Electronic Supporting Information

Separation of Ethane and Ethylene by a Robust Ethane-Selective Calcium-Based Metal-Organic Framework

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Materials and characterizations. All reagents used were purchased from commercial vendors and used without purification. Powder X-ray diffraction (PXRD) patterns were performed on a Bruker D8 Advance diffractometer. Data were collected between 3° and 40° of 2θ with a scan speed of 5.0 deg/min. Thermogravimetric analysis (TGA) data were recorded on a TGA550 (TA Instruments) Analyzer with a temperature ramping rate of 10 °C/min from RT to 600 °C under nitrogen atmosphere. Gas adsorption experiments were performed using a volumetric gas sorption analyzer (3Flex, Miromeritics).

Synthesis of Ca(H$_2$tcpb). CaCl$_2$ (90 mg), H$_4$tcpb (90 mg) were mixed in 10 mL absolute ethanol in a 25-mL autoclave. The mixture was stirred for 1 hour at room temperature, and then heated at 100°C for 3 days. After being cooled to RT, colorless block-shaped crystals were filtered, washed thoroughly with ethanol and dried under air.

Column breakthrough measurements. MOF samples were packed into a stainless steel column (the steel column was 14 cm in length with 10 mm of inner diameter with silica wool filling the void space. The sorbent was vacuumed at 180 °C for 2 hours with a helium flow before the temperature of the column was decreased to room temperature. The flow of He was then turned off while a gas mixture (ethane/ethylene: 50/50, V/V) was sent into the column with a total flow rate of 2ml/min. The downstream was monitored using a mass spectrometer..
Fig. S1. PXRD patterns of Ca(H$_2$tcpb). From bottom to top: black: as-synthesized, red: heating at 120 °C in open air for 2 days, blue: heating at 150 °C in open air for 2 days, purple: heating at 180 °C in open air for 2 days.

Fig. S2. Thermogravimetric analysis (TGA) curve of Ca(H$_2$tcpb)
Fig. S3. Adsorption-desorption isotherm of ethylene at 278, 288, and 298 K.
Fig. S4. Adsorption-desorption isotherm of ethane at 278, 288, and 298 K.

Fig. S5. Adsorption-desorption isotherm of ethane and ethylene at 298 K for samples after being heating at 180 °C for 2 days.
**Fig. S6.** PXRD patterns of Ca(H₂tcpb). From bottom to top: black: as made, red: after exposure under 90%RH for 2 days, blue: after immersed in water for 2 days.

**Fig. S7.** Multicomponent column breakthrough curve for Ethane/Ethylene (90/10) at 298 K.
**Fig. S8.** Consecutive runs of multicomponent column breakthrough curve for an equimolar binary mixture of Ethane/Ethylene (50/50) at 298 K