Electronic Supplementary Material (ESI) for ChemComm.

Pt/Al_2O_3-supported Metal-Organic Framework Film as Size-Selective Core-Shell Hydrogenation Catalyst

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Supporting Information

1. Synthesis of SIM-1

Synthesis of SIM-1 powder

In a typical synthesis a solid mixture of 0.71 g (2.73 mmol) of $Zn(NO_3)_2 \cdot 4H_2O$ and 1.20 g (10.94 mmol) of 4-methyl-5-imidazolecarboxaldehyde is dissolved in 20 ml of DMF. Afterwards the solution is poured into a vial and heated in an oven at 358 K for 72 h. After the synthesis, the resulting powder is washed 3 times with DMF then with EtOH. The samples are dried at 358K for 3h and then overnight under vacuum at room temperature.

SIM-1@Pt/Al_2O_3 film synthesis

Around 20 beads were immersed in a vial containing 0.71 g (2.73 mmol) of $Zn(NO_3)_2 \cdot 4H_2O$ and 1.20 g (10.94 mmol) of 4-methyl-5-imidazolecarboxaldehyde dissolved in 20 ml of DMF. After a solvothermal treatment at 358 K for 48 h, the resulting supported material was washed with ethanol to remove unreacted precursors and fine SIM-1 unsupported particles. The SIM-1 supported on beads is then dried at room temperature.

2. Powder X-Ray analysis

The XRD measurements on the materials were carried out by powder X-Ray diffraction (PXRD) using a Bruker D5005 Diffractometer equipped with a secondary graphite monochromator (CuKα radiation, wavelengths λ = 0.154178 nm) and a scintillation counter. The XRD studies were done at room temperature.

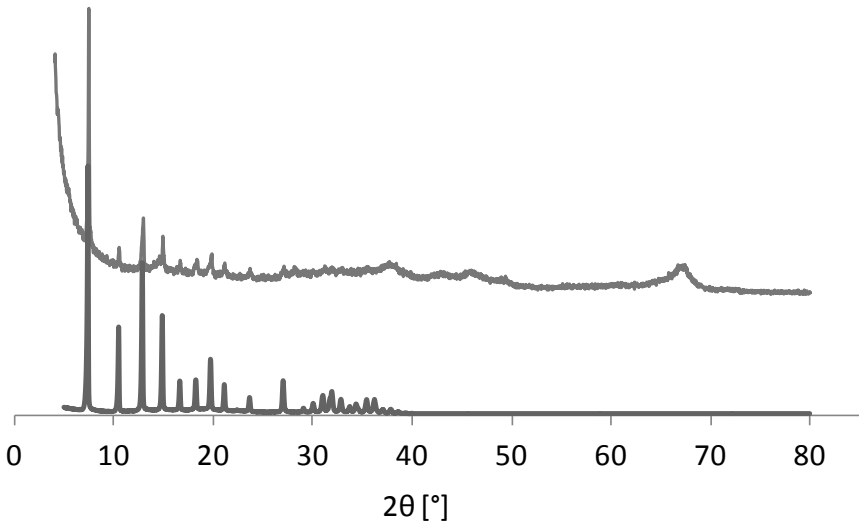


Figure S1: XRD patterns of as-synthesized SIM-1 (bottom) and crushed Pt/alumina beads-supported SIM-1 (top).

3. Gas sorption analysis

The N_2 adsorption isotherms at 77 K were measured on a BELSORP-MINI. The samples were outgassed under vacuum (~ 10^{-4} mbar) at 473K for 12 h before start of the measurements.

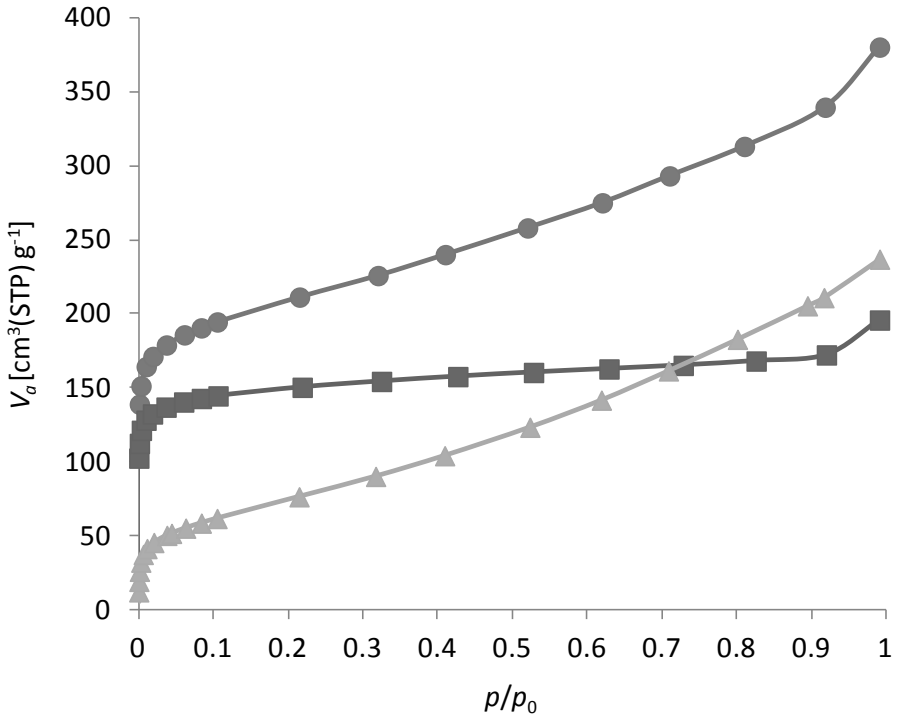


Figure S2. Nitrogen adsorption isotherms (77 K) of Pt/Al_2O_3 beads (bottom), SIM-1 powder (middle) and SIM-1@Pt/Al_2O_3 beads (top).

The C_2H_4 adsorption isotherm at 303 K was measured on a BELSORP-MINI. The samples were outgassed under vacuum (~ 10^{-4} mbar) at 473K for 12 h before start of the measurements.

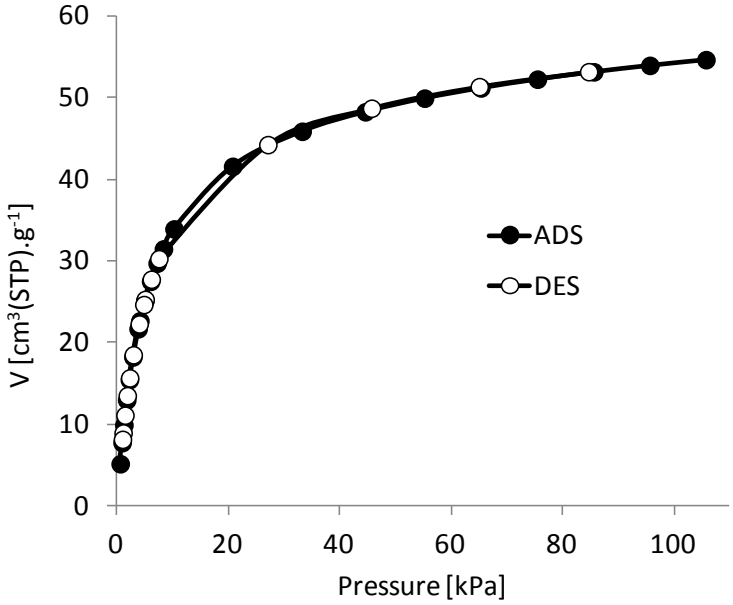


Figure S3. Ethylene isotherm (303 K) measured for SIM-1@Pt/Al_2O_3 beads.

4. SEM-EDS analysis

The surface and cross-section morphology of the as-synthesized supported samples were examined by scanning electron microscopy (SEM) using a JSM 5800LV (JEOL), coupled to an analysis system by energy dispersion spectrometry (EDS) with a diode Si-Li (PGT). The tension range is 0.3-30 kV and the effective resolution is 0.5 nm at 30kV.

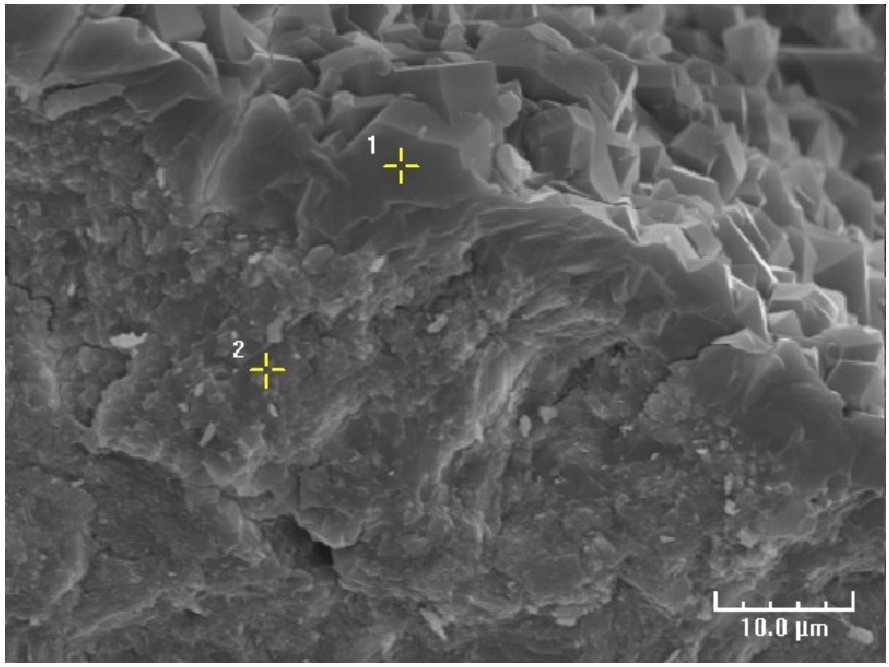
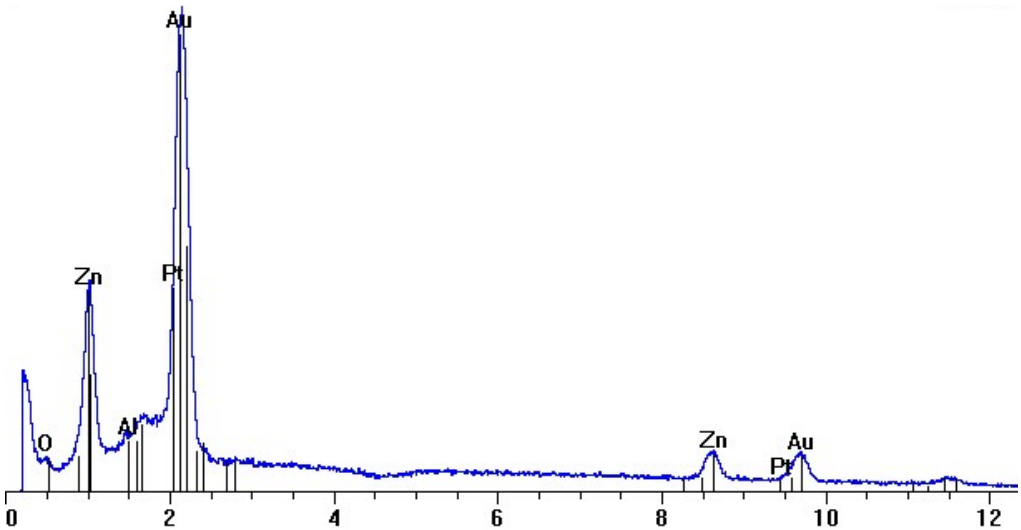
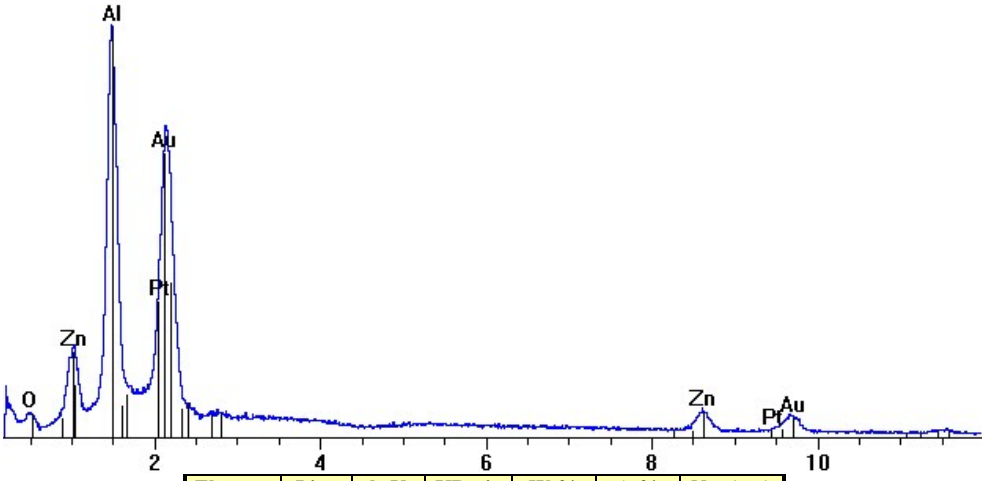


Figure S4. SEM photograph of the cross-section of SIM-1@Pt/Al_2O_3 bead.



Element	Line	keV	KRatio	Wt%	At%	Net (cps)
Al	KA1	1.487	0.0333	8.68	10.48	35.2
Zn	KA1	8.637	0.5896	62.33	31.03	68.0
Au	MA1	2.121	0.0000	0.00	0.00	841.1
Pt	MA1	2.049	0.0016	0.26	0.04	0.6
O	KA1	0.523	0.1071	28.73	58.45	27.1
Total			**0.7316**	**100.00**	**100.00**	

Figure S5. EDS analysis on position 1 in Fig.S4



Element	Line	keV	KRatio	Wt%	At%	Net (cps)
Al	KA1	1.487	0.3404	56.80	60.73	795.2
Zn	KA1	8.637	0.2217	24.98	11.02	56.5
Au	MA1	2.121	0.0000	0.00	0.00	650.9
Pt	MA1	2.049	0.0171	2.77	0.41	14.7
O	KA1	0.523	0.0525	15.45	27.84	29.3
Total			**0.6317**	**100.00**	**100.00**	

Figure S6. EDS analysis on position 2 in Fig.S4

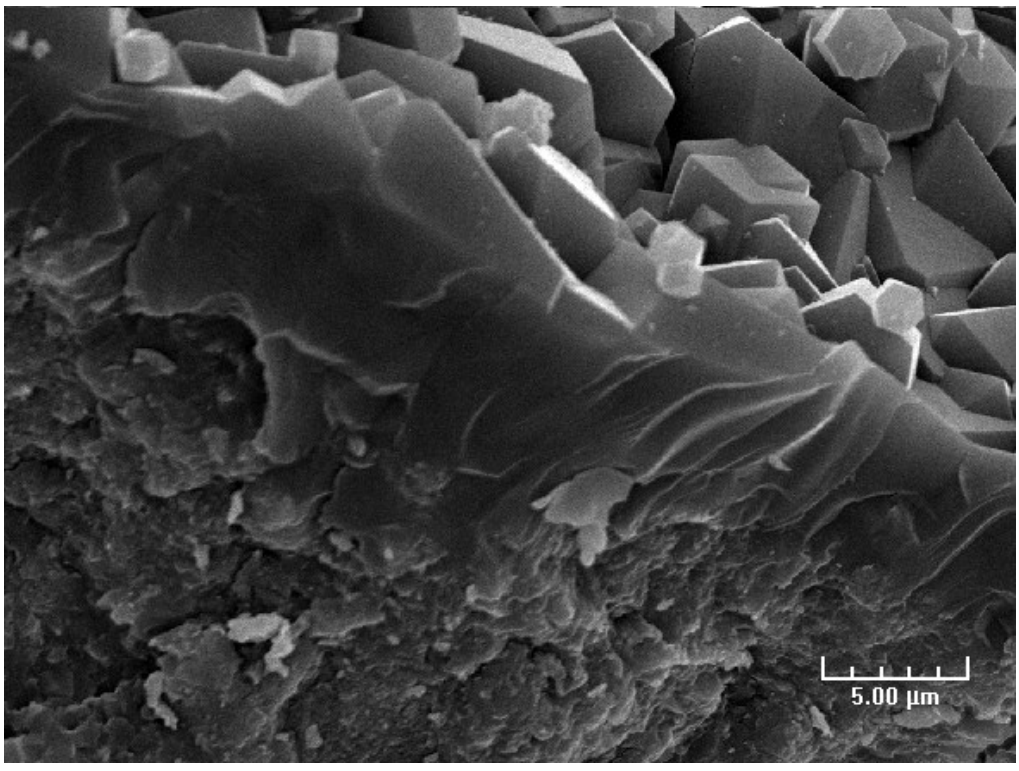


Figure S7. Close view of the cross-section of SIM-1@Pt/Al_2O_3 bead surface.

5. Hydrogenation catalytic tests

Toluene and ethylene hydrogenation tests were carried out using a tubular quartz plug flow reactor (internal diameter 4 mm) placed in a tubular furnace. 50 ± 3 mg of catalysts were used and 16 mg were used for the pure MOF powder, held between quartz wool plugs. This accounted for about 6 to 8 catalyst beads, of about 2 mm diameter each.
The samples were reduced at 150°C under pure flowing H_2 before reactions, which were carried out at atmospheric pressure. Toluene was fed using a saturator kept at 0°C, leading to a partial pressure of 912 Pa. 20 mL/min of pure hydrogen was used as carrier gas and fed through the toluene saturator. The vol.% of toluene was 0.9 %. In the case of ethylene reaction, a 5 vol.% C_2H_4/H_2 feed was used, with a total flow rate of 20 mL/min.
The reactants and reaction products were analysed by FT-IR spectroscopy using a 10 cm path-length gas cell fitted in a Bruker Tensor 27 FT-IR spectrophotometer. The proportion of the reactant and the corresponding saturated product were determined through integration of various spectral regions and calibration curves. For each temperature screened, the measure was performed waiting for steady-state conversion at least 20 min. In the case of toluene, methylcyclohexane was the only product observed, while ethane was the only product obtained in the case of ethylene conversion.

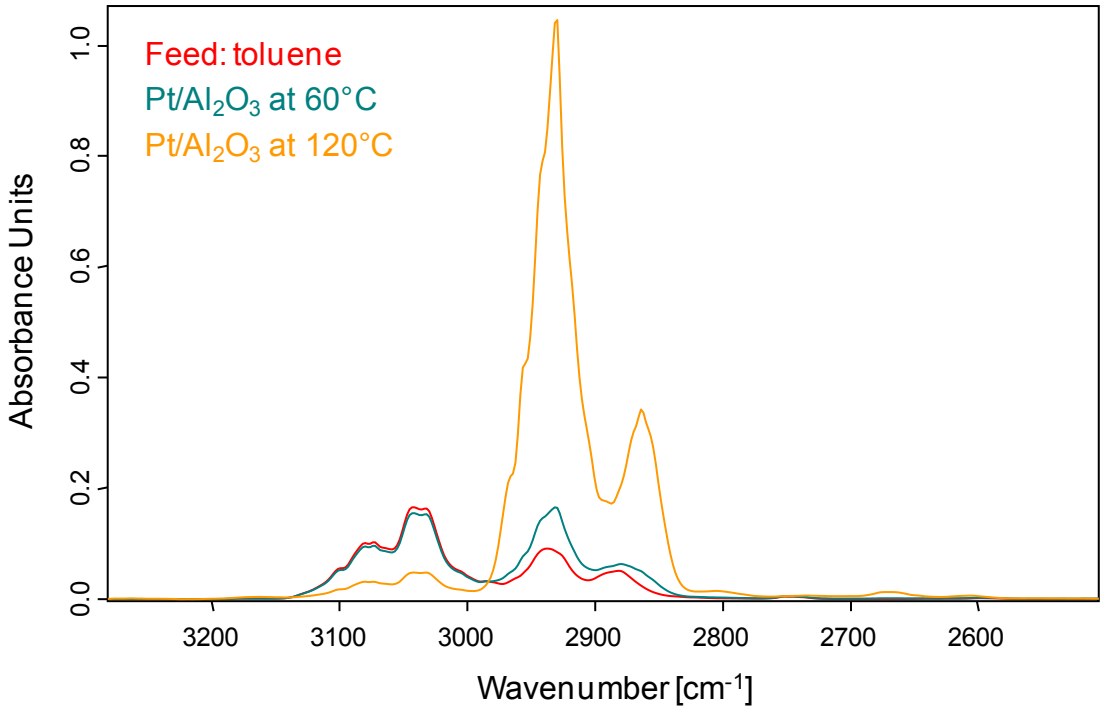


Figure S8. Typical FT-IR spectra obtained for toluene hydrogenation analysis

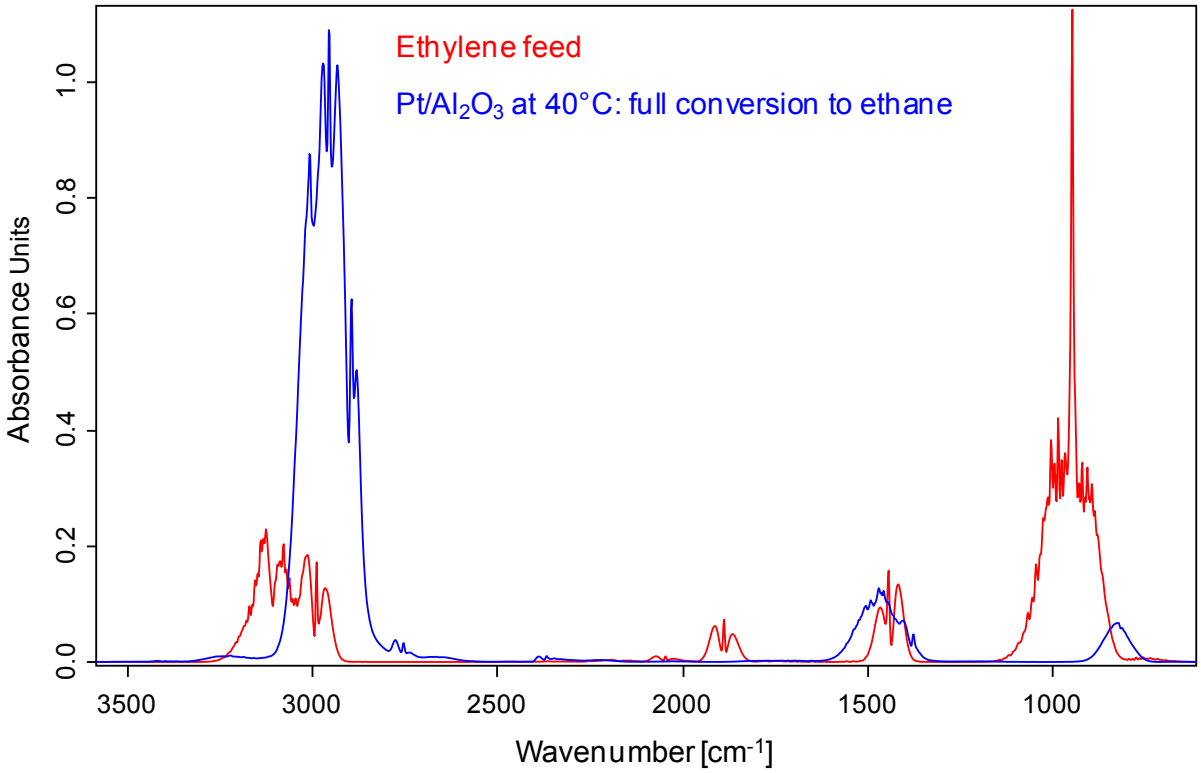


Figure S9. Typical FT-IR spectra obtained for ethylene hydrogenation analysis