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A new MOF-5 homologue compound UTSA-10 has been obtained under solvothermal conditions from a mixture of Zn(NO\textsubscript{3})\textsubscript{2} · 6H\textsubscript{2}O and commercially available linker, 2-methylfumaric acid, in N,N-dimethylformamide. The moderate surface area and suitable pore sizes enable the activated UTSA-10a to separate methane from C\textsubscript{2} hydrocarbons at room temperature. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4897351]

Metal-organic frameworks (MOFs) are a new type of functional porous materials consisting of metal ions or metal containing clusters connected by multidentate organic linkers via metal coordination bonds. By bridging metal ions/clusters with organic linkers, a plethora of compounds with different pore sizes, properties, and functionalities can be systematically designed and synthesized. Compared to conventional porous materials such as zeolites and activated carbons, these hybrid materials have high surface areas and pore volumes, uniform pore sizes, and chemical functionalities. Moreover, their pore sizes and chemical functionalities can be tuned by modifying the metal groups or organic linkers. Hence, MOFs have attracted considerable interest, which has been fueled by the promise of their utilities in gas sorption, separation, heterogeneous catalysis, sensing, and biomedicine.\textsuperscript{1–11}

Nature gas, one of the most important energy resources, mainly consists of methane and also contains small quantities of other hydrocarbons heavier than methane. The removal of these hydrocarbons from natural gas is traditionally carried out by cryogenic distillation, which is very energy-intensive. In contrast, selective adsorption separation near room temperature using porous materials offers an energy-efficient alternative. A few MOF materials have been reported to show the potential for the selective separation of C\textsubscript{2}/C\textsubscript{1} hydrocarbons,\textsuperscript{12–17} but the research in this respect is still somewhat limited to date.

MOF-5 (Zn\textsubscript{4}O(BDC)\textsubscript{3}, BDC = 1,4-benzenedicarboxylate) is a prototypical MOF consisting of a cubic framework built from Zn\textsubscript{4}O clusters connected via benzenedicarboxylates.\textsuperscript{18} Due to the large surface area, exceptional pore volume, and relatively high thermal stability, it has been widely studied in a variety of fields and usually considered to be a benchmark MOF. Yaghi \textit{et al.} employed isoreticular synthesis method to prepare a series of MOF-5 homologues with identical topology but diverse porosity and different chemical functionalization.\textsuperscript{19} One member of this series exhibited a high capacity for methane storage. Xue \textit{et al.} used a fumaric acid to construct...
FIG. 1. Schematic representation of the structure of UTSA-10a with a cubic framework (c) built from Zn₄O clusters (a) connected via 2-methylformate (b).

Another MOF-5 homologue (Zn₄O(FMA)₃, FMA = fumarate) exhibiting moderate gas sorption due to comparatively low surface area. Herein, we report another prototypical MOF-5 homologue, UTSA-10, which is assembled from a readily available dicarboxylate, namely, 2-methylfumarate, in expectation that the methyl group in the organic linker improves the moisture stability and tunes the pore size of the resulting MOF for gas separation application. The activated UTSA-10a shows a good potential for the separation of methane from C₂ hydrocarbons at room temperature, which has been comprehensively established by gas sorption isotherms and transient breakthrough and pulse chromatographic simulations.

UTSA-10 was readily synthesized by a solvothermal reaction of 2-methylfumaric acid and Zn(NO₃)₂·6H₂O in N,N-dimethylformamide (DMF) at 100 °C for 48 h as colorless cubic crystals. The crystal structure was revealed by the similarity of its powder X-ray diffraction (PXRD) pattern to the simulated one from a MOF [Zn₄O(FMA)₃] that is built from the fumarate ligand of the same length as 2-methylfumarate. UTSA-10 adopts a cubic framework structure by connecting Zn₄O(COO)₆ clusters with the 2-methylfumarate linkers (Fig. 1). The presence of methyl groups did not interfere with the formation of the isoreticular structure. UTSA-10 can be formulated as [Zn₄O(MeFMA)₃]·8DMF·2H₂O (MeFMA = 2-methylfumarate) on the basis of thermal gravimetric analysis (TGA, supplementary Fig. S1) and microanalysis. TGA under a nitrogen atmosphere shows that the desolvated MOF is thermally stable up to 360 °C.

The permanent porosity was unambiguously established by the N₂ sorption isotherm at 77 K. Prior to gas sorption measurement, the as-synthesized UTSA-10 was guest-exchanged with dry acetone and evacuated under a dynamic vacuum at room temperature for 24 h to generate the activated UTSA-10a. Its PXRD pattern matches with that of the pristine sample (supplementary Fig. S2), indicating that the structure remains intact after activation. The N₂ sorption isotherm at 77 K shows a characteristic type-I adsorption behavior (Fig. 2), which is typical for microporous materials. UTSA-10a can adsorb 282 cm³ (STP) g⁻¹ of N₂ at 77 K. Based on the N₂ adsorption isotherms, the Brunauer-Emmett-Teller (BET) and Langmuir surface areas are calculated to be 1090
FIG. 2. N\textsubscript{2} sorption isotherm of UTSA-10a at 77 K. The solid and open symbols represent the adsorption and desorption data, respectively. STP = Standard Temperature and Pressure.

and 1146 m\textsuperscript{2} g\textsuperscript{−1}, respectively (supplementary Figs. S3 and S4\textsuperscript{22}). The total pore volume calculated from the maximum amount of N\textsubscript{2} adsorbed is 0.4358 cm\textsuperscript{3} g\textsuperscript{−1}. These values are smaller than those of MOF-5\textsuperscript{18} and [Zn\textsubscript{4}O(FMA)\textsubscript{3}]\textsuperscript{20} materials.

We have recently paid much attention to porous MOFs for the storage and separation of small hydrocarbons because of their very important industrial applications\textsuperscript{12,13,23–30} Given the fact the pore size within UTSA-10a tuned by the methyl group in the organic linker falls in the range of the kinetic diameters of C\textsubscript{1} and C\textsubscript{2} hydrocarbons (3.3–4.4 Å), the low-pressure single-component C\textsubscript{2}H\textsubscript{2}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, and CH\textsubscript{4} adsorption properties were examined accordingly at two different temperatures of 273 and 296 K. As shown in Fig. 3, all isotherms, except the C\textsubscript{2}H\textsubscript{2} one, show good reversible sorption behavior. At 296 K and 1 atm, UTSA-10a takes up a negligible amount of CH\textsubscript{4} (5.8 cm\textsuperscript{3} g\textsuperscript{−1}), but a moderate amount of C\textsubscript{2}H\textsubscript{2} (43.0 cm\textsuperscript{3} g\textsuperscript{−1}), C\textsubscript{2}H\textsubscript{4} (31.0 cm\textsuperscript{3} g\textsuperscript{−1}), and C\textsubscript{2}H\textsubscript{6} (48.5 cm\textsuperscript{3} g\textsuperscript{−1}). The uptakes of C\textsubscript{2} hydrocarbons are higher than those of MOF-5\textsuperscript{31} despite a lower surface area. The higher C\textsubscript{2} hydrocarbon adsorption capacities in comparison with methane indicate that UTSA-10a is a very attractive material for the selective adsorptive separation of C\textsubscript{2} hydrocarbons from methane at room temperature.

Based on the pure-component gas sorption isotherms, the Henry’s law and IAST (Ideal Adsorbed Solution Theory) selectivities were calculated. The Henry’s law selectivities for C\textsubscript{2}H\textsubscript{2}, C\textsubscript{2}H\textsubscript{4}, and C\textsubscript{2}H\textsubscript{6} over CH\textsubscript{4} at 296 K are 8.1, 4.6, and 6.5, respectively, which are moderate compared to those of the best performing MOF materials.\textsuperscript{13} Furthermore, IAST has been applied to calculate adsorption selectivities for an equimolar quaternary CH\textsubscript{4}/C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} gas mixture in UTSA-10a as a function of the total bulk gas phase pressure at 296 K. It was observed from

FIG. 3. The single-component C\textsubscript{2}H\textsubscript{2}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, and CH\textsubscript{4} sorption isotherms of UTSA-10a at 273 K (a) and 296 K (b). The solid and open symbols represent the adsorption and desorption data, respectively.
FIG. 4. Calculations using IAST of Myers and Prausnitz\textsuperscript{32} for C$_2$H$_4$/CH$_4$, C$_2$H$_6$/CH$_4$, and C$_2$H$_8$/CH$_4$ selectivities for an equimolar quaternary CH$_4$/C$_2$H$_2$/C$_2$H$_4$/C$_2$H$_6$ gas mixture maintained at isothermal conditions at 296 K using UTSA-10a.

Fig. 4 that C$_2$H$_2$/CH$_4$ and C$_2$H$_4$/CH$_4$ selectivities decrease, while C$_2$H$_6$/CH$_4$ adsorption selectivities increase, with increasing pressure. The adsorption selectivities of C$_2$ hydrocarbons with respect to CH$_4$ fall in the range of 4–12; this indicates that it is possible to use UTSA-10a for selective adsorption of C$_2$ hydrocarbons from CH$_4$.

To understand the separation selectivity, the isosteric enthalpies of adsorption was calculated using the Clausius-Clapeyron equation by fitting the pure-component adsorption isotherms at 273 K and 296 K to a Langmuir-Freundlich expression (supplementary Fig. S5\textsuperscript{22}). Fig. 5 presents the isosteric enthalpies of adsorption for C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$, and CH$_4$ in UTSA-10a as a function of component loadings. Interestingly, the isosteric enthalpies keep constant, independent of surface coverage. The isosteric enthalpy of adsorption of methane is significantly lower and has a value of 13.2 kJ mol$^{-1}$, whereas the isosteric enthalpy of adsorption of C$_2$ hydrocarbons has a value of about 19–27 kJ mol$^{-1}$. Thus, the preferable adsorption of C$_2$ hydrocarbons relative to C$_1$ methane is attributed to the stronger interaction of the framework with C$_2$ hydrocarbons. Moreover, compared
FIG. 6. (a) Breakthrough characteristics of an adsorber packed with **UTSA-10a** maintained at isothermal conditions at 296 K. The inlet gas is an equimolar 4-component quaternary CH$_4$/C$_2$H$_2$/C$_2$H$_4$/C$_2$H$_6$ gas mixture maintained at isothermal conditions at 296 K and 100 kPa, with partial pressures for each component of 25 kPa. Video animations showing the motion of gas phase concentration fronts traversing the length of the adsorber with an equimolar 4-component CH$_4$/C$_2$H$_2$/C$_2$H$_4$/C$_2$H$_6$ mixture have been provided as the supplementary material. (b) Pulse chromatographic simulations of an adsorber packed with **UTSA-10a** and maintained at isothermal conditions at 296 K. At the inlet to the adsorber, a pulse of an equimolar 4-component quaternary CH$_4$/C$_2$H$_2$/C$_2$H$_4$/C$_2$H$_6$ gas mixture is injected for a duration of 10 s.

to the best-performing materials, the low isosteric enthalpy of adsorption indicates the low regeneration cost. It should be pointed out that an ideal adsorbent for gas separation should possess low regeneration cost, besides high uptake capacity and high adsorption selectivity, which need to be equally taken into consideration.

To further demonstrate the separation feasibility, we carried out transient breakthrough and pulse chromatographic simulations following the methodologies of Krishna and Long.\textsuperscript{13,15,24,33,34} The details are provided in the supplementary material. As shown in Fig. 6(a), for an equimolar 4-component gas mixture of C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$, and CH$_4$ maintained at isothermal conditions at 296 K and a total pressure of 100 kPa at the inlet of the adsorber packed with **UTSA-10a**, the sequence of breakthroughs is CH$_4$, C$_2$H$_6$, C$_2$H$_4$, and C$_2$H$_2$. There is a significant time interval between the breakthrough of CH$_4$ and C$_2$ hydrocarbons. Therefore, it is possible to recover pure methane from this 4-component mixture during the adsorption cycle (see video animations provided in the supplementary material). Fig. 6(b) presents the pulse chromatographic separation of an equimolar 4-component CH$_4$–C$_2$H$_2$–C$_2$H$_4$–C$_2$H$_6$ mixture with **UTSA-10a** at 296 K. The first peak to emerge from the adsorber is that of methane which can be recovered in nearly pure form. The next sets of peaks are for the C$_2$ hydrocarbons. Taken together, these simulated data clearly suggest that **UTSA-10a** can effectively separate methane from C$_2$ hydrocarbons.

In summary, we used a commercially available dicarboxylate to synthesize a new MOF-5 homologue material, namely, **UTSA-10a**. Gas sorption isotherm measurements and simulated breakthrough studies have comprehensively demonstrated that the MOF has a good potential for the separation of methane from C$_2$ hydrocarbons at ambient temperature.

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21 Single-crystal X-ray crystallographic data: Fm3m, a = b = c = 21.643 Å, α = β = γ = 90°, V = 10138 Å3.
22 See supplementary material at http://dx.doi.org/10.1063/1.4897351 for thermal gravimetric analysis; powder X-ray diffraction patterns before and after activation; the BET and Langmuir analysis of N2 adsorption isotherms; and the Langmuir-Freundlich fits of the gas adsorption isotherms.