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# Scalable Room-Temperature Synthesis of Highly Robust Ethane-Selective Metal–Organic Frameworks for Efficient Ethylene **Purification**

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that can separate ethylene from ethane is highly relevant in modern applications. Although adsorption-based separation techniques using metal-organic frameworks (MOFs) have gained increasing attention, the relatively low stability (especially water resistance) and unscalable synthesis of MOFs severely limit their application in real industrial scenarios. Addressing these challenges, we rationally designed and synthesized two new C2H6-selective MOF adsorbents (NKMOF-8-Br and -Me) with ultrahigh chemical and thermal stability, including water resistance. Attributed to the nonpolar/ hydrophobic pore environments and appropriate pore apertures, the MOFs can capture C2 hydrocarbon gases at ambient conditions



even in high humidity. The single-crystal structures of gas@NKMOF-8 realized the direct visualization of adsorption sites of the gases. Both the single-crystal data and simulated data elucidate the mechanism of selective adsorption. Moreover, the NKMOF-8 possesses high  $C_2H_6$  adsorption capacity and high selectivity, allowing for efficient  $C_2H_6/C_2H_4$  separation, as verified by experimental breakthrough tests. Most importantly, NKMOF-8-Br and -Me can be scalably synthesized through stirring at room temperature in minutes, which confers them with great potential for industrial application. This work offers new adsorbents that can address major chemical industrial challenges and provides an in-depth understanding of the gas binding sites in a visual manner.

# INTRODUCTION

As an important chemical feedstock, ethylene  $(C_2H_4)$  is widely used in the chemical industries<sup>1</sup> and in agriculture<sup>2,3</sup> with increasing demand leading to significant consequences for society. In industry, ethylene is mostly produced via the cracking of hydrocarbons.<sup>4</sup> The major byproduct, ethane  $(C_2H_6)$ , needs to be removed to produce polymer-grade ethylene ( $\geq$ 99.95%).<sup>5,6</sup> This process is usually performed in a very large distillation tower (120-180 trays) under energyintensive and high-cost conditions with low temperature and high pressure.<sup>7</sup> Therefore, developing alternative separation techniques with lower-energy consumption is highly desired, yet largely unexplored.<sup>8,9</sup> Recently, adsorption-based separation techniques using porous materials as adsorbents have attracted increasing attention for their high efficiency, easy operation, and low-energy consumption.<sup>10-12</sup> However, the separation of ethylene and ethane is extremely challenging due to their similar physical properties and molecular size<sup>13</sup> (3.28  $\times$  4.18  $\times$  4.84 Å  $^3$  for  $C_2H_4$  and 3.81  $\times$  4.08  $\times$  4.82 Å  $^3$  for  $C_2H_6$  (Scheme 1). Currently, adsorbents used for  $C_2H_6/C_2H_4$ separation mainly consist of two types: C<sub>2</sub>H<sub>4</sub>-selective and

## Scheme 1. Molecular Structures and Physical Properties of Ethane and Ethylene<sup>a</sup>



Kinetic diameter difference: 0.2 Å; b.p (boiling point) difference: 15 K.

<sup>a</sup>b.p. = boiling point.

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 $C_2H_6$ -selective adsorbents. In the first case, separation of  $C_2H_6/C_2H_4$  can be achieved via selecting adsorbents that preferentially adsorb C<sub>2</sub>H<sub>4</sub> over C<sub>2</sub>H<sub>6</sub>. However, in this method,  $C_2H_4$  has to be subsequently harvested in the desorption process which increases the complexity of such a system while reducing energy efficiency due to the higher temperature or vacuum conditions required.<sup>14,15</sup> Separation performance may also be hampered in the event of coadsorption of  $C_2H_6$  residues in the adsorbent.<sup>16</sup> By contrast, C<sub>2</sub>H<sub>6</sub>-selective adsorbents forego many of these obstacles with pure  $C_2H_4$  gas being readily obtained via a one-step process. At present, C<sub>2</sub>H<sub>6</sub>-selective adsorbents are far less reported than  $C_2H_4$ -selective adsorbents as installing  $C_2H_4$ -binding sites (e.g., open metal sites (OMSs)) in adsorbents is far more readily achieved than for C<sub>2</sub>H<sub>6</sub>-binding sites. Additionally, the influence of water vapor requires further study in this field as humidity is ubiquitous in real world applications and often acts as a competitor for binding sites.<sup>17,18</sup> Hence, an ideal adsorbent for  $C_2H_6/C_2H_4$  separation should preferentially adsorb C2H6 and possess poor water adsorptive ability to minimize the effect of humidity on separation capacity.

Metal-organic frameworks (MOFs) with high porosity, ordered structures, and tunable pore size have emerged as promising candidates to address the challenge of gas separation.  $^{19-24}$  To design the MOF platforms for  $C_2H_6$ selective separation, OMSs are undesirable as they preferentially adsorb water molecules and unsaturated hydrocarbons such as  $C_2H_4$ , therefore dampening the adsorption capacity and selectivity for  $C_2H_6^{2.5}$  Introducing and modifying ligand functional groups can be a feasible approach to regulate MOF pore environments to endow specific binding affinities for  $C_2H_6$ .<sup>26–29</sup>  $C_2H_4$  molecules possess a larger quadrupole moment (1.50  $\times$  10<sup>-26</sup> esu cm<sup>2</sup>) than that of C<sub>2</sub>H<sub>6</sub> (0.65  $\times$  $10^{-26}$  esu cm<sup>2</sup>), and thus MOF materials with nonpolar pore environment can often selectively adsorb C<sub>2</sub>H<sub>6</sub> rather than  $C_2H_4$ .<sup>30-32</sup> The C-H... $\pi$  interactions between MOFs and gas molecules are often taken into account when designing this kind of MOF.<sup>33</sup> For example, in MUF-15, the  $C_2H_6$  molecule was capable of interacting with three adjacent phenyl rings of the isophthalic acid ligands via  $C-H\cdots\pi$  interactions.<sup>34</sup> In addition, ideal MOF adsorbents for  $C_2H_6/C_2H_4$  separation should possess both high adsorption capacity and selectivity, which play a vital role in ethylene purity and productivity. Furthermore, scalable room-temperature synthesis of MOF adsorbents is highly desirable toward real industry applications.<sup>35</sup> Currently, the discovery of efficient C<sub>2</sub>H<sub>6</sub>-selective MOF adsorbents fully realizing all the above requirements is yet to be achieved.

With the above considerations in mind, we reasoned that metal-organic building blocks without OMSs (e.g., tetrahedral  $MN_4$  building blocks,  $M = Cu^+$ ,  $Zn^{2+}$ , and  $Co^{2+}$ ) and nonpolar/inert pore surfaces (e.g., small conjugated ligands) are preferred for the construction of  $C_2H_6$ -selective adsorbents. Therefore, a green synthesis reaction of two aromatic imidazole derivative ligands with  $Cu^+$  ions afforded two new  $C_2H_6$ -selective MOF adsorbents, **NKMOF-8-Br** and -**Me**. Attributed to the aromatic imidazole derivative, these MOFs were enriched with nonpolar surfaces and pore channels with a strong affinity to  $C_2H_6$  molecules through  $C-H\cdots\pi$  interactions, thus enabling the selective adsorption of  $C_2H_6$  over  $C_2H_4$ . Moreover, **NKMOF-8-Br** and -**Me** displayed high  $C_2H_6$  adsorption capacity and selectivity, making them among the best adsorbents for ethylene purification.

#### RESULTS AND DISCUSSION

The reaction of the Br-substituted 4,5-dicyanoimidazole with CuI in acetonitrile solution at 100 °C for 1 day afforded colorless crystals of **NKMOF-8-Br**. White crystals of **NKMOF**-8-Me were obtained by a slow evaporation method. Single-crystal X-ray diffraction data revealed that these two isostructural MOFs crystallized in the *Pnna* space group (Table S1). In the structures, each Cu(I) atom coordinates with four N atoms from four ligands, two N atoms from the imidazole groups, and another two from the cyano group. Each ligand links four Cu(I) atoms to generate a 3-dimensional (3D) MOF with a **pts** topology. **NKMOF-8-Br** and -**Me** show narrow square channels along the *a* direction with pore apertures of 6.15 Å × 7.11 and 6.21 Å × 6.96 Å, respectively (Figure 1a). Notably, **NKMOF-8-Br** and -**Me** can be



Figure 1. (a) Synthetic routes and structures of NKMOF-8-Br and -Me. (b) Demonstration of the large-scale synthesis of NKMOF-8-Br (10 g) and -Me (12 g). (c) PXRD patterns of NKMOF-8-Br (left) and -Me (right) after various treatments and large-scale synthesis.

conveniently obtained on a large scale with a high yield (>90%) via a convenient, energy-saving approach: stirring ligands, CuI, and triethylamine (TEA) in acetonitrile at ambient conditions for as short as a few minutes (Figure 1b). Then the white product was obtained by filtration, washed with acetonitrile three times, and dried in an oven at 80 °C. The high purity of the gram-scale NKMOFs was verified by powder X-ray diffraction (PXRD) (Figure 1c) and scanning electron microscope (SEM) measurements (Figure S1). Notably, the acetonitrile solution can be readily recycled via filtration and then reused in the following reaction cycles without further purification, as verified by PXRD (Figure S2). Given the mild reaction conditions and facile scale-up, the fabrication of NKMOF-8-Br and -Me can be considered a Green synthesis, which is desirable for enabling MOFs for industrial application.<sup>36</sup> PXRD results (Figure 1c) and Brunner-Emmet-Teller (BET) tests (Figure S3) reveal that NKMOF-8-Br and -Me maintain high stability and crystallinity after various harsh treatments. NKMOF-8-Br exhibited structural stability even in boiling water, base solution (pH = 13), or 5 M HCl aqueous solutions for over 2 weeks at room

temperature. Thermogravimetric analysis showed that NKMOF-8-Br and -Me have no weight loss before 400 °C under a N<sub>2</sub> atmosphere (Figure S4). NKMOF-8-Br and -Me maintain their structural integrity when heated for an hour at 300 and 270 °C, respectively. The ultrahigh chemical and thermal stability of NKMOF-8-Br and -Me surpass most of the reported  $C_2H_6$ -selective MOF adsorbents (Table S2). The ultramicroporous structure, green synthesis method, and ultrahigh stability make NKMOF-8-Br and -Me ideal platforms for gas separation applications.

The activated MOF adsorbents were prepared directly via heating at 100 °C under a dynamic vacuum without solvent exchange treatment (Figure S5). Single-component equilibrium adsorption behaviors of the activated MOFs were then investigated in detail. Argon gas sorption isotherms at 87 K showed type I sorption curves for both MOFs, indicating their microporous structures. The BET and Langmuir surface areas were 352 and 515  $m^2/g$  and 655 and 907  $m^2/g$  for NKMOF-8-Br, and -Me, respectively. Pore volumes, calculated by the PLATON program,<sup>37</sup> were 0.21 and 0.30 cm<sup>3</sup>/g for NKMOF-8-Br and -Me, respectively. According to the literature,<sup>38</sup> gas molecules can reorder in the pores of MOFs with a larger pore volume, hence leading to the increased argon uptake. Overall, the larger pore volume and lower density (1.803 and 1.369 g/ cm<sup>3</sup> for NKMOF-8-Br, and -Me, respectively) make the surface area of NKMOF-8-Me higher than that of NKMOF-8-Br. A similar case (ZIF-8-Br and ZIF-8-Me) has been observed in a previous study.<sup>39</sup> Pore size distributions obtained by applying nonlocal density functional theory (NLDFT) for the Ar isotherms showed narrow pores of 6.6 and 5.9 Å, for NKMOF-8-Br and NKMOF-8-Me, respectively (Figure 2a and 2b). Subsequently, adsorption of  $C_2H_6$  and  $C_2H_4$  was measured at 273 and 298 K. As shown in Figure 2c and 2d, **NKMOF-8-Br** and **-Me** adsorb more  $C_2H_6$  than  $C_2H_4$  in the full pressure region. NKMOF-8-Br and -Me adsorb 82.27  $cm^3/g$  (3.67 mmol/g) and 104.82  $cm^3/g$  (4.67 mmol/g) of C<sub>2</sub>H<sub>4</sub>, respectively, at 298 K and 1 bar, while the C<sub>2</sub>H<sub>6</sub> adsorption of NKMOF-8-Br and -Me at 298 K and 1 bar reaches 95.01 cm<sup>3</sup>/g (4.22 mmol/g) and 108.12 cm<sup>3</sup>/g (4.82 mmol/g), respectively. Notably, the  $C_2H_6$  uptake for NKMOF-8-Me is higher than most reported C2H6-selective MOFs (Figure 2f). Additionally, we conducted kinetic sorption measurements of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> for NKMOF-8-Br and -Me (Figure S6). Upon increasing pressure from 0 to 1 bar, NKMOF-8-Br reached saturation after 83 s (105.6 mg/g) and 94 s (88.9 mg/g) for  $C_2H_6$  and  $C_2H_4$ , respectively. Similarly, for NKMOF-8-Me, the time to reach saturation for  $C_2H_6$  and C<sub>2</sub>H<sub>4</sub> (139.5 mg/g and 113.6 mg/g) was 85 and 112 s, respectively. These results indicated that both NKMOF-8-Br and -Me exhibited faster kinetic adsorption for C<sub>2</sub>H<sub>6</sub> and slower kinetic adsorption for C<sub>2</sub>H<sub>4</sub>. Desorption kinetic profiles confirmed that the adsorption of both gases is reversible on a very short time scale under vacuum.

Isosteric enthalpies of adsorption ( $Q_{st}$ ) for the NKMOF-8 MOFs were then calculated by the virial equation based on the isotherms collected at 273, 298, and 308 K (Figures S7 and S8). The fitted parameters are provided in Table S3 and Table S4. As shown in Figure 2e, the initial  $Q_{st}$  values of  $C_2H_6$  for NKMOF-8-Br and -Me are 40.8 and 38.4 kJ/mol, respectively, and are higher than those of  $C_2H_4$  (33.6 and 37.6 kJ/mol, respectively). This demonstrates that NKMOF-8-Br and -Me have a stronger thermodynamic affinity toward  $C_2H_6$  than  $C_2H_4$ . The increasing trend in the  $Q_{st}$  for both gases in



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Figure 2. (a,b) Ar adsorption/desorption isotherms of NKMOF-8-Br and -Me at 87 K. Pore size distribution of NKMOF-8-Br and -Me. (c,d) The  $C_2H_6$  and  $C_2H_4$  adsorption isotherms of NKMOF-8-Br and -Me at 298 K. (e)  $Q_{st}$  curves for NKMOF-8-Br and -Me. (f) Comparison of IAST selectivities of the  $C_2H_6/C_2H_4$  (1:1, v/v) mixture and  $C_2H_6$  adsorption of NKMOF-8-Br and -Me with previously reported  $C_2H_6$ -selective MOFs at 298 K and 1 bar.

NKMOF-8-Br could possibly be due to the presence of favorable adsorbate-adsorbate interactions at higher loadings. This behavior is also observed in the literature (e.g., MUF-15,40 ZIF-7,41 and NUP-142). To verify the high binding affinity of NKMOF-8-Br and -Me, the active MOF crystals were exposed to  $C_2H_6$  or  $C_2H_4$  gas via a gas balloon at room temperature. Interestingly, both C2H6 and C2H4 molecules could be captured in the channels of NKMOF-8-Br or NKMOF-8-Me as verified by Fourier transform infrared spectroscopy (FTIR). The characteristic stretching vibration assigned at 2956 and 2846 cm<sup>-1</sup> and bending vibration at 1462  $cm^{-1}$  of  $C_2H_6$  were detected in  $C_2H_6$ @NKMOF-8-Br (i.e.,  $C_2H_6$  trapped in **NKMOF-8-Br**). Stretching vibrations at 2943 and 2843 cm<sup>-1</sup> and a bending vibration at 1460 cm<sup>-1</sup> of  $C_2H_4$ were also found in C<sub>2</sub>H<sub>4</sub>@NKMOF-8-Br (i.e., C<sub>2</sub>H<sub>4</sub> trapped in NKMOF-8-Br)<sup>43</sup> (Figure S9). Notably, gas@NKMOF-8-Br still possessed excellent crystallinity. Thus, the crystals of NKMOF-8-Br after adsorbing C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub> molecules were characterized by single-crystal X-ray diffraction analysis. The crystal structures of gas@NKMOF-8-Br (gas =  $C_2H_6$  or  $C_2H_4$ ) (Figure 3a and 3b) enabled direct visualization of the gas adsorption sites. In the crystal structures, the chemical occupancies for each  $C_2H_6$  or  $C_2H_4$  molecule were approximately 0.5, which correlates with the observation from gas adsorption isotherms at 298 K and 1 bar. As shown in Figure 3c, in the crystal structure of C<sub>2</sub>H<sub>6</sub>@NKMOF-8-Br, there were two binding sites between each C<sub>2</sub>H<sub>6</sub> molecule and the pore wall. Binding sites 1 and 2 were formed by C-H… $\pi$ interactions (a distance of 3.53 Å) between hydrogen atoms of



**Figure 3.** (a) Single crystal structure of  $C_2H_6@NKMOF-8$ -Br viewed along the *a* axis (left) and the 1-D channel (right). (b) Single crystal structure of  $C_2H_4@NKMOF-8$ -Br viewed along the *a* axis (left) and the 1-D channel (right). (c) Binding sites of  $C_2H_6$  (left) and  $C_2H_4$ (right) determined by the crystal structure of  $C_2H_6@NKMOF-8$ -Br and  $C_2H_4@NKMOF-8$ -Br. (d) Binding sites of  $C_2H_6$  (left) and  $C_2H_4$ (right) in NKMOF-8-Me determined by GCMC simulations.

 $C_2H_6$  and C=N double bonds from imidazole groups. On the contrary, there were also two adsorption sites between each  $C_2H_4$  molecule and pore wall. The C-H... $\pi$  interactions (a distance of 3.90 Å) existed between hydrogen atoms of  $C_2H_4$ and  $C \equiv N$  triple bonds from the cyano groups. The binding sites in the crystal structures of gas@NKMOF-8-Br (gas = C<sub>2</sub>H<sub>6</sub> or C<sub>2</sub>H<sub>4</sub>) also agreed well with the results of grand canonical Monte Carlo (GCMC) simulations (Figure S10). Moreover, gas adsorption sites in NKMOF-8-Me were verified by GCMC simulations (Figure S11). Similarly, two binding sites (sites 1' and 2') were formed between the hydrogen atoms of  $C_2H_6$  and C=N double bonds from imidazole groups with a distance of 3.66 Å. Two binding sites (sites 1' and 2') between hydrogen atoms of  $C_2H_4$  and  $C \equiv N$  triple bonds from cyano groups were formed with a distance of 3.94 Å (Figure 3d). For NKMOF-8-Br and -Me, the shorter C- $H \cdots \pi$  interaction indicated a stronger affinity between C<sub>2</sub>H<sub>6</sub> and the MOFs than that with C2H4. Furthermore, static adsorption energies of these binding sites were also revealed by GCMC simulations (Table S5) that showed the same trend as the calculated  $Q_{\rm st}$  results.

In real-world scenarios, water vapor present in gas mixtures is an inevitability.<sup>44</sup> Currently, most of the reported  $C_2H_6$ selective MOFs possess poor water stability and cannot work under humid conditions (Table S2). In the NKMOF-8 platform, each Cu(I) metal center is tetra-coordinated, and no OMS exists to competitively coordinate water molecules. As tested by PXRD, NKMOF-8-Br and -Me maintain their structural integrity for at least 20 days (Figure S12) under 90% RH (relative humidity). Adsorption isotherms of water vapor were carried out at 298 K, showing that only a small amount of water vapor (15.6 cm<sup>3</sup>/g and 17.8 cm<sup>3</sup>/g for NKMOF-8-Br and -Me, respectively, at 90% RH) could be absorbed within NKMOF-8-Br and -Me (Figure 4a). In addition, we found that



**Figure 4.** (a) Water sorption isotherms for **NKMOF-8-Br** and -**Me** at 298 K. (b) FTIR spectra of **MIL-142A** exposed to the  $C_2H_6/C_2H_4$  mixture under 90% RH (shaded area corresponding to the infrared absorption peak of water). (c,d) FTIR spectra of **NKMOF-8-Br** and -**Me** exposed to  $C_2H_4$ ,  $C_2H_6$ , and a  $C_2H_4/C_2H_6$  (1:1, v/v) mixture in 90% RH (shaded and boxed areas corresponding to the infrared absorption peaks of  $C_2H_4$  and  $C_2H_6$ ).

NKMOF-8-Br and -Me can maintain their crystallinity after the water vapor sorption experiment (Figure S13). We also studied the dynamic sorption of water vapor at 298 K for NKMOF-8-Br and -Me (Figure S14). When the RH rose to 90%, the mass change only increased 0.92% and 0.70% for NKMOF-8-Br and -Me, respectively, further validating their low water vapor uptakes. These low water uptakes could be attributed to the introduction of hydrophobic groups, i.e., bromine and methyl, into the pores.<sup>45,46</sup> The combined effect of hydrophobic pores and a lack of OMS sites allow for **NKMOF-8-Br** and **-Me** to act as  $C_2H_6$ -selective materials that operate under high humid conditions. To verify this prediction, FTIR was applied to track the signal of water molecules under high humid conditions. The tested MOFs were separately exposed to  $C_2H_6$ ,  $C_2H_4$ , or  $C_2H_6/C_2H_4$  (1:1, v/v) mixture under 90% RH, respectively. The characteristic peak (3548- $3300 \text{ cm}^{-1}$ ) assigned to water molecules was absent, while the characteristic peaks  $(2956-2843 \text{ cm}^{-1} \text{ and } 1462-1460 \text{ cm}^{-1})$ assigned to C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub> appeared, indicative of waterrepellent effect (Figure 4c and 4d). By contrast, the reported C<sub>2</sub>H<sub>6</sub>-selective MOFs, MIL-142A,<sup>47</sup> yielded an opposite result to the NKMOF-8 platforms. An obvious infrared peak of water molecules was present in MIL-142A after exposure to humid conditions (Figure 4b). These results demonstrate that NKMOF-8-Br and -Me could potentially operate with excellent  $C_2H_6/C_2H_4$  separation capacity even under high humid conditions, making them more applicable to realistic industrial environments.

Attributed to the nonpolar pore environments and appropriate pore sizes, **NKMOF-8-Br** and **-Me** exhibited differences in adsorption between  $C_2H_6$  and  $C_2H_4$ . The ideal adsorbed solution theory (IAST) was used to calculate their  $C_2H_6/C_2H_4$  gas mixture selectivities. The fitted parameters are provided in Table S6. The initial adsorption selectivities of the

 $C_{2}H_{6}/C_{2}H_{4}$  (1:1, v/v) mixture at 298 K were 2.7 and 1.9 for NKMOF-8-Br and -Me, respectively (Figure S15). Notably, NKMOF-8-Br possessed superior comprehensive performance for  $C_2H_6/C_2H_4$  separation. The selectivity of the  $C_2H_6/C_2H_4$ (1:1, v/v) mixture at 298 K for NKMOF-8-Br outperformed most  $C_2H_6$ -selective MOFs under the same conditions (Figure 2f) while only being lower than  $Fe_2(O_2)(dobdc)^{48}$  (4.4) and Cu(Qc)<sub>2</sub> (3.4).<sup>49</sup> However, NKMOF-8-Br possessed a higher absorption capacity for  $C_2H_6$  (4.22 mmol/g) than  $Fe_2(O_2)$ -(dobdc) (3.40 mmol/g) and  $Cu(Qc)_2$  (1.85 mmol/g) at 298 K and 1 bar. To further confirm the separation performance, breakthrough experiments of NKMOF-8-Br and -Me for a  $C_2H_6/C_2H_4$  (1:1, v/v) mixture with He as the carrier gas (70%, vol %) were purged into a packed column with a total inlet flow rate of 3.0 mL/min at 298 K. It was found that  $C_2H_6/C_2H_4$  separation was well achieved by the NKMOF-8 MOFs (Figure 5a). When a  $C_2H_6/C_2H_4$  mixture was passed



**Figure 5.** (a) Experimental breakthrough curves of the  $C_2H_6/C_2H_4$  (1:1, v/v) mixture with He as the carrier gas (70%, vol %) for NKMOF-8-Br and -Me at 298 K and 1 bar. The total flow rate was 3 mL/min. (b) Experimental breakthrough curves of a  $C_2H_6/C_2H_4$  (1:9, v/v) mixture with He as the carrier gas (70%, vol %) for NKMOF-8-Br and -Me at 298 K and 1 bar. The total flow rate was 3 mL/min. (c,d) Five cycles of experimental breakthrough curves of the  $C_2H_6/C_2H_4$  (1:1, v/v) mixture with He as the carrier gas (70%, vol %) for NKMOF-8-Br and -Me at 298 K and 1 bar. The total flow rate was 3 mL/min.

over the packed column of NKMOF-8-Br, as predicted, C<sub>2</sub>H<sub>4</sub> was the first to elute through the packed column, followed by C<sub>2</sub>H<sub>6</sub> 112 min later. Similarly, the breakthrough time difference between C2H6 and C2H4 was 44 min for **NKMOF-8-Me**. Notably,  $C_2H_4$  of high purity >99.99% was produced from the above separation process. We also have conducted the  $C_2H_6/C_2H_4$  (1:1, v/v) breakthrough measurement without He (Figure S16). As predicted, both NKMOF-8-Br and -Me can efficiently separate  $C_2H_6/C_2H_4$ . The results showed the  $C_2H_4$  first passed the packed column and was detected from the outlet gas within a high purity >99.99%, and then after 68 and 22 min, C2H6 eluted through the packed column for NKMOF-8-Br and -Me, respectively. Overall, the separation result and trend for the  $C_2H_6/C_2H_4$  (1:1, v/v) mixture without He are consistent with those for the  $C_2H_6/$  $C_2H_4$  (1:1, v/v) mixture with He. To further evaluate the performance of NKMOFs, we also conducted the break-

through experiments of NKMOF-8-Br and -Me for a  $C_2H_6/$  $C_{2}H_{4}$  (1:9, v/v) mixture with He as the carrier gas (70%, vol %) (total flow rate 3.0 mL/min, 298 K). For NKMOF-8-Br and -Me, C2H4 first passed the packed column and was detected in the outlet gas with a high purity of >99.99%, and then after 85 and 60 min, respectively, C<sub>2</sub>H<sub>6</sub> eluted through the packed column (Figure 5b). NKMOF-8-Br and -Me exhibited excellent regeneration and reusability. NKMOF-8-Br and -Me could be recycled for at least five cycles in a dynamic  $C_2H_6/C_2H_4$  column breakthrough test without any deterioration in separation performance (Figure 5c, 5d, and S17). For comparison, control breakthrough experiments of  $Cu(Qc)_{2}^{49}$ PCN-250,<sup>50</sup> and MIL-142A<sup>47</sup> were also examined using the same device under the same testing conditions  $(C_2H_6/C_2H_4)$ (1:1, v/v) mixture with He as the carrier gas (70%, vol %)). The breakthrough time difference between  $C_2H_6$  and  $C_2H_4$  for Cu(Qc)<sub>2</sub>, PCN-250, and MIL-142A was 68 min, 52 min, and 12 min (Figures S18-S20), respectively, shorter than that of NKMOF-8-Br. Moreover, MCIF-1<sup>51</sup> constructed by 4,5dicyanoimidazole was also examined for comparison. MCIF-1 possessed a similar structure as NKMOF-8 but different connectivity (a face-to-face comparison in Figure S21). The breakthrough results showed no separation effect for MCIF-1 under the same testing conditions (Figure S22).

## CONCLUSION

In conclusion, we rationally designed and synthesized two new highly robust ethane-selective MOFs, NKMOF-8-Br and -Me, which can be conveniently fabricated on a large scale at room temperature within minutes. These two isostructural MOFs possess a regular ultramicroporous 3D pts network and exhibited remarkably high stability against harsh treatments such as boiling water, acid/base, or heating at 300 °C. The nonpolar pore environments and appropriate pore apertures enabled the preferential adsorption of  $C_2H_6$  over  $C_2H_4$ . Thus, NKMOF-8-Br and -Me possessed both high C2H6/C2H4 selectivity and  $C_2H_6$  uptake that surpass most reported C<sub>2</sub>H<sub>6</sub>-selective MOFs. Breakthrough experiments verified the C<sub>2</sub>H<sub>6</sub>/C<sub>2</sub>H<sub>4</sub> separation performance of NKMOF-8-Br and -Me, with C<sub>2</sub>H<sub>4</sub> of high purity >99.99% being produced, and these two MOFs possessed excellent reusability. NKMOF-8-Br and -Me were able to selectively capture C2 hydrocarbon gases even under high humidity conditions due to the presence of hydrophobic pores. Moreover, the gas adsorption sites can be observed directly in a visual way through single-crystal structures of gas@NKMOF-8-Br and are further verified by simulation results. Therefore, this work provides important guidance to fabricate ideal C2H6-selective adsorbents for  $C_2H_6/C_2H_4$  separation in real industrial scenarios.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c02108.

Experimental procedures, simulation details, NMR data, PXRD, gas sorption data, extra figures, and tables (PDF)

 $C_2H_4$ @NKMOF-8-Br (CIF)  $C_2H_6$ @NKMOF-8-Br (CIF) NKMOF-8-Br (CIF) NKMOF-8-Me (CIF)

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#### Notes

The authors declare no competing financial interest.

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#### REFERENCES

(1) Gong, S.; Shao, C.; Zhu, L. Energy efficiency enhancement of energy and materials for ethylene production based on two-stage coordinated optimization scheme. *Energy* **2021**, *217*, 119401.

(2) Khan, N. A.; Khan, M. I. R.; Ferrante, A.; Poor, P. Editorial: ethylene: a key regulatory molecule in plants. *Front. Plant Sci.* **2017**, *8*, 1–4.

(3) Tucker, G.; Yin, X.; Zhang, A.; Wang, M.; Zhu, Q.; Liu, X.; Xie, X.; Chen, K.; Grierson, D. Ethylene. *Food Qual. Saf.* **2017**, *1*, 253–267.

(4) Ren, T.; Patel, M.; Blok, K. Olefins from Conventional and heavy feedstocks: energy use in steam cracking and alternative processes. *Energy* **2006**, *31*, 425–451.

(5) Sadrameli, S. M. Thermal/catalytic cracking of hydrocarbons for the production of olefins: a state-of-the-art review I: thermal cracking review. *Fuel* **2015**, *140*, 102–115.

(6) Sadrameli, S. M. Thermal/catalytic cracking of liquid hydrocarbons for the production of olefins: a state-of-the-art review II: catalytic cracking review. *Fuel* **2016**, *173*, 285–297.

(7) Safarik, D. J.; Eldridge, R. B. Olefin/paraffin separations by reactive absorption: a review. *Ind. Eng. Chem. Res.* **1998**, 37, 2571–2581.

(8) Sholl, D. S.; Lively, R. P. How innovation modes have evolved. *Nature* **2016**, 532, 435–437.

(9) Chu, S.; Cui, Y.; Liu, N. The path towards sustainable energy. *Nat. Mater.* **2017**, *16*, 16–22.

(10) Sholl, D. S.; Lively, R. P. Seven chemical separations to change the world. *Nature* **2016**, *532*, 435–437.

(11) Rungta, M.; Xu, L.; Koros, W. J. Carbon molecular sieve dense film membranes derived from matrimid for ethylene/ethane separation. *Carbon* **2012**, *50*, 1488–1502.

(12) Bereciartua, P. J.; Cantín, Á.; Corma, A.; Jordá, J. L.; Palomino, M.; Rey, F.; Valencia, S.; Corcoran, E. W.; Kortunov, P.; Ravikovitch, P. I.; et al. Control of zeolite framework flexibility and pore topology for separation of ethane and ethylene. *Science* **2017**, 358, 1068–1071.

(13) Bao, Z.; Wang, J.; Zhang, Z.; Xing, H.; Yang, Q.; Yang, Y.; Wu, H.; Krishna, R.; Zhou, W.; Chen, B.; et al. Molecular sieving of ethane from ethylene through the molecular cross-section size differentiation in gallate-based metal-organic frameworks. *Angew. Chem., Int. Ed.* **2018**, *57*, 16020–16025.

(14) Lin, R. B.; Li, L.; Zhou, H. L.; Wu, H.; He, C.; Li, S.; Krishna, R.; Li, J.; Zhou, W.; Chen, B. Molecular sieving of ethylene from ethane using a rigid metal–organic framework. *Nat. Mater.* **2018**, *17*, 1128–1133.

(15) Bloch, E. D.; Queen, W. L.; Krishna, R.; Zadrozny, J. M.; Brown, C. M.; Long, J. R. Hydrocarbon separations in a metal-organic framework with open iron(II) coordination sites. *Science* **2012**, *335*, 1606–1610.

(16) Mukherjee, S.; Sensharma, D.; Chen, K. J.; Zaworotko, M. J. Crystal engineering of porous coordination networks to enable separation of C2 hydrocarbons. *Chem. Commun.* **2020**, *56*, 10419–10441.

(17) Schoenecker, P. M.; Carson, C. G.; Jasuja, H.; Flemming, C. J. J.; Walton, K. S. Effect of water adsorption on retention of structure and surface area of metal-organic frameworks. *Ind. Eng. Chem. Res.* **2012**, *51*, 6513–6519.

(18) Decoste, J. B.; Peterson, G. W.; Schindler, B. J.; Killops, K. L.; Browe, M. A.; Mahle, J. J. The effect of water adsorption on the structure of the carboxylate containing metal-organic frameworks Cu-BTC, Mg-MOF-74, and UiO-66. *J. Mater. Chem. A* **2013**, *1*, 11922–11932.

(19) Zhou, H. C.; Kitagawa, S. Metal-organic frameworks (MOFs). *Chem. Soc. Rev.* **2014**, *43*, 5415–5418.

(20) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. The chemistry and applications of metal-organic frameworks. *Science* **2013**, *341*, 1230444–1230456.

(21) Maurin, G.; Serre, C.; Cooper, A.; Férey, G. The new age of MOFs and of their porous-related solids. *Chem. Soc. Rev.* 2017, 46, 3104–3107.

(22) Li, H.; Wang, K.; Sun, Y.; Lollar, C. T.; Li, J.; Zhou, H. C. Recent advances in gas storage and separation using metal-organic frameworks. *Mater. Today* **2018**, *21*, 108–121.

(23) Li, H.; Li, L.; Lin, R.-B.; Zhou, W.; Zhang, Z.; Xiang, S.; Chen, B. Porous metal-organic frameworks for gas storage and separation: status and challenges. *EnergyChem.* **2019**, *1*, 1–39.

(24) Ryu, U.; Jee, S.; Rao, P. C.; Shin, J.; Ko, C.; Yoon, M.; Park, K. S.; Choi, K. M. Recent advances in process engineering and upcoming applications of metal-organic frameworks. *Coord. Chem. Rev.* **2021**, 426, 213544–213587.

(25) You, W.; Liu, Y.; Howe, J. D.; Sholl, D. S. Competitive binding of ethylene, water, and carbon monoxide in metal-organic framework materials with open Cu sites. *J. Phys. Chem. C* **2018**, *122*, 8960–8966.

(26) Nguyen, J. G.; Cohen, S. M. Moisture-resistant and superhydrophobic metal-organic frameworks obtained via postsynthetic modification. J. Am. Chem. Soc. 2010, 132, 4560-4561.

(27) Logan, M. W.; Adamson, J. D.; Le, D.; Uribe-Romo, F. J. Structural stability of N-alkyl-functionalized titanium metal-organic frameworks in aqueous and humid environments. *ACS Appl. Mater. Interfaces* **2017**, *9*, 44529–44533.

(28) Nandi, S.; Haldar, S.; Chakraborty, D.; Vaidhyanathan, R. Strategically designed azolyl-carboxylate MOFs for potential humid CO<sub>2</sub> capture. *J. Mater. Chem. A* **2017**, *5*, 535–543.

(29) Cao, H.; Lu, Z.; Hyeon-Deuk, K.; Chang, I-Y.; Wang, Y.; Xin, Z.; Duan, J.; Jin, W. Enhanced breakthrough efficiency by a chemically stable porous coordination polymer with optimized nanochannel. *ACS Appl. Mater. Interfaces* **2018**, *10*, 39025–39031.

(30) Lin, R.; Xiang, S.; Zhou, W.; Chen, B. Microporous metalorganic framework materials for gas separation. *Chem.* **2020**, *6* (2), 337–363.

(31) Lan, T.; Li, L.; Chen, Y.; Wang, X.; Yang, J.; Li, J. Opportunities and critical factors of porous metal-organic frameworks for industrial light olefins separation. *Mater. Chem. Front.* **2020**, *4*, 1954–1984.

(32) Wang, T.; Lin, E.; Peng, Y. L.; Chen, Y.; Cheng, P.; Zhang, Z. Rational design and synthesis of ultramicroporous metal-organic frameworks for gas separation. *Coord. Chem. Rev.* **2020**, *423*, 213485–213518.

(33) Lin, R. B.; Wu, H.; Li, L.; Tang, X. L.; Li, Z.; Gao, J.; Cui, H.; Zhou, W.; Chen, B. Boosting ethane/ethylene separation within isoreticular ultramicroporous metal-organic frameworks. *J. Am. Chem. Soc.* **2018**, *140*, 12940–12946.

(34) Qazvini, O. T.; Babarao, R.; Shi, Z. L.; Zhang, Y. B.; Telfer, S. G. A Robust ethane-trapping metal-organic framework with a high capacity for ethylene purification. *J. Am. Chem. Soc.* **2019**, *141*, 5014–5020.

(35) Reinsch, H. Green" synthesis of metal-organic frameworks. *Eur. J. Inorg. Chem.* **2016**, *27*, 4290–4299.

(36) Kumar, S.; Jain, S.; Nehra, M.; Dilbaghi, N.; Marrazza, G.; Kim, K. H. Green synthesis of metal-organic frameworks: a state-of-the-art review of potential environmental and medical applications. *Coord. Chem. Rev.* **2020**, 420, 213407–213434.

(37) Spek, A. L. Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. 2003, 36, 7–13.

(38) Ania, C. O.; Garcia-Perez, E.; Haro, M.; Gutierrez-Sevillano, J. J.; Valdes-Solis, T.; Parra, J. B.; Calero, S. Understanding gas-induced structural deformation of ZIF-8. *J. Phys. Chem. Lett.* **2012**, *3*, 1159–1164.

(39) Chaplais, G.; Fraux, G.; Paillaud, J.; Marichal, C.; Nouali, H.; Fuchs, A.; Coudert, F.; Patarin, J. Impacts of the imidazolate linker substitution (CH<sub>3</sub>, Cl, or Br) on the structural and adsorptive properties of ZIF-8. *J. Phys. Chem. C* **2018**, *122*, 26945–26955.

(40) Qazvini, O. T.; Babarao, R.; Shi, Z.-L.; Zhang, Y.-B.; Telfer, S. G. A Robust Ethane-trapping metal-organic framework with a high capacity for ethylene purification. *J. Am. Chem. Soc.* **2019**, *141*, 5014–5020.

(41) Liao, P. Q.; Zhang, W. X.; Zhang, J. P.; Chen, X. M. Efficient purification of ethene by an ethane-trapping metal-organic framework. *Nat. Commun.* **2015**, *6*, 8697–8705.

(42) Zhu, B.; Cao, J.; Mukherjee, S.; Pham, T.; Zhang, T.; Wang, T.; Jiang, X.; Forrest, K. A.; Zaworotko, M. J.; Chen, K. Pore engineering for one-step ethylene purification from a three-component hydrocarbon mixture. *J. Am. Chem. Soc.* **2021**, *143*, 1485–1492.

(43) Hallett, L. T. Optical society of america. *Anal. Chem.* **1948**, *20*, 1125–1129.

(44) You, W.; Liu, Y.; Howe, J. D.; Tang, D.; Sholl, D. S. Tuning binding tendencies of small molecules in metal-organic frameworks with open metal sites by metal substitution and linker functionalization. *J. Phys. Chem. C* **2018**, *122*, 27486–27494.

(45) Yeşilbaş, M.; Boily, J. F. Particle Size Controls on Water Adsorption and Condensation Regimes at Mineral Surfaces. *Sci. Rep.* **2016**, *6*, 1–10.

(46) Canivet, J.; Fateeva, A.; Guo, Y.; Coasne, B.; Farrusseng, D. Water adsorption in MOFs: fundamentals and applications. *Chem. Soc. Rev.* **2014**, *43*, 5594–5617.

(47) Chen, Y.; Wu, H.; Lv, D.; Shi, R.; Chen, Y.; Xia, Q.; Li, Z. Highly Adsorptive Separation of Ethane/Ethylene by An Ethane Selective MOF MIL-142A. *Ind. Eng. Chem. Res.* **2018**, *57*, 4063–4069. (48) Li, L.; Lin, R. B.; Krishna, R.; Li, H.; Xiang, S.; Wu, H.; Li, J.;

Zhou, W.; Chen, B. ethane/ethylene separation in a metal-organic framework with iron-peroxo sites. *Science* **2018**, *362*, 443–446.

(49) Lin, R. B.; Wu, H.; Li, L.; Tang, X. L.; Li, Z.; Gao, J.; Cui, H.; Zhou, W.; Chen, B. Boosting ethane/ethylene separation within isoreticular ultramicroporous metal-organic frameworks. *J. Am. Chem. Soc.* **2018**, *140*, 12940–12946.

(50) Chen, Y.; Qiao, Z.; Wu, H.; Lv, D.; Shi, R.; Xia, Q.; Zhou, J.; Li, Z. An ethane-trapping MOF PCN-250 for highly selective adsorption of ethane over ethylene. *Chem. Eng. Sci.* **2018**, *175*, 110–117.

(51) Zhao, N.; Li, P.; Mu, X.; Liu, C.; Sun, F.; Zhu, G. Facile synthesis of an ultra-stable metal-organic framework with excellent acid and base resistance. *Faraday Discuss.* **2017**, *201*, 63–70.