Lithium-Ion Battery Materials as Tunable, Redox Non-Innocent Catalyst Supports

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Abstract The development of general strategies for the electronic tuning of a catalyst’s active site is an ongoing challenge in heterogeneous catalysis. To this end, herein we describe the application of Li-ion battery cathode and anode materials as redox non-innocent catalyst supports that can be continuously modulated as a function of lithium intercalation. A zero-valent nickel complex was oxidatively grafted onto the surface of lithium manganese oxide (Li,xMn2O4) to yield isolated Ni2+ occupying the vacant interstitial octahedral site in the Li diffusion channel on the surface and subsurface of the spinel structure (Ni/Li,xMn2O4). The activity of Ni/Li,xMn2O4 for olefin hydrogenation, as a representative probe reaction, was found to increase monotonically as a function of support reductive lithiation. Simulation of Ni/Li,xMn2O4 reveals the dramatic impact of surface redox states on the viability of the homolytic oxidative addition mechanism for H2 activation. Catalyst control through support lithiation was extended to an organotantalum complex on Li4TiO2, demonstrating the generality of this phenomenon.

The discovery of general strategies for the stereoelectronic modulation of active site structure toward tunable activity and selectivity is a grand and ongoing challenge in heterogeneous catalysis.1,2 Heterogeneous catalysts dominate industrial applications due to the necessity for continuous processing and separation on scale, but intrinsically lack some of the attractive attributes of homogeneous catalysts, such as the electronically tunable nature of the supporting organic ligand architecture.2 Furthermore, the redox properties of conjugated organic ligands, referred to as “redox non-innocent” ligands, also play an
active role in the reversible storage of electrons during the catalytic process, especially for first-row transition metals, facilitating key chemical steps and enabling multi-electron redox elementary transformations (Figure 1b).³⁻⁵ While heterogeneous supports are often more decoupled from catalytic reactivity compared to supporting ligands in homogeneous catalysis, they can play an important role in determining the properties of a supported catalyst. The dynamic relationship between nanoparticles and reducible support materials is often rationalized by Strong Metal Support Interactions (SMSI).⁶ Electronic Metal Support Interactions (EMSI), a subset of SMSI, can be viewed as a heterogeneous analogy to redox non-innocent ligand interactions.⁷ Given the ability to modulate their Fermi levels, band structures, and surface potentials, EMSI capable supports could facilitate catalytic transformations analogous to their “redox non-innocent” molecular counterparts. Efforts to control catalysis via metal-surface interactions including EMSI through support doping⁸, surface modification,⁹ and particle morphology¹⁰,¹¹ have proven effective, but continuous tunability and clear structure-function relationships that enable rational catalyst design are not always achievable.⁶

Surface organometallic chemistry (SOMC) is a powerful strategy for the synthesis of well-defined, homogeneous-in-function, heterogeneous catalysts.²,¹² For SOMC catalysts, the support material, most commonly silica (SiO₂) or alumina (Al₂O₃), often plays a crucial role in stabilizing and site-isolating reactive intermediates, however, the chemical properties of the support are seldom employed to modulate catalyst reactivity.¹³⁻¹⁵ The treatment of catalyst supports as chemically dynamic ligands, leveraging the electronic structure of the support to tune the activity of surface species represents an opportunity for innovation in the design of heterogenized catalyst systems.¹ While examples of catalysts on reducible support materials, such as titania and ceria, synthesized through SOMC techniques have been reported, the presence of EMSI has not been demonstrated or leveraged (Figure 1b).¹⁶⁻¹⁹
Figure 1. (a) Application of lithium intercalation as a mechanism for electronic modulation of catalyst activity (b) Analogy between redox non-innocent molecular ligands and comparable redox noninnocence of a solid catalyst support. (c) surface potentials achievable by redox tuning of two battery anode/cathode materials, lithium titanium oxide and lithium manganese oxide.

Lithium-ion battery cathode and anode materials, such as lithium manganese oxide (LMO, $\text{Li}_x\text{MnO}_2$) and lithium titanium oxide (LTO, $\text{Li}_x\text{TiO}_2$), are attractive candidates for redox-active supports due to their broad range of available charge states and the ability to tune surface potentials as a function of lithium intercalation (Figure 1c). Modulating the degree of lithiation for $\text{Li}_x\text{Mn}_2\text{O}_4$ affords a series of materials with continuously varying surface potentials (0 to +2V vs SHE), making them ideal for tunable catalysis;
likewise, Li$_x$TiO$_2$ spans a similar range at lower potential, from -2 to -0.2V. Thus, with these two support
materials, a span of nearly 4V of surface potential is accessible, which may imbuo previously inaccessible
levels of catalyst tunability. Herein, we report a series of catalysts supported on Li-ion battery materials
that exhibit activity tunable as a function of the charge state of the support material. This work represents
a proof-of-principle for this generalizable strategy of electronic catalyst modulation through continuous and
systematic chemical manipulation of the charge state of the support by lithium intercalation.

Results and Discussion
Synthesis and Characterization of Ni/LiMn$_2$O$_4$. The relatively low density of hydroxyl groups on the
surface of LMO precludes traditional SOMC grafting techniques such as protonolysis and condensation
(See Figure S4d). However, the oxidizing nature of the support affords the possibility of an orthogonal
chemisorption mechanism by abstraction of one or more electrons from a low-valent molecular
precursor. To evaluate the viability of this approach, a solution of the low-valent organonickel complex
bis(cyclooctadiene)nickel(0) (Ni(COD)$_2$) was added to a suspension of LiMn$_2$O$_4$ in benzene, which was
monitored by $^1$H NMR spectroscopy (Figure 2a). A sharp decrease in the concentration of Ni(COD)$_2$ was
observed upon exposure to LMO, with concomitant appearance of free cyclooctadiene and saturation was
achieved after 24 hours, affording the metalated Ni/LiMn$_2$O$_4$ (0.50 wt % Ni) (Figure 2b, S1). In contrast,
when Ni(COD)$_2$ was exposed to silica (redox inactive) or the pre-reduced Li$_2$Mn$_2$O$_4$ (insufficiently
oxidizing), chemisorption of nickel was not observed, underscoring the role of the oxidizing surface in
the grafting reaction (Figure S2-5). Analysis of Ni/LiMn$_2$O$_4$ by diffuse reflectance infrared Fourier
transform spectroscopy (DRIFTS) and thermogravimetric analysis (TGA-MS) revealed no evidence of
residual COD, suggesting that nickel was fully deligated upon chemisorption (Figure S6-7). The effect of
the oxidative grafting process on the valency of nickel was established by X-ray Absorption Spectroscopy
(XAS) and X-ray Photoelectron Spectroscopy (XPS). The pre-edge and white line features (8331.6 and
8349.2 eV, respectively) in the Ni K-edge X-ray Absorption Near Edge Structure (XANES) of Ni/LiMn$_2$O$_4$
were consistent with Ni(II) (Figure 2c). Similarly, the XPS of Ni/LiMn$_2$O$_4$ exhibited two peaks (855.2
and 873.1 eV corresponding to 2p$_{3/2}$ and 2p$_{1/2}$ respectively), consistent with a Ni(II) ion in an oxygen rich environment distinct from Ni(II)O and Ni(0) (2p$_{3/2}$ binding energies of 853.5 and 852.5 eV, respectively) (Figure S8). Depth profiling by angle-resolved XPS indicates that the redox state of Mn was uniform between the surface and bulk, suggesting that the electrons absorbed by the support are homogeneously distributed within the crystallite (Figure 2d). Energy-dispersive X-ray spectroscopy (EDS) of Ni/LiMn$_2$O$_4$ (Figure 2f, S9-10), corroborates the dispersity of nickel on the surface with no agglomeration to clusters or nanoparticles. The Ni K-edge XAS Extended X-ray Absorption Fine Structure (EXAFS) is consistent with an oxygen-rich environment with 5-6 nearest neighbors and was most consistent with Mn as the nearest neighbor$^{27}$ (Figure S11-12, Table S1). The relatively high density of nickel on the crystallite (~14 Ni / nm$^2$) precludes a submonolayer of isolated Ni$^{2+}$ ions on the surface, and the EXAFS data suggest that Ni is in a manganese oxide environment, as opposed to a segregated nickel oxide environment; therefore, it was hypothesized that the nickel ions may have been incorporated into the surface and subsurface of the spinel crystal structure.

Three distinct sites in the cubic spinel structure could accommodate nickel upon oxidative grafting. Nickel incorporation could occur by (i) substitutional doping at the octahedral 16d manganese site by displacement of Mn (or at an existing Mn defect), (ii) interstitial doping within the Li diffusion channels of the spinel, with Ni occupying the tetrahedral 8a site typically occupied by Li, or (iii) interstitial doping at the vacant octahedral 16c site, which sits directly between two 8a sites (Figure 2g). While incorporation at the tetrahedral 8a site can be categorically ruled out by EXAFS fitting (5-6 oxygen donors), the EXAFS data cannot discriminate between the octahedral 16d manganese site or interstitial 16c site. Changes in the $^6$Li NMR spectrum upon Ni chemisorption provided the first evidence for interstitial doping on Ni at the 16c vacant site (Figure 2e). A resonance at ~720 ppm appears upon metalation, consistent with Li adjacent to Ni in the surface layer.$^{28}$ The remaining 8a Li signals shift to slightly lower frequency ($\Delta\delta \approx -2$ ppm), consistent with a slight decrease in average Mn oxidation state, and the population shifts from pristine tetrahedral 8a sites (520 ppm) to 8a sites adjacent to a defect (545-576 ppm) as would be expected for more
densely packed Li (8a Li adjacent to 16c Li) if Li is displaced by Ni from the surface to the core of the particle.  

Figure 2. (a) The oxidative grafting of Ni(COD)$_2$ onto LiMn$_2$O$_4$ to make Ni/LiMn$_2$O$_4$, (b) reaction profile for the chemisorption of Ni(COD)$_2$ onto LiMn$_2$O$_4$, (c) XANES spectra of Ni/Li$_{0.96}$Mn$_2$O$_4$, and nickel standards, (d) Angle dependent Mn $2p_{3/2}$ and $2p_{1/2}$ XPS indicating Mn oxidation state is depth independent, (e) $^6$Li NMR spectra of LiMn$_2$O$_4$ and Ni/LiMn$_2$O$_4$, (f) Ni and Mn EDS maps of Ni/LiMn$_2$O$_4$, (g) HRTEM image of the (111) facet of Ni/LiMn$_2$O$_4$ viewed down the [0-11] axis, orange diamonds denoting eight atomic columns surrounding Li diffusion channels, as indicated in the model (O=red, Mn=pink, Li=yellow, Ni=blue), and inset composite multi-slice TEM simulation of Ni/LiMn$_2$O$_4$ composed of individual simulations one unit cell wide decreasing in Ni occupancy of 0.25, 0.125, 0.0625, 0.0312, and 0 (simulation inset with red border), (h) hyperspectral elemental profiles of Ni and Mn showing antiphase oscillations in intensity at the surface layer of Ni.
High-resolution microscopy and hyperspectral imaging were employed to further interrogate the hypothesis that the oxidative grafting of Ni(COD)$_2$ led to the population of the interstitial octahedral vacancy. Aberration corrected High-Resolution Transmission Electron Microscopy (HRTEM) images of Ni/LiMn$_2$O$_4$ revealed a characteristic diamond pattern formed by the eight manganese-containing atomic columns surrounding the spinel Li diffusion channel in the bulk of the particle, and a qualitatively rocksalt-like structure at the edge of the particle, with a bright spot appearing in the center of the Li channel (Figure 2g, S20). The signal in the Li channel is most intense at the surface and decreases in intensity as a function of distance from the surface, consistent with partial Ni occupancy in the 16c site in the Li channels as compared to multislice HRTEM simulations for varying occupancies of Ni at the 16c site, decreasing from 0.25 (Ni$_{0.5}$Mn$_2$O$_4$) at the surface to 0 (LiMn$_2$O$_4$) after four repeating layers (Figure 2g, inset). This feature is consistent with Ni in the 16c interstitial site, but may be contributed to by manganese defects, or residual potassium from the KMnO$_4$ precursor, which has increased concentration at the surface (Figure S21). To further support this assignment, high resolution hyperspectral imaging of a Ni/LiMn$_2$O$_4$ particle viewed down the (111) facet was collected, which afforded elemental profiles of Ni and Mn, with a Mn signal that oscillated in intensity with a period of 0.46 nm, matching the fringe spacing by HAADF-STEM (Figures 2h,S21-25), and a Ni signal that was concentrated in the first 1-2 nm of the particle, and oscillated with the same period but antiphase relative to Mn (Figure 2h, S21-25). The Ni:Mn EDS signal ratio was ~1:5 at the surface, and decreased as a function of penetration depth. In conjunction with the depth independence of Mn oxidation state based on XPS analysis, this observation suggests that the majority of Li atoms in the first surface unit cell are displaced by Ni to approach a NiMn$_4$O$_8$ stoichiometry at the surface (Figure S25). Antiphase EDS signals for Mn and Ni suggest that the two must not be co-located in the structure, providing strong evidence that Ni occupies the vacant interstitial 16c site.

Electronic modulation of Ni/Li$_x$Mn$_2$O$_4$. Reductive lithiation of Ni/LiMn$_2$O$_4$ was performed via the addition of varying mole fractions of $n$-butyllithium to a suspension of Ni/LiMn$_2$O$_4$ (Figure 2a, Li:Mn = 0.63 to 1.13, Table S7). HAADF-STEM and EDS maps of the fully reduced material, Ni/Li$_{2.26}$Mn$_2$O$_4$, show that upon lithiation nickel remains dispersed on the surface of the support (Figure 3e, S26-27), and no
The Ni K-edge XANES of the variably reduced materials exhibit small differences in pre-edge peak and edge energies relative to the parent Ni/LiMn$_2$O$_4$ suggesting that the majority of sites remain in the 2+ oxidation state, however, as the extent of lithiation increases, a small increase in the rising edge is observed, possibly indicative of a partially reduced minor species or the presence of a more electron rich local environment (Figure 3b). While isolation of the putative reduced Ni species from the XAS spectra was not possible, a combination of principle component analysis and linear combination fitting suggests that the reduced nickel species is likely in an oxide environment, and is not consistent with a segregated metallic Ni phase (see pages S20-S22, Figures S16-18 for full analysis). In contrast, the Mn XANES of Ni/Li$_x$Mn$_2$O$_4$ underwent a decrease in edge energy and growth of the pre-edge feature at 6545 eV upon lithiation, consistent with full conversion to manganese 3+ (Figure 3c). Upon reduction, a gradual decrease in the main $^6$Li NMR resonance at ~520 ppm is observed, accompanied by the formation of a new resonance around 100 ppm (Figure 3d), characteristic of the cubic to tetragonal crystallographic transition induced by Jahn-Teller distortion as the concentration of Mn(III) increases, consistent with the phase change observed in the X-ray powder diffraction data (Figure S31, Table S8).
Figure 3. (a) Reduction of Ni/LiMn$_2$O$_4$ with n-BuLi to afford Ni/Li$_x$Mn$_2$O$_4$ (Li:Mn = 0.63 to 1.13). Lithiation biproducts include octane, butane and butenes. (b) Ni and (c) Mn K-edge XANES spectra of variably reduced Ni/Li$_x$Mn$_2$O$_4$, (d) $^6$Li NMR spectra of Ni/Li$_x$Mn$_2$O$_4$; Li in the cubic spinel in the 500-600 ppm region, and Li in the tetragonal spinel-related structure in the 100-130 ppm region (cubic spinel nomenclature is maintained for clarity when referring to the tetragonal crystallographic sites), (e) Ni and Mn EDS maps of Ni/Li$_{2.06}$Mn$_2$O$_4$, showing that Ni remains dispersed after lithiation, (f) Weiner filtered bright field HRTEM image of the (002) facet of Ni/Li$_{2.06}$Mn$_2$O$_4$ viewed down the [-100] axis of the tetragonal phase, showing rocksalt-like surface layer at the surface, and tetragonal Li$_2$Mn$_2$O$_4$ structure in the core, consistent with multislice TEM simulations (simulations inset with red border, surface layer modeled with 0.25 Ni occupancy at the 16c site), (g) EELS measurements collected with HRTEM images showing detectable Ni only at the surface layer, and changes in the O and Mn edges consistent with marginally lower Mn oxidation state in the surface layer.
HRTEM images of Ni/Li$_{2.06}$Mn$_2$O$_4$ were collected to determine if Ni remains in the octahedral 16c site of the Li channel (Figure 3f, S32$^{35}$). Like the parent material, Ni/Li$_{2.06}$Mn$_2$O$_4$ features a rock-salt-like pattern at the exposed surface facet, which is crystallographically aligned with the Li$_x$Mn$_2$O$_4$ core, suggesting that the Li channel at the surface remains doped at partial occupancy with Ni, however it is possible that some Mn$^{2+/3+}$ ions also enter the lithium channel after reductive oxygen abstraction.$^{36}$ While the qualitative appearance of the surface layer is rock-salt-like, the observation of systematic alternation in intensity mapping profiles suggests that the spinel structure remains intact, and is inconsistent with full conversion to a rock-salt-like NiO/MnO (Figure S32). Electron Energy Loss Spectroscopy (EELS) was conducted at the edge and the bulk of the material (Figures 3g, S33). The Ni L$_{2,3}$-edge at 855 eV was only detectable at the surface layer, and an increase of the Mn L$_3$/L$_2$ ratio (2.18 in the bulk 2.31 in the surface layer) and slightly diminished O pre-edge feature are consistent with a small decrease in the average oxidation state of Mn at the surface.$^{37}$ Plausible explanations for the appearance of these reduced manganese atoms include Mn$^{3+}$ reduced to Mn$^{2+}$ to charge balance Ni$^{2+}$ substituting Li$^+$ with adjacent 16c sites fully populated by Li, or Mn$^{2+}$ migration into the Li channel associated with deoxygenation as mentioned above.

**Catalytic reactivity of Ni/Li$_x$Mn$_2$O$_4$.** Hydrogenation of alkenes was chosen as a probe reaction to test the activity of the variably reduced Ni/Li$_x$Mn$_2$O$_4$, with the hypothesis that reduction of the support would increase electron density at the Ni active site, facilitating the two-electron oxidative addition of H$_2$ (Figure 4a). Initial screening for catalytic reactivity by *in situ* $^1$H NMR spectroscopy revealed that Ni/LiMn$_2$O$_4$ was inactive in the hydrogenation of olefins, however, hydrogenation was observed for materials with a Li:Mn ratio $\geq$0.90 (Figures S35-36). A series of ethereal and aliphatic olefins and alkynes were hydrogenated by Ni/Li$_{2.26}$Mn$_2$O$_4$, however, more polar functional groups were not tolerated due to side reactions with the surface (Table S9). Control experiments with nickel-free Li$_{2.23}$Mn$_2$O$_4$ did not result in hydrogenation, and the reaction mixture filtered at partial conversion was inactive, ruling out desorption of a catalytically active species (Figures S37-38). No evidence of surface Mn/Ni hydride or butyl groups that could plausibly contribute to catalysis were found by DRIFTS or protonolysis/hydrogenolysis experiments for catalytically active Ni/Li$_x$Mn$_2$O$_4$ materials (Figures S28-30,36).
Kinetic measurements on the full range of reduced materials were performed by monitoring hydrogen uptake for a solution of cyclohexene in toluene with Ni/Li$_{x}$Mn$_2$O$_4$ (1 mol% Ni) (Figure 4b, S39-47). An onset of activity was observed for the material with Li:Mn ratio of 0.90, and catalytic rates increased monotonically with the degree of further support lithiation (Figures 4c, Table S10). Post-catalysis XAS spectra of Ni/Li$_{2.16}$Mn$_2$O$_4$ were similar to those of the pristine material (Figure S48), with a slight decrease in the concentration of the minor reduced Ni species (Table S4) and no induction period is observed (Figure 4b), suggesting that significant structural rearrangement does not occur under reaction conditions. The correlation between catalytic rates and the Li:Mn ratios of Ni/Li$_{x}$Mn$_2$O$_4$ suggests that lithiation plays a critical role in the generation of the catalytically active nickel species and/or stabilization of reactive intermediates. The hydrogen pressure dependence on the rate of the reaction was found to follow saturation kinetics with a linear double reciprocal plot of rate and H$_2$ pressure (Figure 4d). The kinetic dependence of the reaction on cyclohexene concentration was also found to display saturation behavior with moderate inhibition of the reaction at high olefin concentration, and the reaction is first order in catalyst loading (Figure 4e,f). These data are consistent with a plausible mechanism involving an unsaturated Ni resting state under standard conditions, which activates hydrogen (homolytically or heterolytically) followed by olefin insertion and elimination, either of which could constitute the rate limiting transition state.
Figure 4. (a) Reaction scheme for the hydrogenation of cyclohexene catalyzed by Ni/Li$_x$Mn$_2$O$_4$. (b) Reaction profile for the hydrogenation of cyclohexene with Ni/Li$_x$Mn$_2$O$_4$ (Li:Mn = 0.9 – 1.13) monitored by hydrogen uptake, pseudo-zero-order initial rates for cyclohexene hydrogenation as a function of (c) degree of lithiation (Li:Mn = 0.9 – 1.13), (d) H$_2$ pressure (Li:Mn = 0.98), (e) cyclohexene concentration (Li:Mn = 0.95), and catalyst loading (Li:Mn = 0.98), measurements for lithium dependence were performed in triplicate and measurements for kinetic dependence on H$_2$, cyclohexene and catalyst were performed in duplicate. Data is compared within the same batch of Ni/Li$_x$Mn$_2$O$_4$ to eliminate potential batch-to-batch variability. Vertical error bars represent one standard deviation. Standard conditions 95 psi H$_2$, 0.1 M cyclohexene, 1 mol % Ni, 5 mL toluene, 23 °C. (g) DFT calculated reaction coordinates for oxidative addition of H$_2$, insertion of cyclohexene, and elimination of cyclohexane to regenerate the catalyst for Ni/LiMn$_2$O$_4$ and Ni/Li$_2$Mn$_2$O$_4$ models, (h) DFT optimized structure of Ni/LiMn$_2$O$_4$ and Ni/Li$_2$Mn$_2$O$_4$, and thermodynamics of oxidative addition of H$_2$, (i) $\text{Ni}^d$-Density of States comparing Ni/LiMn$_2$O$_4$ and Ni/Li$_2$Mn$_2$O$_4$, showing a significant increase in occupied d-states below the Fermi level for the reduced catalyst model.

A periodic computational model of the hypothesized active site was developed to gain further insight into how surface lithiation might impact the reactivity of a nickel active site.$^{40, 41}$ This model is intended to serve as a representative structure to provide insight into the changes in electronics and activity of nickel as a result of surface lithiation, as opposed to a definitive assignment of the active site and mechanism in this system. Intriguingly, while homolytic activation of H$_2$ at the unreduced Ni/LiMn$_2$O$_4$ was prohibitively high in energy ($\Delta G = 79.6$ kcal/mol), the product of H$_2$ oxidative addition on the reduced material was dramatically stabilized, with a catalytically relevant reaction energy of only 7.9 kcal/mol (Figure 4g,h).

Upon oxidative addition of H$_2$ at the reduced Ni site, the nickel atom migrates out from the 5-coordinate binding pocket in the lithium channel, retaining two oxygen donors and adopting a distorted square planar geometry (Figure 4h). Completing the putative reaction pathway, olefin insertion is energetically favorable by 4.5 kcal/mol, and elimination of the hydrogenated product is downhill by a further 19.7 kcal/mol (Figure 4g, S44). To understand this disparate reactivity, the electronics of the active site was assessed as a function of Ni magnetization and the Ni $d$-orbital density of states (d-DOS). The magnetization of nickel on LiMn$_2$O$_4$ was 1.76, suggesting Ni(II), while, Ni on Li$_2$Mn$_2$O$_4$ had a magnetization of 0.46, interpreted as Ni(I).$^{42}$

Upon oxidative addition of H$_2$, the magnetization of the reduced nickel species increases from 0.46 to 1.15$^{43}$, consistent with an increase in formal oxidation state of Ni(I) to Ni(II). As oxidative addition requires two electrons, an increase in oxidation state from Ni(I) to Ni(II) suggests that an additional electron must be withdrawn from the support, underscoring the analogy to redox non-innocent ligands in the
homogeneous catalysis literature\(^3\), and EMSI in the heterogeneous catalysis literature\(^6\). This electronic change is also captured in the contrasting Ni d-DOS, with a significant increase in the density of occupied states just below the fermi level for the Ni/Li\(_2\)Mn\(_2\)O\(_4\), plausibly facilitating H\(_2\) activation (Figure 4i). The observation of a reduced minor phase in the XAS spectra of variably reduced Ni/Li\(_x\)Mn\(_2\)O\(_4\) (Figures 3a, S18) is consistent (though not exclusively) with the formation of a site similar to the Ni(I) structure identified in the computational model of Ni/LiMn\(_2\)O\(_4\).

**Extension to Anode Material Lithium Titanium Oxide.** To evaluate the generality of lithium intercalation as a strategy for modulation of catalyst reactivity, an analogous system was targeted on the anode material Li\(_x\)TiO\(_2\). Tris(neopentyl)tantalum dichloride (Ta(CH\(_2\)C(CH\(_3\))\(_3\))\(_2\)Cl\(_2\)) was chemisorbed on anatase TiO\(_2\) nanoparticles, which resulted in the release of two equivalents of neopentane per tantalum complex based on in situ \(^1\)H NMR spectroscopy, suggesting a bipodal complex on the surface, Ta/TiO\(_2\) (0.80 wt % Ta. Figures 5a, S59-63).\(^4\) This material was reduced with an excess of lithium naphthalide (LiNap), to afford Ta/Li\(_{0.77}\)TiO\(_2\). Upon lithiation, the Ti K-edge XANES displayed a decrease in white line intensity and in the energy of the edge and pre-edge features, consistent with a decrease in average oxidation state of titanium (Figure 5c). In contrast, the Ta L\(_3\)-edge XANES of Ta/TiO\(_2\) and Ta/Li\(_{0.77}\)TiO\(_2\) exhibited qualitatively similar edge and white line features, suggesting that the oxidation state of Ta remains constant upon lithiation (Figure 5b, S64). In the hydrogenation of cyclohexane, no measurable activity was observed for either unreduced Ta/TiO\(_2\) or tantalum-free Li\(_x\)TiO\(_2\), while Ta/Li\(_{0.77}\)TiO\(_2\) catalyzed the reaction with a half-life of approximately nine hours (Figures 5d, S65-68).
Figure 5. (a) The chemisorption and lithiation of tris(neopentyl)tantalum dichloride on titania to afford Ta/TiO$_2$ and Ta/Li$_{0.77}$TiO$_2$. (b) Tantalum and (c) titanium XANES spectra for Ta/TiO$_2$ and Ta/Li$_{0.77}$TiO$_2$. (d) Reaction profile for the hydrogenation of cyclohexene with Ta/TiO$_2$ and Ta/TiO$_2$ monitored by hydrogen uptake (95 psi H$_2$, 0.1 M cyclohexene, 1 mol % Ta, 5 mL toluene, 23 °C)

Conclusions

This work describes a generalizable approach to the modulation of the activity of single atom heterogeneous catalyst systems by a continuously tunable variable, reductive intercalation of lithium into the catalyst support. The Ni/Li$_x$Mn$_2$O$_4$ materials represent an example of a system in which the support acts as a redox active ligand and its electronic properties are used to control its catalytic performance. The extension of these results to the Ta/Li$_x$TiO$_2$ system demonstrates the generalizability of this approach. The utilization of this continuous variable to modulate catalytic outcomes represents a new approach to rational catalyst design at the interface of organometallics, catalysis, and material science. Work in this area will draw on the wealth of knowledge surrounding lithium intercalation derived from the development of Li-ion battery cathode and anode materials. Further, leveraging the “redox non-innocent” properties of cathode materials towards catalysis is expected to result in novel systems capable of facilitating difficult transformations through innovative mechanisms.
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Notes

The authors declare the following competing financial interest(s): A patent application partially based on this work has been filed (US Patent Application 17/077,630).

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Data Availability The authors declare that the main data supporting the findings of this study are available within the article and its Supplementary Information files. Additional raw data are available from the corresponding author upon request.

Code Availability No custom computer code was generated or used in this research.


21. A process similar to this approach had previously been reported in the grafting of in situ generated Au(0) and Ag(0) on MnO₂ nano materials, although a comprehensive understanding of this process is difficult in the absence of a well-defined molecular precursor.


25. SiO₂ was partially dehydroxylated under vacuum at 700 °C.


27. Long-range order beyond the second nearest neighbor, such as seen in NiO, LiMn₂O₄, or LiMnO₂ was not observed, ruling out the formation of large nickel oxide nanoparticles.


29. A fringe spacing of 0.46 nm confirms that the (111) exposed facet, and fast Fourier transform analysis of the image is consistent with the expected cubic LiMn₂O₄ spinel structure.

30. EXAFS analysis suggests that the Ni local structure changes after reduction to increase the Ni-O bond length and the Ni-Mn path length by an average of 0.023 Å and 0.046 Å, respectively (See SI, Pages S16-S18).

31. Alternatively, the increase in rising edge intensity and the decrease in white line may indicate lower Ni site symmetry.


34. With increasing lithium content two peaks are observed at ~101 ppm and ~118 ppm, with the major peak shifting from the former to the latter as Li atoms shift from the tetrahedral 8a site to the more densely packed octahedral 16c site.

35. Surface roughness in the reduced sample is likely contributed to by strain release upon undergoing the cubic to tetragonal structural transition upon reduction as previously reported.


38. Pressures expected to achieve complete saturation were inaccessible with the experimental apparatus.

39. The rate of the reaction was found to be first order in catalyst loading as expected for a non-diffusion limited heterogeneous catalytic process, however this behavior was observed above a certain threshold of catalyst loading, below which no activity was observed (Figure 4f). This
suggests that the first equivalents of catalyst are quantitatively poisoned by a small impurity in the reaction mixture despite rigorous air and moisture free technique, consistent with a minority of highly reactive active sites.


42. Notably, the subsurface Ni in the same reduced Ni/Li$_2$Mn$_2$O$_4$ model does not undergo a significant change in magnetization, suggesting that exposure to the structure termination and/or the presence of the oxygen vacancy plays a key role on the electronics of the nickel.

43. The magnitude of this value may be partially diminished by pairing of electrons in the pseudo-square planar geometry.