MIL-100Cr with open Cr sites for a record N₂O capture

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Supporting Information

1. Experimental

1.1. Materials

MIL-100Cr was synthesized and purified according to the literature. [1] Mixed metallic chromium (0.104 g), H₃BTC (0.3 g), HF (40%, 0.2 mL) and deionized water (9.6 mL) evenly. The slurry was introduced in a 23 mL Teflon liner, which was then put into an oven. The system was heated from room temperature up to 493 K in 12h, and keep at 493 K for 4 days before being cooled to room temperature in 24 h. The resulting light green product was filtered off, immersed in ethanol at 343 K for 5 h at a ratio of 1 g / 250 mL to remove the excess of unreacted organic ligand and then filtered again. The solid was finally dried for 3 h in vacuum at 323 K. The resulting solid material was denoted as MIL-100Cr. MIL-101Cr was synthesized in our laboratory too. [2]

1.2. Characterization

The crystallinity and phase purity of the materials were measured by powder X-ray diffraction (PXRD) on a Bruker D8 ADVANCE X-ray diffractometer with Cu-K α (λ = 1.5418 Å) radiation operated at 40 kV and 40 mA. Scanning was performed over the 2 θ range of 2-20° at 5°/min. The N₂O, N₂, CO₂, CH₄, and O₂ adsorption/desorption isotherms were obtained using a Micromeritics ASAP 2460 surface area and pore size analyzer after the samples were activated (the temperature was 423 K and 523 K, vacuum was 1*10⁻¹⁰ bar) for 12 h. H₂O adsorption isotherms were obtained using a Micromeritica activated for 12 h (the temperature was 423 K and 523 K, vacuum was 423 K and 523 K, vacuum was 423 K and 523 K, vacuum was 1*10⁻¹⁰ bar) for 12 h. H₂O adsorption isotherms were obtained using a Micromeritica material of 12 h (the temperature was 423 K and 523 K, vacuum was 1*10⁻¹⁰ bar).



Fig. S1 XRD patterns of MIL-100Cr samples after activation at 423 K (MIL-100Cr-150) and 523 K (MIL-100Cr-250), respectively.



Fig. S2 N_2 adsorption and desorption isotherms of MIL-100Cr at 77 K and the pore size distribution calculated by the H-K method after activation at 423 K and 523 K.



Fig. S3 Adsorption isotherms of H₂O on MIL-100Cr activated from 423 K and 523 K at 298 K



Fig. S4 High-resolution XPS spectra of Cr^{3+} 3/2p and Cr^{3+} 1/2p peaks for MIL-100Cr before (a) and after activation (b) at 523 K (MIL-100Cr-250), and also the N₂O adsorption on MIL-100Cr-250



Fig. S5 Adsorption isotherms of N₂O on MIL-100Cr-250 at 298 K and 273 K.



Fig. S6 Adsorption heat of N₂O on MIL-100Cr-250.



Fig. S7 Adsorption isotherms of N_2 on MIL-100Cr-150 and MIL-100Cr-250 at 298 K.



Fig. S8 Adsorption isotherms of CH₄ on MIL-100Cr-150 and MIL-100Cr-250 at 298 K.



Fig. S9 Adsorption isotherms of O₂ on MIL-100Cr-150 and MIL-100Cr-250 at 298 K.



Fig. S10 Adsorption isotherms of CO₂ on MIL-100Cr-150 and MIL-100Cr-250 at 298 K.



Fig. S11 Comparison of the ideal adsorbed solution theory (IAST) gas selectivity of 50/50 N_2O/CH_4 mixtures in MIL-100Cr-150 and MIL-100Cr-250 at 298 K.



Fig. S12 Comparison of the ideal adsorbed solution theory (IAST) gas selectivity of $50/50 \text{ N}_2\text{O}/\text{O}_2$ mixtures in MIL-100Cr-150 and MIL-100Cr-250 at 298 K.



Fig. S13 Comparison of the ideal adsorbed solution theory (IAST) gas selectivity of 50/50 N₂O/CO₂ mixtures in MIL-100Cr-150 and MIL-100Cr-250 at 298 K.

2. Calculation

2.1. Density-functional theory calculations

Our First-principles density-functional theory (DFT) calculations were performed using the Quantum-Espresso package.^[3] A semi-empirical addition of dispersive forces to conventional DFT was included in the calculation to account for van der Waals interactions.^[4] We used Vanderbilt-type ultrasoft pseudopotentials and the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange correlation. Due to the large size of the MIL-100Cr unit cell and the large number of atoms, direct calculation on the MOF crystal structure is highly difficult. Therefore, we adopted a simplified cluster model (similar to the one used in ref. 5) to evaluate the gas binding. The Cr trimer metal center was cleaved from the periodic crystal structure of MIL-100Cr, and put in a $20 \times 20 \times 20$ supercell. The carboxylate groups were terminated by H atoms, and the terminal F group on Cr was removed, which results in a net charge of +1 for the cluster. For this system, a cutoff energy of 544 eV and a $2 \times 2 \times 2$ *k*-point mesh (generated using the Monkhosrt-Pack scheme) were found to be enough for total energy to converge within 0.01 meV/atom. The cluster

model (with "+1" charge) was first fully optimized with respect to atomic coordinates. The lowestenergy spin configuration for the three Cr ions is (+3, -3, +3), with the total spin value of the cluster being S=3. For gas adsorption, various possible binding configurations were considered and fully relaxed. The lowest-energy structures were identified as the optimal binding structures. To obtain the gas binding energies, a single gas molecule placed in a supercell with the same cell dimensions was also relaxed as a reference. The static binding energy (at T = 0 K) was calculated using: $E_B = E(MOF) + E(gas) - E(MOF+gas)$.

2.2. Fitting of pure component isotherms

The unary isotherm data for N_2 , O_2 , and CH_4 in MIL-100Cr, measured at 298 K, were fitted with the single-site Langmuir model

$$q = q_{sat} \frac{bp}{1 + bp} \tag{1}$$

The unary isotherm data for N_2O and CO_2 in MIL-100Cr, measured at 298 K, were fitted with the Dual-site Langmuir model

$$q = q_{A,sat} \frac{b_A p}{1 + b_A p} + q_{B,sat} \frac{b_B p}{1 + b_B p}$$

$$\tag{2}$$

The isotherm fit parameters are provided in Table 1 to Table 5.

Table 1. Dual-site Langmuir fit parameters for N₂O in MIL-100Cr.

	<i>q</i> _{A,sat}	b_{A}	$q_{ m B,sat}$	$b_{ m B}$
	mol kg ⁻¹	Pa^{-1}	mol kg ⁻¹	Pa^{-1}
MIL-100Cr 150	0.28	0.000475089	5.3	4.65563E-06
MIL-100Cr 250	2.1	0.024589204	5.7	1.61106E-05

Table 2. Dual-site Langmuir fit parameters for CO₂ in MIL-100Cr.

<i>q</i> _{A,sat}	b _A	$q_{\mathrm{B,sat}}$	$b_{ m B}$
mol kg ⁻¹	Pa ⁻¹	mol kg ⁻¹	Pa ⁻¹

MIL-100Cr 150	0.6	0.000268518	4.5	4.95596E-06
MIL-100Cr 250	2.4	0.004856163	5.8	1.34482E-05

Table 3. Single-site Langmuir fit parameters for N_2 in MIL-100Cr.

	$q_{\rm sat}$	b
	mol kg ⁻¹	Pa^{-1}
MIL-100Cr 150	14	1.25717E-07
MIL-100Cr 250	1.4	4.38906E-05

Table 4. Single-site Langmuir fit parameters for CH₄ in MIL-100.

	$q_{ m sat}$	b
	mol kg ⁻¹	Pa ⁻¹
MIL-100Cr 150	14	2.40748E-07
MIL-100Cr 250	3	2.59055E-06

Table 5. Single-site Langmuir fit parameters for O_2 in MIL-100Cr.

	$q_{\rm sat}$	b
	mol kg ⁻¹	Pa ⁻¹
MIL-100Cr 150	1	2.5E-06
MIL-100Cr 250	1	5.6E-06

2.3 Qst calculation

Qst is the adsorption isosteric enthalpy ($-\Delta H$), which can be calculated as a function of loading using adsorption data at different temperatures via the Clausius–Clapeyron equation:

$$ln\frac{P_2}{P_1} = \frac{\Delta H}{R}(\frac{1}{T_1} - \frac{1}{T_2})$$

Where P is the pressure in bar, T is the temperature in K, R is the gas constant (8.314).

2.4. IAST calculations of adsorption selectivities, and uptake capacities

IAST calculations were performed to determine the separation selectivities of MIL-100Cr.

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