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Exploiting the Gate Opening Effect in a Flexible MOF for Selective Adsorption of Propyne from C1/C2/C3 Hydrocarbons

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Libo Li,^a Rajamani Krishna,^b Yong Wang,^a Jiangfeng Yang,^{a,*} Xiaoqing Wang,^a and Jinping Li^{a,*}

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The separation of propyne from light hydrocarbon mixtures is of technological importance but poses considerable technical challenges. This article reports the potential of a flexible metal-organic framework [Cu(dhbc)₂(4,4'-bipy)], with gate-opening characteristics, that exhibits adsorption selectivity in favor of propyne in a C1/C2/C3 mixture of hydrocarbons. The separation potential of the flexible MOF is established using a judicious combination of measurements of unary isotherms, IAST calculations of mixture adsorption equilibrium, transient breakthrough simulations, along with transient breakthrough experiments. Our multi-tier investigation strategy confirms that propyne can be selectively adsorbed from C1/C2/C3 hydrocarbons in fixed bed adsorbers that are commonly employed in the process industries.

Light hydrocarbons such as C₂H₄, and C₃H₆ are important feedstocks in the petrochemical industries for production of polyethylene and polypropylene. The separation and isolation of such feedstocks from hydrocarbon mixtures is traditionally carried out in distillation columns that are energy demanding. Adsorptive separation is an alternative method to cryogenic distillation and is more sustainable. At early age, some zeolites have been considered the adsorbent for light hydrocarbons separation: Miltenburg tested the separation of ethane/ethylene mixtures working with CuCl/NaX;^{1a} Rodrigues reported the use of zeolite 13X for separation of propane/propylene mixtures;^{1b} Al-Baghli suggest that Na-ETS-10 have great potential as adsorbents for ethylene/ethane separations.^{1c} However, these zeolites have an average kinetic diameter of 8-10 Å, which is larger than the molecular diameter of light hydrocarbons, so the

separation selectivity on zeolites would be based on equilibrium competitive adsorption.^{1d} In recent years, there has been considerable research on the synthesis of metal-organic frameworks (MOFs) that offer energy-efficient alternatives to distillation technology.² The potential of MOFs has been well established for a variety of separations: C₂H₂/C₂H₄,^{2d, 3} C₂H₄/C₂H₆,^{2d, 3a, 4} C₃H₆/C₃H₈,^{2d, 3a, 5a} CH₄/C₂H₂/C₂H₄/C₂H₆,^{3a, 5b, 5c} and CH₄/C₂H₂/C₂H₄/C₂H₆/C₃H₆/C₃H₈ mixtures.^{3a, 5d} The feedstock to polymerization reactors need to be free of impurities such as C₂H₂ (acetylene = ethyne) and C₃H₄ (methyl acetylene = propyne) that have a tendency to poison the catalysts. While there has been considerable published research on C₂H₂/C₂H₄ separations, there is no published work on selective adsorption of C₃H₄. In this work, we present the first example where separations of C₃H₄ from CH₄/C₂H₂/C₂H₄/C₂H₆/C₃H₆/C₃H₈ mixtures are achieved with a single flexible MOF [Cu(dhbc)₂(4,4'-bipy)] utilizing guest-induced structural changes and the resulting differences in gate-opening pressures.

Flexible MOFs as promising materials for gas separation have attracted a lot of attention, but such expectations have commonly been based solely on inspection of their pure-component adsorption isotherms. The efficacy of flexible MIL-53 for a variety of separations is established in a number of publications.⁶

The flexible MOF [Cu(dhbc)₂(4,4'-bipy)] exhibits unique gate-opening behavior at certain pressures of nitrogen, oxygen, or methane, corresponding to a subnetwork displacement in its structure; this was first reported by Kitagawa in 2003.⁷ As a consequence of such structural changes, [Cu(dhbc)₂(4,4'-bipy)] exhibits adsorption selectivity between two kinds of guest molecules that exploits the differences in the gate opening pressures. In recent work, carried out using an in-house-constructed separation apparatus, controlled and targeted CO₂ and CH₄ capture, respectively, from binary mixtures (CO₂/CH₄ or CH₄/N₂) has been realized with [Cu(dhbc)₂(4,4'-bipy)].⁸

^a College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, Shanxi, P. R. China. Email: jpli211@hotmail.com (Jinping Li), yangjiangfeng@tyut.edu.cn (Jiangfeng Yang)

^b Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands.

Electronic Supplementary Information (ESI) available: [Experimental details, Fitting of experimental data on pure component isotherms, GCMC simulation details, Breakthrough curves for equimolar 3-component C₂H₆/C₂H₄/C₂H₂ and CH₄-C₂H₆-C₃H₆ mixtures and equimolar 2-component C₂H₄/C₃H₆ mixtures, and a video animations of the transient traversal of gas phase concentrations along the length of the fixed bed adsorber].

In this article we investigate the potential of $[\text{Cu}(\text{dhbc})_2(4,4'\text{-bipy})]$ for light hydrocarbon separations. Unary isotherms for C1-C3 hydrocarbons adsorption were measured on $[\text{Cu}(\text{dhbc})_2(4,4'\text{-bipy})]$ at 273 and 298 K. Figure 1 presents a comparisons of experimental data for unary isotherms for CH_4 , C_2H_2 , C_2H_4 , and C_2H_6 , C_3H_4 , C_3H_6 , and C_3H_8 in $[\text{Cu}(\text{dhbc})_2(4,4'\text{-bipy})]$ at (a) 273 K, and (b) 298 K with multi-site Langmuir-Freundlich model fits; the fit parameters are provided in the Supplementary material accompanying this article. The fits are of good accuracy at both temperatures.

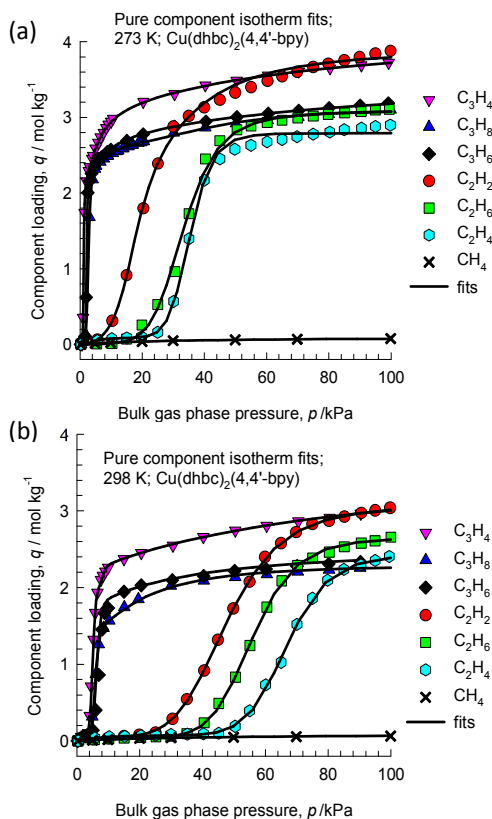


Fig. 1 Comparisons of experimental data for unary isotherms for CH_4 , C_2H_2 , C_2H_4 , and C_2H_6 , C_3H_4 , C_3H_6 , and C_3H_8 at (a) 273 K, and (b) 298 K in $[\text{Cu}(\text{dhbc})_2(4,4'\text{-bipy})]$ with multi-site Langmuir-Freundlich model fits.

The unary isotherm of each C2-C3 hydrocarbon displays gate opening characteristics (Fig. 1). The structural transformation in flexible MOFs was due to the guest-induced phenomenon, the stronger intermolecular interactions between guest molecular and flexible MOFs leads to a lower gate-opening pressure. So at lower temperature, thermal motion of gases would be lower, the gas molecules can get adsorbed on the flexible MOFs easier, therefore caused a lower gate-opening pressure.⁸⁻¹⁰ And as a common sense in flexible MOFs, the interaction energy between MOFs structures and guest molecule is dependence to the gate-opening phenomenon. The results show that the interaction energy is larger for C3 hydrocarbons vs C2 hydrocarbons molecules. Therefore, the

longer the chain of the guest hydrocarbon, the more likely the flexible MOF structures are affected by this interaction and the lower the pressure opening point, as shown in Figure 1.^{2a} And C_3H_4 has the lowest gate-opening pressure to induce the structural transitions of the flexible MOFs $[\text{Cu}(\text{dhbc})_2(4,4'\text{-bipy})]$, which indicated that the flexible framework can highly selective adsorb C_3H_4 at very low pressure. Interestingly, there is a discernible trend in the gate-opening pressures of guest molecules in $[\text{Cu}(\text{dhbc})_2(4,4'\text{-bipy})]$, as will be outlined below.

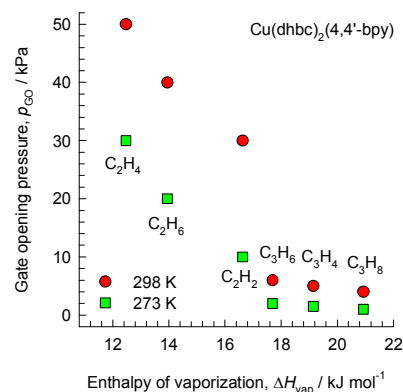


Fig. 2 The gate opening pressures of C_2H_2 , C_2H_4 , C_2H_6 , C_3H_4 , C_3H_6 , and C_3H_8 at 273 K, and 298 K in $[\text{Cu}(\text{dhbc})_2(4,4'\text{-bipy})]$ plotted as a function of latent heats of vaporization.

The gate-opening pressures of C2-C3 hydrocarbon on $[\text{Cu}(\text{dhbc})_2(4,4'\text{-bipy})]$ at 273 and 298 K are found to be inversely correlate very well with the latent heat of vaporization, whose values are respectively, 16.6, 12.5, 13.9, 20.9, 17.7, and 19.1 kJ/mol; see Figure 2. And the molar enthalpy of gate opening are correlates with the molar enthalpy of vaporization, see Figure S2. Thus, we speculate that a condensation phenomenon occurs during adsorption of light hydrocarbons in the flexible MOF, triggering the gate-opening process. A similar phenomenon was reported by Yaghi on rigid MOFs.¹¹ Yaghi et al. have explained the unusual shape of adsorption isotherms in IRMOF-1, though combination with GCMC simulations and experiment results. They explained that the attractive electrostatic interactions between gas molecules were responsible for the unusual shape of the adsorption isotherms, and the pore was filled with the guest molecules in the condensed phase.

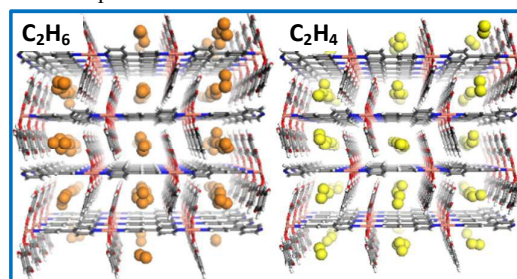


Fig. 3 A schematic from a GCMC simulation for C_2H_6 (brown), C_2H_4 (yellow) adsorption in the channels of $[\text{Cu}(\text{dhbc})_2(4,4'\text{-bipy})]$ at 1 bar and 273 K.

The simulation results were presented in Figure 3 as a snapshots of the locations and conformations of C_2H_6 and C_2H_4 adsorbed within the channels of the structure.¹⁴ It is noticed that, in the one-dimensional channel, C_2H_6 and C_2H_4 align along the center of the channels. These snapshots also validate the hypothesis that light hydrocarbons adsorb in $[Cu(dhbc)_2(4,4'-bipy)]$ following a condensation process. The reason may be attributed to the suitable pore sizes fixed the hydrocarbon molecule isolate in the one-dimensional channel. To further study the mechanism of gases diffusion through the one-dimensional pores of $[Cu(dhbc)_2(4,4'-bipy)]$, a newly models was designed for MD (Molecule Dynamic) simulations. And the results showed that light hydrocarbon molecules can easily diffusion through the one-dimensional channels, and no pore size limitation to diffusion were found (Fig.S4). A similar behavior was reported by Kitagawa et al, who showed that C_2H_2 adsorbed in the channels of $Cu_2(pzdc)_2(pyz)$ ($pzdc =$ pyrazine-2,3-dicarboxylate and $pyz =$ pyrazine) through the electrostatic attraction and electron delocalization effect between hydrogen atom of C_2H_2 and the free oxygen atom.¹⁵

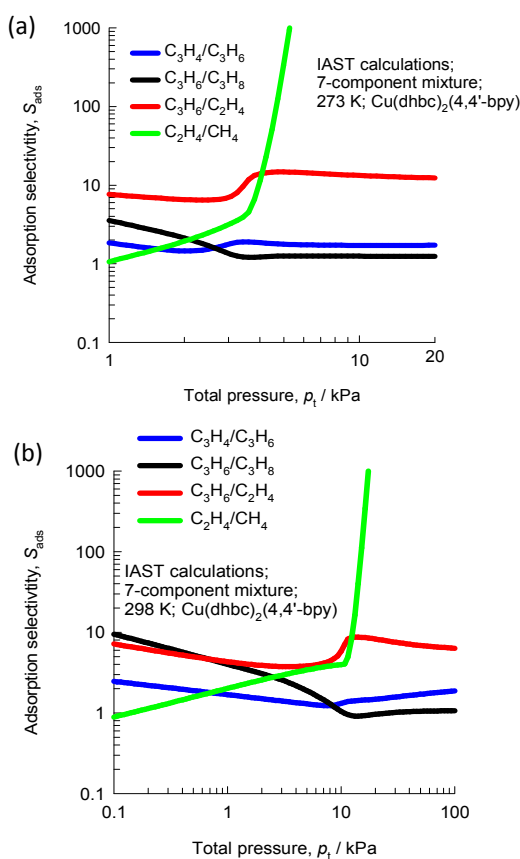


Fig. 4 IAST calculations for component loadings for adsorption of 7-component $CH_4/C_2H_2/C_2H_4/C_2H_6/C_3H_4/C_3H_6/C_3H_8$ gas mixtures in $[Cu(dhbc)_2(4,4'-bipy)]$ at (a) 273 K, and (b) 298 K.

The strength of C1-C3 hydrocarbons binding within $[Cu(dhbc)_2(4,4'-bipy)]$ was determined quantitatively through analysis of the gas adsorption data. The binding energy of

adsorbate that is reflected in the isosteric heat of adsorption, Q_{st} , was determined using the pure component isotherm fits using the Clausius-Clapeyron equation (Fig.S3). The results show that C_3H_4 has the highest binding energy in C1-C3 hydrocarbons, which implies that $[Cu(dhbc)_2(4,4'-bipy)]$ can selectively adsorb C_3H_4 from hydrocarbon mixtures.

Furthermore, the ideal adsorbed solution theory (IAST) was calculated to estimate the adsorption of equimolar 7-component $CH_4/C_2H_2/C_2H_4/C_2H_6/C_3H_4/C_3H_6/C_3H_8$ gas mixtures (Fig. 4), and adsorption selectivities of C_3H_4/C_3H_6 , C_3H_6/C_3H_8 , C_3H_6/C_2H_4 , and C_2H_4/CH_4 in $[Cu(dhbc)_2(4,4'-bipy)]$ (Fig. 5). The component loadings were bunched into three fractions: C3, C2 and C1 hydrocarbons with different carbon numbers. The longer the chain of the guest hydrocarbon, the stronger binding energy between MOF structures. And at both temperatures C_3H_4 has the highest component loading in $[Cu(dhbc)_2(4,4'-bipy)]$, which indicate that C_3H_4 can be selectively adsorbed from hydrocarbon mixtures. For adsorption of equimolar 7-component $CH_4/C_2H_2/C_2H_4/C_2H_6/C_3H_4/C_3H_6/C_3H_8$ gas mixtures, the calculated C_2H_4/CH_4 selectivities are 1000, and this value is much higher than the recently reported (300 for $Fe_2(dobdc)$).^{2d}

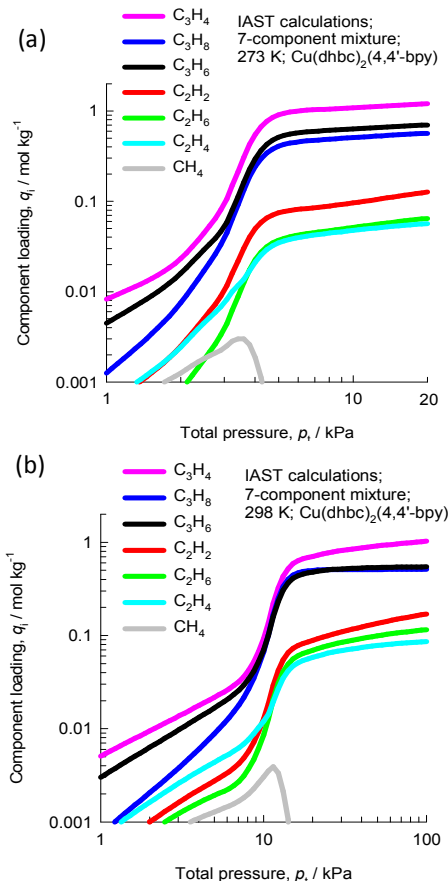


Fig. 5 IAST calculations for C_3H_4/C_3H_6 , C_3H_6/C_3H_8 , C_3H_6/C_2H_4 , and C_2H_4/CH_4 adsorption selectivities for 7-component $CH_4/C_2H_2/C_2H_4/C_2H_6/C_3H_4/C_3H_6/C_3H_8$ gas mixture adsorption in $[Cu(dhbc)_2(4,4'-bipy)]$ maintained at isothermal conditions at (a) 273 K, and (b) 298 K.

To confirm the selective adsorption of C_3H_4 over C_3H_6 and C_3H_8 under mixture conditions, several breakthrough experiments were performed on an in-house-constructed apparatus, which was reported in our previous work (Fig. S5).^{8, 16} The breakthrough experiments were performed to demonstrate the selective adsorption of C_3H_4 using $[Cu(dhbc)_2(4,4'-bipy)]$, in which an equimolar 3-component $C_3H_4/C_3H_6/C_3H_8$ mixtures was flowed over a packed bed with a total flow of 30 mL/min at 298 K. As shown in Figure 6a, with the high adsorption selectivity of $[Cu(dhbc)_2(4,4'-bipy)]$, C_3H_6 and C_3H_8 are breaks first, while C_3H_4 breaks through after some further period of time. And C_3H_4 can be effectively separated from the $C_3H_4/C_3H_6/C_3H_8$ mixtures as a nearly pure form with the gas phase concentrations is more than 99.9 % (detection limit ~ 0.1 %). And the breakthrough experiments results are in agreement with the expectations of the IAST calculations of mixture adsorption shown in Figure 4 and 5.

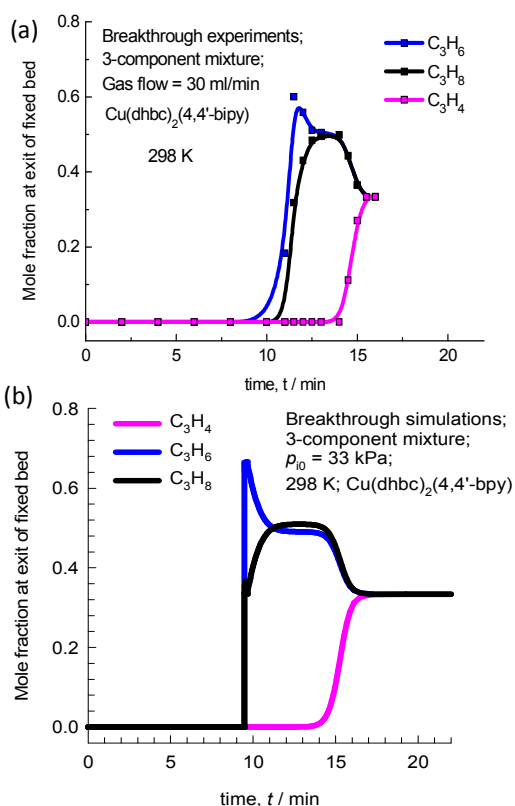


Fig. 6 Breakthrough experiments (a) and simulations (b) of $[Cu(dhbc)_2(4,4'-bipy)]$ for separation equimolar 3-component C_3H_4 - C_3H_6 - C_3H_8 mixture in a fixed bed of adsorbent at 298 K.

The experimental breakthroughs for $C_3H_4/C_3H_6/C_3H_8$ mixtures are in very good agreement with transient breakthrough simulations (Fig. 6b) carried out using the methodology described in earlier work.^{2f} In both experiments and simulations, we note that C_3H_4 is the last component to elute from the fixed bed confirming that this component can be selectively adsorbed from the C3 hydrocarbons.

Breakthrough experiments were also performed on equimolar 3-component $C_2H_6/C_2H_4/C_2H_2$ and CH_4 - C_2H_6 - C_3H_8 mixtures

and equimolar 2-component C_2H_4/C_3H_6 mixtures; see Figures S6, S7 and S8 of the Supplementary material accompanying this article. These breakthrough experiments confirm the adsorption hierarchy observed in Figure 4: $CH_4 < C_2H_4 < C_2H_6 < C_3H_6 < C_3H_8 < C_3H_4$. By combination with the IAST calculations and breakthrough experiments, we can conclude that flexible MOFs $[Cu(dhbc)_2(4,4'-bipy)]$ can selectively adsorb C_3H_4 from C1-C3 hydrocarbon mixtures with its unique gate-opening phenomenon.

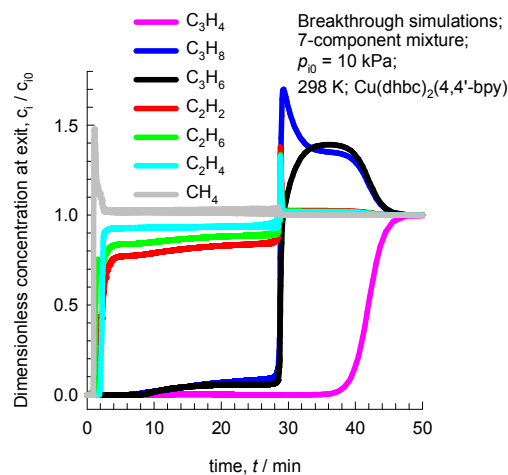


Fig. 7. Breakthrough simulation with an equimolar 7-component $CH_4/C_2H_2/C_2H_4/C_2H_6/C_3H_4/C_3H_6/C_3H_8$ mixture in to a fixed bed of adsorbent. The inlet partial pressures are 10 kPa for each hydrocarbon.

To further confirm this conclusion, we carried out transient breakthrough simulations with a 7-component $CH_4/C_2H_2/C_2H_4/C_2H_6/C_3H_4/C_3H_6/C_3H_8$ feed to a fixed bed adsorber operating at 298 K; see Figure 7. The sequence of breakthroughs is CH_4 , C_2H_6 , C_2H_4 , C_2H_2 , C_3H_8 , C_3H_6 , and C_3H_4 . This sequence indicates that C_3H_4 can also be selectively adsorbed from a C1/C2/C3 mixture. And C1-C2 hydrocarbons cannot get adsorbed on $[Cu(dhbc)_2(4,4'-bipy)]$ at that pressure, they were diffused through the fixed bed at the very beginning, which is because this pressure are lower than their gate-opening pressure. Particular noteworthy is the long time interval between the breakthroughs of C2 and C3 hydrocarbons, which showed that flexibility is being used to effect a more efficient separation. This is a direct consequence of the large differences in the gate-opening pressures of C3 hydrocarbons as compared to C2 hydrocarbons as witnessed in Figure 7. The separation potential of $[Cu(dhbc)_2(4,4'-bipy)]$ is best appreciated by video animations of the transient traversal of gas phase concentrations along the length of the fixed bed adsorber; this video has been uploaded as Supplementary Material to this publication.

Conclusions

In summary, the flexible MOF $[Cu(dhbc)_2(4,4'-bipy)]$ with unique gate-opening behavior has been studied for separation of C_3H_4 from C1-C3 hydrocarbon mixtures. The separation

potential of the flexible MOF is established by a combination of measurements of unary isotherms, IAST calculations of mixture adsorption equilibrium, transient breakthrough simulations, along with transient breakthrough experiments. The results exhibited that [Cu(dhbc)₂(4,4'-bipy)] is promising for selective adsorb C₃H₄ form C1-C3 hydrocarbon mixtures.

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