Title: Simultaneously Trapping C2H2 and C2H6 into a Robust Metal-Organic Framework from a Ternary Mixture of C2H2/C2H4/C2H6 for Purification of C2H4

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Simultaneously Trapping C$_2$H$_2$ and C$_2$H$_6$ into a Robust Metal-Organic Framework from a Ternary Mixture of C$_2$H$_2$/C$_2$H$_4$/C$_2$H$_6$ for Purification of C$_2$H$_4$

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Abstract: The removal of C$_2$H$_2$ and C$_2$H$_6$ from C$_2$H$_4$ streams is of great significance for the purification of feedstock to produce polyethylene and other commodity chemicals, while the simultaneous absorption of C$_2$H$_4$ and C$_2$H$_6$ over C$_2$H$_4$ from a ternary mixture has never been realized. Herein, a robust metal-organic framework (MOF) TJT-100 was design and synthesized, which demonstrates remarkably selective adsorption of C$_2$H$_2$ and C$_2$H$_6$ over C$_2$H$_4$. Breakthrough experiments show that TJT-100 can be used as an adsorbent for high-performance purification of C$_2$H$_4$ from a ternary mixture of C$_2$H$_2$/C$_2$H$_4$/C$_2$H$_6$ (0.5/99/0.5), to afford a C$_2$H$_4$ purity greater than 99.997%, beyond that required for ethylene polymerization. Computational studies reveal that the uncoordinated carboxylate oxygen atoms and coordinated water molecules towards the pore can trap C$_2$H$_2$ and C$_2$H$_6$ through the formation of multiple C=O electrostatic interactions, while the corresponding 'C$_2$H$_4$-framework' interaction is unfavorable.

Light hydrocarbons, such as ethane, ethylene, and acetylene, are the most widely used feedstock molecules in the petrochemical industry. 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 via steam cracking of naphtha and the dehydrogenation of ethane. 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 acetylides, which have been known to cause gas flow blockages and explosion. While the presence of high levels of C$_2$H$_6$ can result in higher reactor residence times and decrease production per unit time. In addition, the non-reactive C$_2$H$_2$ 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$_2$H$_4$/C$_2$H$_2$/C$_2$H$_6$ mixture is perceived as one of the most challenging yet important industrial processes, due to the similar molecular sizes and volatilities of C$_2$H$_4$ and C$_2$H$_6$. At present, the most commonly used method for the industrial separation of C$_2$H$_4$/C$_2$H$_2$/C$_2$H$_6$ mixture is high pressure cryogenic distillation, an extremely costly and energy intensive process. To up to now, new approaches for effective C$_2$H$_4$/C$_2$H$_2$/C$_2$H$_6$ separations have focused on membrane separations, organic solvent sorbent based separations, and MOF adsorbents based separations.

In the past decades, MOFs have emerged as a new type of advanced functional porous materials for the separation of C$_2$H$_2$/C$_2$H$_4$ or C$_2$H$_2$/C$_2$H$_6$ mixtures. Up to now, many MOFs have shown outstanding performance in the separation of C$_2$H$_2$/C$_2$H$_4$ or C$_2$H$_2$/C$_2$H$_6$. For C$_2$H$_4$/C$_2$H$_2$, it is well known that the unsaturated C$_2$H$_4$ can be easily bound to the open metal sites to achieve the highly selective uptake of C$_2$H$_4$ over C$_2$H$_2$. However, in such a process, the inert C$_2$H$_6$ is recovered first, with C$_2$H$_2$ only being obtained through heating or by purging with an inert-gas. As such, it is difficult to obtain the desired C$_2$H$_4$ product with high purity if utilizing C$_2$H$_4$ as the mobile phase. The examination of adsorbents with highly selective adsorption of C$_2$H$_2$ from C$_2$H$_4$/C$_2$H$_6$ mixture, could reduce the energy consumption of these separation processes, affording high-purity C$_2$H$_4$. Until now, only a few low polarity or hydrophobic MOFs have been reported to possess such an unusual adsorption behavior. To our knowledge, MOFs that can simultaneously and selectively absorb C$_2$H$_4$ and C$_2$H$_6$ over C$_2$H$_2$ from a ternary mixture of C$_2$H$_2$/C$_2$H$_4$/C$_2$H$_6$ have never been achieved.

Herein, we report such a rare example, a stable porous MOF, (Me$_2$NH)$_2$[Co$_3$(DCPN)$_2$][(μ$_3$-OH)(H$_2$O)].11H$_2$O (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 C$_2$H$_2$ and C$_2$H$_6$ through the formation of weak electrostatic interactions with the C-H bonds of C$_2$H$_6$ and C$_2$H$_2$, a situation that does not appear to occur with C$_2$H$_4$. This lead to the efficient purification of C$_2$H$_4$ (purity > 99.997%) from a ternary mixture of C$_2$H$_2$/C$_2$H$_4$/C$_2$H$_6$ using this MOF as an adsorbent in a single breakthrough operation at room temperature.

TJT-100 crystallizing in the orthorhombic space group Pbca, exhibits a three-dimensional (3D) porous structure with high density of carboxylate oxygen atoms on the surface of 1D pores (Figures 1a and S1-S3). In one asymmetric unit, there are three...
crystallographically independent Co$^{2+}$ ions to form a tri-nuclear Co$_8$(μ$_3$-OH)(O$_2$C)$_4$ ((Co$_3$) cluster as a secondary building unit (SBU, Figure 1b). In Co$_3$ SBU, both Co1 and Co3 show a six-coordinated octahedral configuration. As shown in Figure 1b, Co1 is coordinated by four carboxylate oxygen atoms, one μ$_3$-OH, and one pyridyl N atom, and Co3 is coordinated by four carboxylate oxygen atoms, one coordinated water molecule, and one μ$_3$-OH oxygen atom. Co2 is five-coordinated with three carboxylate O atoms, one pyridyl N atom, and one μ$_3$-OH, showing a distorted trigonal bipyramidal configuration. It is noteworthy that there are two uncoordinated carboxylate oxygen atoms around Co1 and Co3 centers, which are potentially sites to interact with guest molecules via electrostatic interactions. Furthermore, the Co$_3$ SBUs are linked together by DCPN ligands, generating an anionic skeleton with 1D pores running along the $b$ axis (about 8.7×11.6 Å$^2$). The negative charge of the host framework is balanced by Me$_3$NH$^+$ cations (Figure S2). The phase purity of the bulk product was confirmed by the comparison of its experimental and simulated PXRD patterns (Figure S4a).

**Figure 1.** a) The structure of TJT-100 viewed along the $b$ axis (Me$_3$NH$^+$ and guest water molecules are omitted for clarity); b) tri-nuclear Co$_3$ SBU in TJT-100; preferential adsorption sites for c) C$_2$H$_4$, d) C$_2$H$_6$, and e) C$_2$H$_2$ in TJT-100 as revealed by computational simulations.

Remarkably, TJT-100 exhibits high thermal and chemical stability (Figures S4-S7), which prompts us to investigate its gas adsorption and separation properties.$^{[14-17]}$ To examine the gas adsorption capacity, $N_2$ adsorption isotherm of activated TJT-

**Figure 2.** a) $N_2$ adsorption and desorption isotherms at 77 K for activated TJT-100 (inset: pore-size distributions); adsorption and desorption isotherms of activated TJT-100 for b) C$_2$H$_6$, c) C$_2$H$_4$, and d) C$_2$H$_2$ at 273, 298 and 318 K, respectively.

**Figure 3.** a) The calculated $Q_v$ values of activated TJT-100 for C$_2$H$_6$, C$_2$H$_4$, and C$_2$H$_2$ at 298 K. Breakthrough curves of activated TJT-100 for b) C$_2$H$_6$/C$_2$H$_4$/C$_2$H$_2$ (0.5/0.5/99), c) C$_2$H$_2$/C$_2$H$_4$ (1/99), and d) C$_2$H$_2$/C$_2$H$_6$ (1/99) measured at 298 K and 1 bar. G and C are the concentrations of the inlet and outlet gases, respectively.

porosity of TJT-100, with a BET (Brunauer-Emmett-Teller) surface area of 890 m$^2$g$^{-1}$ (Langmuir surface area of 1077 m$^2$g$^{-1}$) and a pore size distribution of ca. 8.0 Å. Measurements of C$_2$H$_2$, C$_2$H$_4$, and C$_2$H$_6$ gas adsorption capacities of activated TJT-100 were also performed. Single-component adsorption isotherms for C$_2$H$_2$, C$_2$H$_4$, and C$_2$H$_6$ up to 1 atm were measured at 273, 298, and 318 K, respectively (Figure 2, Table S2-S5). As expected, the amount of adsorbed gas in activated TJT-100 decreases along with increasing temperature. In addition, it is interesting to note that the adsorption capacity of activated TJT-100 for C$_2$H$_2$ is lower than those of C$_2$H$_4$ and C$_2$H$_6$ at all temperatures analyzed (Figure 2), being inconsistent with those of previously reported MOFs, in which the adsorption capacities are in the order of C$_2$H$_2$ > C$_2$H$_4$ > C$_2$H$_6$ (Table S2). The isosteric

100 was investigated at 77 K (Figure 2a), which shows typical Type-I microporous isotherm and confirms the permanent

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heats of adsorption ($Q_h$) were calculated to evaluate the binding energy between C$_2$ gases and T10-100 framework. As shown in Figure 3a and Table S2, the order of $Q_h$ values at zero coverage are C$_2$H$_4$ (31 kJ mol$^{-1}$) > C$_2$H$_2$ (29 kJ mol$^{-1}$) > C$_2$H$_6$ (25 kJ mol$^{-1}$), which is consistent with the uptake amounts shown via adsorption isotherms. Typically, $Q_h$ values for C$_2$H$_2$, C$_2$H$_4$, and C$_2$H$_6$ are in the order of C$_2$H$_4$ > C$_2$H$_2$ > C$_2$H$_6$ in the reported MOFs (Table S2). The higher C$_2$H$_4$ $Q_h$ value in activated T10-100 indicates that the position of functional groups within this framework can efficiently adsorb the inert C$_2$H$_2$ molecule. Single-component isotherms for 1:99 C$_2$H$_2$/C$_2$H$_4$ and C$_2$H$_2$/C$_2$H$_6$ at 273 and 298 K were fitted via ideal adsorbed solution theory (IAST). As shown in Figure S10, the adsorption selectivity for C$_2$H$_2$/C$_2$H$_4$ and C$_2$H$_2$/C$_2$H$_6$ at a pressure of 1 atm and 298 K was calculated to be 1.8 and 1.2, respectively, indicating the feasibility of activated T10-100 for practical applications in the separation of C$_2$H$_4$ from C$_2$H$_2$ and C$_2$H$_6$.

To evaluate the separation potential of activated T10-100 for C$_2$H$_4$/C$_2$H$_2$ and C$_2$H$_2$/C$_2$H$_6$ gas mixtures, breakthrough experiments were carried out with binary mixtures of C$_2$H$_4$/C$_2$H$_2$ (1:99, v/v) and C$_2$H$_2$/C$_2$H$_6$ (1:99, v/v), which are typical compositions of industrial mixtures. As shown in Figures 3b and 3c, the high-efficiency separation of C$_2$H$_2$ from a 1:99 gas mixture of C$_2$H$_4$/C$_2$H$_2$ can be achieved by flowing the mixture over a packed column of activated T10-100. It can be observed that C$_2$H$_2$ achieves a breakthrough first, with no evidence of C$_2$H$_4$ or C$_2$H$_6$ flow before its breakthrough point. Thus, the concentrations of C$_2$H$_2$ and C$_2$H$_6$ 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 selectivity for 1:99 v/v C$_2$H$_2$/C$_2$H$_4$ and 1:99 v/v C$_2$H$_2$/C$_2$H$_6$ gas mixtures are 8.5 and 5.75, respectively, as determined by dual component breakthrough experiments. Breakthrough experiments were also conducted using a ternary mixture of C$_2$H$_2$/C$_2$H$_4$/C$_2$H$_6$ (0.5:0.5:0.5) v/v/v with activated T10-100 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. These results suggest T10-100 as a high-performance adsorbent for potential purification of ternary mixtures of C$_2$’s into high-purity ethylene for use in petrochemical industry.

The investigation of gas-framework interaction is significant for understanding the above unique adsorption behavior. One of the most effective methods is to determine the gas binding sites via single-crystal diffraction.[20,21] However, the single-crystal data of activated T10-100 with absorbed C$_2$’s 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 the framework,[22-25] were used to study the adsorption properties of C$_2$ gases on activated T10-100. GCMC results reveal that the simulated C$_2$H$_2$, C$_2$H$_4$, and C$_2$H$_6$ isotherms for activated T10-100 at 298 K and 1 bar are 105, 80 and 86 cm$^3$ g$^{-1}$ for C$_2$H$_2$, C$_2$H$_4$, and C$_2$H$_6$, respectively. These values are close to those of experimental results, validating the GCMC method for T10-100 system. The calculated potential fields for these gases were shown by the way of slice (Figures S14-S16). As shown in Figure S14, the highest potential values for C$_2$H$_2$ are near uncoordinated carboxylate oxygen atoms, Me$_2$NH$_2^+$ cations, and phenyl rings of the ligand. The slice of calculated potential field for C$_2$H$_4$ shows the highest potential values are located around the coordinated water molecules, uncoordinated carboxylate oxygen atoms and Me$_2$NH$_2^+$ cations (Figure S15).[26] For C$_2$H$_6$, the slice suggests no obvious strong affinity between C$_2$H$_2$ molecules and the framework (Figure S16). These results are in good agreement with the breakthrough experiments that show a low affinity of C$_2$H$_2$ towards activated T10-100.

Electrostatic interactions between donor oxygen atoms and gas molecules are known to play important roles in the separation of light hydrocarbons by MOFs.[26] In most cases, C-H···O interactions were identified with C···O distances in the range of 3.2 < C····O < 4.0 Å.[27,28] GCMC calculations revealed that C$_2$H$_2$ molecules are bound to two uncoordinated carboxyl oxygen atoms C-H···O (H···O 2.612 Å) and C-H···O (H···O 2.996 Å) via hydrogen bonding interactions (Figures 1e and 4). In addition, C$_2$H$_4$ molecules are close to Me$_2$NH$_2^+$ cations and DCPN linkers in the framework of T10-100, resulting in beneficial intermolecular van der Waals interactions (distances of C···C range from 3.342 to 4.133 Å, Figure 4a). The high uptake of C$_2$H$_2$ in activated T10-100 can be attributed to the existence of large number of weak interactions between the anionic oxygen atoms and the slightly polarizable C-H bonds of C$_2$H$_2$. As shown in Figure 1c and 4d, an ethane molecule can form four interactions with the uncoordinated carboxylate oxygen atom and coordinated water molecules through its polarizable C-H bonds. These interactions are aided by the polarization provided by the Me$_2$NH$_2^+$ cations (Figure 4d). For C$_2$H$_6$, only weak van der Waals interactions between C$_2$H$_6$ molecules and Me$_2$NH$_2^+$ cations were observed (Figure 1d and 4c). Due to the shorter C-C and C-H bond distances of C$_2$H$_6$ compared to those of C$_2$H$_2$, the C-H bonds in C$_2$H$_6$ cannot be polarized enough by Me$_2$NH$_2^+$ to force a C-H···O interaction. Because of this, C$_2$H$_6$ has the lowest framework affinity amongst the three gases. All the above results reveal an unusual affinity of T10-100 toward the inert C$_2$H$_6$ instead of unsaturated C$_2$H$_4$, giving an affinity order of C$_2$H$_2$ > C$_2$H$_4$ > C$_2$H$_6$. This hierarchy also agrees with the results of break-through experiments, which can achieve high...
separation selectivity of C_{2}H_{4} from a ternary mixture of C_{2}H_{4}/C_{2}H_{6}/C_{4}H_{6} at room temperature. To further prove the interactions between the C_{2} molecules and the framework, in-situ IR measurements of C_{2} adsorption at room temperature were conducted on TJT-100, which confirm the existence of stronger hydrogen bonding interactions between C_{2}H_{4}/C_{2}H_{6} and the uncoordinated carboxylate oxygen of the framework, compared to those between C_{2}H_{4} and TJT-100, and the existence of weak van der Waals interactions between C_{2}H_{4} and the phenyl ring of the ligand (see the supporting information, Figures S17-S18).

In conclusion, we have synthesized a new porous MOF, TJT-100, with high thermal and acid/alkali stability. This framework possesses relatively high uptake capacity of C_{2}H_{4}, C_{2}H_{6} and C_{2}H_{2}, and shows unique selective adsorption of C_{2}H_{4} over C_{2}H_{6} from a ternary mixture of C_{2}H_{4}/C_{2}H_{6}/C_{4}H_{6} (0.5:0.5:9.9, v/v), achieving a C_{2}H_{4} purity greater than 99.997% by a single-breakthrough operation. This can be mostly attributed to the existence of a high density of uncoordinated carboxylate oxygen atoms and coordinated water molecules on the surface of the pore, which can enable the capture of C_{2}H_{4} and C_{2}H_{2} molecules through multiple electrostatic interactions. Me_{2}NH_{2}^{+} 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 provides a new stable material for potentially producing high-purified C_{2}H_{4} from a ternary mixture of C_{2}H_{4}/C_{2}H_{6}/C_{4}H_{6} but also supplies a new insight for exploring the effect of functional oxygen atoms on the separation of C_{2} species in MOFs.

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Keywords: metal organic framework, light hydrocarbon, selective adsorption, gas separation, electrostatic interaction

A robust porous metal-organic framework was synthesized, and firstly utilized for high-separation selectivity of \( \text{C}_2\text{H}_4 \) from a ternary mixture of \( \text{C}_2 \) hydrocarbons, with a \( \text{C}_2\text{H}_4 \) purity greater than 99.997% after a single-breakthrough operation.

Simultaneously Trapping \( \text{C}_2\text{H}_2 \) and \( \text{C}_2\text{H}_6 \) into a Robust Metal-Organic Framework from a Ternary Mixture of \( \text{C}_2\text{H}_2/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6 \) for Purification of \( \text{C}_2\text{H}_4 \)