Simultaneous Trapping of C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}H\textsubscript{6} from a Ternary Mixture of C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} in a Robust Metal–Organic Framework for the Purification of C\textsubscript{2}H\textsubscript{4}

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Abstract: The removal of C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}H\textsubscript{6} from C\textsubscript{2}H\textsubscript{4} streams is of great significance for feedstock purification to produce polyethylene and other commodity chemicals but the simultaneous adsorption of C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}H\textsubscript{6} over C\textsubscript{2}H\textsubscript{4} from a ternary mixture has never been realized. Herein, a robust metal–organic framework, TJT-100, was designed and synthesized, which demonstrates remarkably selective adsorption of C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}H\textsubscript{6} over C\textsubscript{2}H\textsubscript{4}. Breakthrough experiments show that TJT-100 can be used as an adsorbent for high-performance purification of C\textsubscript{2}H\textsubscript{4} from a ternary mixture of C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} (0.5-99:0.5) to afford a C\textsubscript{2}H\textsubscript{4} purity greater than 99.997\%, beyond that required for ethylene polymerization. Computational studies reveal that the uncoordinated carboxylate oxygen atoms and coordinated water molecules pointing towards the pore can trap C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}H\textsubscript{6} through the formation of multiple C–H···O electrostatic interactions, while the corresponding C\textsubscript{2}H\textsubscript{4}–framework interaction is unfavorable.

Light hydrocarbons, such as ethane, ethylene, and acetylene, are the most widely used feedstock molecules in the petrochemical industry.\cite{1,2} In particular, ethylene, one of the most essential chemical feedstocks in the world, is widely utilized in the production of multiple commodity chemicals, including polyethylene. Within the petrochemical industry, ethylene is mainly obtained by steam cracking of naphtha and the dehydrogenation of ethane.\cite{3} During these processes, two major impurities are acetylene and ethane. Acetylene is a known poison for many common ethylene polymerization catalysts, reacting with catalytic metals to form acetylidies, which have been known to cause gas flow blockages and explosions.\cite{3} The presence of high levels of C\textsubscript{2}H\textsubscript{4} on the other hand, can result in longer reactor residence times and decreases the production output per unit time. In addition, non-reactive C\textsubscript{2}H\textsubscript{2} will often end up leaving the process after off-gassing from the finished polymer, which can be a source of health and safety concerns. The separation of a C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} mixture is perceived as one of the most challenging yet important industrial processes, owing to the similar molecular sizes and volatilities of C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{6}. At present, the most commonly used method for the industrial separation of C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} mixture is high-pressure cryogenic distillation, an extremely costly and energy-intensive process.\cite{4} Up to now, new approaches for effective C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} or C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{4} separation have focused on membrane separations, organic solvent sorbent based separations, and metal–organic framework (MOF) adsorbent based separations.

In the past decades, MOFs have emerged as a new type of advanced functional porous materials for the separation of C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} or C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} mixtures.\cite{5–13} Up to now, many MOFs have shown outstanding performance in the separation of C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4}.\cite{5} For C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{6}, it is well known that unsaturated C\textsubscript{2}H\textsubscript{4} can easily bind to the open metal sites, leading to highly selective uptake of C\textsubscript{2}H\textsubscript{4} over C\textsubscript{2}H\textsubscript{6}.\cite{6} However, in such a process, the inert C\textsubscript{2}H\textsubscript{6} is recovered first, with C\textsubscript{2}H\textsubscript{4} only being obtained through heating or by purging with an inert gas. As such, it is difficult to obtain the desired C\textsubscript{2}H\textsubscript{4} product with high purity if C\textsubscript{2}H\textsubscript{6} is utilized as the mobile phase. The examination of adsorbents with highly selective adsorption of C\textsubscript{2}H\textsubscript{2} from a C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} mixture could reduce the energy consumption of these separation processes affording high-purity C\textsubscript{2}H\textsubscript{4}. Until now, only a few low-polarity or hydrophobic MOFs have been reported to possess such an unusual adsorption behavior.\cite{4,11,12} To the best of our knowl-
edge, MOFs that can simultaneously and selectively absorb C₂H₆ and C₂H₅ over C₂H₄ from a ternary mixture of C₂H₆/C₂H₅/C₂H₄ have never been described.

Herein, we report such a rare example, a stable porous MOF, [(Me₂NH)₂][Co₃(DCPN)₂(H₂O)]:11H₂O (TJT-100, DCPN = 5-(3,5-dicarboxyphenyl)nicotinate). The proper positioning of uncoordinated carboxylate oxygen atoms and coordinated water molecules on the microporous pore surface can simultaneously trap C₂H₆ and C₂H₅ through the formation of weak electrostatic interactions with the C–H bonds of C₂H₆ and C₂H₅, a situation that does not appear to occur with C₂H₄. This leads to the efficient purification of C₂H₆ (purity > 99.997%) from a ternary mixture of C₂H₆/C₂H₅/C₂H₄ with this MOF as an adsorbent in a single breakthrough operation at room temperature.

TJT-100 crystallizes in the orthorhombic space group Pbcn, and exhibits a three-dimensional (3D) porous structure with a high density of carboxylate oxygen atoms on the surfaces of the 1D pores (Figure 1; see also the Supporting Information, Figures S1–S3). In one asymmetric unit, there are three crystallographically independent Co²⁺ ions that form a trinuclear Co₃(µ₂-OH)(O₂C)₃ ([Co₃]) cluster as a secondary building unit (SBU; Figure 1b). In [Co₃] SBU, both Co1 and Co3 adopt a six-coordinated octahedral configuration. As shown in Figure 1b, Co1 is coordinated by four carboxylate oxygen atoms, one µ₂-OH, and one pyridyl N atom, and Co3 is coordinated by four carboxylate oxygen atoms, one coordinated water molecule, and one µ₂-OH oxygen atom. Co2 is five-coordinated with three carboxylate O atoms, one pyridyl N atom, and one µ₂-OH, showing a distorted trigonal-bipyramidal configuration. It is noteworthy that there are two uncoordinated carboxylate oxygen atoms around the Co1 and Co3 centers, which might be able to interact with guest molecules through electrostatic interactions. Furthermore, the [Co₃] SBU’s are linked together by DCPN ligands, generating an anionic skeleton with 1D pores running along the a axis (ca. 8.7 × 11.6 Å). The negative charge of the host framework is balanced by Me₄N⁺ cations (Figure S2). The phase purity of the bulk product was confirmed by comparison of its experimental and simulated PXRD patterns (Figure S4a).

Remarkably, TJT-100 exhibits high thermal and chemical stability (Figures S4–S7), which prompted us to investigate its gas adsorption and separation properties.[14–17] To examine the gas adsorption capacity, the N₂ adsorption isotherm of activated TJT-100 was investigated at 77 K (Figure 2a). A typical type I microporous isotherm was generated, confirming the permanent porosity of TJT-100, with a Brunauer–Emmett–Teller (BET) surface area of 890 m² g⁻¹ (Langmuir surface area of 1077 m² g⁻¹) and a mean pore size of approximately 8.0 Å. Measurements of the C₂H₆, C₂H₅, and C₂H₄ gas adsorption capacities of activated TJT-100 were also performed. Single-component adsorption isotherms for C₂H₆, C₂H₅, and C₂H₄ up to 1 atm were measured at 273, 298, and 318 K, respectively (Figure 2 and Tables S2–S5). As expected, the amount of adsorbed gas in activated TJT-100 decreased with increasing temperature. In addition, the adsorption capacity of activated TJT-100 is lower for C₂H₅ than for C₂H₆ and C₂H₄ at all analyzed temperatures (Figure 2), which contrasts those of previously reported MOFs, with adsorption capacities in the order of C₂H₆ > C₂H₅ > C₂H₄ (Table S2). The isosteric heats of adsorption (Qₛₑ) were calculated to evaluate

Figure 1. a) The structure of TJT-100 viewed along the b axis (Me₂NH⁺ and guest water molecules are omitted for clarity). b) Trinuclear [Co₃] SBUs in TJT-100. Preferential adsorption sites for c) C₂H₆, d) C₂H₅, and e) C₂H₄ in TJT-100 as revealed by computational simulations.

Figure 2. a) N₂ sorption and desorption isotherms at 77 K for activated TJT-100 (inset: pore-size distribution). Adsorption and desorption isotherms of activated TJT-100 for b) C₂H₆, c) C₂H₅, and d) C₂H₄ at 273, 298, and 318 K, respectively.
the binding energies between the C₂ gases and the TJT-100 framework. As shown in Figure 3a and Table S2, the order of \( Q_\text{ads} \) values at zero coverage is \( \text{C}_2\text{H}_6 \) (31 kJ mol\(^{-1}\) > \( \text{C}_2\text{H}_4 \) (29 kJ mol\(^{-1}\) > \( \text{C}_2\text{H}_2 \) (25 kJ mol\(^{-1}\) ), which is consistent with component breakthrough experiments. Breakthrough experiments were also conducted using a ternary mixture of \( \text{C}_2\text{H}_6/\text{C}_2\text{H}_4/\text{C}_2\text{H}_2 \) (0.5:0.5:99 v/v/v) with activated TJT-100 as the adsorbent (Figure 3d). Again, only a single adsorption-desorption cycle was required to achieve an ethylene purity of greater than 99.997\% (Figure S13). This purity is much higher than that required for a typical ethylene polymerization reactor.\(^{[23]}\) These results suggest TJT-100 as a high-performance adsorbent for the potential purification of ternary mixtures of C₂ hydrocarbons into high-purity ethylene for use in the petrochemical industry.

The investigation of gas-framework interactions is significant for understanding the above unique adsorption behavior. One of the most effective methods is to determine the gas binding sites by single-crystal diffraction.\(^{[20,21]}\) However, single-crystal data of activated TJT-100 with absorbed C₂ molecules could not be obtained even after several attempts. Therefore, grand canonical Monte Carlo (GCMC) simulations, which have been widely used to understand the nature of gas adsorption sites within such frameworks,\(^{[22–25]}\) were used to study the adsorption properties of C₂ gases on activated TJT-100. The GCMC results gave simulated C₂ uptake amounts determined from the adsorption isotherms. Typically, the \( Q_\text{ads} \) values for \( \text{C}_2\text{H}_6 \), \( \text{C}_2\text{H}_4 \), and \( \text{C}_2\text{H}_2 \) decrease in the order of \( \text{C}_2\text{H}_6 \geq \text{C}_2\text{H}_4 > \text{C}_2\text{H}_2 \)\(^{[26]}\) in previously reported MOFs (Table S2). The higher \( \text{C}_2\text{H}_6 \) \( Q_\text{ads} \) value of activated TJT-100 indicates that the positioning of the functional groups within this framework enables efficient adsorption of the inert \( \text{C}_2\text{H}_6 \) molecule. Single-component isotherms for 1:99 \( \text{C}_2\text{H}_6/\text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_4/\text{C}_2\text{H}_2 \) mixtures at 273 and 298 K were fitted by ideal adsorbed solution theory (IAST).\(^{[27]}\) As shown in Figure S10, the adsorption selectivities for \( \text{C}_2\text{H}_6/\text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_4/\text{C}_2\text{H}_2 \) at a pressure of 1 atm and 298 K were calculated to be 1.8 and 1.2, respectively, indicating the feasibility of using activated TJT-100 for practical applications in the separation of \( \text{C}_2\text{H}_6 \) from \( \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_2 \).\(^{[2,4,19]}\)

To evaluate the separation potential of activated TJT-100 for \( \text{C}_2\text{H}_6/\text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_4/\text{C}_2\text{H}_2 \) gas mixtures, key experiments were carried out with binary mixtures of \( \text{C}_2\text{H}_6/\text{C}_2\text{H}_4 \) (1:99 v/v) and \( \text{C}_2\text{H}_4/\text{C}_2\text{H}_2 \) (1:99 v/v), which are typical compositions of industrial mixtures. As shown in Figure 3b,c, highly efficient separation of \( \text{C}_2\text{H}_6 \) from a 1:99 gas mixture of \( \text{C}_2\text{H}_6/\text{C}_2\text{H}_4 \) was achieved by passing the mixture over a packed column of activated TJT-100. It can be observed that \( \text{C}_2\text{H}_6 \) achieves a breakthrough first, with no evidence of \( \text{C}_2\text{H}_4 \) or \( \text{C}_2\text{H}_2 \) flow before its breakthrough point. Thus the concentrations of \( \text{C}_2\text{H}_6 \) and \( \text{C}_2\text{H}_4 \) in the outlet gas are both below 3 ppm (lower than the detection limit of the GC, 0.003%), enabling the collection of ethylene with an extremely high purity greater than 99.997% after only a single-breakthrough operation (Figures S11 and S12). The actual gas separation selectivities for 1:99 v/v \( \text{C}_2\text{H}_6/\text{C}_2\text{H}_4 \) and 1:99 v/v \( \text{C}_2\text{H}_4/\text{C}_2\text{H}_2 \) gas mixtures were 8.5 and 5.75, respectively, as determined by dual-component breakthrough experiments.
polarization provided by the Me$_2$NH$_3^+$ cations (Figure 4d). For C$_2$H$_4$, only weak van der Waal interactions between C$_2$H$_4$ molecules and Me$_2$NH$_3^+$ cations were observed (Figures 1d and 4c). Owing to the shorter C–C and C–H bond lengths of C$_2$H$_4$ compared to those of C$_2$H$_6$, the C–H bonds in C$_2$H$_4$ cannot be polarized enough by Me$_2$NH$_3^+$ to enforce a C–H···O interaction. Because of this, C$_2$H$_4$ has the lowest framework affinity amongst the three gases. All of the above results reveal an unusual affinity of TJT-100 towards inert C$_2$H$_6$ instead of unsaturated C$_2$H$_4$, giving an affinity order of C$_2$H$_6$ > C$_2$H$_4$ > C$_2$H$_4$. This hierarchy also agrees with the results of the breakthrough experiments, which achieved a high separation selectivity of C$_2$H$_6$ from a ternary mixture of C$_2$H$_6$/C$_2$H$_4$/C$_2$H$_4$ at room temperature. To further confirm the interactions between the C$_2$ molecules and the framework, in situ IR measurements of C$_2$H$_6$ adsorption at room temperature were conducted on TJT-100, which confirmed the existence of stronger hydrogen-bonding interactions between C$_2$H$_6$/C$_2$H$_4$ and the uncoordinated carboxylate oxygen atoms of the framework, compared to those between C$_2$H$_6$ and TTT-100, and the existence of weak van der Waals interactions between C$_2$H$_4$ molecules and the phenyl rings of the ligands (Figures S17 and S18).

In conclusion, we have synthesized a new porous MOF, TJT-100, with high thermal and acid/base stability. This framework possesses a relatively high uptake capacity of C$_2$H$_4$, C$_2$H$_4$, and C$_2$H$_4$, and shows unique selective adsorption of C$_2$H$_6$ and C$_2$H$_4$ over C$_2$H$_4$ from a ternary mixture of C$_2$H$_6$/C$_2$H$_4$/C$_2$H$_4$ (0.5:0.5:99 v/v/v), achieving a C$_2$H$_6$ purity greater than 99.997% by a single-breakthrough operation. This was mostly attributed to the existence of a high density of uncoordinated carboxylate oxygen atoms and coordinated water molecules on the surfaces of the pores, which enables the capture of C$_2$H$_4$ and C$_2$H$_4$ molecules through multiple electrostatic interactions. Me$_2$NH$_3^+$ also plays an important role in polarizing C$_2$H$_4$ for the high affinity of TJT-100 toward C$_2$H$_4$ by forcing C–H···O interactions. This work not only reports a new stable material for potentially producing very pure C$_2$H$_4$ from a ternary mixture of C$_2$H$_6$/C$_2$H$_4$/C$_2$H$_4$, but also provides insight for exploring the effect of functional oxygen atoms on the separation of C$_2$ species in MOFs.


