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Size Effect of the Active Sites in UiO-66-Supported Nickel Catalysts Synthesized via Atomic Layer Deposition for Ethylene Hydrogenation^{†,‡}

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Abstract

Ni(II) ions have been deposited on the Zr₆ nodes of a metal–organic framework (MOF), UiO-66, via an ALD-like process (ALD = atomic layer deposition). By varying the number of ALD cycles, three Ni-decorated UiO-66 materials were synthesized. A suite of physical methods has been used to characterize these materials, indicating structural and high-surface-area features of the parent MOF are retained. Elemental analysis via X-ray photoelectron spectroscopy (XPS) indicates that the anchored Ni ions are mainly on surface and near-surface MOF defect sites. Upon activation, all three materials are catalytic for ethylene hydrogenation, but their catalytic activities significantly vary, with the largest clusters displaying the highest per-nickel-atom activity. The study highlights the ease and effectiveness ALD in MOFs (AIM) for synthesizing, specifically, UiO-66-supported Ni_yO_x catalysts.

Graphical abstract

[†]Dedicated to Professor Mercurio G. Kanatzidis on the occasion of his 60th birthday

[‡]Electronic Supplementary Information (ESI) available: Synthesis, characterization of the catalysts, post-catalysis analysis data. See DOI: 10.1039/x0xx00000x

Introduction

Atomic layer deposition (ALD) is used industrially to fabricate high quality ultrathin films.¹ ALD offers atomic-level control over thickness/composition of the deposited films because of the inherent self-limiting and temporally separated surface reactions for chemically complementary pairs of reactants (A and B). During one conventional AB cycle of the ALD process, chemical functionalities (e.g. hydroxyls) on a surface chemically react with a volatile organometallic or coordination complex, thereby binding the metal (A cycle). A second precursor (e.g., H₂O,² H₂S,³ or NH₃⁴) is then delivered in vapor form to the surface-bound metal atom, with which it reacts (B cycle). This step serves to regenerate the metal-anchoring sites, thereby setting the surface up for another round of metal binding. After each A or B half-cycle a purge step removes unreacted precursor, as well as volatile byproducts. With appropriately chosen precursors, the two-stage synthesis scheme engenders film growth that is both self-limiting (for any given step) and conformal (and, therefore, applicable to porous platforms and high-area surfaces).⁵ By varying the chemical identities of the molecular precursors, as well as the number of AB cycles (growth cycles), the composition and thickness of the fabricated films can be meticulously controlled.⁶

Over the past few years, ALD has increasingly been used either to synthesize catalysts on conventional solid supports, such as metal-oxides, or to stabilize, again on conventional supports, nanometer-sized catalysts prepared in other ways.⁷ More recently, mesoporous metal-organic frameworks (MOFs),^{8, 9} especially those based on hexa-zirconium(IV) nodes, have been shown to be excellent platforms for ALD-like synthesis of supported catalysts. Thus, the nodes behave as tiny pieces of zirconia¹⁰ that present reactive aqua and hydroxo groups (ligands) to molecular precursors.¹¹ However, in contrast to bulk metal-oxides, which favor film growth, these discrete units favor the formation of clusters.¹² Furthermore, the systematic separation/isolation of nodes by the organic components of MOFs, may serve to inhibit sintering/agglomeration, even under catalytic conditions.^{13, 14}

From previous studies, the metal nodes of Zr-MOFs can be post-synthetically decorated with many different metal-oxides/sulfides.¹⁵ The decoration can be accomplished *via* ALD in MOFs (AIM)^{16–18} or solvothermal deposition in MOFs (SIM)^{19–22}—as well as by AIM and SIM in combination.²³ Depending, of course, on their specific chemical composition, the resulting MOF-supported clusters or single metal ions can be rendered competent for photocatalytic H₂ generation,²⁴ electrocatalytic O₂ production,²⁵ solution-phase alkene epoxidation,^{26, 27} and gas-phase ethylene hydrogenation and oligomerization,^{13, 21, 28} hexene polymerization,²⁰ and propane oxidative dehydrogenation,²⁹ among other reactions.^{22, 30}

It is well-known, especially for neutral metal clusters, that the size of a cluster can affect its catalytic performance tremendously.^{31–35} Conventional approaches to installation of nanometer and sub-nanometer sized catalysts on supports include impregnation, ion exchange, and sol-gel encapsulation. While undeniably versatile, these approaches, especially when used with conventional supports, often yield overly broad distributions of catalyst sizes.³⁶ Due to the structural uniformity of the MOF supports,³⁷ the metal ions installed on nodes of MOFs, *via* AIM or SIM, tend to adopt, for a given set of synthesis

conditions, well-defined structures of uniform size.²² Intentional modulation of the size of AIM-installed clusters can be achieved varying the number AB synthesis cycles.

For the current study, we chose UiO-66³² (Figure 1) as the MOF support and the Ni(II)-catalyzed hydrogenation of ethylene as the test reaction, where the overall objective was to gauge the effect of catalyst size on catalytic activity. UiO-66 was selected, in part, because of its outstanding stability as well as the ease with which it can be synthesized.^{38, 39} It was also chosen because of the comparative enhanced variability with which single-metal-atom active sites can be introduced.^{19, 21, 40, 41} Briefly, the nodes of UiO-66 are ideally twelve-connected to carboxylate-terminated linkers, leaving no sites for the nodes to present ALD-reactive aqua or terminal hydroxo ligands. (In contrast, mesoporous Zr-MOFs such as PCN-222 (MOF-545),^{42, 43} NU-1000,¹⁶ NU-1200,⁴⁴ and MOF-808⁴⁵ are six- or eight-connected, with the unused linker-connection sites instead being occupied by ligated water or hydroxide, *i.e.* ligands that are ideal for reacting with metal ions (SIM)²² or metal-containing ALD precursors (AIM and SIM).^{23, 26}) Real UiO-66 samples, in contrast, are characterized by missing linkers,⁴⁶ leaving the nodes eleven- (or ten-) connected. Thus, these defect sites serve to present the node ligands needed for reaction with metal complexes. UiO-66 is further characterized by comparatively small pores and apertures, a consequence of employing benzene di-carboxylate as the linker. Indeed, in the absence of missing-linker-type defects, the apertures are sufficiently small to size-exclude the ALD precursor molecule of choice, bis(N,N'-di-*tert*-butylacetoamidinato)nickel(II) (Figure S1). Nevertheless, in the presence of defects, the nickel precursor should be capable of sampling, for the initial A cycle, much of the MOF interior. For subsequent AB cycles, however, sampling the interior should be much more difficult, and deposition of additional nickel ions should be limited mainly to sites at or near the exterior of the MOF.

Results and Discussion

In this work, we prepared UiO-66-supported catalysts, based on 1, 2 or 3 AB cycles, where water vapor was the B-step reactant. (See SI for detailed procedures, and they are denoted as Ni-UiO-66 1 cycle, Ni-UiO-66 2 cycles and Ni-UiO-66 3 cycles) Scheme I shows qualitative representations of the resulting catalyst active sites at or near MOF crystallite exterior surfaces.

The MOF particle morphology and crystallinity of all three samples, as well as their thermal stability, are retained after nickel installation, as evidenced by scanning electron microscopy (SEM), powder X-ray diffraction pattern (PXRD) (Figure 2 a,b) and thermogravimetric analysis (TGA, Figure S2). SEM-energy dispersive spectroscopy measurements (Figure S4) corroborate the presence of nickel in the AIM-treated MOF samples. X-ray photoelectron spectroscopy (XPS, Figure 2c) confirms that the valence of the installed Ni ions is +2, as a peak at 854.5 eV, attributable to the 2p_{3/2} electrons of Ni(II), is present in the spectrum. The content of Ni in the samples was determined *via* inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and corresponded to $\sim 1.1 \pm 0.05$, 1.3 ± 0.1 and 1.6 ± 0.1 nickel ions for each Zr₆ node in the 1, 2, and 3 cycles samples (these values are equivalent to 3.7%, 4.3% and 5.2% *wt.* of Ni loading), respectively. (Note that these numbers refer to the

average installation/loading per node. At specific locations the loadings are much more widely varying, *viz.* sites at or near the MOF crystallite external surface; see below.)

The Ni(II) binding sites for the first cycle of AIM are almost certainly the water and terminal hydroxo ligands present on the nodes at missing-linker-type defect sites.¹⁹ This assertion is in line with diffuse reflectance Fourier transform infrared spectra (DRIFTS) for the MOF before and after single-AIM-cycle nickel incorporation. Relative to the “before” spectrum, the “after” spectrum shows a modest decrease in intensity of a peak at 3674 cm^{-1} , which is known to be due to O-H stretches associated with node water and terminal-hydroxide ligands;⁴⁷ see Figure S3. Additional AIM cycles yield no obvious further attenuation of the intensity of the O-H stretch. An appealing explanation is that Ni deposition in the second and third AB cycles occurs mainly on newly-generated Ni–(OH)(OH₂) sites (Scheme 1). Thus, the remaining unreacted Zr–(OH)(OH₂) sites are largely or completely inaccessible after the initial AIM cycle.

Measurements of N₂ adsorption isotherms show that Ni(II) installation decreases the Brunauer–Emmett–Teller (BET) surface area of UiO-66 from $1150\text{ m}^2\text{ g}^{-1}$ to $\sim 680\text{ m}^2\text{ g}^{-1}$. This finding is broadly consistent with observations in previous AIM studies.^{13, 24} Notably, despite the introduction of more nickel, additional AB cycles leave the experimental BET surface area unchanged. Together with the DRIFTS data, we interpret the observation as strong circumstantial evidence that metalation during the second and third AB cycles is restricted to Ni–OH(OH₂) sites at or near the MOF exterior surface.

Direct evidence of spatially preferential metal ion deposition was obtained via XPS assessment of MOF composition, under conditions of depth profiling (via ion-beam etching; see SI). XPS selectively interrogates the outermost few nanometers of a material. For UiO-66, the XPS signal from Zr provides an internal calibration, as the Zr content is uniform throughout the samples. Comparisons of Ni content before and after etching to a depth of several nanometers revealed that all three Ni-AIM UiO-66 samples feature substantially higher nickel loadings at and near the MOF exterior versus within the MOF crystallites (Table S1). As we would expect, the surface and near-surface Ni loading increases with the number of AB AIM growth cycles. The 2-cycle sample has ~ 2.3 times greater surface/near-surface loading of nickel than does the 1-cycle sample. The 3-cycle sample has ~ 4.4 times the surface/near-surface nickel of the 1-cycle sample (Table S1). UV-Vis reflectance measurements reveal for the AIM-treated samples, but not the nickel-free sample, a broad absorption at $\sim 700\text{ nm}$ (Figure S5). The location is consistent with an assignment as Ni(II) d→d transition. Closer inspection reveals that the band is slightly red-shifted for the 3-cycle sample relative to the 1-cycle sample, pointing to larger Ni_yO_x clusters in the 3-cycle sample.⁴⁸

Turning to catalysis, we targeted ethylene hydrogenation since many supported Ni moieties have been shown (after activation) to be catalytic for this reaction.⁴⁹ Similar to Ni-AIM + NU-1000, the as-installed UiO-66-supported atoms and clusters show no catalytic activity. However, heating in a flow of H₂ at $200\text{ }^{\circ}\text{C}$ for 2 h renders them catalytically active.¹³ By varying the molar space time of ethylene (W/F) (Figure S6), the per-nickel-atom turnover frequencies (TOFs) $100\text{ }^{\circ}\text{C}$ were determined to be 0.04 ± 0.01 , 0.05 ± 0.02 and $0.15\pm 0.04\text{ s}^{-1}$

for 1-, 2-, and 3-cycles samples, respectively (with all nickel atoms being counted, See Figure 3).⁵⁰

These TOF values, especially in the 3-cycle case, are similar to those observed for Ni-AIM+NU-1000 under the same experimental conditions,¹³ *i.e.* $\sim 0.12 \text{ s}^{-1}$ at 100 °C. Nevertheless, the per-nickel-atom TOF for Ni-AIM+UiO-66 3 cycles is about four times greater the TOF for Ni-AIM+UiO-66 1 cycle (and Ni-AIM+UiO-66 2 cycles). Thus, AIM-synthesized oxo,hydroxo clusters of Ni(II) are significantly more active for ethylene hydrogenation than AIM-synthesized single- or few-nickel-ion catalysts. If we recognize further that only a fraction of the nickel atoms in the 3 cycles sample (perhaps 30 or 40%) are present as clusters, the true difference in per-nickel-atom TOF values for single-nickel-ion or few-nickel-ion catalysts versus several-nickel-ion catalysts cluster-based may be closer to ten-fold. It will be interesting to see the outcome of computational modeling of activity for the latter, as the initial computational studies (*i.e.* for Ni-AIM+NU-1000) were intentional simplified by evaluating node-supported single-nickel-ion catalysts.

Notably, for all three samples, no change in catalytic activity was observed after 24 h on stream. The catalysts are completely deactivated, however, by exposure to laboratory air of finite humidity. Their catalytic activity can be restored by re-exposing them to flowing H₂ at 200 °C for 2 h (Figure S7).

Finally, based on comparisons of “before” and “after” PXRD patterns (Figure S8) no evidence for catalysis-induced degradation of crystallinity was found. From the SEM images of the post-catalysis samples (Figure S9), there are slight changes in the morphology of a small fraction of MOF crystallites. The changes might be related to apparent decreases in gravimetric surface area following catalysis measurements (Figures S10 and S11); alternatively, they might be artefactual as we cannot exclude contamination of the sample with similarly sized fragments of quartz wool from the catalytic reactor.

Conclusions

In summary, AIM is a facile way of anchoring Ni(II) ions to UiO-66. By varying the number of the AB cycles used, the size of the Ni_yO_x clusters formed at or near the external surface of the MOF crystallite can be readily tuned. Upon thermal activation under flowing H₂, the samples are catalytic for ethylene hydrogenation process under mild conditions. A clear active-site size effect on the catalytic activity is observed, with the largest catalyst sites displaying the highest activity. Overall, the findings highlight the potential of the AIM methodology for fabricating MOF-supported catalytic atoms and clusters, and the utility of defective UiO-66 for focusing cluster growth at or near the external surface of the microporous support.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Structural features of UiO-66 with the emphasis of its perfect Zr₆ node and defected node. The anchored Ni atoms are sited on the defective nodes. Zr, green; O, red; C, gray; Ni, purple.

Figure 2.

Characterization of the as-synthesized UiO-66 supported Ni materials. (a). powder X-ray patterns of the three samples (b). SEM image of Ni-AIM+UiO-66 1 Cycle; (c). XPS spectrum of Ni-AIM+UiO-66 in the Ni region. Blue: Ni-AIM+UiO-66 1 Cycle, Orange: Ni-AIM+UiO-66 2 Cycles, Black: Ni-AIM+UiO-66 3 Cycles. (d). N_2 isotherms of the three samples

Figure 3.
The TOFs of the three UiO-66-supported Ni catalysts for ethylene hydrogenation upon activation. Reaction conditions: 100 °C, 1.5 bar pressure, ethylene: H₂ = 1:2.[‡]

[‡]Notes

Available experimental diffusivity data for ethane in UiO-66 (see ref. 50), together with measured TOFs (this study) imply that for 800 nm diameter crystallites, ethylene can fully sample the MOF crystallite interior (and associated catalyst active-sites). In other words, intracrystalline mass-transport resistance effects can reasonably be neglected and the full complement of installed catalyst active-sites can be viewed as reactant-accessible. These conclusions, in turn, justify the inclusion of all nickel atoms and clusters in estimating per-nickel-atom TOFs.

Scheme 1. Schematic Representations of Exterior Ni_yO_x Sites for Three UiO-66-supported Ni(II) Catalysts Synthesized *via* AIM^{a,b}

a. For simplicity (and in the absence of detailed information) aqua and hydroxo ligands are omitted. b. The exact catalyst compositions are unknown; the scheme is meant to convey our best estimates of the metal nuclearity of catalysts obtained via 1, 2, and 3 AIM synthesis cycles.