Electronic Supplementary Information

From equilibrium based MOF adsorbent to kinetic selective carbon molecular sieve for paraffins/iso-paraffins separation

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1. Experimental Details

All reagents were purchased from Sigma-Aldrich, Alfa or TCI and used as received unless otherwise indicated.

Synthesis of CMS-PMOF-1:

CD-MOF-2 was synthesized according to the literature.[1] γ-CD (1.30 g, 1 mmol) and RbOH (0.82 g, 8 mmol) were dissolved in H_2O (20 mL). The aqueous solution was filtered and methanol was allowed to vapor diffuse into the solution one week. Colorless cubic crystals were isolated, filtered and washed with methanol before thermolysis.

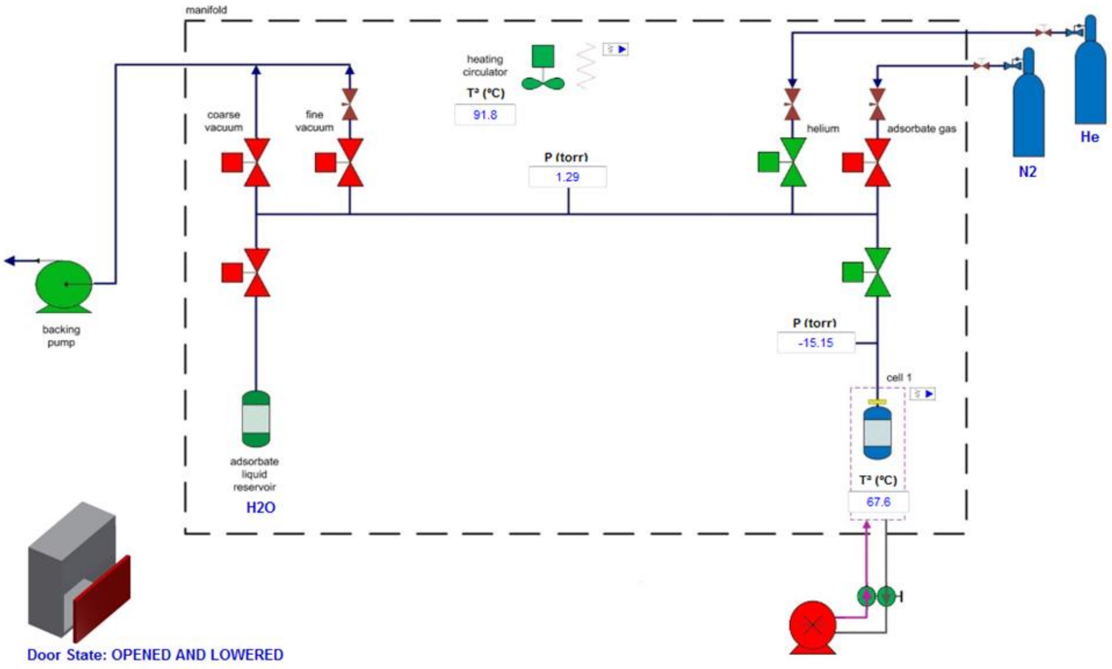
The crystals of CD-MOF-2 was heat-treated in a horizontal quartz reactor under an N_2 flow 20 mL/min at 600 ºC for 5 h and then at 900 ºC for 1 h to afford the carbonized materials. Then the obtained carbon materials was soaked into a 2 M HCl solution at room temperature for 24 h followed by washing with water and methanol. This wash procedure were performed twice to afford the final microporous carbon material designated as **CMS-PMOF-1**.

Vapor and Gas sorption:

A volumetric apparatus Vstar1 vapor sorption analyzer from Quantachrome instruments was used for collecting pentane, iso-pentane, n-butane and iso-butane adsorption isotherms at 293 K. Schematic diagram of the instrument is shown in the scheme 1, from the screenshot of the software window.

For the vapor sorption experiments, high purity liquid pentane and iso-pentane was taken in adsorbate liquid reservoir, while n-butane and iso-butane cylinders were connected to adsorbate gas port. In a typical experiment sample was activated in-situ at 105 °C under dynamic vacuum for 6 hours. Temperature was increased to 105 °C from room temperature at the rate of 1 °C/min. Activated sample was used for corresponding isotherm measurement. All the sorption of hydrocarbon was carried out at 20 °C sample temperature. Manifold temperature was maintained at 40 °C throughout the measurement. Sorption data was processed by using Helmholtz equation. It is a real gas Schmidt-Wenzel equation, which is defined in terms of Helmholtz residual free energy and is an improvement of Benedict-Webb-Rubin equation for pentane,1 isopentane,2 butane3 and isobutane.4 This equation is recommended from NIST (National Institute of

Standards and Technologies) of USA for pentane and iso-pentane. It is suitable for pentane at temperatures between 143.47-600 K and pressures to 1000 bar; for iso-pentane at temperatures between 112.65-600 K and pressures to 10000 bar; for n-butane at temperatures between 134.895-575 K and pressures to 690 bar and for iso-butane at temperatures between 113.73-575 K and pressures 350 bar.

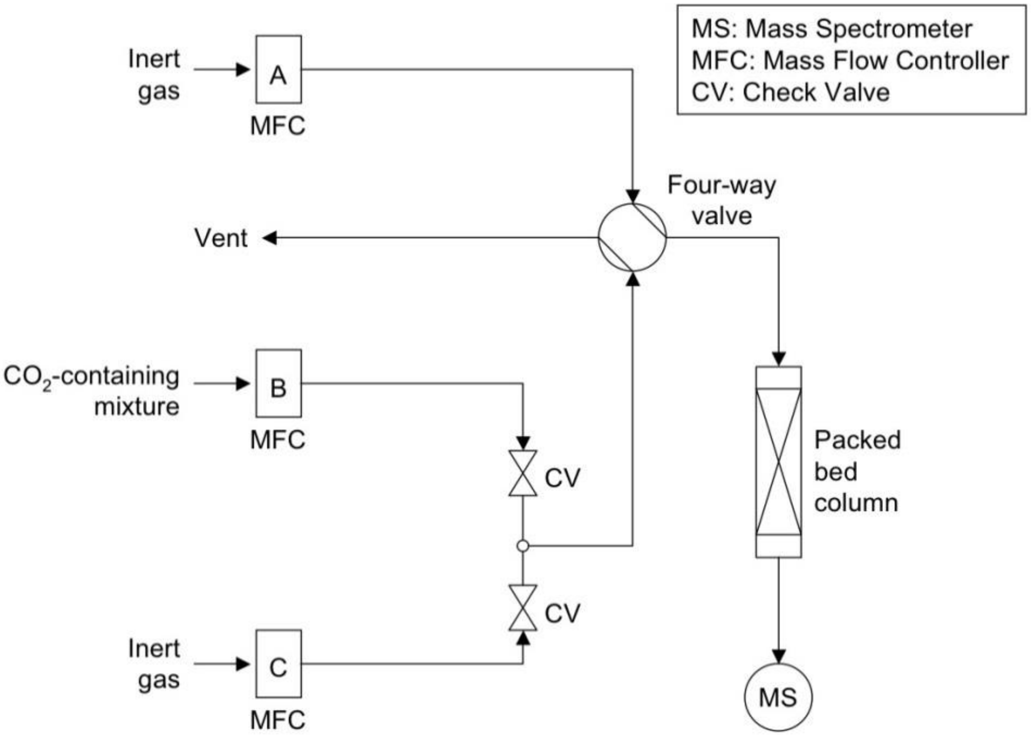


Scheme S1. Schematic diagram of Vstar1 vapor sorption analyzer.

Column Breakthrough Test Set-up, Procedure and Measurements:

The experimental set-up used for dynamic breakthrough measurements is shown in Scheme 2. The gas manifold consisted of three lines fitted with mass flow controllers Line "A" is used to feed an inert gas, most commonly helium, to activate the sample before each experiment. The other two lines, "B" and "C" feed a pure or pre-mixed gases. Whenever required, gases flowing through lines "B" and "C" may be mixed before entering a column packed with **CMS-PMOF-1** using a four-way valve. In a typical experiment, 0.5 g of adsorbent (in the column) was treated at 278 K overnight under vacuum in a separate oven.

After the sample is degassed, the column is backfilled with argon and mounted in the set-up. Before starting each experiment, helium reference gas is flushed through the column and then the gas flow is switched to the desired gas mixture at the same flow rate of 8 cm^3/min. The gas mixture downstream the column was monitored using a Hiden mass-spectrometer.



Scheme 2 Representation of the column breakthrough experiment.

2. Characterization

PXRD data were collected on a Bruker D8 Advance (Cu or Mo) X-ray diffractometer. Gas sorption experiments were carried out on the surface area analyzer ASAP-2020. N_2 gas sorption isotherm was measured at 77 K using a liquid N_2 bath. CO_2 isotherms were measured at 273 K using a water-ice bath and at 295 K with a water bath. Prior to the measurements, **CMS-PMOF-1** was degassed at 150 °C for 10 h.

A very small amount of the sample was directly placed on an aluminium stage without any extra treatment. The stage was then transferred into a Magellan XHR scanning electron microscope (FEI) for SEM studies. SEM images were taken at an acceleration voltage of 2kV and a working distance of 1 mm to reduce charging effects.

A very small amount of the sample was firstly dispersed in ethanol for an ultrasonic treatment (2 min). A drop of the suspension was then transferred to a copper grid supported holey carbon film in order to perform transmission electron microscopy (TEM) studies. All the TEM data were collected on a Titan G2 80-300 ST transmission electron microscope operated at 300 kV. A 2K*2K Gatan UltraScan CCD camera was used for recording the TEM images.

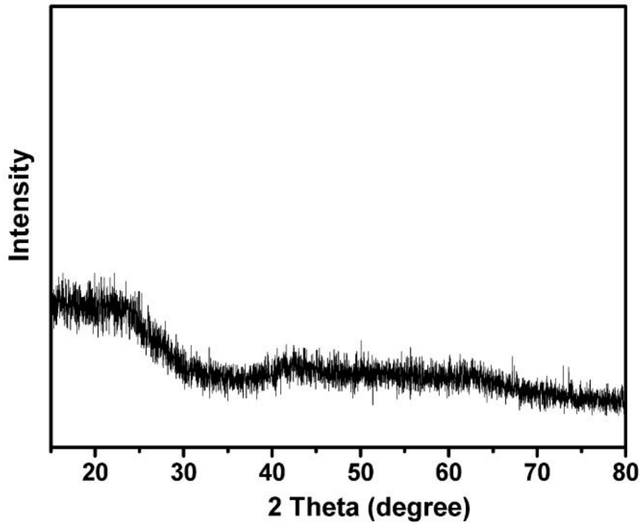


Fig. S1. Powder XRD patterns of the porous carbons **CMS-PMOF-1**.

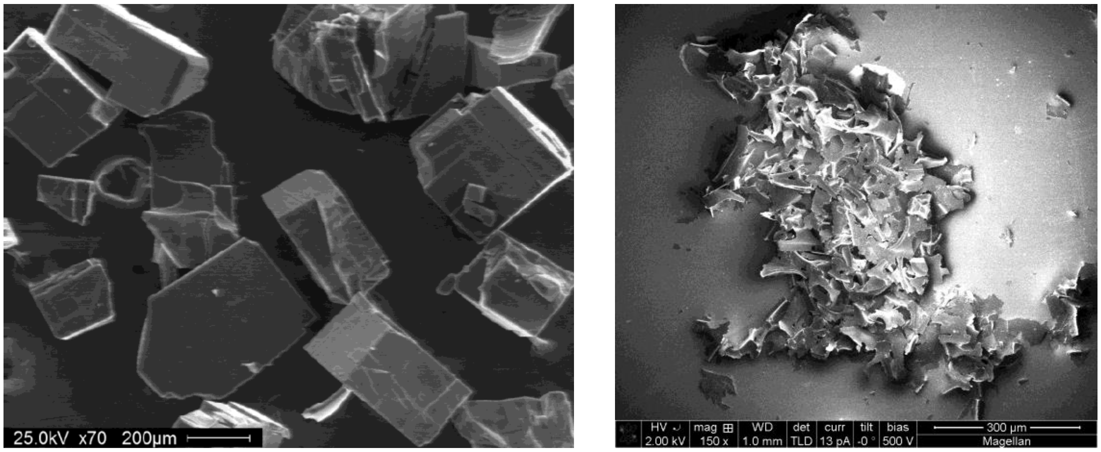


Fig. S2. Scanning electron microscopy (SEM) image of CD-MOF-2 (left) and the porous carbons **CMS-PMOF-1** (right).

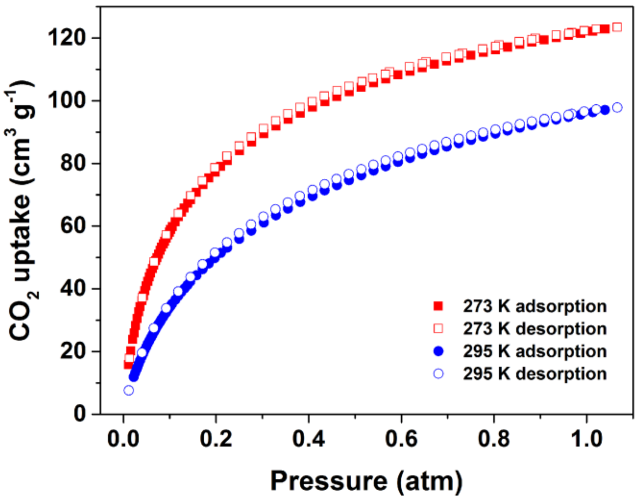


Fig. S3. CO_2 sorption isotherms of **CMS-PMOF-1** at 273 K and 295 K.

Column Breakthrough Experiments:

Column breakthrough experiments were carried out as described in materials and general procedures section.

For these experiments, the need of continuous analysis in column breakthrough adsorption test limits our choice or gas analyzers to mass-spectrometry. n-Butane and iso-butane being very similar molecule with same molecular weight, it is difficult to distinguish them by mass spectrometer simultaneously. n-Butane and iso-butane have almost identical fragmentation pattern except intensities of few fragments, irrespective of the mass fragment selected. There will be always overlap of mass fragments of one component over the other in this case. After several blank experiments (without sample) with pure gases and mixture, we selected mass 29 and mass 39 for *n*-butane and iso-butane respectively. Although mass 29 for n-butane overlaps with iso-butane and mass 39 for isobutane overlaps with *n*-butane, they were the mass fragment pair with minimum overlap. Blank experiments with pure gases and mixture suggest that despite the overlap it is possible to distinguish between pure *n*-butane and iso-butane with their mixture qualitatively by mass spectrometer as shown in Fig. S4-S6.

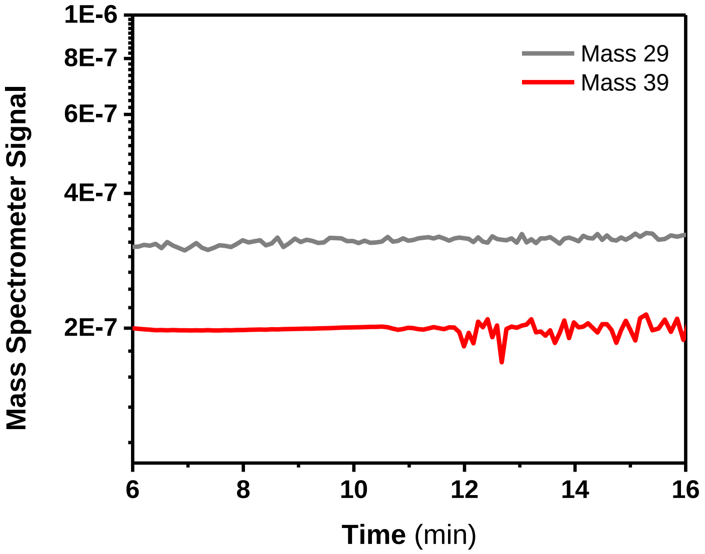


Fig. S4. Mass fragmentation for pure n-butane during blank experiment without column. It can be seen that n-butane produces both mass 29 and mass 39 fragments with similar intensity. Mass 29 fragment intensity is approximately 1.5 times higher than that of mass 39 fragment in case of n-butane.

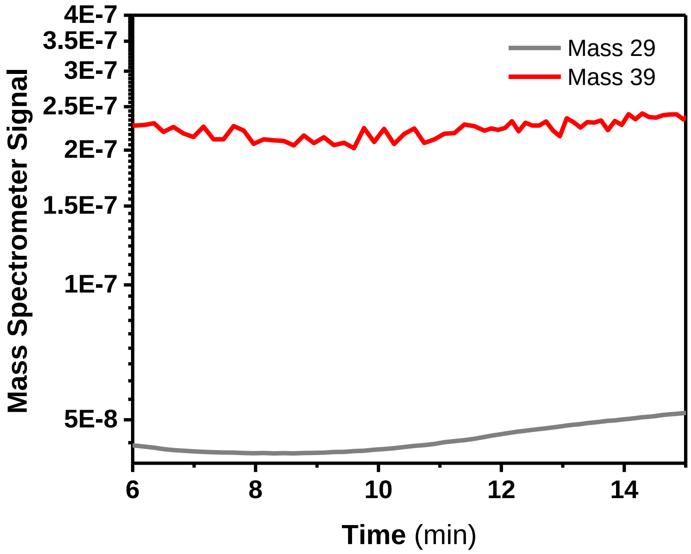


Fig. S5. Mass fragmentation for pure isobutane during blank experiment without column. It can be seen that isobutane produces both mass 39 and mass 29 fragments. Mass 39 fragment intensity is approximately 4-5 times higher than that of mass 29 fragment in case of iso-butane.

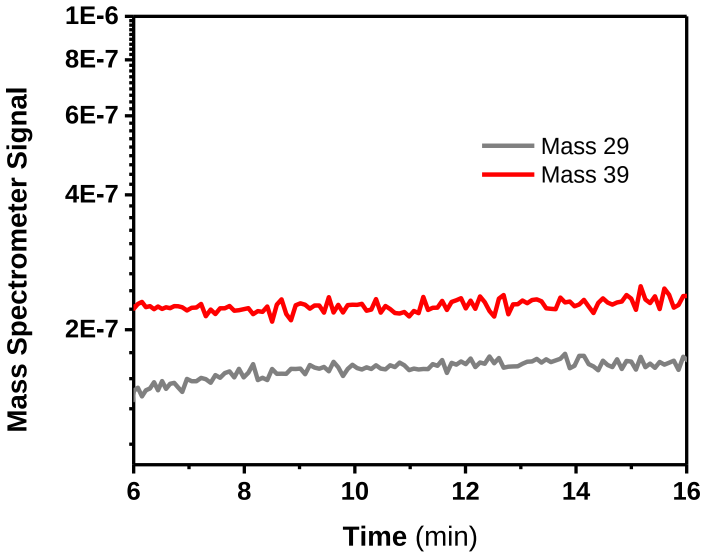


Fig. S6. Mass fragmentation for1:1 mixture of n-butane and isobutane during blank experiment without column. It can be seen that 1:1 mixture of *n*-butane and isobutane produces both mass 39 and mass 29 fragments with similar intensity. Mass 39 fragment intensity is approximately 1.5 times higher than that of mass 29 fragment in case of 1:1 mixture of n-butane and isobutane.

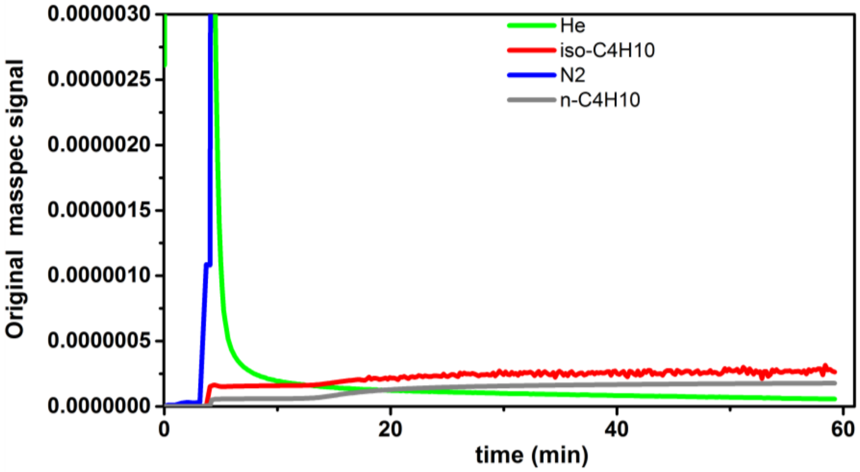


Fig. S7. Raw data of adsorption column breakthrough test of mixed n-butane (5%) and iso-butane (5%) in balance with N_2 (n-C_4H_{10}/iso-C_4H_{10}/N_2: 5/5/90 mixture) with the flow rate of 8 cm^3 min^{-1} on **CMS-PMOF-1**. The present figure show the massspec signal of all gases (with zoom on M29 and M39 signal) before normalization.

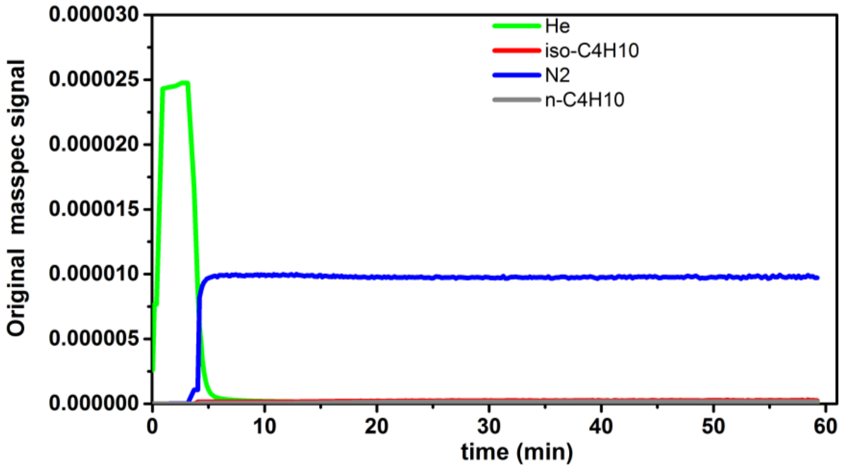


Fig. S8. Raw data of adsorption column breakthrough test of mixed n-butane (5%) and iso-butane (5%) in balance with N_2 (n-C_4H_{10}/iso-C_4H_{10}/N_2: 5/5/90 mixture) with the flow rate of 8 cm^3 min^{-1} on **CMS-PMOF-1**. The present figure show the zoom of N_2 and He (initial pressurization gas)| massspec signal.

Note: While plotting the breakthrough curve, we removed contribution of isobutane to mass fragment 29 (M29)(used for n-butane) by subtracting the intensity of M29 after isobutane breakthrough from the intensity of the M29 over the whole range(from isobutane breakthrough to end of experiment) to obtain the contribution of M29 for n-butane. In another hand, the N2 signal help in detecting the change in the signal of less selective gas (in this case iso-butane). This methodology was described in details in ref 2.

Reference:

1. R. A. Smaldone, R. S. Forgan, H. Furukawa, J. J. Gassensmith, A. M. Z. Slawin, O. M. Yaghi, J. F. Stoddart, *Angew. Chem. Int. Ed.*, 2010, **49**, 8630.

2. A. H. Assen, Y. Belmabkhout, K. Adil, P. M. Bhatt, D.-X. Xue, H. Jiang, M. Eddaoudi, *Angew. Chem. Int. Ed.*, 2015, **54**, 14353.