## Supporting information

# Snowflake Porous Multi-Metal Oxide Nanocatalysts from Metallocene@Metal Organic Framework Precursors

Ignacio Luz\*, Sameer Parvathikar, Michael Carpenter, Brittany Grillo, John Carpenter and Marty Lail

RTI International, 3040 E. Cornwallis Rd, Research Triangle Park, NC 27709-2194.

#### Material synthesis and characterization

Metallocene@MIL-53 precursors were synthetized according to literature<sup>1</sup>.

 $N_2$  sorption isotherms. The samples were analysed in a Micromeritics ASAP (Accelerated Surface Area and Porosimetry) 2020 System. Samples were weighted into tubes with seal frits and degassed under vacuum (<500 μm Hg) with heating. Samples were initially heated at 150 °C and held for 4 h, and finally cooled to room temperature and backfilled with N<sub>2</sub>. The samples were re-weighted before analysis. The analysis adsorptive was N<sub>2</sub> at 77 K. A multi-point BET surface area was determined from 6 measurements at relative pressures (P/P<sub>0</sub>) ranging from 0.05 to 0.30. Single point adsorption total pore volume was measured near saturation pressure (P<sub>0</sub> ≈ 770 mmHg). Adsorption average pore width was also calculated. Pore size distribution plot was determined by Horvath-Kawazoe method using the Cylinder Pore Geometry (Saito-Foley) with Cheng-Yang Correction.

**X-ray diffraction.** XRD was used to study the crystalline structure of the MOF catalyst. XRD patterns were recorded using a Panalytical Empyrean X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda$ =1.54778 Å). The samples were prepared by filling the holder with the dry powder. Crystalline phase stability was investigated using an XRK900 high temperature oven chamber. Sample was first heated in the chamber from 25 °C to 800 °C with a heating rate of 3 °C/min. Diffraction patterns were measured throughout the whole heat treatment using Cu K $\alpha$  X-ray radiation with a wavelength of 1.5418 Å and a 20 range of 4.5°– 60°. Each pattern was measured for 4 min using a step size and count time of 20 = 0.0263° and 147 s/step, respectively.

**CO** Chemisorption. CO chemisorption analyses were performed using an AutoChem II 2920 reactor (Micromeritics) equipped with a built-in TCD detector. Samples were activated at 350 °C under 10% H2/He and were measured under CO at 35 °C.

**Transmission electron microscopy (TEM)**. TEM experiments were performed in a JEOL JEM-2000FX S/TEM microscope with LaB6 emitter at 200kV with a 120  $\mu$ m condenser lens aperture and 80  $\mu$ m objective lens aperture inserted. STEM-HAADF images were acquired in a FEI Titan 80-300 probe aberration corrected scanning transmission electron microscope (STEM) with monochromator.

**Catalyst testing.** The catalytic performance for ammonia synthesis was tested in a Micromeritics PID Effi Microreactor. The Microreactor is a stand-alone, fully automated system with inlet gas flows metered through mass flow controllers. Feed gases consisted of nitrogen and hydrogen, with argon used as an internal standard. The reactor consisted of a 9mm stainless-steel tube in a furnace. The reactor and the furnace are contained in a hot box, with pressure controlled downstream by a back-pressure regulator. Pressure, temperature, and gas flow rates were all controlled by the Microreactor's process control software. The catalyst was diluted with silicon carbide (SiC) in a 1:22 ratio and was placed between two beds of SiC in the reactor, such that the reactor thermocouple was in the middle of the catalyst bed. All catalysts were reduced in 75%  $H_2/25\%$   $N_2$  at 470 °C for 16 h, prior to catalytic activity tests at 95 bar. Downstream of the reactor system, the composition of the process gases was analysed by gas chromatography (for quantifying nitrogen, hydrogen, and argon) and MKS MultiGas FTIR Continuous Gas Analyzer (for quantifying ammonia).



Scheme 1. Generality of the approach metallocene@MOF precursor to multimetal oxide catalysts.



**Figure S1.** TGA in nitrogen for  $\operatorname{FeCp}_2(AI)$ MIL-53 compared to  $\operatorname{FeCp}_2$  and (AI)MIL-53.

	% Al	% M	M : Al ratio			
FeCp_@(Al)MIL-53	25.9	17.3	1 Fe: 3 Al			
NiCp @(Al)MIL-53	30.1	17.5	1 Ni: 3.75 Al			

31.0

22.2

1 Co : 3 Al

CoCp\_@(AI)MIL-53

#### Table S1. ICP analysis.



Figure S2. Thermo-XRD analysis for FeCp<sub>2</sub>@(AI)MIL-53 at increasing temperatures under air.



Figure S3. XRD phase analysis for  $FeCp_2@(AI)MIL-53$  treated at different temperatures under air compared to  $FeAl_2O_4$  spinel.



Visible	Ref. Code	Score	Compound	Displacement	Scale Factor	Chemical
			Name	[°2Th.]		Formula
*	01-080-5414	17	Iron Oxide	0.000	0.520	Fe2 O3
*	04-014-4971	15	Iron Oxide	0.000	0.503	Fe3 O4
*	04-002-4945	21	Iron Aluminum Oxide	0.000	0.260	Fe1.53 Al0.47 O3
*	01-071-4915	13	Iron Aluminum Oxide	0.000	0.192	Fe Al2 O4
*	04-012-6907	18	Aluminum Oxide	0.000	0.475	Al2 O3

Figure S4. XRD phase analysis for FeCp $_2$ @(Al)MIL-53 treated at 500  $^{\circ}$ C under air.



**Figure S5.** FTIR spectra for FeCp<sub>2</sub>@(AI)MIL-53 treated at increasing temperatures under air compared to bare (AI)MIL-53.



**Figure S6.** DRIFT for FeCp<sub>2</sub>@(AI)MIL-53 and bare (AI)MIL-53 treated at 300  $^{\circ}$ C under air and measured after treating under nitrogen at 200  $^{\circ}$ C.



Figure S7. TEM images for FeCp<sub>2</sub>@(AI)MIL-53 and bare (AI)MIL-53 treated at 300 °C under air.



100 nm

**Figure S8.** TEM images for FeCp<sub>2</sub>@(AI)MIL-53 treated at increasing temperatures under air.



Figure S9. TEM images for  $FeCp_2@(AI)MIL-53$  treated at 500 °C under air.



Figure S10. HAADF-STEM-EDS analysis for FeCp<sub>2</sub>@(AI)MIL-53 treated at 280 °C under air.



**Figure S11.** HAADF-STEM-EDS analysis for FeCp<sub>2</sub>@(AI)MIL-53 treated at 400 °C under air.



Figure S12. TGA in air for metallocene@(AI)MIL-53.



Figure S13. FTIR for different metallocene@(AI)MIL-53.



Figure S14. XRD for different metallocene@(AI)MIL-53 at different treatment temperatures under air.



Figure S15. TEM images for different metallocene@(AI)MIL-53 treated at 500 °C under air.



**Figure S16.** TGA in air for NiCp<sub>2</sub>@(Al)MIL-53 and NiCp<sub>2</sub>@(Fe)MIL-53.



**Figure S17.** TEM images for NiCp<sub>2</sub>@(Al)MIL-53, NiCp<sub>2</sub>@(Fe)MIL-53, and (Fe)MIL-53 treated at 500 °C under air. Note that (Fe)MIL-53 without NiCp<sub>2</sub> sinters into large particles.



**Figure S18.** TEM images for second metallocene loading (NiCp<sub>2</sub>) on FeCp<sub>2</sub>@(AI)MIL-53<sub>300C</sub> after two treatment temperatures under air: 300 °C and 500 °C.



Figure S19. HAADF-STEM-EDS analysis for NiCp<sub>2</sub>@[FeCp<sub>2</sub>@(AI)MIL-53<sub>300C</sub>]<sub>500C</sub>.

**Table S2.** Surface area, Fe loading and CO chemisorption data for some Fe catalysts compared to MOFderived Fe catalyst.

SAMPLE	Fe%	CO (µmol g <sub>cat</sub> <sup>-1</sup> )	Fe dispersion (%)	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Ref.
FeCp@MOF	17.3	33	2%	287	This work
Commercial Fe catalyst	64	0.04	<0.1	<1	This work
FeO /γ-Al O	3.3	16.3	6.2%	168	2
FeO /SiO	3.2	4.3	2%	218	2



**Figure S20.** Ammonia synthesis activity and stability demonstrated on MOF-derived  $FeCp_2@MOF$  catalysts (promoted with 2wt.% K, 2wt.% Ca) and compared with commercial Fe catalysts from United Catalysts Inc. All tests reported here were carried out at 95 barg with a feed gas composition of 75%H<sub>2</sub>/25% N<sub>2</sub> at a gas hourly space velocity of 60,000 h<sup>-1</sup> to ensure operation away from equilibrium.



**Figure S21:** (left) N<sub>2</sub> sorption isotherms and pore distribution plot for FeCp<sub>2</sub>@(Al)MIL-53 prepared at 500 °C compared to commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. (right) TPR-H<sub>2</sub> for FeCp<sub>2</sub>@(Al)MIL-53 prepared at 500 °C.

### References

(1) Meilikhov, M.; Yusenko, K.; Fischer, R. A. The adsorbate structure of ferrocene inside [al(oh)(bdc)]x (mil-53): A powder x-ray diffraction study. Dalton Trans. 2009, (4), 600-602,

(2) Mosallanejad, S.; Dlugogorski, B. Z.; Kennedy, E. M.; Stockenhuber, M. On the chemistry of iron oxide supported on γ-alumina and silica catalysts. ACS Omega 2018, 3 (5), 5362-5374,