### Size Effect of the Active Sites in UiO-66 Supported Nickel Catalysts Synthesized *via* Atomic Layer Deposition for Ethylene Hydrogenation

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#### **Experimental Methods**

Zirconyl chloride octahydrate, acetic acid, hydrochloric acid, hydrogen peroxide, high purity silica, nickel and zirconium ICP standards were purchased from Sigma Aldrich Chemicals Company, Inc. (Milwaukee, WI) and were used as received. The used MOF UiO-66 is synthesized *via* a reported procedure.<sup>1</sup> Concentrated sulfuric acid was purchased from VWR Scientific, LLC (Chicago, IL). Compound *bis*(N,N'-*di*-Butyl-acetamidinato)Ni(II) (98%) was obtained from Strem Chemicals, and used without further purification. Acetone, N,N-dimethylformamide (DMF) were obtained from Fisher Scientific and used without further purification. Ultrapure deionized water (18.2 MB•cm resistivity) was obtained from a Millipore Milli-Q Biocel A10 instrument (Millipore Inc., Billerica, MA).

All gases used for the adsorption and desorption measurements were Ultra High Purity Grade 5 and they were obtained from Airgas Specialty Gases (Chicago, IL).

Atomic layer deposition of Ni in UiO-66 was carried out on a Savannah 100 (Cambridge Nanotech, Inc).

Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku X-ray Diffractometer Model ATX-G (Tokyo, Japan) equipped with an 18 kW Cu rotating anode, an MLO monochromator, and a high-count-rate scintillation detector. Measurements were made over the range  $5^{\circ} < 2\theta < 60^{\circ}$  in 0.05° step width with a 3°/min scanning speed.

 $N_2$  adsorption and desorption isotherms were measured on a Micromeritics Tristar II 3020 (Micromeritics, Norcross, GA) instrument at 77 K. Pore-size distributions were obtained using DFT calculations using a carbon slit-pore model with a  $N_2$  kernel. Before each run, samples were activated at 120 °C for 12–24 h under high vacuum on a Smart Vacprep. Around 30 mg of sample was used in each measurement and BET surface area was calculated in the region  $P/P_0 = 0.005-0.05$ .

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was conducted on an iCAP<sup>TM</sup> 7600 ICP-AES Analyzer (Thermo Scientific<sup>TM</sup>) over the 166–847nm spectral range. Samples (2–3 mg) were digested in a small amount (1 mL) of a mixture of 3:1 v/v conc.  $H_2SO_4:H_2O_2$  (30 wt % in  $H_2O$ ) by heating in a Biotage (Uppsala, Sweden) SPX microwave reactor (software version 2.3, build 6250) at 150 °C for 5 minutes. The acidic solution was then diluted to a final volume of 15 mL with Millpore  $H_2O$  and analyzed for Ni (221.647, 231.604 and 341.476 nm) and Zr (327.305, 339.198, and 343.823 nm) content as compared to standard solutions.

Scanning electron microscopy (SEM) images were collected on a Hitachi SU8030 FE-SEM (Dallas, TX) microscope at Northwestern University's EPIC/NUANCE facility.

Diffuse reflectance infrared Fourier transform spectra (DRIFTS) were recorded on a Nicolet 6700 FTIR spectrometer (Thermo Scientific) equipped with an MCT detector and a Harrick praying mantis accessory. Samples were activated at 120 °C under high vacuum for 24 h before each measurement. The spectra were collected at 1 cm<sup>-1</sup> resolution over 64 scans.

Diffuse reflectance ultraviolet-visible spectra were recorded on a Shimadzu 3600 UV-visible-NIR spectrophotometer equipped with a Harrick praying mantis accessory. Spectra were collected from 500–1000 nm with a 3 nm slit width and 1 nm sample interval. Teflon was used a white light standard.

Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 in a flow of  $N_2$  at a heating rate of 10 °C/min from 25 to 600 °C.

X-ray photoelectron spectroscopy (XPS) measurements were carried out at the KECK-II/NUANCE facility at NU on a Thermo Scientific ESCALAB 250 Xi (Al K $\alpha$  radiation, hv = S5 1486.6 eV) equipped with an electron flood gun. XPS data was analyzed using Thermo Scientific Avantage Data System software and all spectra were referenced to the C1s peak (284.8 eV).

Catalyst activity and selectivity measurements were recorded using a packed-bed flow reactor (Microactivity Efficient, MAE). Using an Agilent 7890A GC system, the amount of ethylene and ethane were analyzed by an FID detector using an Agilent J&W GC column (GS-Alumina, 30 m X 0.535 mm).

Ni-AIM+UiO-66 1 Cycle: Compound *bis*(N,N'-diiso-butyl-acetamidinato)Ni(II), Ni(MeC(N*i*-Bu)<sub>2</sub>)<sub>2</sub> (reactant A), was chosen as the Ni precursor from our previous work for Ni-AIM+NU-1000.<sup>2</sup> Room temperature deionized H<sub>2</sub>O is used as the co-reactant (reactant B) to produce the Ni–O(H) motif. In a typical experiment, a custom-made stainless steel powder sample holder containing microcrystalline UiO-66 (60.0 mg, 0.037 mmol) was placed in the ALD chamber, which was held at 125 °C for 30 min to remove any physisorbed water before dosing with the Ni precursor. A cylinder containing Ni(MeC(N*i*-Bu)<sub>2</sub>)<sub>2</sub> is held at 120 °C, and each of its pulses followed the time sequence of  $t_1-t_2-t_3$ , where  $t_1$  is the precursor pulse time,  $t_2$  is the substrate exposure time, and  $t_3$  is the N<sub>2</sub> purge time ( $t_1 = 1 \text{ s}, t_2 = t_3 = 300 \text{ s}$ ). To ensure full metalation of the Zr<sub>6</sub> sites throughout the microcrystals, the NiMeC(N*i*-Bu)<sub>2</sub>)<sub>2</sub> pulsing cycle was run 100× before exposing the MOF to H<sub>2</sub>O pulses, which adopts the same time sequence as the Ni pulse ( $t_1 = 0.015 \text{ s}, t_2 = t_3 = 120 \text{ s}$ ).

Ni-AIM+UiO-66 2 Cycles and Ni-AIM+UiO-66 3 Cycles: They are synthesized in a similar fashion where the AB cycle is repeated two and three times, respectively.



**Figure S1.** Structural representation of the used Ni precursor, bis(N,N'-di-tertbutyl-acetamidinato)nickel(II), Ni(MeC(Nt-Bu)<sub>2</sub>)<sub>2</sub>.



Figure S2. TGA profile for the three UiO-66 supported Ni materials as well as that for UiO-66.



Figure S3. DRIFTS of the three UiO-66 supported Ni materials, as compared to the assynthesized UiO-66.



**Figure S4**. (a)-(c) SEM images of the as-synthesized Ni-AIM+UiO-66 1 Cycle, 2 Cycles and 3 Cycles sample and (d) SEM-EDS result from the Ni-UiO-66 1 Cycle sample.



**Figure S5**. Diffuse reflectance UV-Vis spectra of the three Ni-AIM+UiO-66 samples and the nickel-free MOF.



**Figure S6**. Plots of percent conversion versus W/F or determination of TOFs for Ni-AIM+UiO-66 1 Cycle, Ni-AIM+UiO-66 2 Cycles and Ni-AIM+UiO-66 3 Cycles for ethylene hydrogenation catalysis at 100 °C, 1.5 bar total pressure.



**Figure S7**. Stability test as well as the regeneration test of the three UiO-66 supported Ni catalysts for ethylene hydrogenation catalysis.

**Table S1**. The mol ratio between Ni and Zr probed by different techniques at different sampling depths. The indicated etching depth of 5 nm is based on instrument calibration for hard, nonporous materials. The true etching depth is likely greater.

		ICP-AES (bulk)	XPS (surface)	XPS (~5 nm etching)
Ni-AIM+UiO-66 1 Cycle	e	0.18	2.6	0.25
Ni-AIM+UiO-66 Cycles	2	0.22	6.1	0.39
Ni-AIM+UiO-66 Cycles	3	0.27	12	1.5



Figure S8. PXRD patterns of the three UiO-66 supported Ni samples recovered after catalysis.



Figure S9. (a)-(c) SEM images of Ni-AIM+UiO-66 1 Cycle, 2 Cycles and 3 Cycles recovered after catalysis.



Figure S10. N<sub>2</sub> isotherms of recovered UiO-66 supported Ni catalysts after catalysis.



**Figure S11**. Comparison of the pore size distribution of the three UiO-66 supported Ni catalysts before and after catalysis.

#### References

- 1. H. G. T. Nguyen, N. M. Schweitzer, C. Y. Chang, T. L. Drake, M. C. So, P. C. Stair, O. K. Farha, J. T. Hupp and S. T. Nguyen, *ACS Catal.*, 2014, **4**, 2496-2500.
- Z. Li, N. M. Schweitzer, A. B. League, V. Bernales, A. W. Peters, A. Getsoian, T. C. Wang, J. T. Miller, A. Vjunov, J. L. Fulton, J. A. Lercher, C. J. Cramer, L. Gagliardi, J. T. Hupp and O. K. Farha, *J. Am. Chem. Soc.*, 2016, **138**, 1977-1982.