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Rationally tuning the separation performances of $[M_3(HCOO)_6]$ frameworks for CH_4/N_2 mixtures via metal substitution

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ABSTRACT

A series of isostructural ultra-microporous metal-organic framework (MOF) compounds $[M_3(HCOO)_6]$ (M = Mg, Mn, Co and Ni) have been readily synthesized in large-scale, characterized, and evaluated for the separation of CH_4 and N_2. Results indicate that the metallic formates exhibit different CH_4 adsorption capacities and distinct CH_4/N_2 selectivity in a sequence of Ni > Co > Mg > Mn analogue owing to their varied CH_4 affinities. Thereinto, $[Ni_3(HCOO)_6]$ shows the highest CH_4 adsorption capacity of 1.09 mmol/g and CH_4/N_2 selectivity up to 6.5 at 0.4 MPa and 298 K in the dynamic experiments, which suggests the most suitable synergistic effect between constricted pores and surface properties among $[M_3(HCOO)_6]$ frameworks. At the same time, the adsorption behaviour in $[M_3(HCOO)_6]$ is investigated by NH_3-TPD, revealing that the adsorbed NH_3 molecules should have two different states. One is that gas molecules stay inside the pores, the other is that gas molecules are adsorbed on the adsorption sites induced by the coordinated metal ions or exposed oxygen of the $[M_3(HCOO)_6]$, which directly affects the adsorption capacity, the ratio of two states of molecules and the final selectivity. These results confirm that alteration of metal ion plays an important role in the tuning of pore size and internal surface properties, thus providing new clues to design MOFs with different pore characteristics for enhanced gas sorption and separation.

1. Introduction

Methane, clean energy, is widely agreed to induce less adverse effects on the environment than other conventional fuels like coal and petroleum [1,2], and has become one of the fastest growth energy sources throughout the world. Therefore, considerable efforts have been devoted to exploit and utilize a variety of sources of methane gas in order to meet the rapidly increasing demands in natural gas. In particular, the unconventional natural gases like coal-bed methane, landfill gas and shale gas, are effective supplements to natural gas. However, the removal of N_2 severely impedes the utilization of these low-quality natural gases since the separation of CH_4/N_2 is difficult because of their very similar properties [3–6]. Among various separation methods, Pressure Swing Adsorption (PSA) is the most potential candidate for purifying the nitrogen-rich natural gas owing to its high energy efficiency, intrinsic economic feasibility and operating flexibility [7]. In this process, obtaining the desired adsorbent is a bottleneck problem for the separation of CH_4/N_2 mixtures. Up to date, various available porous solids such as activated carbon (AC) [8–11], carbon molecular sieves (CMS) [12–14], zeolites [15–20], silica gels [21] and some new types of molecular sieves like ETS-4 [22,23], DDR [24] and SAPO-34 [25] have been actively investigated and evaluated for the CH_4/N_2 separation. Among these adsorbents, only clinoptilolite and ETS-4 exhibit a certain application prospect. However, they still cannot match the requirement of the high efficiency separation of CH_4 from N_2. The discouraging industrial application of reported adsorbents is attributed to several structural features, including (a) the highly polar surfaces can also enhance the strength of interaction between N_2 and the channel resulting in a negative contribution to the selectivity, (b) the chaotic pore structure of adsorbents like AC deteriorates the selectivity, (c) the uncomfortable size and geometry of the nanopores bring about pore obstruction or weak adsorption of CH_4.

From above-mentioned reports, the adjustments of aperture and internal surface property are the keys to improve separation

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performance for adsorbents, but the modifications of molecular sieves and AC cannot satisfy the requirements of the separation of CH_4/N_2 owing to their own inferiors [17,22,26]. In the last decades, porous metal-organic frameworks (MOFs) as a relatively new class of materials exhibit great potential in gas storage, gas purification and separation due to their exceptional specific surface area, adjustable pore size and controllable properties [27–36]. Compared with the conventional adsorbents, the most intriguing characteristic of MOFs is the infinite number of combinations of metal ions and organic linkers, which makes rational design of the pore functionality and size easier [37–40]. Thus, many MOFs have been applied in selective gas adsorption, such as CO_2/CH_4, CO_2/N_2, CH_4/H_2 and CH_4/N_2 [41–47]. However, few porous MOFs reported so far have been potentially used in the separation of CH_4 from nitrogen-rich natural gases.

Among the current MOFs materials, a series of isostructural ultra-microporous metal-organic framework (MOF) compounds $[M_3(HCOO)_6]$ (M = Mg, Mn, Co and Ni) with permanent porosity, high thermal stability exhibit excellent performance of gas adsorption and separation. $[M_3(HCOO)_6]$ frameworks have a diamond network and contain one-dimensional zigzag-shaped channels with a pore width of ca. 4 × 5 Å. Wang [48–50], Kim [27,51] and Jeffrey [52] et al. and our group have successfully synthesized these MOFs and studied their gas adsorption properties. Among the possible applications, we recently discovered that the ultra-microporous $[Ni_3/Co_3(HCOO)_6]$ frameworks presented high adsorption selectivities for the separation of CH_4/N_2 mixtures, especially $[Ni_3(HCOO)_6]$ with extraordinary selectivity up to 7.0 [45]. This result is ascribed to the possible synergistic effect between uniform ultra-micropore and moderate polarity on channel surfaces. According to the previous studies, we synthesized other members in this series by using different divalent metal ions to tune the pore size and polarity in order to get a better understanding towards the enhanced separation performance of the adsorbent for CH_4/N_2 mixtures.

In this work, the isostructural ultra-microporous MOF compounds $[M_3(HCOO)_6]$ (M = Mg, Mn, Co and Ni) are synthesized by using an HF-assisted solvent-thermal method, and the structures of these frameworks are carefully analyzed. The CH_4 adsorption capacity and selectivity of CH_4/N_2 for $[M_3(HCOO)_6]$ frameworks were evaluated by the methods of pure gas adsorption, dynamic binary-gas breakthrough separation, and the Henry's law constants, isosteric heats of adsorption (Q_{st}) and selectivity of CH_4/N_2 were calculated as well. Furthermore, we demonstrate that $[M_3(HCOO)_6]$ frameworks have higher selectivity in comparison to the traditional adsorbents. In order to elucidate the intriguing differences in CH_4 adsorption and separation from N_2, NH_3-TPD has been employed to investigate the tuning of pore size and internal surface properties arising from alteration of metal ion. These fundamental studies will be helpful for the insight into how adsorbed CH_4 interacts with the internal surface and provide a facile route to design MOFs for gas sorption and separation.

2. Experimental section

2.1. Synthesis of the MOFs

All reagents and solvents for synthesis were obtained from commercial vendors and of analytical grade without further treatment prior to use. The compounds of the $[M_3(HCOO)_6]$ frameworks, where M = Mg, Mn, Co and Ni, were synthesized through different methods by other authors [27,48,52]. In this work, the $[M_3(HCOO)_6]$ frameworks were prepared in a similar synthetic process with minor modifications. The preparation of $[Mg_3(HCOO)_6]$ was described as an example. 1.5 ml HF solution was dissolved into 250 ml *N*,*N*-dimethylformamide (DMF). And then, the mixtures and magnesium(II) nitrate hexahydrate (38.5 g, 150 mmol) were added to a 500 ml round-bottle flask equipped with a magnetic stirrer. After stirring at room temperature for 30 min to form a homogenous mixtures, formic acid (15 ml, 400 mmol) was added drop-wise over 5 min. The resultant solution was then transferred to a 500 ml Teflon-lined stainless steel autoclave and sealed. Then, the reaction was carried out at 100 °C for 6 h under autogenous pressure by solvent-thermal synthesis. After cooling to room temperature, colourless crystals were obtained and washed with fresh acetone three times and then dried in an oven at 100 °C for 10 h. The as-synthesized samples of $[M_3(HCOO)_6]\cdot DMF$ (M = Mg, Mn, Co and Ni) were evacuated at 160 °C under dynamic vacuum conditions for 12 h. For each case, the yield was high (92–98%).

2.2. Material characterization

2.2.1. Adsorption of argon

Argon (Ar) adsorption isotherms were measured at 87 K using a Quantachrome Autosorb-iQ2 instrument. Before the analysis, the samples were degassed at 150 °C for 12 h under vacuum. The specific surface areas of the samples were calculated employing the Brunauer–Emmett–Teller (BET) model in a relative pressure (P/P_0) ranging from 0.001 to 0.05. Total pore volumes (V_{total}) were determined directly from the amount of Ar adsorbed at the relative pressure $P/P_0 = 0.95$. The pore size distribution (PSD) and micropore volume were calculated from the adsorption branch by non-local density function theory (NLDFT) and Dubinin-Raduskevitch (D-R) method, respectively.

2.2.2. PXRD

Powder X-ray diffraction (PXRD) patterns were collected on a PANalytical X'pert diffractometer using Cu $K_{\alpha 1}$ radiation, 40 kV and 40 mA current with a scan speed of 8° min^{-1} and a step size of 0.02° in 2θ.

2.2.3. FT-IR

The Fourier transform infrared (FT-IR) spectra were carried out using a Nicolet 6700 FT-IR instrument equipped with a KBr beam splitter and an MTC nitrogen-cooled detector. The spectra data were collected at the frequency region of 4000–650 cm^{-1} with a resolution of 4 cm^{-1}.

2.2.4. TGA

Thermal gravimetric analysis (TGA) was performed on a NETZSCH STA 449 F3 analyzer. The samples were measured under argon atmosphere (flow rate 30 ml/min) in the temperature range of 30–800 °C with a heating rate of 10 °C/min.

2.3. Pure gas adsorption measurements

Methane and nitrogen adsorption experiments were conducted on a modified Quantachrome Autosorb-iQ2 gas sorption analyzer. Isothermic data of CH_4 and N_2 on $[M_3(HCOO)_6]$ frameworks were recorded at three different temperatures (288, 298 and 308 K) with a pressure range of 0–100 kPa. The temperatures were regulated by using a recirculating thermostatic bath with an accuracy of 0.01 K. By using a mixture of ethylene glycol and de-ionized water as heating fluid and filling the sample cell with rod, the error of volumetric adsorption is greatly reduced. About 1 g sample was used for adsorption measurements. Prior to the experiments, all samples were degassed at 150 °C for 12 h under vacuum condition. According to these isotherms measured at 288, 298 and 308 K, respectively, the isosteric heats of adsorption can be calculated from the plot of ln *P* versus $1/T$. Herein, the isosteric heats of