Facile shaping of an imidazolate based MOF on ceramic beads for adsorption and catalytic applications

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Supporting Information

1.- Synthesis and characterization 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.

Characterization of SIM-1 powder

- Elemental analysis

Elemental analysis was carried out by Inductively Coupled Plasma ICP (Activa Horiba) after dissolution of the samples.

Elem. anal. calcd for $[C_{10}H_{10}N_4O_2Zn]$: C, 42.35; H, 3.55; N, 19.76; Zn, 23.06, found C, 42.29; H, 3.61; N, 19.71; Zn, 23.01.

- Liquid ^{1}H NMR

The ^{1}H NMR spectrum was recorded on a Brücker 250 MHz spectrometer at room temperature.

In a NMR tube, around 3mg of **SIM-1** were dissolved with a minimum of DCl/D_2O solution and then diluted in DMSO-d6 (c.a. 400µL). ^{1}H NMR δ (250 MHz, DMSO-d6, 294K) = 2.51 (s, 3H, CH_3), 8.81 (s, 1H, CH), 9.75 (s, 1H, CHO) ppm. Pics at 4.85 and 2.50 ppm correspond respectively to water (H_2O) and DMSO from the NMR solvent. No signal from DMF can be detected by NMR, thus showing the efficiency of the washing procedure.

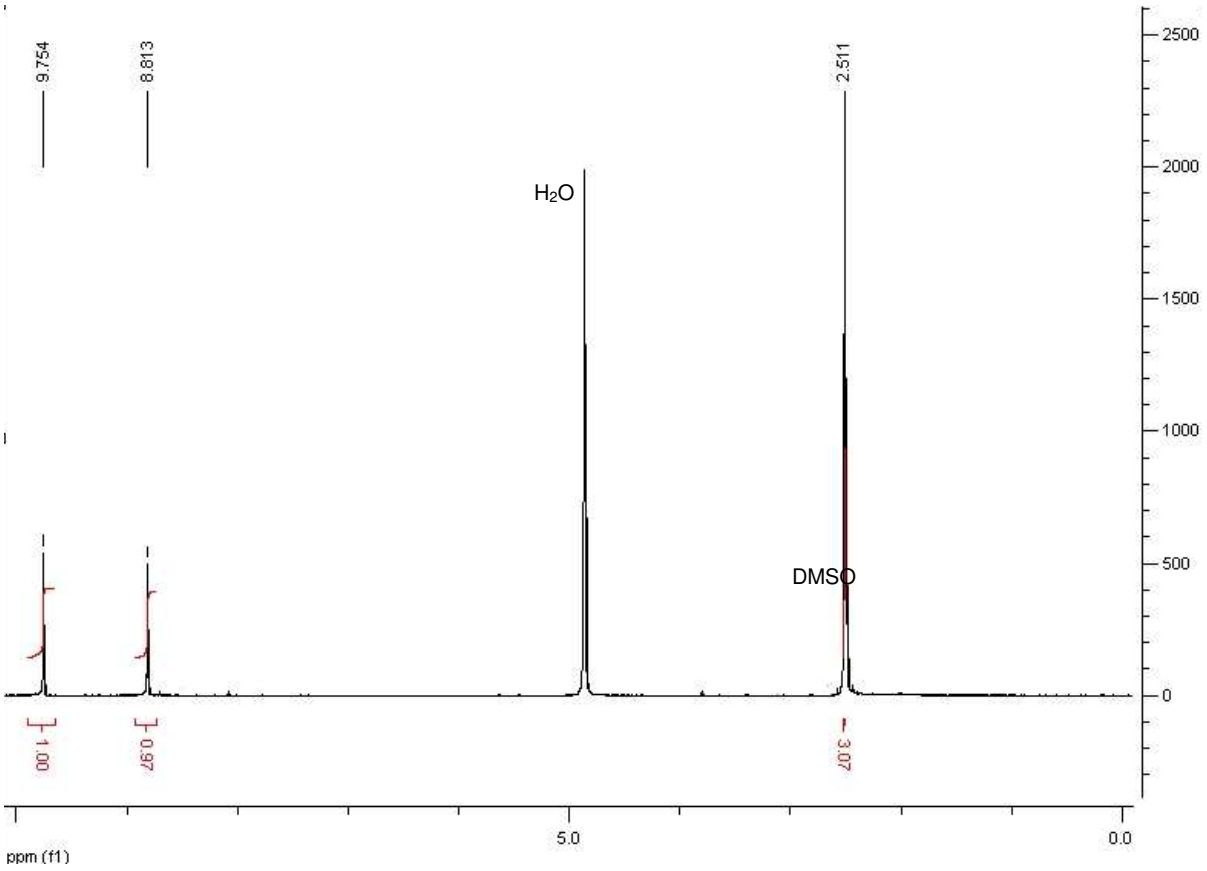


Figure S1: ^{1}H NMR of SIM-1.

2.- X-ray diffraction (XRD)

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.

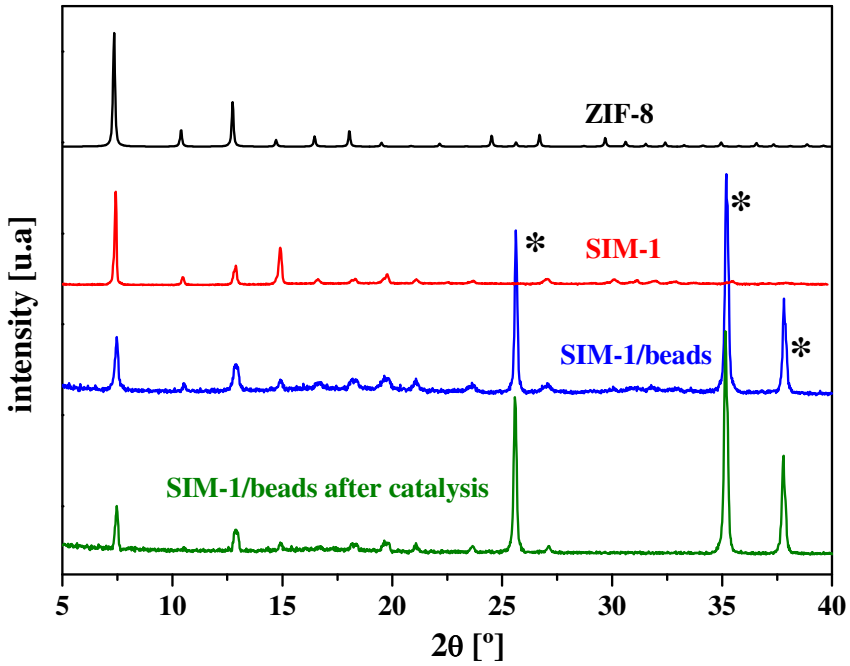


Figure S2: XRD patterns of as-synthesized SIM-1 and supported SIM-1. Reflections marked by (*) correspond to the alumina support

3.- Structural 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.

4.- Gas sorption analysis

The N_2 adsorption/desorption isotherms qt 77 K were measured on a BELSORP-MAX. The samples were outgassed under vacuum (~ 10^{-4} mbar) at 473K for 12 h before start of the measurements. The specific surface was determined by BET method, the micropore volume by t-plot analysis, and the mesopore volume by BJH.

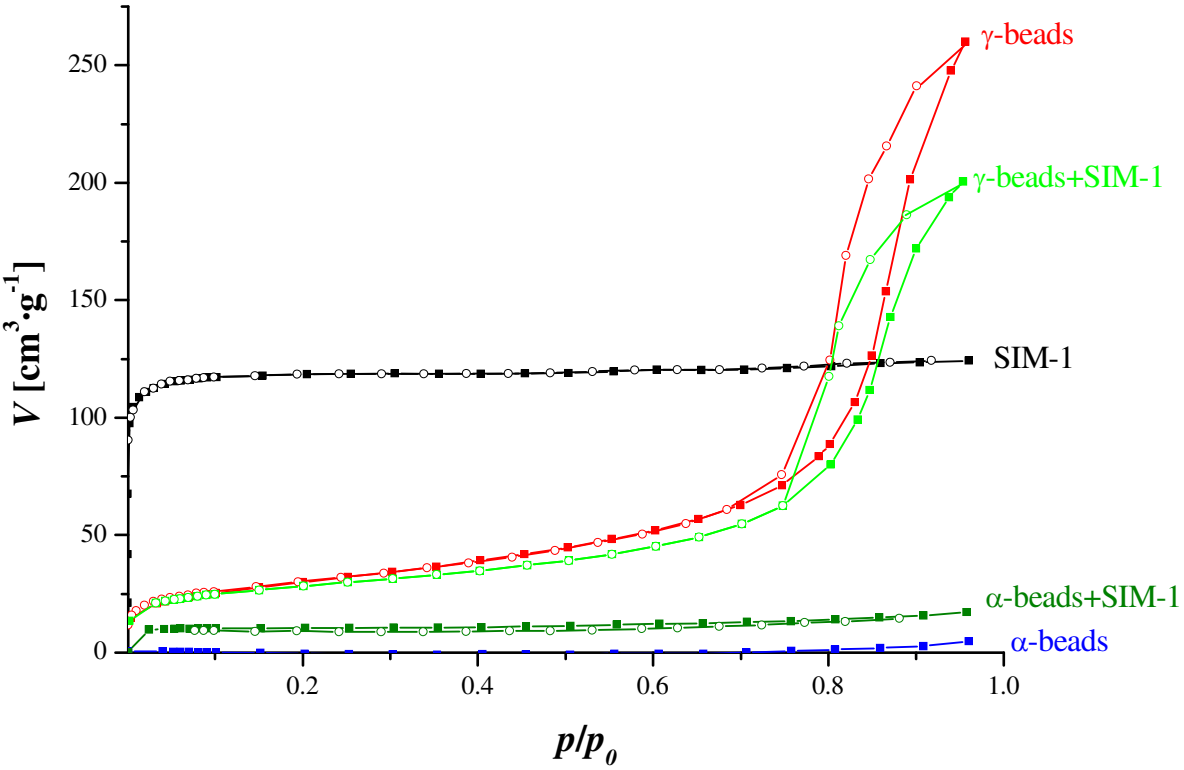


Figure S3: Nitrogen isotherms (77 K) represented as linear-linear diagrams. Close and open symbols correspond to adsorption and desorption data, respectively.

Table S4: Specific surface area of SIM-1 and beads supported SIM-1.

sample	BET area [$m^2 \cdot g^{-1}$]	p/p_0 range	V_{micro} [$cm^3 \cdot g^{-1}$]	V_{meso} [$cm^3 \cdot g^{-1}$]
SIM-1	471	0.04-0.10	0.19	0.01
γ-beads	100	0.03-0.25	0.06	0.39
SIM-1/γ-beads	110	0.04-0.25	0.06	0.30
α-beads	2	0.01-0.08	-	-
SIM-1/α-beads	57	0.03-0.15	0.02	-

The CO_2 adsorption/desorption isotherms at 303 K were measured on a BELSORP-HP. The sample was outgassed under vacuum (~ 10^{-4} mbar) at 473K for 12 h before start of the measurements.

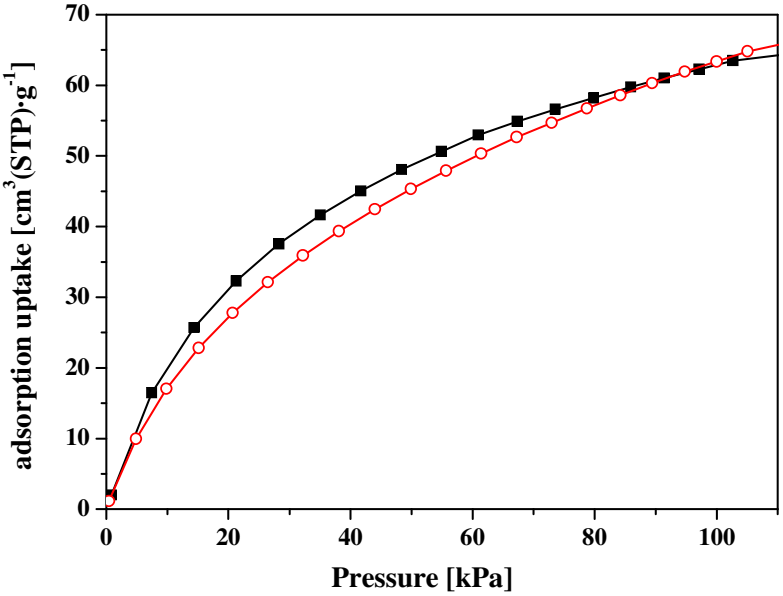


Figure S5: CO_2 adsorption isotherms of SIM-1 (■) and SIM-1/alumina composite (○) at 303 K.

5.- Infrared analysis

The sample is loaded in a DRIFT cell from Harricks Sci equipped with KBr window. The samples are desorbed at 100°C under inert gas for 30 min. The spectra are collected with a Nicolet 8700 spectrometer at a resolution of 4 cm^{-1}, 32 scans.

Synthesis of ZIF-7, ZIF-8 and corresponding α-alumina composites

The synthesis was carried out with clear synthesis solutions with a molar composition of Zn^{2+}/2*H*-bIm/DMF=1:4:100 and Zn^{2+}/2*Me*-Im/DMF=1:4:100, and then heated at 100ºC for 72 hours.

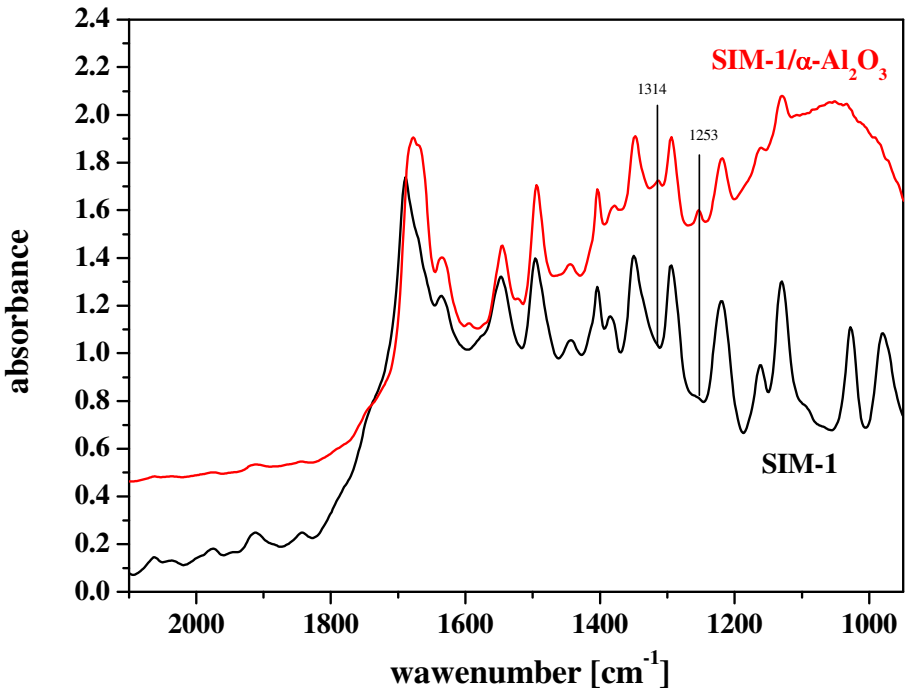


Figure S6: DRIFT spectra of SIM-1 powder (blue) and ground SIM-1/α-Al_2O_3 composite (red).

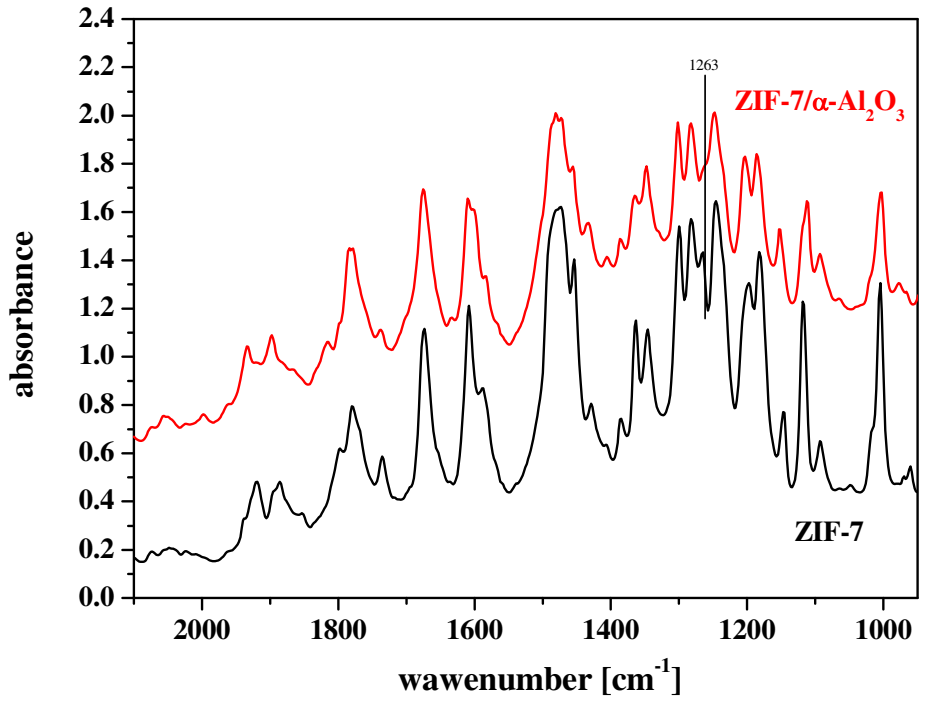


Figure S7: DRIFT spectra of ZIF-7 powder and ground ZIF-7/α-Al_2O_3 composite.

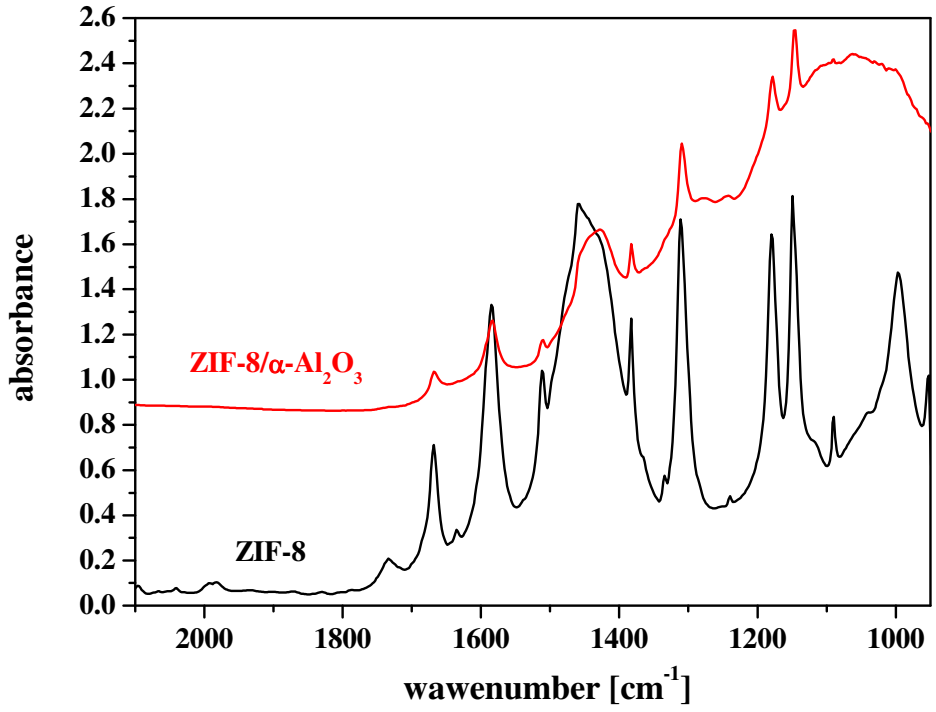


Figure S8: DRIFT spectra of ZIF-8 powder and ground ZIF-8/α-Al_2O_3 composite.

7.- Catalytic reaction

The transfer hydrogenation reactions of acetophenone (1 mmol), using SIM-1/g-Al_2O_3 (5 mol% SIM-1) as catalyst, were carried out in isopropanol (5 mL) used as solvent and hydrogen source in the presence of KOH (14 mg) under inert atmosphere. In a typical experiment, the solution was heated for the indicated time at 353 K, and then the reaction was quenched by cooling to 273 K. The organic products were extracted by Et_2O and identified after filtration through silica gel by GC on Cyclodex-B. Conversion was determined by integration of the signals.

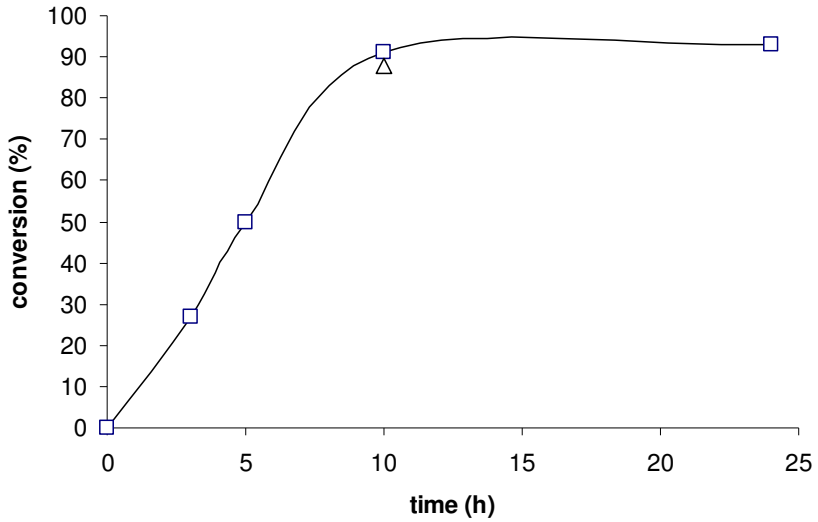
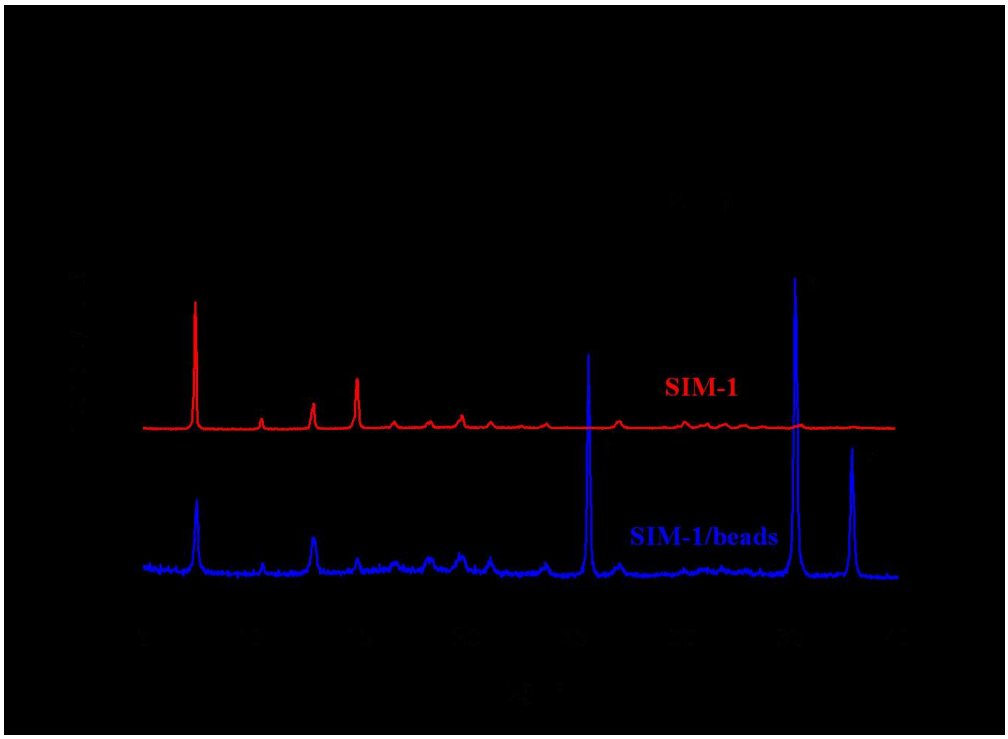


Figure S9: Time dependence of conversion (1st run: □; 2nd run: Δ) for transfer hydrogenation of acetophenone (1 mmol) using SIM-1/γ-Al_2O_3 beads as catalyst (5 mol% SIM-1) and KOH (14 mg) in isopropanol (5 mL) at 353 K.

Table S10: Catalyst screening for the transfer hydrogenation of acetophenone (1 mmol) using KOH (14 mg, 0.25 mmol, 25 mol%) in isopropanol (5 mL) at 353 K.

sample (quantity)	Time / h	conversion %
none	10	0
γ-Al_2O_3 (5 beads, 125 mg, ~245 mol% Al)	10	< 10
SIM-1 (14 mg, 0.05 mmol, 5 mol%)	12	87
SIM-1/γ-Al_2O_3 (5 beads, 5 mol% SIM-1)	10	90



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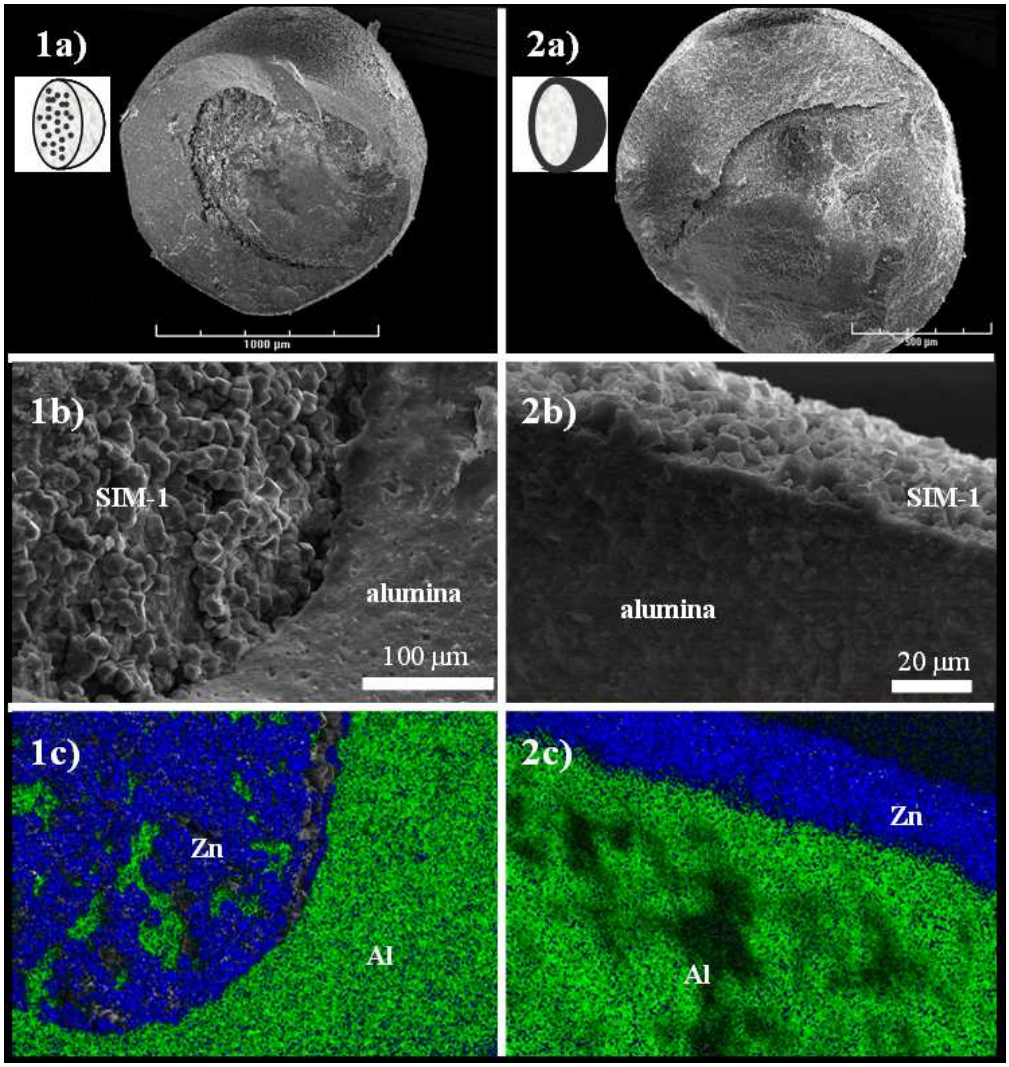

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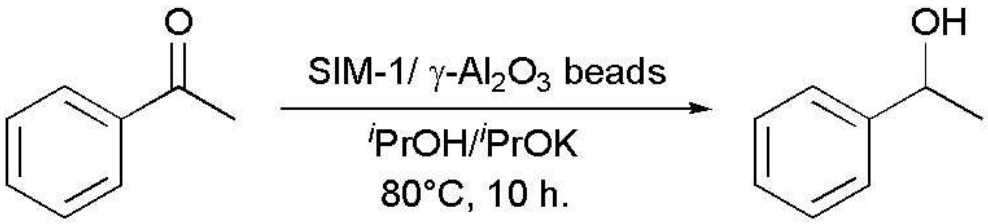

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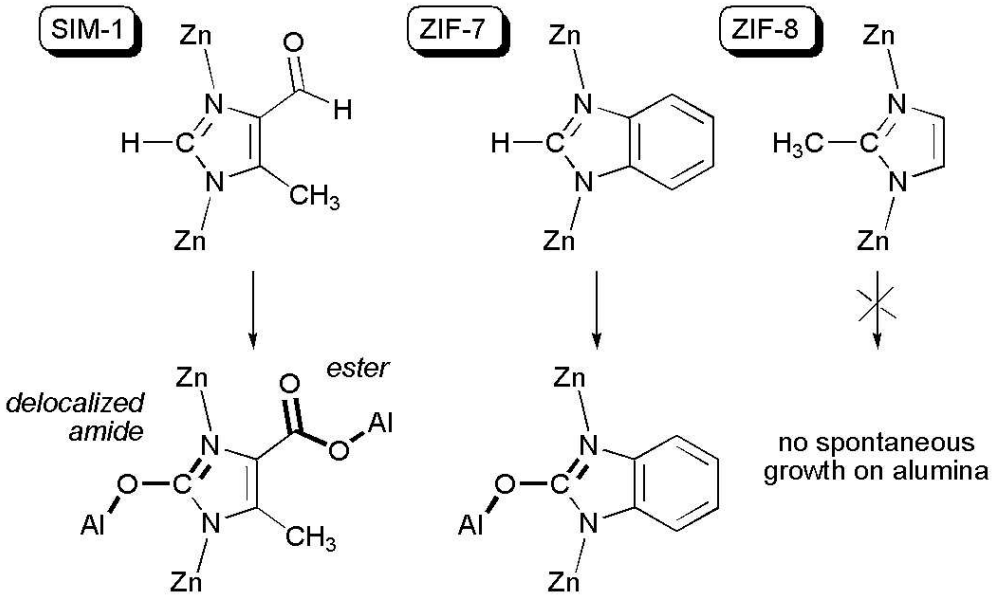

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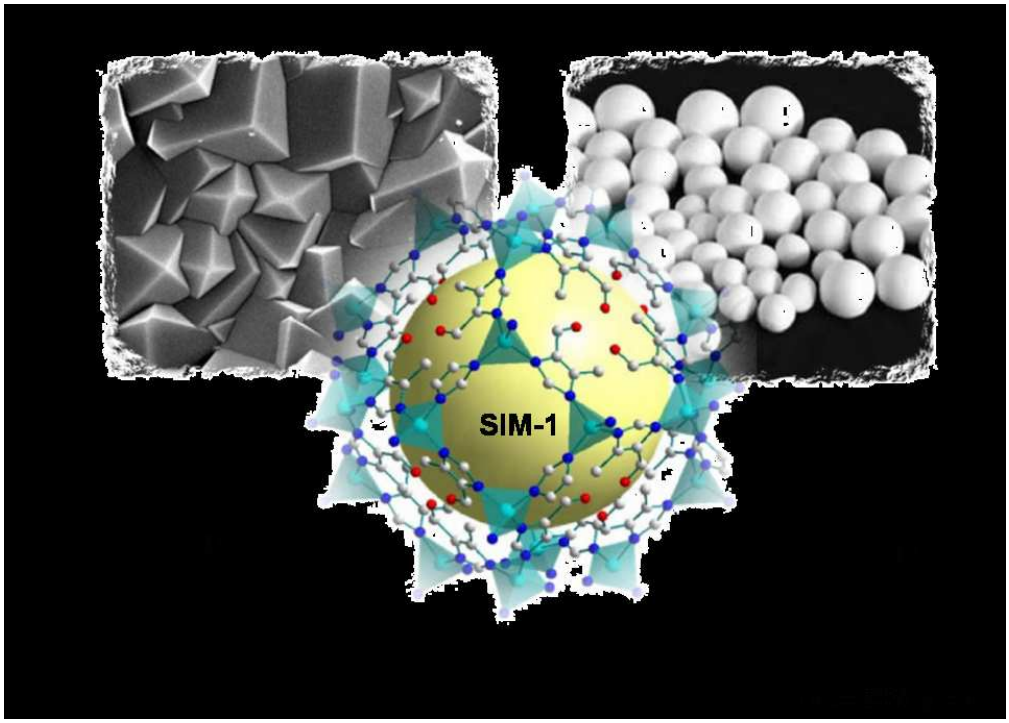

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