# Synthesis and Modification of Water-Stable CPL-2 MOF for Ethylene/Ethane Separation.

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**Highlights**

* CPL-2 MOF exhibits preferential adsorption of ethylene over ethane.
* CPL-2 MOF is relatively hydrophobic and shows excellent water stability under humid conditions.
* Ethylene/ethane adsorption selectivity was enhanced six-fold by silver ions modification.

**1. Introduction**

Adsorptive separation of ethylene/ethane mixture has growing interest in petrochemical industries compared to the conventional energy-intensive cryogenic distillation.[1] Metal-organic frameworks (MOFs) have attracted considerable attention in gas adsorption and separation due to their combined properties of large surface area, functionalised and adjustable pore structure and surface.[2] However, the open metal sites in MOFs interact strongly with water molecules, resulting in material decomposition and poor water stability,[3] limiting their potential in practical settings. Therefore, development of water-stable materials with high selectivity is of great importance to accomplish the ethylene/ethane separation.

In this work, pillared-layer CPL-2 MOF was selected as the model MOF and synthesised at room temperature for separating binary ethylene/ethane mixture. The water stability of CPL-2 was evaluated under dynamic humid conditions. Ag(I) ions modification of CPL-2 was also conducted to explore the possibility of improving the selectivity of CPL MOFs in ethylene/ethane separation.

**2. Methods**

Hydrothermal synthesis was used to prepare CPL-2. Silver ions modified CPL-2 MOFs (denoted as Ag/CPL-2) were prepared using the incipient wetness impregnation method. Dynamic water vapour adsorption analyses at 25 °C and 50 °C with relative humidity values ranging from 0% to 90% (10% per step) were measured using a dynamic vapour sorption (DVS 1) equipment. Prior to the water vapour adsorption, all samples were dried at 0% relative humidity for 3 h. Intelligent gravimetric analyser (IGA-001) based on the static gravimetric technique was applied to determine ethylene and ethane adsorption isotherms on developed CPL-2 and Ag/CPL-2 materials at a constant temperature of 25 °C, 35 °C and 50 °C, respectively. The adsorption selectivity was calculated as a ratio of Henry’s constants.

**3. Results and discussion**

CPL-2 can be easily synthesised at room temperature, which was confirmed by XRD and SEM analysis. Characteristic peaks at 2*θ* = 6.4°, 8.8°, 10.3° and 12.6°, matching the simulated results, were identified in all the synthesised CPL-2 MOFs, confirming the presence of the pillared-layer structure in the crystalline domain. All SEM images show squared slab-shaped crystals aggregated together with sizes ranging from 0.2 μm to 2.5 μm. The synthesised CPL-2 has excellent water stability confirmed by the dynamic water vapour adsorption analysis under 90% relative humidity, showing no significant framework decomposition, even at 50 °C. The calculated selectivity based on gravimetric single-component gas adsorption experiments shows the significantly improved C2H4/C2H6 selectivity from 1.2 to 6.6 after loading 10% (theoretical) of sliver ions on CPL-2.

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**Figure 1.** Schematic presentation of CPL-2 framework and its water stability and adsorption performance in C2H4/C2H6 separation.

**4. Conclusions**

The synthesis of CPL-2 is facile with fast crystallization, *i.e.* 3 h is sufficient to prepare CPL-2 MOF at room temperature. CPL-2 demonstrated the outstanding water stability under dynamic humid conditions at 25 °C and 50 °C, showing the reversible water vapour adsorption under the conditions used. Gas adsorption study shows that 10 wt.% Ag/CPL-2 by Ag(I) impregnation gave the best adsorption performance considering both capacity and selectivity towards C2H4 over C2H6. The good selectivity combined with the water stability makes it promising and potentially feasible to use CPL-2 in the separation of ethylene/ethane mixtures, especially under conditions where water vapour exists.

**References**

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