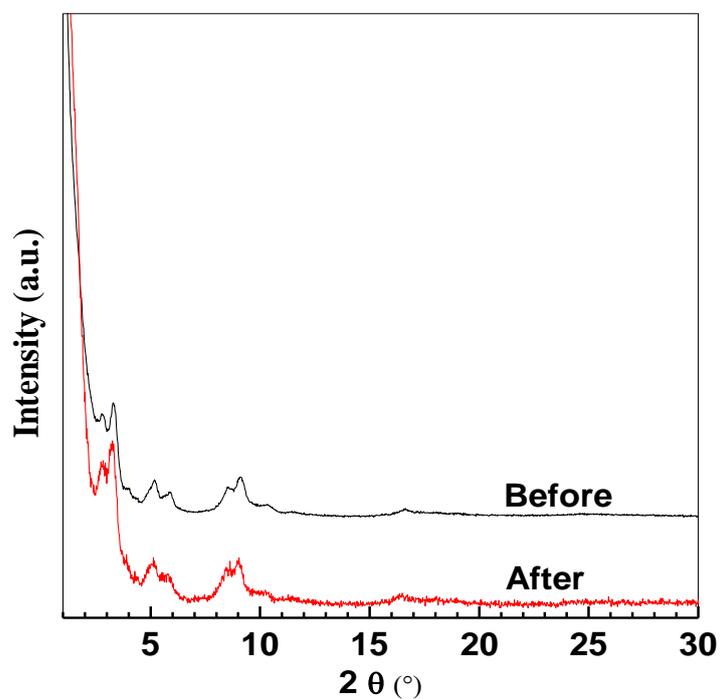


Fig. S1 PXRD patterns of amine-MIL-101 before and after immersing in water at 70 °C for 4 days.

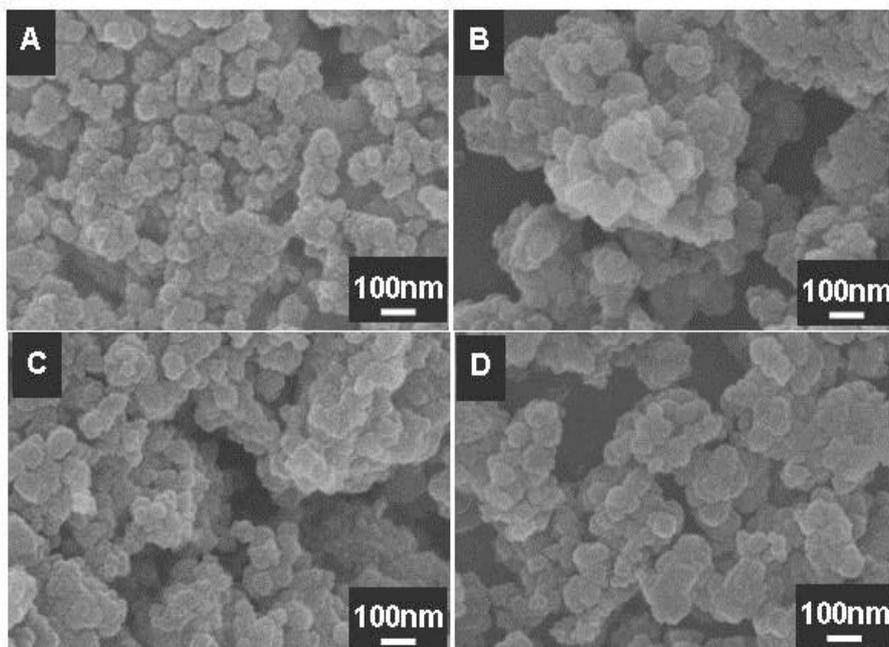


Fig. S2 SEM images of amine-MIL-101(Cr) (A) and PEI-decorated amine-MIL-101  
(Cr) (B, a; C, b; D, c).

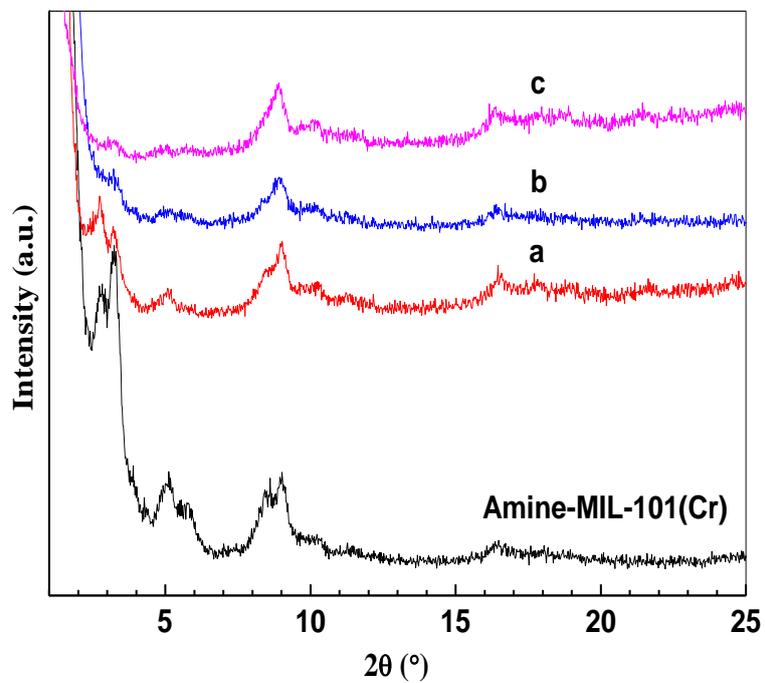


Fig. S3 PXRD patterns of amine-MIL-101(Cr), a, b and c.

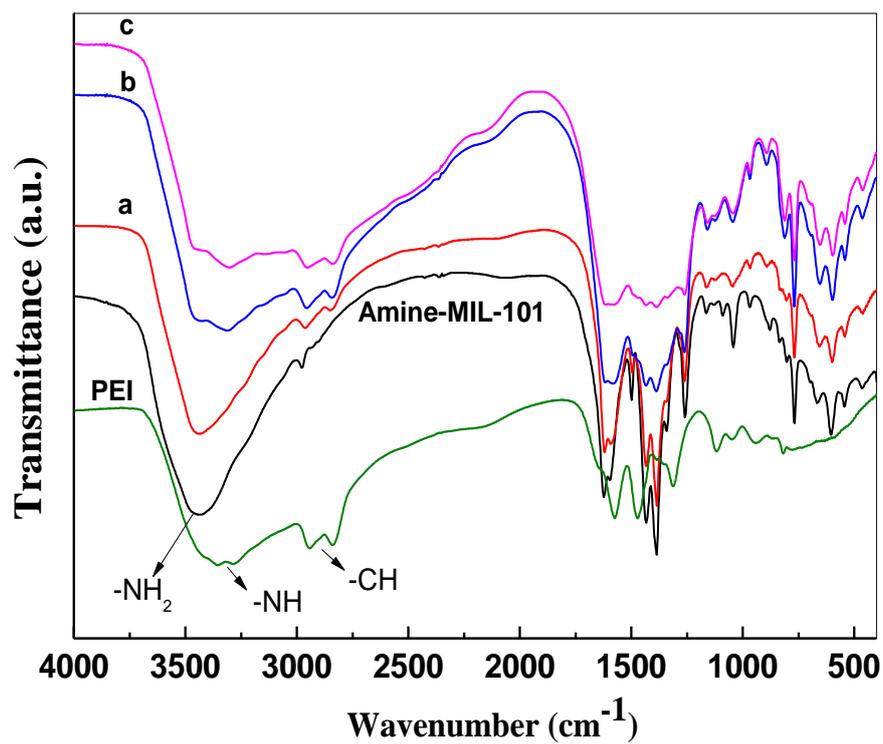


Fig. S4 Infrared spectra of PEI, amine-MIL-101(Cr), a, b and c.

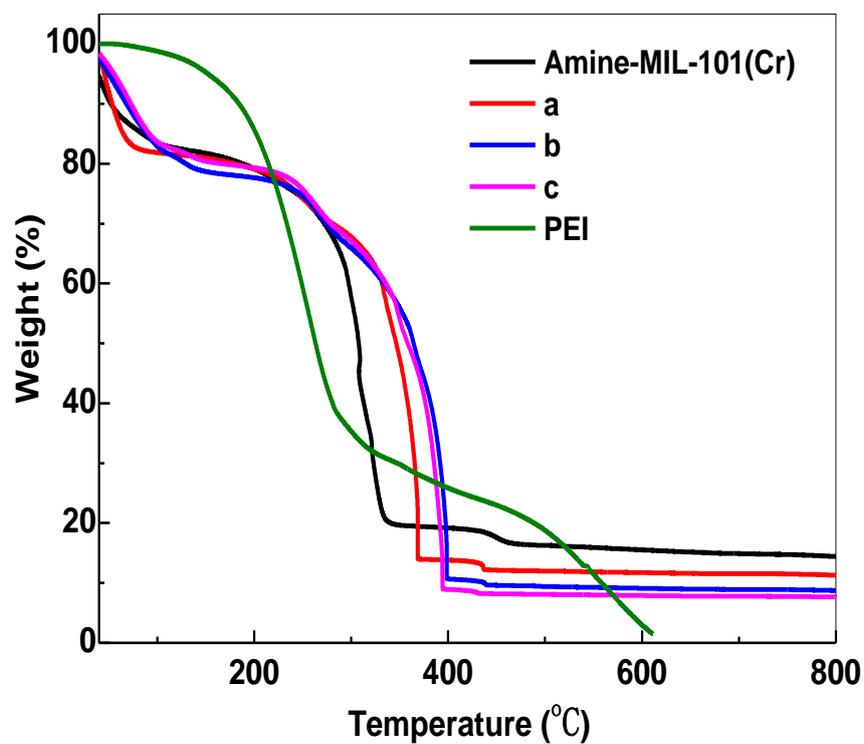


Fig. S5 Thermogravimetric analysis of PEI, amine-MIL-101(Cr), a, b and c.

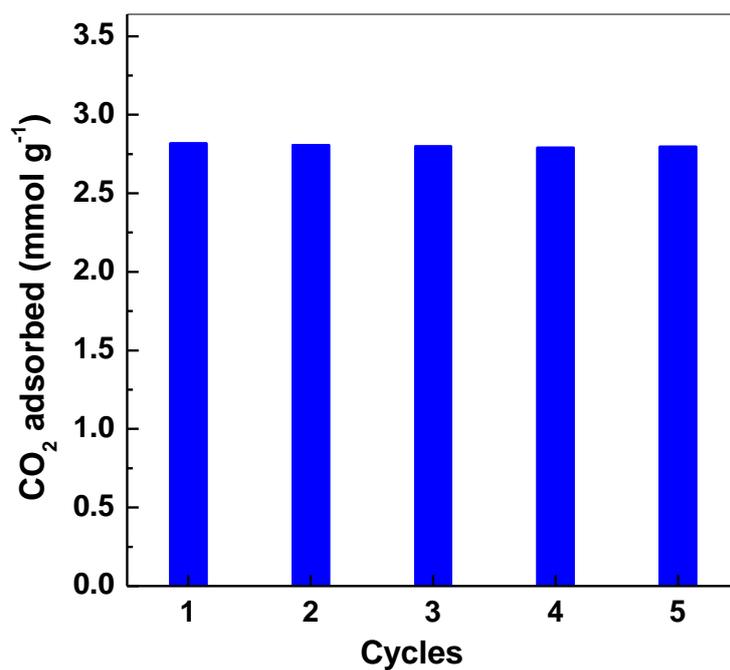


Fig. S6 Cyclic sorption processes for **b** sample at 25 °C and 0.15 bar.

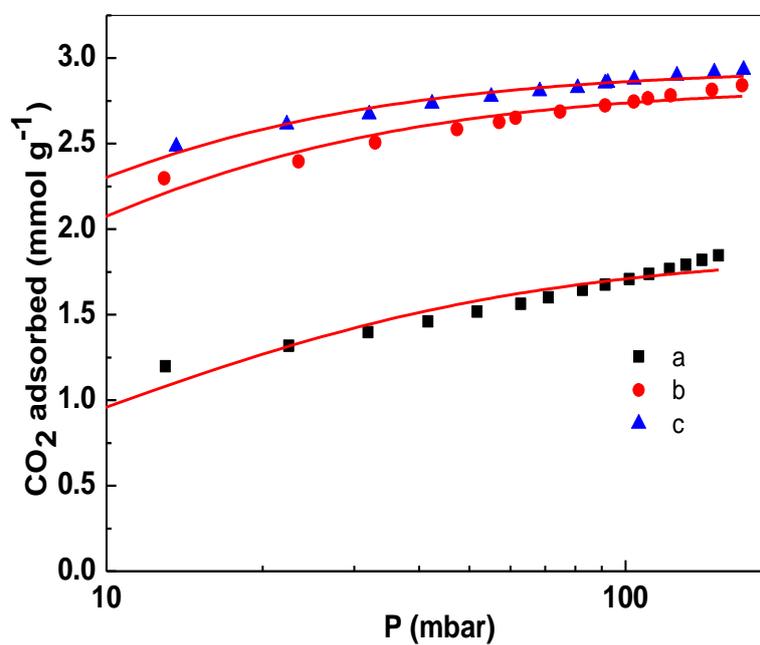


Fig. S7 CO<sub>2</sub> adsorption isotherms of **a**, **b** and **c** at low pressures and 25 °C. Line: the simulated Langmuir isotherms.

Langmuir isotherm model :

$$q = \frac{q_m b P}{1 + b P}$$

The constants of the simulated isotherms:

Sample **a**:

$$q_m=1.87211, b=0.10524$$

Sample **b**:

$$q_m=2.83814, b=0.27212$$

Sample **c**:

$$q_m=2.94176, b=0.36099$$

Dimensional Henry's law adsorption equilibrium constants:  $K_H \sim q_m b$

$K_H$  for sample **a**: 0.19702;

$K_H$  for sample **b**: 0.77231;

$K_H$  for sample **c**: 1.06194.

So, we have:

$K_H$  for sample **c** >  $K_H$  for sample **b** >  $K_H$  for sample **a**

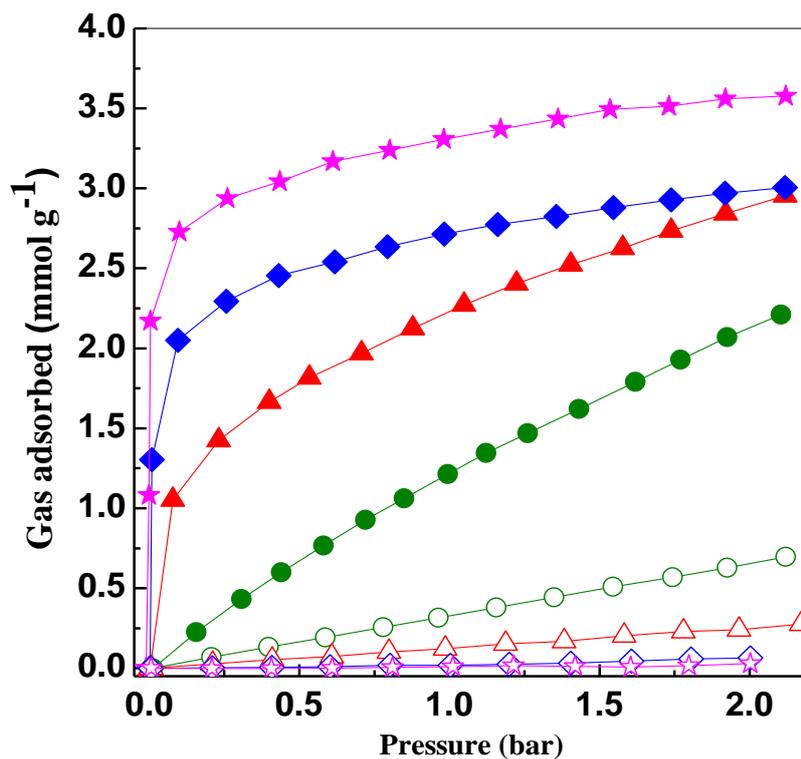


Fig. S8 CO<sub>2</sub> and CH<sub>4</sub> adsorption isotherms for amine-MIL-101(Cr) (circles), **a** (triangles), **b** (squares) and **c** (stars) at 50 °C. Symbols: Filled, CO<sub>2</sub> adsorption; Hollow, CH<sub>4</sub> adsorption.

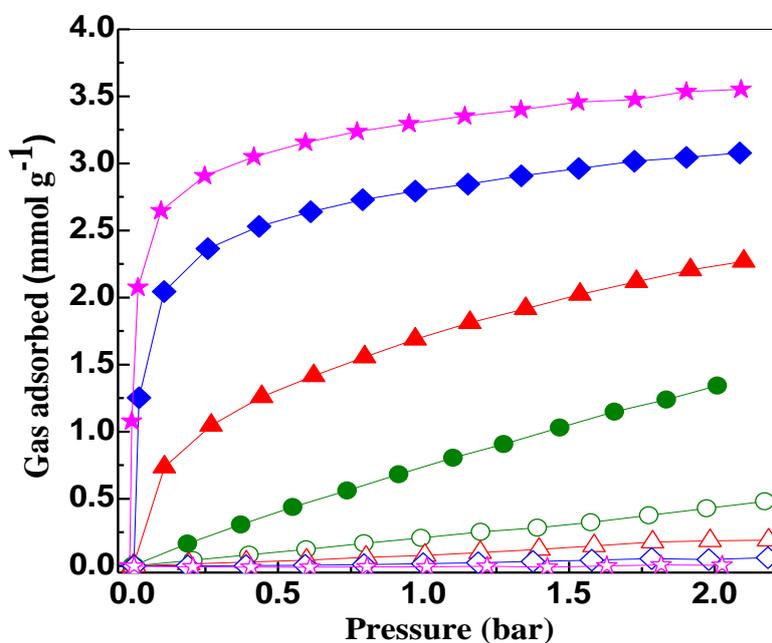


Fig. S9 CO<sub>2</sub> and CH<sub>4</sub> adsorption isotherms for amine-MIL-101(Cr) (circles), **a** (triangles), **b** (squares) and **c** (stars) at 75 °C. Symbols: Filled, CO<sub>2</sub> adsorption; Hollow, CH<sub>4</sub> adsorption.

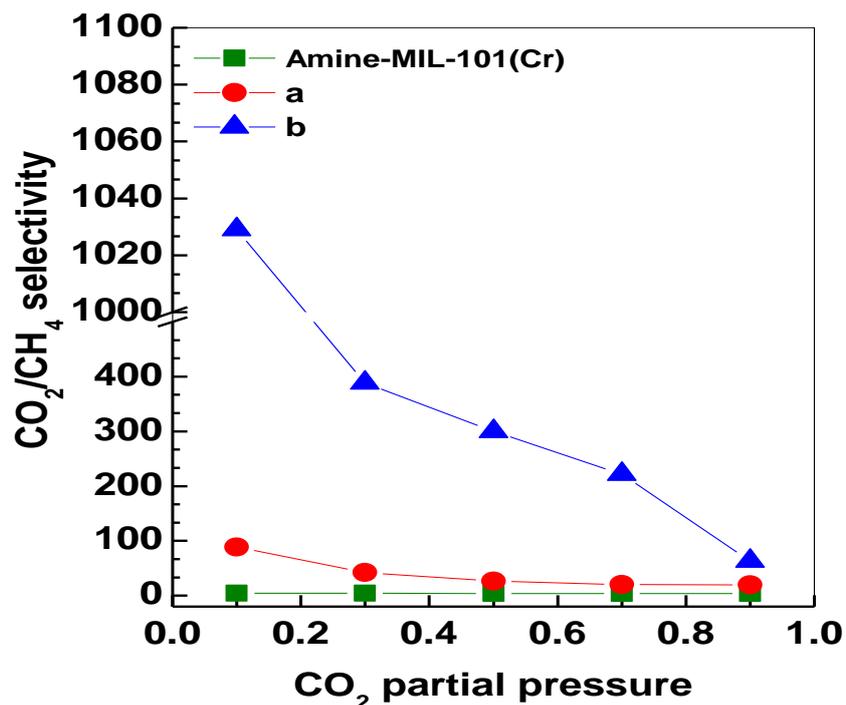


Fig. S10 The selectivities of the CO<sub>2</sub>/CH<sub>4</sub> mixture for amine-MIL-101(Cr), **a** and **b** at a total pressure of 1 bar and 50 °C.

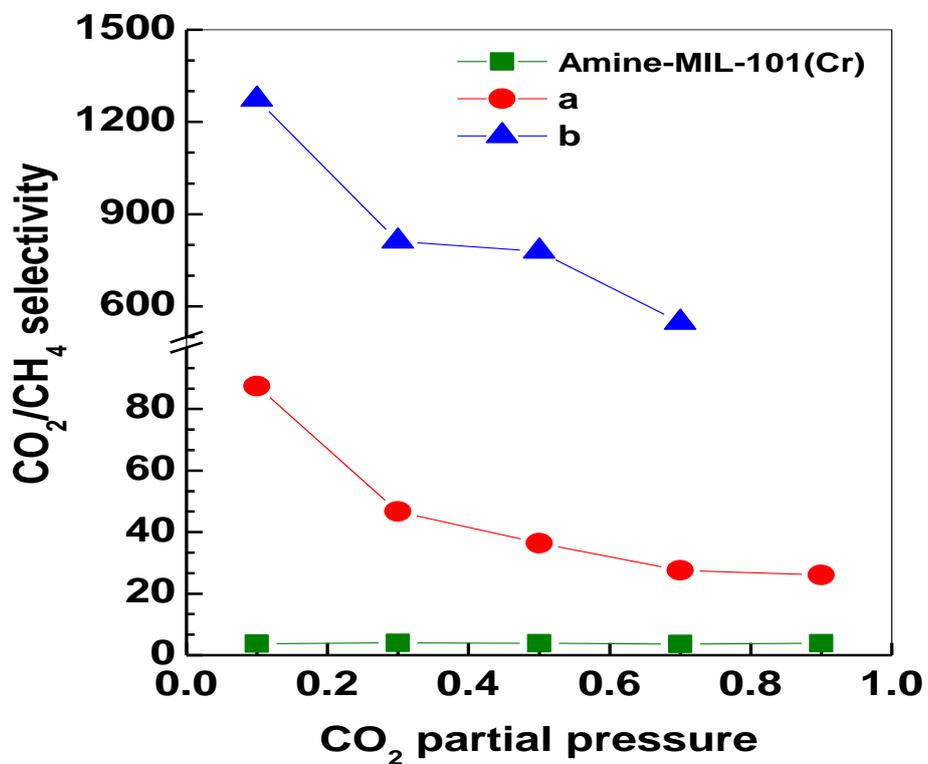


Fig. S11 The selectivities of the CO<sub>2</sub>/CH<sub>4</sub> mixture for amine-MIL-101(Cr), **a** and **b** at a total pressure of 1 bar and 75 °C.

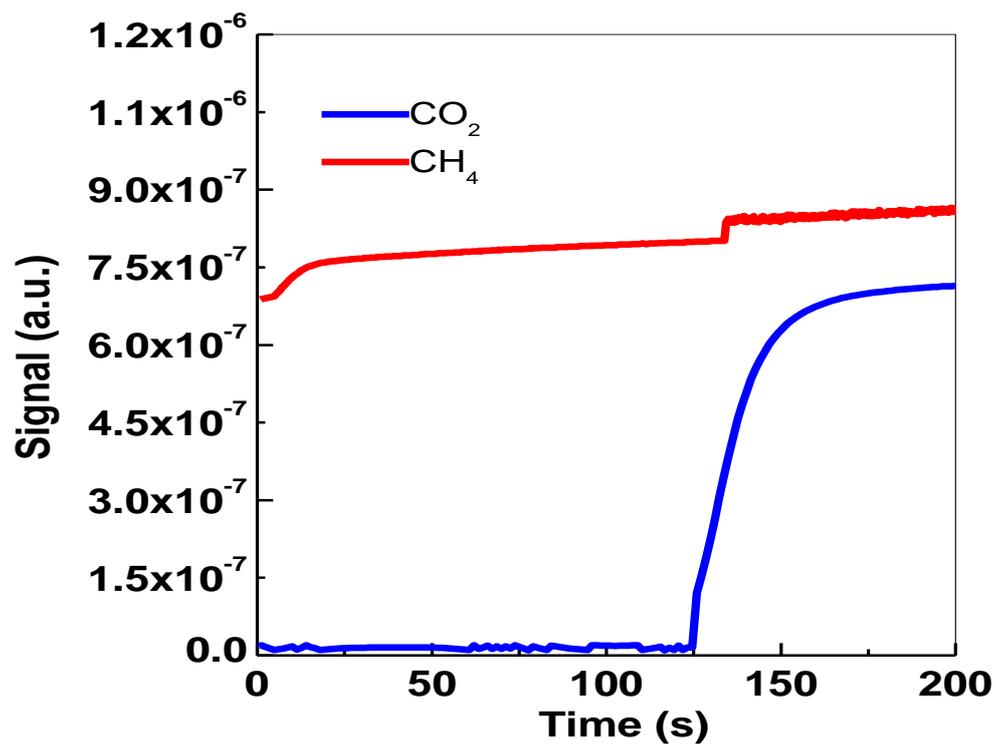


Fig. S12 Single-component gas breakthrough curves of CO<sub>2</sub> and CH<sub>4</sub> for c sample at 25 °C.

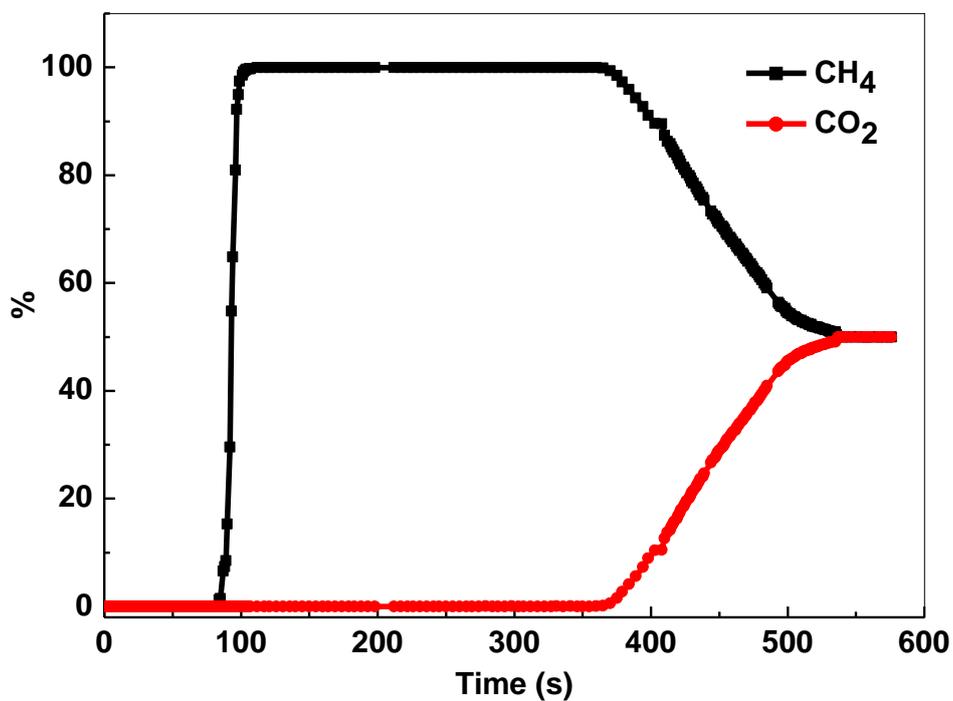


Fig. S13 Gas breakthrough curves of CO<sub>2</sub> and CH<sub>4</sub> mixture (50 wt%:50 wt%) for sample c at 25 °C.

## Reference

- [1] T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, and G. Férey, *Chem. Eur. J.* 2004, **10**, 1373.
- [2] K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae and J. R. Long, *Chem. Rev.* 2012, **112**, 724.
- [3] T. M. McDonald, D. M. D'Alessandro, R. Krishna, J. R. Long, *Chem. Sci.*, 2011, **2**, 2022.
- [4] Y. Liu, Z. U. Wang, H.-C. Zhou, *Greenh. Gas.: Sci. and Technol.*, 2012, **2**, 239.