Bridging Zirconia Nodes within a Metal–Organic Framework via Catalytic Ni-hydroxo Clusters to Form Hetero-Bimetallic Nanowires

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Synthesis

Zirconyl chloride octahydrate, acetic acid, hydrochloric acid, hydrogen peroxide, high purity silica, nickel and zirconium ICP standards were used as received from Sigma Aldrich Chemicals Company, Inc. (Milwaukee, WI). Concentrated sulfuric acid was purchased from VWR Scientific, LLC (Chicago, IL). *bis*(N,N'-*di*-Butyl-acetamidinato)Ni(II) (98%) was used as obtained from Strem Chemicals. Acetone and N,N-dimethylformamide (DMF) were used as obtained from Fisher Scientific. Ultrapure deionized water (18.2 MB•cm resistivity) was obtained from a Millipore Milli-Q Biocel A10 instrument (Millipore Inc., Billerica, MA). NU-1000 was synthesized *via* a reported procedure.[1]

Atomic layer deposition of Ni in NU-1000 was carried out on a Savannah 100 (Cambridge Nanotech, Inc). *Bis*(N,N'-diiso-butyl-acetamidinato)Ni(II), $Ni(MeC(N\textit{i}\text{-}Bu)_2)_2$ (reactant A), was chosen as the Ni precursor.[2] Room temperature deionized H_2O was 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 NU-1000 (30.0 mg, 0.014 mmol) was placed in the ALD chamber. The sample was held at 125 °C for 30 min before exposure to reagents to remove physisorbed water. *"A" cycle*: a cylinder containing $Ni(MeC(N\textit{i}\text{-}Bu)_2)_2$ was 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_2 purge time (t_1 = 1 s, $t_2 = t_3$ = 300 s). To ensure full metalation of the Zr_6 sites throughout the microcrystals, the $NiMeC(N\textit{i}\text{-}Bu)_2)_2$ pulsing cycle was run 50 times. *"B" cycle:* The sample was subsequently exposed to H_2O pulses for 20 times, using the same time sequence as the Ni pulse (t_1 = 0.015 s, $t_2 = t_3$ = 120 s). For 1, 2, and 3 cycle Ni-AIM the "A"+"B" sequence was repeated 1, 2, and 3 times, respectively. Following the ALD, the samples were thermally activated at 120 °C for 12–24 h under high vacuum on a Smart Vacprep from Micromeritics.

Inductively coupled plasma–atomic emission spectroscopy (ICP–AES) was conducted on an iCAP™ 7600 ICP-AES Analyzer (Thermo Scientific™) 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 10 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.

Surface Area and Pore Analyses: N_2 adsorption and desorption isotherms were measured on a Micromeritics Tristar II 3020 (Micromeritics, Norcross, GA) instrument at 77 K. All gases were Ultra High Purity Grade 5 obtained from Airgas Specialty Gases (Chicago, IL). Pore-size distributions were obtained using DFT calculations using a carbon slit-pore model with a N2 kernel. Before each run, samples were activated at 120 °C for 12–24 h under high vacuum on a Smart Vacprep from Micromeritics. 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.

Brunauer–Emmett–Teller (BET) analysis of the N_2 isotherms of activated samples (120 °C, evacuated for 12 h) indicates surface areas of 2300, 1450, 1130 and 925 $m^2 \cdot g^{-1}$ for NU-1000 and Ni-AIM after 1, 2 and 3 ALD cycles, respectively, in agreement with our previous work (Figure S1).[3] These correspond to surface areas of 2300, 1725, 1560, and 1450 $m^2 \cdot g^{-1}$ normalized per gram of NU-1000 (based 4, 8 and 12 Ni deposited per node).

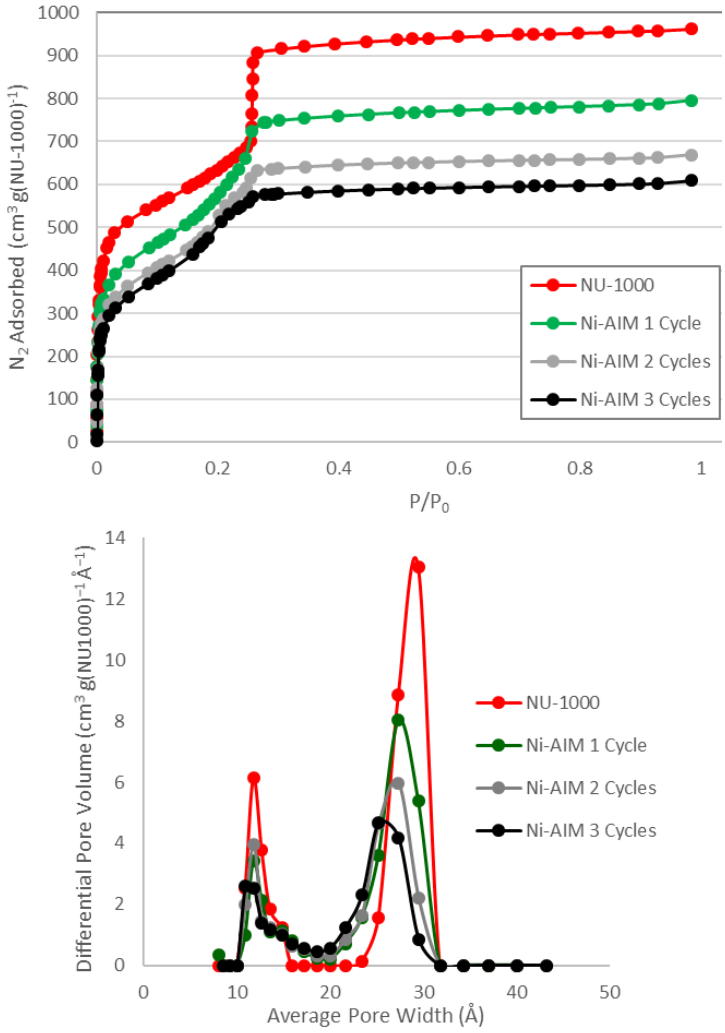

Figure S1. N_2 isotherms (top) and pore distributions (bottom) within NU-1000 and Ni-AIM. The data for the Ni-AIM samples are normalized per gram of NU-1000.

X-ray Absorption Spectroscopy

Transmission geometry XAS measurements were performed at 10-ID and 20-BM at the Advanced Photon Source at Argonne National Laboratory. Ni K-edge XAFS spectra were acquired using 12 min (k = 18 Å^{-1}) acquisition times. At 10-ID,[4] *in situ* XAS measurements were performed under flow conditions using a high temperature cell described previously;[5] data were collected at the Ni and Zr K-edges. At 20-BM, *in situ* XAS measurements were performed under batch conditions at 50 bar using a micro-reactor cell[6]. The data analysis and background removal were performed within ATHENA and ARTEMIS.[7] The Fourier transform of the k-space EXAFS data were fitted to theoretical models derived using the FEFF9 code.[8]

Zr-EXAFS analysis and comparison of NU1000 to Ni-AIM following 1, 2, and 3 ALD cycles

Zr-EXAFS measurements were performed to determine the structural changes occurring in the node of NU1000 of 1, 2, and 3 ALD cycles. The Zr-EXAFs spectra are shown in Figure S1. The Img[χ(R)] and k^2-χ(k) spectra of k^2-weighted fits and experimental data of NU1000 and Ni-AIM samples are presented in Figures S2-S5. The obtained parameters from the FEFF fit are listed in Table S1. Change in the coordination numbers of Zr-Zr and Zr-O bonds after Ni deposition indicates the node distortion.

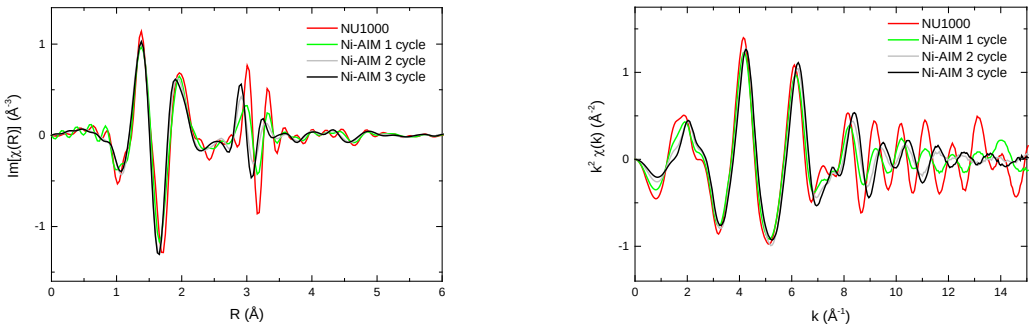

Figure S2. The k^2-weighted Zr-EXAFS Img[χ(R)] (left) and k^2-χ(k) Zr-EXAFS spectra (right) of NU1000 and Ni-AIM following 1, 2, and 3 ALD cycles.

Table S1. Coordination numbers [a] from K_2-weighted fit of the Zr-K-edge data collected at 10-ID.

	Zr-O (2.14 Å)	Zr-O (2.28 Å)	Zr-Zr (3.39 Å)	Zr-Zr (3.517 Å)
NU-1000	4	4	—	4
1Ni-AIM	4.5	3.2	1.1	2.9
2Ni-AIM	5.2	2.8	1.9	2.1
3Ni-AIM	5.4	2.4	2.7	1.3

[a]Absolute uncertainty is approximately 15%.

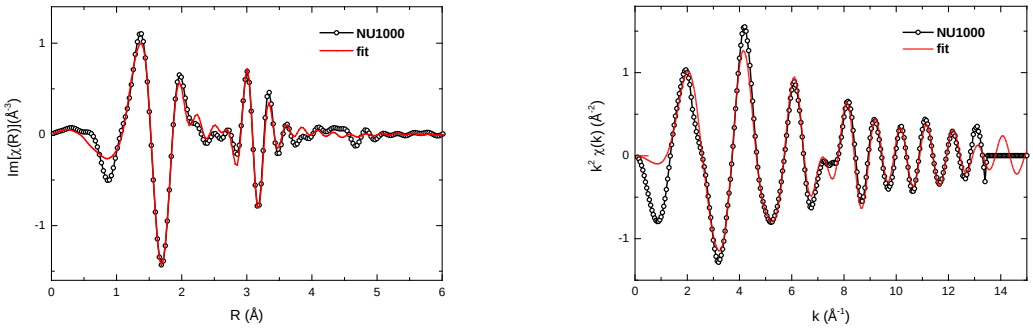

Figure S3. The k^2-weighted Zr-EXAFS Img[χ(R)] and k^2-χ(k) spectra of NU1000 (black) and the FEFF fitted spectra (red).

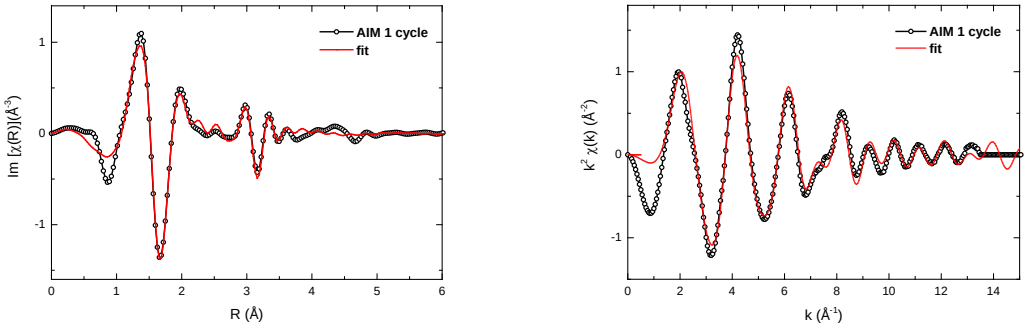

Figure S4. The k^2-weighted Zr-EXAFS Img[χ(R)] and k^2-χ(k) spectra of Ni-AIM 1 cycle (black) and the FEFF fitted spectra (red).

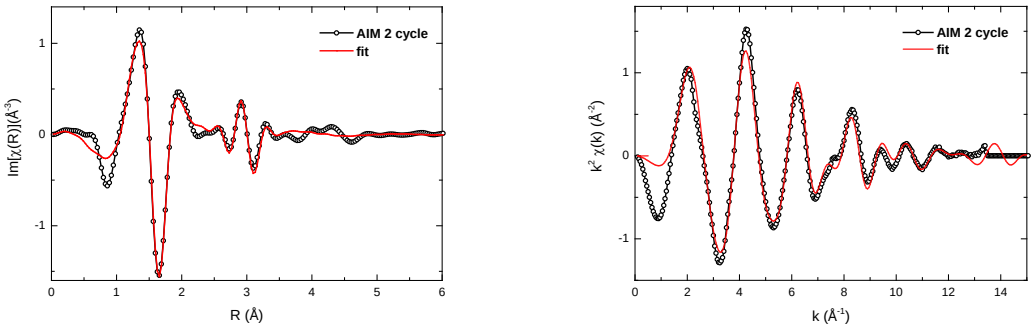

Figure S5. The k^2-weighted Zr-EXAFS Img[χ(R)] and k^2-χ(k) spectra of Ni-AIM 2 cycle (black) and the FEFF fitted spectra (red).

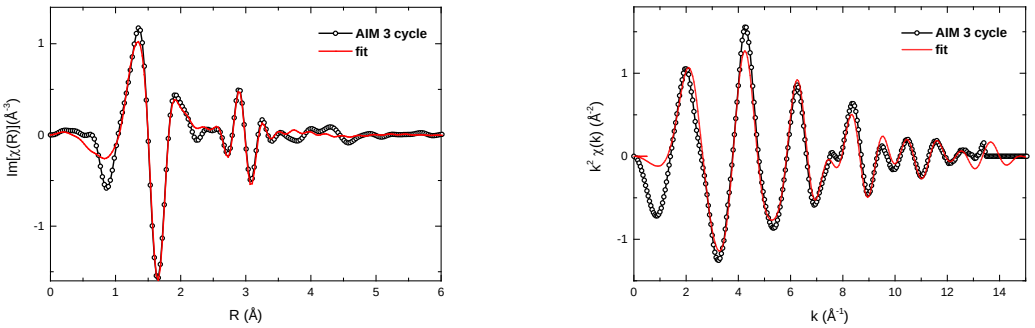

Figure S6. The k^2-weighted Zr-EXAFS Img[χ(R)] and k^2-χ(k) spectra of Ni-AIM 3 cycle (black) and the FEFF fitted spectra (red).

Ni-EXAFS fits of standards and Ni-AIM following 1, 2, and 3 ALD cycles

Table S2. Parameters from a k^2-weighted fit of the EXAFS data collected at 10-ID.

	1 cycle	1 cycle (activated)	2 cycle	3 cycles
Ni-O				
d/Å	2.046(2)	2.033(2)	2.047(3)	2.049(2)
CN	5.4(2)	4.9 (2)	5.3(2)	5.4(2)
DWF	0.0077(7)	0.0084 (6)	0.0078(7)	0.0085(8)
Ni…Ni				
d/Å	3.035(9)	2.997(10)	3.030(7)	3.021(5)
CN	2.9(8)	3.6(1.1)	4.4(1.0)	5.4(9)
DWF	0.0145(32)	0.0193(33)	0.0149(24)	0.0161(20)

d = distance, CN = coordination number. The passive electron reduction factor (S02) and E-shift (E_0) are fixed to 0.88 and -8.15 based on the average value from α-$Ni(OH)_2$ and Ni foil standards. The relative uncertainties in CN are reported; absolute uncertainty is at least 15%.

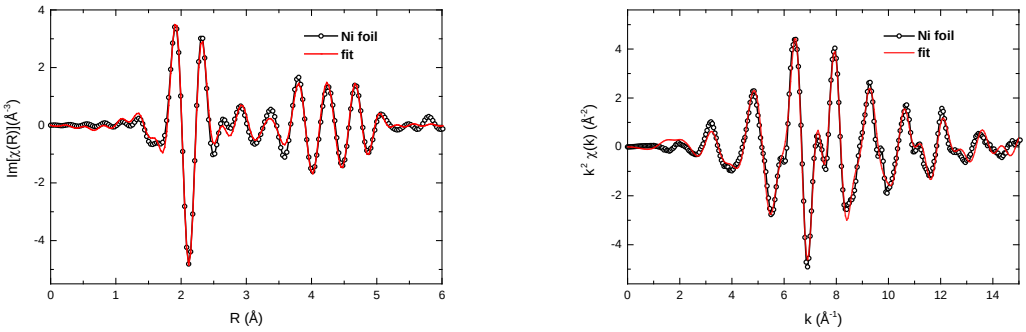

Figure S7. The k^2-weighted Ni-EXAFS Img[χ(R)] and k^2-χ(k) spectra of Ni foil standard (black) and the FEFF fitted spectra (red).

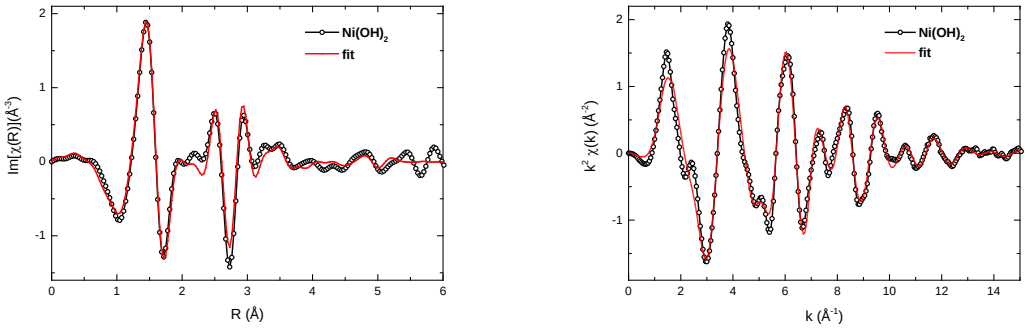

Figure S8. The k^2-weighted Ni-EXAFS Img[χ(R)] and k^2-χ(k) spectra of $Ni(OH)_2$ standard (black) and the FEFF fitted spectra (red).

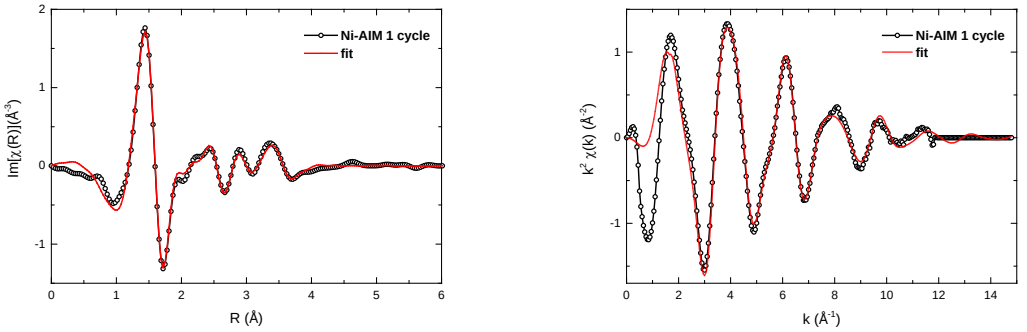

Figure S9. The k^2-weighted Ni-EXAFS Img[χ(R)] and k^2-χ(k) spectra of Ni-AIM 1 cycle (black) and the FEFF fitted spectra (red).

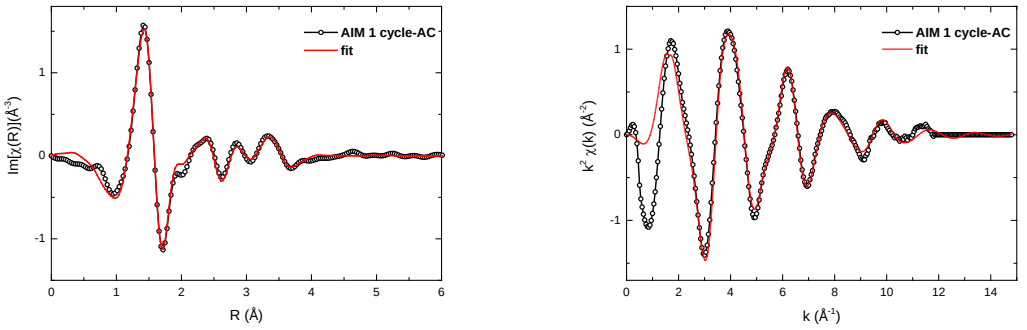

Figure S10. The k^2-weighted Ni-EXAFS Img[χ(R)] and k^2-χ(k) spectra of Ni-AIM 1 cycle-**activated** (black) and the FEFF fitted spectra (red).

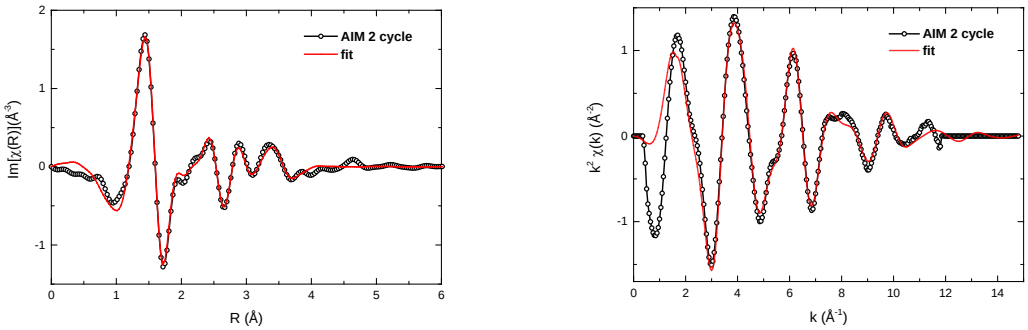

Figure S11. The k^2-weighted Ni-EXAFS Img[χ(R)] and k^2-χ(k) spectra of Ni-AIM 2 cycle (black) and the FEFF fitted spectra (red).

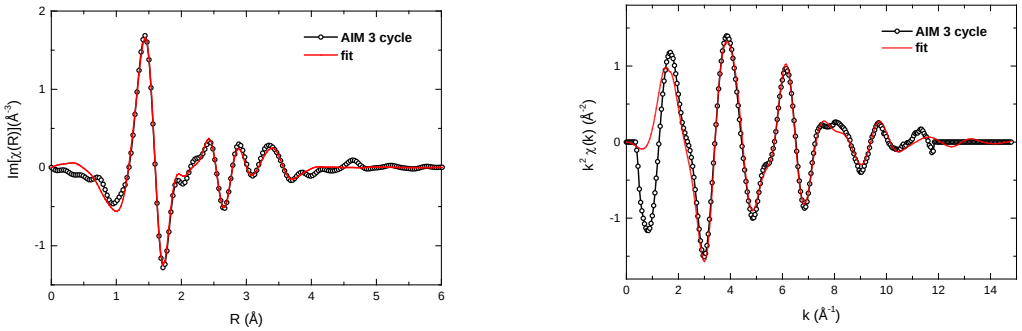

Figure S12. The k^2-weighted Ni-EXAFS Img[χ(R)] and k^2-χ(k) spectra of Ni-AIM 3 cycle (black) and the FEFF fitted spectra (red).

Simultaneously Ni-Zr scattering in Ni-AIM 1 cycle (10-ID data)

The simultaneous fit of the Ni- and Zr-EXAFS data allows analysis of the Ni- and Zr-EXAFS that are independent measurements of the Ni-Zr structure. The Ni-Zr correlations present in the Ni-EXAFS, should be present in the Zr-EXAFS with identical Ni-Zr distance and disorder parameters. Thus, we compare the fits of Ni-AIM EXAFS with and without Zr-Ni paths to see whether the overall fit quality can be improved. We attempted to let all of the Ni-Zr parameters be adjustable, but did not get reasonable values. Subsequently, coordination numbers were assigned based on the simple model (Figure S12) of a Ni_4 cluster bridging two Zr_6 nodes: 2 Ni atoms from Ni_4 cluster are linked to 4 Zr atoms from two different Zr_6 nodes. Similarly, 2 Zr atoms from each Zr_6 node are linked to 1 Ni atom of the Ni_4 clusters. Thus, the coordination numbers for Ni-Zr and Zr-Ni are defined to $CN_{Zr\text{-}Ni} = 0.667\ CN_{Ni\text{-}Zr}$. Thus, we fixed the $CN_{Zr\text{-}Ni}$ to 0.667 and $CN_{Ni\text{-}Zr}$ to 1. The Ni EXAFS was fit to an α-$Ni(OH)_2$ model with one of the second shell Ni atoms substituted by Zr. The Zr EXAFS was fit to the NU1000 model with one of the Zr atoms substituted by Ni. We used the following four protocols: 1) fit without Zr-Ni path, 2) fit with Zr-Ni path, 3) fit with Zr-Ni path with fixed distance (3.26 Å), and 4) fit with Zr-Ni path with fixed both distance (3.26 Å) and DWF (0.008). The parameters determined by the fits are listed in Table S3. We find that the inclusion of a Ni-Zr path does not reduce the chi square (χ^2).

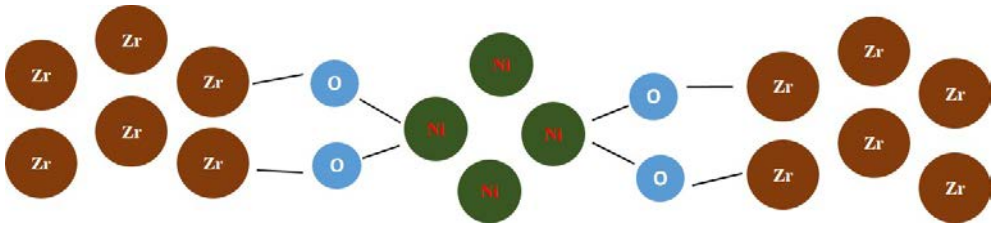

Figure S13: A simple Zr_6-Ni_4 model

Table S3. Average interatomic distances, Debye-Waller-Factors, and reduced χ^2 values from simultaneously fitting the Ni- and Zr-EXAFS k^2-weighted spectra of Ni-AIM 1 cycle.

Fit parameter [a]	Fit without a Ni-Zr path	Fit with a Ni-Zr path	Fit with a Ni-Zr path fixed d to 3.26 Å	Fit with a Ni-Zr path fixed both d and DWF
CN $_{Ni\text{-}O\ (SS)}$	6 (set)	6 (set)	6 (set)	6 (set)
d (Å) $_{Ni\text{-}O\ (SS)}$	2.048	2.048	2.048	2.048
DWF $_{Ni\text{-}O\ (SS)}$	0.0090	0.0091	0.0091	0.0091
CN $_{Ni\text{-}Ni\ (SS)}$	3 (set)	3 (set)	3 (set)	3 (set)
d (Å) $_{Ni\text{-}Ni\ (SS)}$	3.031	3.034	3.032	3.033
DWF $_{Ni\text{-}Ni\ (SS)}$	0.0142	0.0137	0.0142	0.0165
CN $_{Ni\text{-}Zr\ (SS)}$	N/A	1 (set)	1 (set)	1 (set)
CN $_{Zr\text{-}O1\ (SS)}$	3 (set)	3 (set)	3 (set)	3 (set)
d (Å) $_{Zr\text{-}O1\ (SS)}$	2.168	2.168	2.168	2.0167
DWF $_{Zr\text{-}O1\ (SS)}$	0.0071	0.0073	0.0072	0.0069
CN $_{Zr\text{-}O2\ (SS)}$	5 (set)	5 (set)	5 (set)	5 (set)
d (Å) $_{Zr\text{-}O2\ (SS)}$	2.232	2.232	2.233	2.235
DWF $_{Zr\text{-}O2\ (SS)}$	0.0159	0.0155	0.0156	0.0157
CN $_{Zr\text{-}Zr\ (SS)}$	4 (set)	4 (set)	4 (set)	4 (set)
d (Å) $_{Zr\text{-}Zr\ (SS)}$	3.52	3.518	3.515	3.528
DWF $_{Zr\text{-}Zr\ (SS)}$	0.0098	0.0097	0.0099	0.0116
CN $_{Zr\text{-}Ni\ (SS)}$	N/A	0.667 (set)	0.667 (set)	0.667 (set)
d (Å) $_{Zr\text{-}Ni\ (SS)}$	N/A	3.150 ± 0.125	3.26 (set)	3.26 (set)
DWF $_{Zr\text{-}Ni\ (SS)}$	N/A	0.0209 ± 0.0198	0.0336 ± 0.0627	0.008 (set)
Reduced χ^2	1771	1803	1787	1851

[a] CN = average coordination number, SS = single scattering, MS = multiple scattering, d = bond distance, N/A = not available from the fit.

EXAFS spectra for DFT-derived models

To differentiate between the DFT-derived Ni-cluster models, we compare the experimental Ni-EXAFS spectra to the spectra obtained by calculating the Ni scattering paths based on the DFT-optimized models. Vjunov et al. previously reported a conceptually similar approach for the Al-EXAFS analysis of zeolite samples.[9] To generate the EXAFS spectrum of the DFT-optimized structure *first* all of the atom positions and CN's are adopted from the simulated structure. This produces the primary input for the ab initio EXAFS scattering code (FEFF9 code) that includes *all* the single and multiple scattering paths out to 6 Å, e.g. a total of 819 scattering paths for structure in Figure 10a. Next, an approximate treatment of the bond disorder at 300 K is applied by setting a universal value of DWF of 0.003. While this is a good estimate of the first shell disorder, it will tend to overestimate the order in the higher shells that will manifest as slight over-prediction of the amplitudes. The σ^2 could be exactly calculated from ab initio molecular dynamics (MD) as previously described.[9,10] The obtained spectra are then averaged and the E_0 is applied to match experimental values (oscillations in χ(k) converge at k = 0).

Powder X-ray diffraction

Lattice parameters and peak intensities were quantified based on the diffraction data via Le Bail whole-pattern fitting. Structure envelopes were generated using The intensities of low-index reflections.

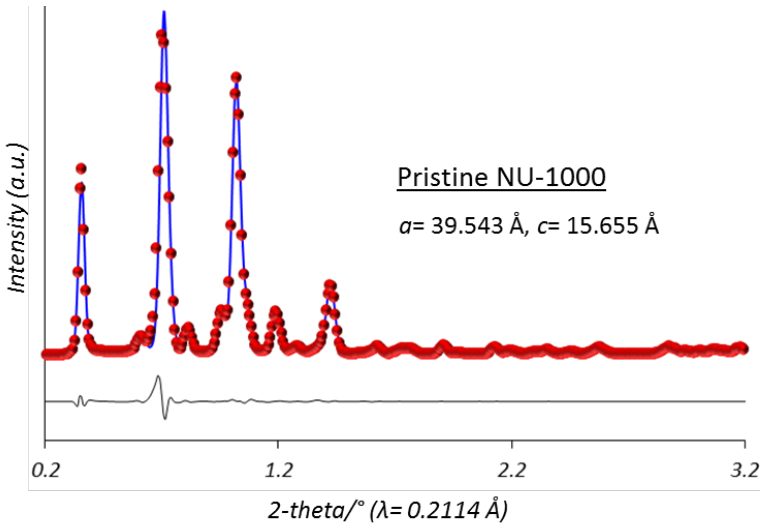

Figure S14. Le Bail whole-pattern fit for pristine NU-1000. Experimental data (red circles), simulated pattern (blue line) and residual (grey line).

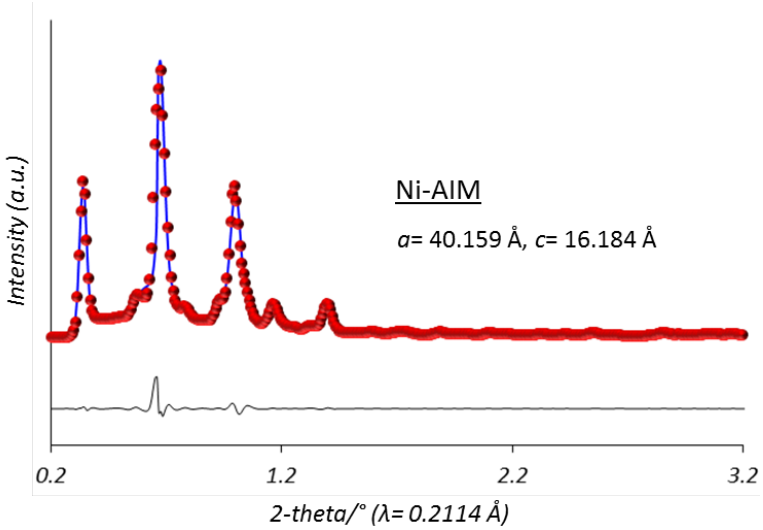

Figure S15. Le Bail whole-pattern fit for fresh Ni-AIM, 1-ALD cycle. Experimental data (red circles), simulated pattern (blue line) and residual (grey line).

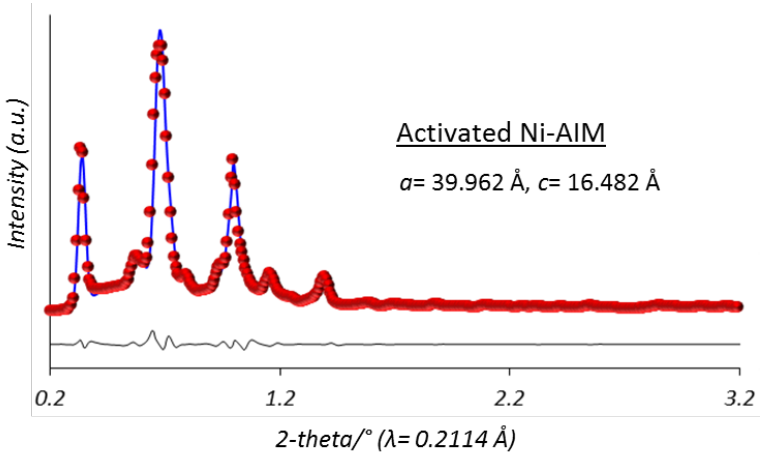

Figure S16. Le Bail whole-pattern fit for activated Ni-AIM, 1-ALD cycle. Experimental data (red circles), simulated pattern (blue line) and residual (grey line).

Pair Distribution Function Analyses

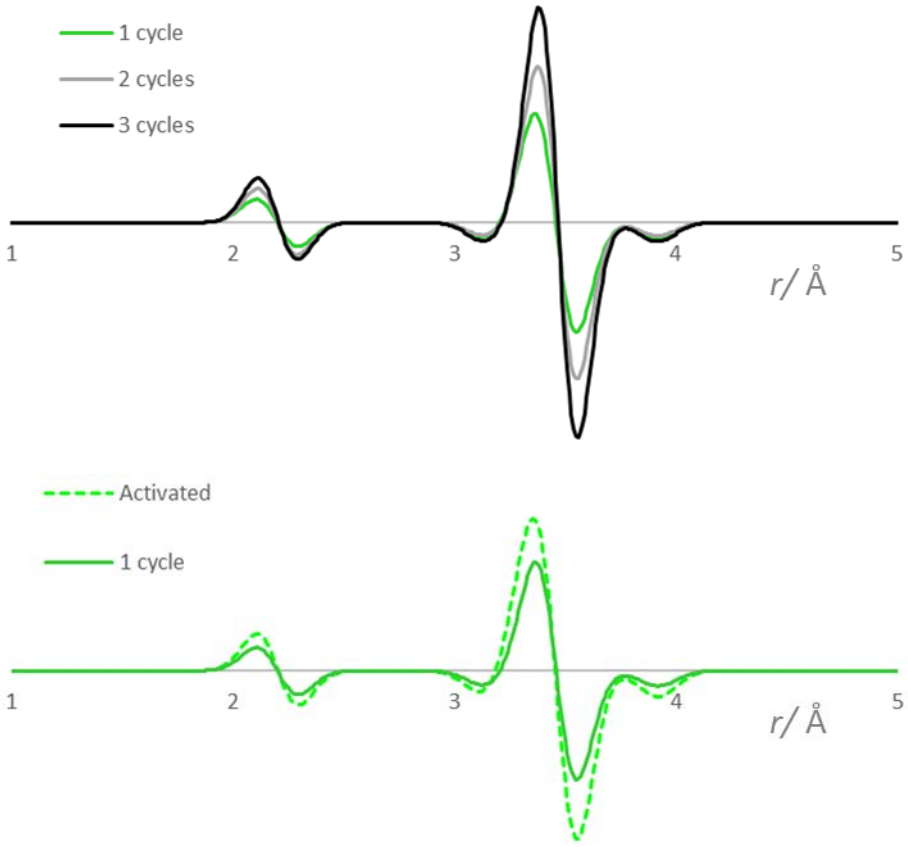

Figure S17: The changes in G(r) associated with changes to the Zr-O and Zr-Zr distances during node distortion based on the Zr K-edge EXAFs fits. These were used to adjust the differential PDFs to separate the contribution from node distortion.

Table S4. Peak positions and areas of the d-PDFs for fresh and activated Ni-AIM (node-distortion corrected)

	Center / Å	Area	Width	Assigned Atom pair	normalized CN
1 cycle, Activated					
Peak 1	2.004	0.664	0.16	Ni-O	6
Peak 2	3.013	1.001	0.26	Ni…Ni (edge), O…O	2.58
Peak 3	3.270	0.576	0.17	Ni…Zr	1.04
1 cycle					
Peak 1	2.032	0.577	0.18	Ni-O	6
Peak 2	3.002	0.670	0.25	Ni…Ni (edge), O…O	1.99
Peak 3	3.267	0.709	0.18	Ni…Zr	1.041
				+ Ni…Ni (corner)	0.62
2 cycles					
Peak 1	2.023	0.911	0.18	Ni-O	6
Peak 2	3.010	1.284	0.27	Ni…Ni (edge), O…O	2.42
Peak 3	3.263	1.026	0.18	Ni…Zr	
3 cycles					
Peak 1	2.008	1.186	0.18	Ni-O	6
Peak 2	3.008	2.466	0.27	Ni…Ni (edge), O…O	4.64
Peak 3	3.254	0.940	0.18	Ni…Zr	

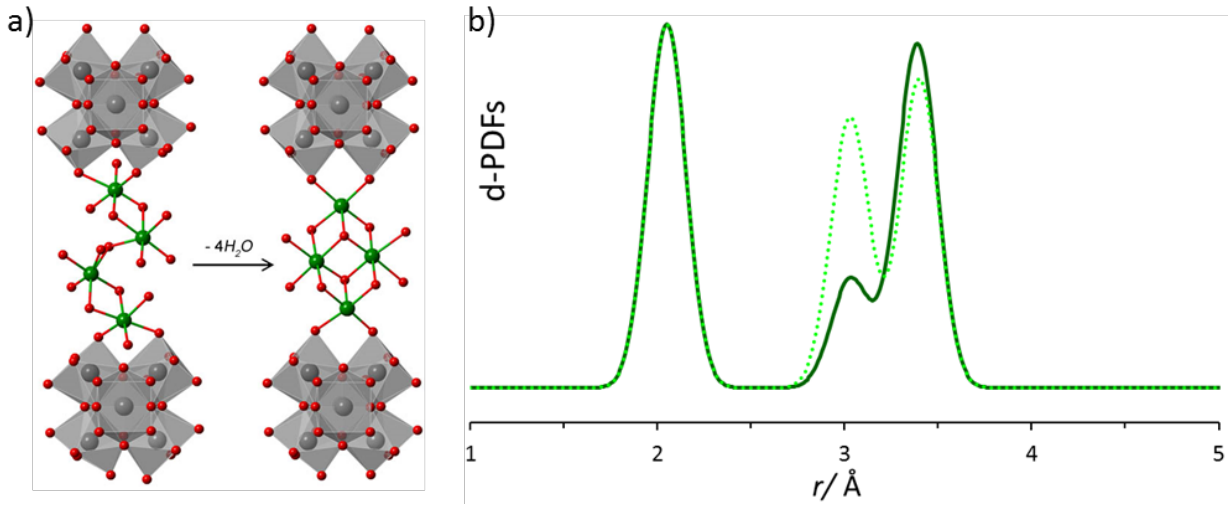

Figure S18. a) A structural mechanism for activation that is consistent with the observed changes to edge sharing Ni…Ni coordination number. b) Calculated d-PDFs for the models proposed before (dot line) and after activation (solid line).

Computational Methods and Models

A variety of Ni clusters were investigated computationally in an effort to reproduce the EXAFS spectra for Ni-NU-1000 and thereby elucidate what species make up the deposited metal. Our preliminary effort built off of our previous work on Ni-NU-1000,[2] where we assumed that two Ni atoms would deposit, one on each of the μ_3-O and μ_3-OH of a node face, and that any additional layers would deposit directly on top of those first two atoms. Following this line of reasoning, we obtained the cubic cluster shown in Figure S16.

Based on our interpretation of the EXAFS spectra, we believed that the Ni–Ni and Ni–Zr distances in Ni-NU-1000 were longer than in the cubic model. We therefore examined clusters which are bound to the node through one Ni atom, which is not bound to a μ_3-O on the node. These model systems are shown in Figure S16.

The relative energies, enthalpies, and free energies of all systems relative to the bare node, free Ni precursors, and free water molecules are shown in Tables S5 and S6. Note that because the AIM process is performed under a flow of gas, it is not clear which standard state would be most useful for the free nickel precursors and water molecules. The free energies reported here assume a standard state of 22.4 L mol^{-1} for all species, and the reader should keep that in mind when drawing conclusions.

The relative enthalpy values for the model systems show a trend where increasing the number of nickel atoms or coordinating oxygen atoms (indicated by the number of water molecules needed to form each cluster) results in increased cluster stability. This trend is unsurprising, considering that the factor that one would expect to most limit cluster growth is the greater entropy that water molecules enjoy when free in solution, rather than trapped in a cluster – a factor not accounted for by the enthalpy values. We therefore reason that, based on these energies alone, none of the clusters can confidently be said to be more stable than the others, and that matching the experimental EXAFS spectra must be the litmus test we use to determine which model or models are closest to reality.[i]

[i] Atoms whose positions were kept fixed do not contribute to the thermal and entropic contributions to the energy (for more details see ref: *J. Phys. Chem. C*, 2013, 117(24), pp 12648–12660).

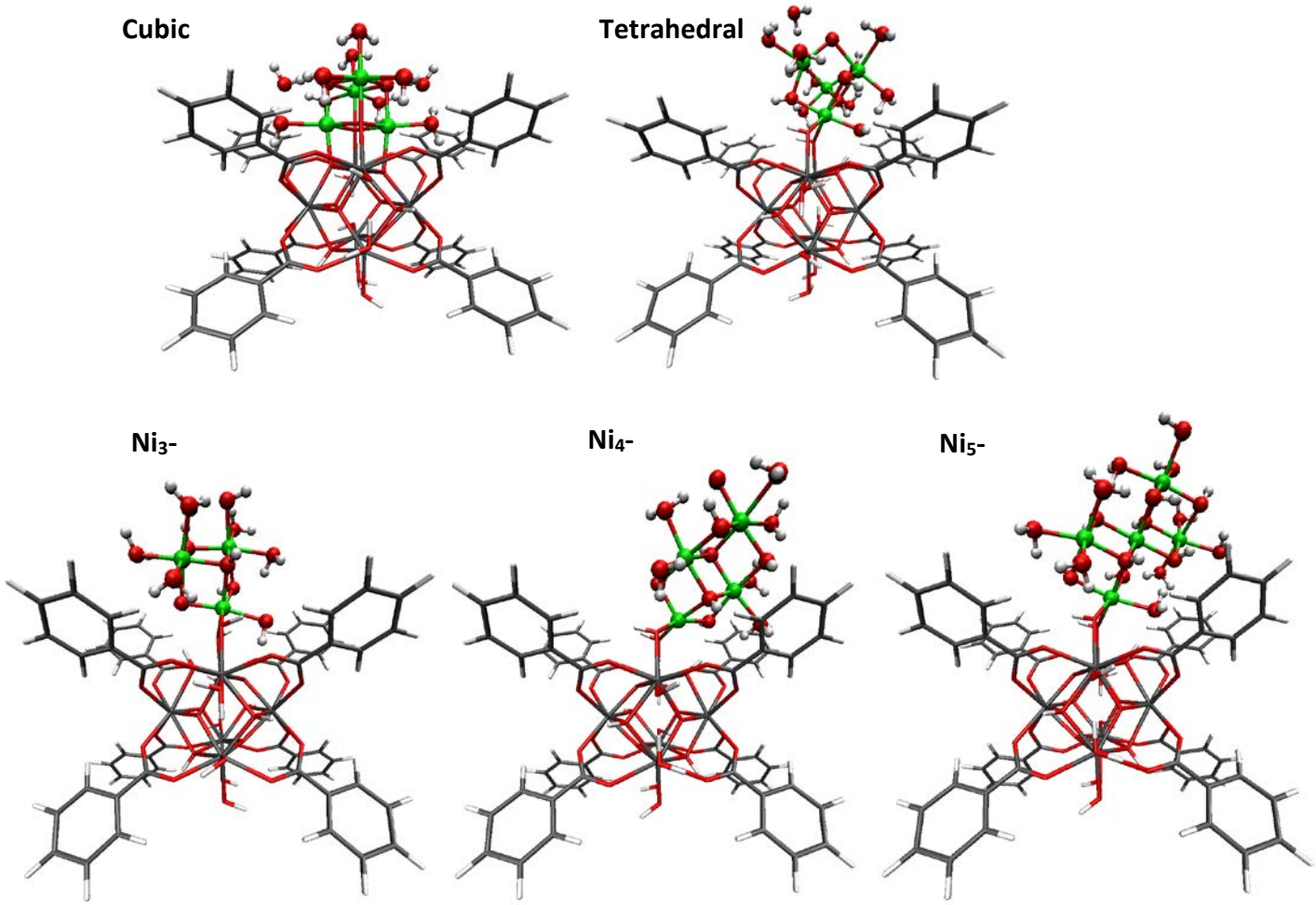

Figure 19. Depictions of the model systems for the cubic, tetrahedral, Ni_3-, Ni_4- and Ni_5-layered clusters.

Table S5. Relative energies calculated at 298 K for different Ni_x-cluster models (x = 3, 4, and 5).[a]

Energy [kcal/mol]	Cubic	Tetrahedral	Ni_3-Layered	Ni_4-Layered	Ni_5-Layered
Number of water[b]	12	15	11	13	18
ΔE_{rel}	-212.3	-258.8	-193.9	-237.7	-326.6
ΔH_{rel}	-198.8	-232.3	-174.5	-215.5	-296.5
ΔG_{rel}	-106.9	-117.1	-91.61	-122.7	-159.2

[a] Energies relative to bare NU-1000 node, water molecules, and Ni precursor. [b] Molecules needed to form the Ni cluster.

Table S6. Electronic energies, enthalpies, and free energies calculated at 298 K for different Ni_x-cluster models (x = 3, 4, and 5).[a]

Energy [a.u.]	Cubic	Tetrahedral	Ni_3-Layered	Ni_4-Layered	Ni_5-Layered
$<S^2>$	20.0169	20.0145	12.0000	20.0000	30.0001
E	-6455.640667	-6684.913616	-6209.347593	-6532.080640	-7084.084593
H	-6455.034785	-6684.225113	-6208.749882	-6531.449966	-7083.336425
G	-6455.210847	-6684.413972	-6208.920705	-6531.631687	-7083.538152

[a] Energies relative to bare NU-1000 node, water molecules, and Ni precursor.

- **Cartesian coordinates in Å**

Cubic model

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C 1.340895 4.646950 2.668763
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C 3.284964 -3.734926 -3.665279
C 2.398411 4.508172 3.579227
C 4.176628 -4.421719 4.401567
C 3.020890 5.393525 -4.403496
C 4.174979 -4.677385 -4.173032
C 3.035107 5.632351 4.097815
C 4.097239 -5.795781 4.101329
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C 3.053865 -6.231292 3.261926
C 1.523805 6.906865 -3.263474
C 3.054446 -6.409661 -2.919183
C 1.546586 7.057484 2.837642
C -4.716901 5.133995 -2.632503
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C -5.586629 6.049614 -3.216107
C -3.990353 -7.063701 3.317376
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C 1.358527 -3.114232 -2.151572
C 1.282949 -2.998575 2.400887
C -3.112570 -3.510698 2.347400
C -3.956970 2.938699 2.026322
C -3.915420 2.793458 -2.255531
C 0.699904 3.361185 -2.207977
C -3.033405 -3.640885 -2.215473
C 0.668404 3.454357 2.074666
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H 1.386692 -5.758619 -1.710438
H 0.088982 6.033970 1.614205
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H 3.371680 -2.687187 -3.938010
H 2.710541 3.509910 3.871637
H 4.972018 -4.057250 5.046478
H 3.845771 5.215938 -5.088811
H 4.955444 -4.358019 -4.858820
H 3.857325 5.505266 4.797286
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H 1.176427 7.915198 -3.053173
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H 1.205667 8.047682 2.546084
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H -6.344962 -5.681654 -4.786834
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H -5.462982 7.303122 2.628140
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H 4.785392 -6.766481 -4.189183
H 3.108503 7.558234 -4.603520
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H -5.635339 -7.985046 -4.104971
H -7.269915 6.598778 4.209793
H 3.129509 7.805833 4.128781
H -7.292042 6.340190 -4.534309
H 4.819127 -6.498052 4.505663
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H 1.987682 -1.515184 0.140343
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H -1.605820 -0.031835 4.060380
H -2.764571 -1.159727 -4.362790
H -5.269417 -0.550765 -0.353224
H -5.674266 0.206017 1.617668
H -5.546956 0.307193 -1.661914
H -1.532971 1.944077 2.781163
H -3.870004 -2.366248 0.001357
H 0.437114 -0.491226 4.444276
H -0.852705 -0.203268 -4.051362
H 0.531653 -0.972570 -4.188622
H 2.900136 1.014485 2.416829
H 2.927385 1.214724 -1.985077

O -1.166540 -1.111596 1.475969
O -2.242724 -3.799982 1.464786
O -2.147257 -3.864384 -1.335310
O 0.525131 -3.474133 1.489654
O 1.279348 -1.812664 2.818841
O 2.597499 0.291338 1.844894
O 1.099186 2.320037 2.420742
O 1.154880 2.202600 -2.459152
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O -0.258108 3.628260 -1.420542
O -3.076520 3.374885 1.218594
O -3.008266 3.282629 -1.512052
O -4.091346 1.556501 -2.485472
O -4.140809 1.720131 2.331347
O -2.822000 0.787414 -0.087590
O -1.466223 1.345758 2.023204
O -0.027767 0.210829 3.966259
O -2.614943 -0.192280 3.959177
O 0.157186 -0.107829 -3.950651
O 0.197808 1.213398 0.021888
O 1.067077 -1.181330 0.107826
O 1.473380 -1.906582 -2.534095
O 2.752069 0.347796 -1.581581
O 0.553592 -3.544212 -1.275746
O -5.148922 -0.527761 1.266931
O -5.185049 -0.547186 -1.371383
O -3.148265 -1.721725 -0.026013
O -3.461765 -2.336510 2.678620
O -3.400415 -2.491980 -2.620957
O -2.480425 -0.337326 -3.937881
O -1.328881 1.224251 -2.106441
O -1.049388 -1.187121 -1.434857
Zr -1.533422 2.393866 -0.066502
Zr 0.487255 0.144806 1.915380
Zr -3.102602 -0.243249 1.705035
Zr -2.926516 -0.380264 -1.880202
Zr -0.939403 -2.596290 0.091703
Zr 0.615204 0.089751 -1.682889
Ni 3.824259 0.641081 0.251384
O 5.493238 1.027472 -0.914894
O 4.294811 -1.316965 0.174319
O 5.065955 1.440940 1.707179
O 2.894296 2.651841 0.093978
H 5.612356 1.344104 -1.820493
Ni 6.010058 -0.961169 -0.867132
Ni 6.799614 1.373955 0.627071
H 4.490827 -1.562906 1.091031
H 5.193639 0.816743 2.435683
H 1.962956 2.337992 0.031782
H 2.969644 2.905350 1.029574
O 6.611515 -3.032213 -0.443931
O 4.720202 -1.348137 -2.476512
O 7.640039 -0.341699 -2.081221
O 7.096318 -0.654141 0.830321
O 8.534078 1.437104 -0.424700
O 6.228433 3.558031 0.718125
O 8.291867 1.934218 2.149505
H 6.858744 -2.623165 0.416208
H 7.456697 -3.284761 -0.842275
H 3.966189 -0.747332 -2.215384
H 4.392609 -2.211502 -2.171117
H 8.336745 -0.961807 -2.331672
H 8.086687 0.366739 -1.477562
H 8.047331 -0.642344 0.636739
H 8.593087 2.273917 -0.905230
H 5.599776 3.146036 1.359888
H 5.680059 3.675013 -0.073571
H 8.156951 2.892519 2.212180
H 8.855123 1.829498 1.338228

Ni_4-Birnessite type

SCF = -6532.08064 hartrees

185 atoms

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C 2.042251 6.179971 -1.856542
C -3.673978 -2.016753 -2.453221
C 1.786370 4.660013 3.335379
C -2.956544 -2.616724 3.267548
C 1.035457 5.248540 -2.150995
C -4.500826 -1.095110 -3.113009
C 0.888934 4.869118 4.393034
C -3.538693 -1.909143 4.329818
C -0.090337 5.669299 -2.873897
C -5.796967 -1.447270 -3.482214
C 0.911028 6.061746 5.109722
C -4.674113 -2.399616 4.968901
C -0.219914 6.998435 -3.267217
C -6.302463 -2.734504 -3.213900
C 1.827467 7.082808 4.790916
C -5.261058 -3.617130 4.571444
C 0.774489 7.946560 -2.955349
C -5.458156 -3.655795 -2.564851
C 2.747251 6.846651 3.752034
C -4.647620 -4.336227 3.527601
C 1.915170 7.505897 -2.257946
C 7.356944 2.555792 2.070695
C 0.375872 -6.299340 -3.118287
C 6.716793 3.139304 -2.825841
C 1.017341 -6.854979 1.973836
C 6.885633 1.257164 2.313963
C 1.301224 -5.299104 -3.453358
C 6.172690 1.895189 -3.178129
C 2.009183 -5.913989 2.291314
C 7.694618 0.359914 3.025983
C 2.196839 -5.530373 -4.508711
C 6.734978 1.182812 -4.247718
C 3.161367 -6.344450 2.966764
C 8.960686 0.743035 3.458027
C 2.191800 -6.747073 -5.185407
C 7.837686 1.689816 -4.928452
C 3.325857 -7.687380 3.298278
C 9.454106 2.035975 3.195965
C 1.286945 -7.769363 -4.836919
C 8.413458 2.921413 -4.560264
C 2.340329 -8.641023 2.975868
C 8.619773 2.939219 2.510723
C 0.366040 -7.511069 -3.802829
C 7.818376 3.644429 -3.509580
C 1.179390 -8.194496 2.315489
C -1.780061 -2.079669 2.522625
C -2.317915 -1.625897 -1.976978
C 1.332382 -4.032359 -2.662677
C 5.026861 1.325067 -2.419079
C 5.542315 0.852555 1.807982
C 1.724253 3.405410 2.536424
C 1.862025 -4.498477 1.847856
C 1.176749 3.836258 -1.690065
H -3.524478 -4.008557 -1.669179
H 3.424211 5.482365 2.218653
H -3.059218 -4.390908 2.064620
H 2.915078 5.843953 -1.305520
H -4.120141 -0.096927 -3.307059
H 0.177070 4.086752 4.637077
H -3.103981 -0.958341 4.624194
H -0.857051 4.940805 -3.120681
H -6.426706 -0.715536 -3.981601
H 0.203042 6.210356 5.921076
H -5.119113 -1.827012 5.778547
H -1.102511 7.307775 -3.821099
H -5.822622 -4.656670 -2.347838
H 3.477074 7.610945 3.497383
H -5.070897 -5.285977 3.210292
H 2.703508 8.214520 -2.016906
H 6.719495 3.246823 1.528199
H -0.320579 -6.111800 -2.307170
H 6.268105 3.689100 -2.004153
H 0.130437 -6.517431 1.446693
H 7.315614 -0.636630 3.232525
H 2.913023 -4.755402 -4.765885
H 6.297055 0.230279 -4.529256
H 3.932237 -5.616637 3.201472
H 9.577360 0.032605 4.002493
H 2.906403 -6.912857 -5.987532
H 8.266239 1.121366 -5.749907
H 4.231847 -8.002645 3.809420
H 8.972185 3.947683 2.309411
H -0.354753 -8.275350 -3.523270
H 8.232492 4.606097 -3.217569
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H -6.150380 -3.996068 5.064610
H 1.837451 8.016316 5.344334
H 1.289173 -8.720032 -5.360236
H 2.471002 -9.687644 3.231213
H 9.279419 3.311187 -5.085693
H 0.671166 8.983328 -3.259125
H 10.443445 2.332872 3.529098
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H 5.788390 -2.040027 0.899571
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H 2.851682 -3.540321 -0.477154
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H 0.261542 -0.714421 4.440930
H -1.531862 2.885494 -0.826325
H -1.353501 2.566929 2.281297

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O 0.571595 -3.983835 -1.643308
O 0.842142 -4.223289 1.142877
O -1.708482 -2.478975 -1.265997
O -1.922696 -0.462791 -2.282459
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O 0.827565 2.558047 2.838505
O 2.243328 3.546825 -1.057117
O 2.582106 3.278225 1.610376
O 4.564351 2.031098 -1.469465
O 4.856681 1.751426 1.230699
O 5.179831 -0.352044 1.989360
O 4.593200 0.183732 -2.771229
O 3.378761 -0.275571 -0.175908
O 2.109402 1.005654 -2.030300
O 0.032113 0.765832 -3.689222
O 2.153434 -0.714690 -4.145073
O 0.938568 -0.081848 4.147267
O 0.906054 1.341097 0.222353
O -0.963382 -0.373823 0.286204
O -1.215471 -1.038022 2.973523
O -1.529880 1.628145 2.119145
O -1.455457 -2.707958 1.464865
O 4.622291 -2.362503 -1.926701
O 5.041081 -2.618055 0.670136
O 2.515652 -2.646963 -0.315378
O 2.116272 -3.109251 -3.039760
O 2.773946 -3.677540 2.181083
O 3.148819 -1.463495 3.674229
O 2.552679 0.609137 2.086485
O 1.132220 -1.375303 1.456373
Zr 2.942634 1.735228 0.042877
Zr -0.135270 0.811290 -1.585239
Zr 2.891874 -1.153706 -1.998459
Zr 3.208480 -1.508450 1.569864
Zr 0.203599 -2.429388 -0.057120
Zr 0.262547 0.503285 2.005311
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O -4.431011 0.795802 -0.612925
O -3.822185 -0.064118 1.720269
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Ni -5.277364 2.691587 -0.581048
H -4.183450 0.434505 -1.472075
Ni -5.638895 -0.113165 0.752396
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O -6.390306 4.486050 -0.541947
O -6.416630 1.765116 0.910504
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O -7.230352 -0.435520 -0.494741
O -6.869421 -0.816485 2.389533
H -7.045272 2.951947 -2.251750
Ni -7.902540 1.500651 -0.445006
H -3.208345 2.693132 -1.953450
H -4.473730 2.669263 -2.880239
H -6.126341 5.035357 0.208081
H -7.340594 4.164586 -0.369631
H -6.632627 2.171615 1.758933
H -4.198238 -1.927921 1.124877
H -4.802306 -2.473654 -0.206868
H -6.902012 -0.576032 -1.394326
H -6.831587 -1.766186 2.187534
H -7.770352 -0.536184 2.131805
O -8.750219 3.326109 -0.339657
O -9.649913 1.382756 -1.820826
O -9.227448 0.130070 0.946338
H -9.222310 3.453683 0.493287
H -9.152034 1.441449 -2.651154
H -9.658981 2.322868 -1.479879
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Ni_5-Birnessite type

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C -1.115826 -4.601022 3.355768
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C -0.956713 -5.166930 -2.182003
C 3.255986 2.000509 -3.823340
C -0.072593 -4.633322 4.293018
C 3.092704 2.793659 3.681856
C 0.127032 -5.407420 -3.040832
C 4.417664 2.559225 -4.351214
C 0.197362 -5.797422 5.006103
C 4.197772 3.482314 4.174551
C 0.431484 -6.701785 -3.446782
C 4.725431 3.918704 -4.147291
C -0.563754 -6.965213 4.803537
C 4.515105 4.773115 3.707700
C -0.340351 -7.798435 -3.014249
C 3.822824 4.697045 -3.397369
C -1.631107 -6.909642 3.887722
C 3.664305 5.356295 2.749027
C -1.445042 -7.542657 -2.179602
C -7.076213 -3.496444 2.797517
C -2.399578 6.303173 -3.216697
C -6.953591 -4.064304 -2.140988
C -2.494660 6.847388 1.916004
C -6.806889 -2.132030 2.980878
C -3.174951 5.154061 -3.434276
C -6.677110 -2.753604 -2.557678
C -3.264829 5.758887 2.354215
C -7.663116 -1.370110 3.788842
C -4.219871 5.208560 -4.369461
C -7.479929 -2.168929 -3.548271
C -4.381495 6.002031 3.168447
C -8.782384 -1.952943 4.375286
C -4.505667 6.394313 -5.040738
C -8.555341 -2.869188 -4.086363
C -4.730451 7.304317 3.518732
C -9.076602 -3.315872 4.176055
C -3.752432 7.561967 -4.807276
C -8.862953 -4.172580 -3.649956
C -3.969222 8.404112 3.076431
C -8.191278 -4.078867 3.391479
C -2.680799 7.484673 -3.896369
C -8.028588 -4.762588 -2.682206
C -2.839397 8.146934 2.276044
C 1.121928 2.626795 2.108465
C 1.171240 2.177622 -2.423656
C -2.892116 3.916928 -2.646717
C -5.560628 -1.982259 -1.947203
C -5.624811 -1.516544 2.311427
C -1.367152 -3.370902 2.556238
C -2.934177 4.379814 1.894973
C -1.278822 -3.790151 -1.706229
H 1.982483 4.735927 -2.267143
H -2.714259 -5.711588 2.451666
H 1.922020 5.111132 1.495766
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H 3.030099 0.948506 -3.968983
H 0.520028 -3.736907 4.446773
H 2.866029 1.789304 4.027612
H 0.721198 -4.563097 -3.378649
H 5.096605 1.934448 -4.925746
H 1.014721 -5.807273 5.722657
H 4.830099 3.010137 4.921971
H 1.279031 -6.869113 -4.106978
H 4.035220 5.749431 -3.226922
H -2.245657 -7.791518 3.725677
H 3.877144 6.357212 2.381959
H -2.065220 -8.369341 -1.842415
H -6.401979 -4.080699 2.179277
H -1.586882 6.253003 -2.498968
H -6.320064 -4.513136 -1.382067
H -1.634919 6.653972 1.282084
H -7.437059 -0.319747 3.947083
H -4.819579 4.318421 -4.535716
H -7.248847 -1.162050 -3.881668
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Periodic Calculations

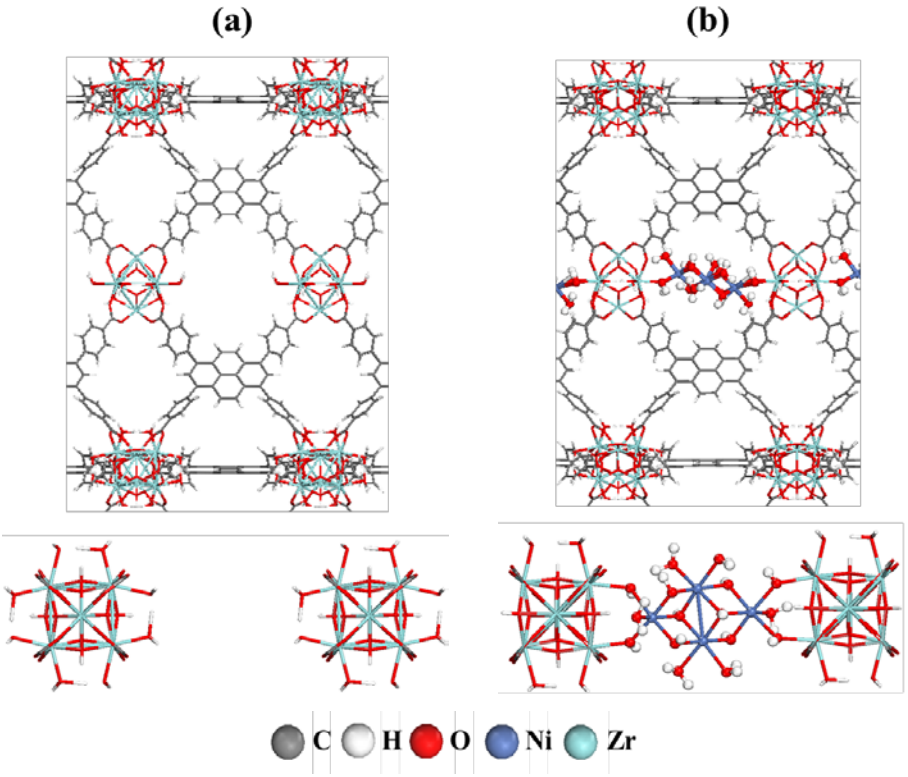

Figure S20. The small pore of NU-1000, where the the c axis runs horizontally in the figure: (a) without a nickel cluster and (b) with one Ni_3-hydroxo cluster ($Ni_3(OH)_4(OH_2)_6$)

Our calculations are based on one unit cell, which has a formula of $Zr_{18}O_{96}H_{180}C_{264}$; this corresponds to three Zr_6 nodes, allowing us to study three degrees of Ni-hydroxo cluster loading. These are denoted as *n*Ni_4-NU1000 with *n* = 1, 2, or 3. The number of Ni_4-hydroxo clusters in each unit cell and the number of Ni atoms deposited per node are *n* and *m*, respectively, where *m* = *4n*/3. For example, 2Ni_4-NU1000, has two $Ni_4O_6H_6{\cdot}6H_2O$ clusters in one NU-1000 unit cell; this corresponds to an average loading of 8/3 Ni atoms per Zr_6 node. The lattice constants of the optimized unit cell of NU-1000 and *n*Ni_4-NU1000 are summarized in Table 2.

Figure S18 shows that this trend is in a good agreement with the experimental trend; this agreement is consistent with the Ni_4-hydroxo cluster being the dominant component in the Ni-NU-1000(AIM) sample.

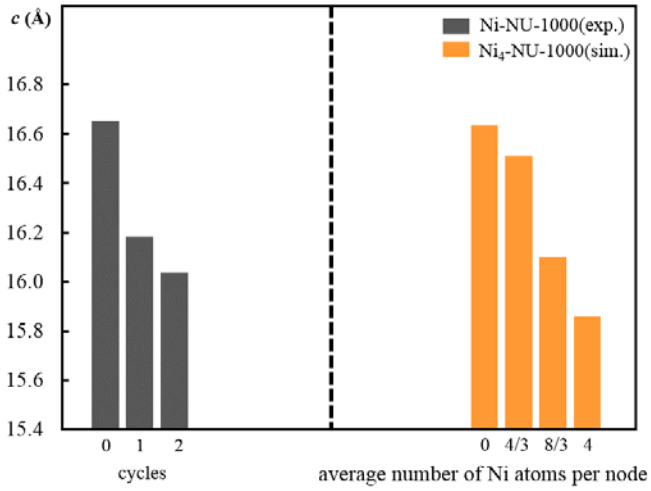

Figure S21. Comparison of lattice constants *c* obtained from experiments and simulations.

Table S7. The Ni-O and Ni-Ni bond distances in the optimized unit cell of *n*Ni$_x$-NU-1000. The Ni-O and Ni-Ni bond distances are averaged over all Ni-O bonds and all Ni-Ni nearest-neighbor pairs, respectively.

Material	***Ni-O(Å)***	***Ni…Ni(Å)***
1Ni$_4$-NU1000	2.152	3.060
2Ni$_4$-NU1000	2.125	3.077
3Ni$_4$-NU1000	2.120	3.102

Table S8. The Ni-O and Ni-Ni bond distances in the optimized unit cell of *n*Ni$_x$-NU-1000. The Ni-Ni distances are averaged over all Ni-Ni nearest-neighbor pairs, and the Ni-O distances are averaged over all Ni-O bonds excluding the Ni-O bond distances that are larger than 2.2 Å and over all Ni-Ni bonds, respectively.

Material	***Ni-O(Å)***	***Ni…Ni(Å)***
1Ni$_4$-NU1000	2.069	3.060
2Ni$_4$-NU1000	2.075	3.077
3Ni$_4$-NU1000	2.076	3.102

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