Direct observation of Ni–Mo catalyst formation via thermal reduction of nickel molybdate nanorods

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Abstract

We used in situ transmission electron microscopy to directly image the formation of a Ni–Mo composite nanocatalyst via thermal reduction of NiMoO₄ nanorods. Two clear structural changes were observed as the temperature was increased from 25 to 500 °C in the presence of H₂(g): the first involved nucleation of nanoscale Ni-rich particles, and the second involved general collapse of the remaining oxide phase along with substantial sintering of the alloy particles. The activity of the catalyst toward alkaline hydrogen evolution was found to reach a maximum in a narrow range of reduction temperatures from 375–425 °C. This resulted in the formation of a mixed-phase

product comprising sub-10 nm $\text{Ni}_{0.91}\text{Mo}_{0.09}$ particles embedded in a porous NiMoO_x matrix. Thus, the most active Ni–Mo catalyst apparently requires intimate contact between the metallic alloy component and the oxide phase, lending support to a catalytic mechanism involving oxidized surface sites.

Keywords

Transmission electron microscopy, in situ, ETEM, nickel, molybdenum, molybdate, nanorod, catalyst, hydrogen

Introduction

Nickel-molybdenum composites are used to catalyze numerous redox reactions involving hydrogen intermediates. Examples include thermochemical processes like the water gas shift reaction,¹ hydrotreating reactions,^{2–6} and CO_2 methanation⁷ as well as electrochemical water splitting.^{8–13} Ni–Mo catalysts are often generated via thermal reduction of mixed oxide precursors like nickel molybdate, NiMoO_4 , and prior reports have shown that the details of precursor oxide preparation and thermal reduction have a major influence on the resulting catalytic activity.^{14–19} Nonetheless, very little is known about the structural evolution of these materials during thermal reduction. Herein, we report a study involving the use of environmental transmission electron microscopy (ETEM) to directly observe the formation of a multiphase Ni–Mo composite catalyst.

Our interest in Ni–Mo primarily centers on its potential as a nonprecious catalyst for alkaline anion exchange membrane (AAEM) electrolyzer cathodes. Oxide-derived Ni–Mo alloys have been shown to exhibit excellent catalytic activity toward the alkaline hydrogen evolution reaction (HER).^{10,12,20–24} Several of these prior reports note that the final catalyst contains both metallic and oxidized phases; hence, it remains unclear whether the HER active site is a metallic alloy, an oxide, or a mixture of the two. Moreover, the specific details of how

the competent catalyst forms from the oxide precursor has not been thoroughly explored.

We recently reported that thermal reduction of compositionally homogeneous Ni–Mo oxide precursors results in spontaneous phase segregation into a core-shell nanocatalyst with excellent alkaline HER activity.²⁵ This result is intriguing for several reasons: first, the thermodynamically stable product under these treatment conditions is a single intermetallic with the empirical formula Mo_7Ni_7 rather than the observed mixture containing a face-centered cubic (fcc) alloy and a mixed oxide.^{26–30} Second, applying the same thermal reduction treatment to Mo oxide alone does not yield metallic Mo, but instead the sub-oxide $\text{MoO}_{3-\delta}$.^{31,32} Accordingly, the dynamics of Ni–Mo oxide reduction apparently depend on kinetic factors that may include cooperative interactions between the respective metals.

Recent advances in *in situ* analytical methods have made it possible to understand nonequilibrium solid-state chemical transformations in fine detail. Several prior studies have focused on the dynamics of nickel molybdate reduction to the alloy component using *in situ* methods like X-ray diffraction,³³ Raman spectroscopy,³⁴ X-ray photoelectron spectroscopy³⁵ and temperature programmed reduction.^{36,37} These studies collectively suggest that the thermal reduction of NiMoO_4 commences with preferential reactions at Ni sites, which subsequently activate hydrogen to reduce neighboring Mo-oxides. This mechanistic formulation is plausible, as Mo is not a good hydrogen activator; accordingly, Mo-oxide reduction in these systems may only proceed via hydrogen spillover from Ni.³⁸

Transmission electron microscopy (TEM) is a uniquely powerful tool for local characterization of nanomaterials, providing a wealth of structural, compositional, and chemical information that is spatially resolved over the μm - to $\text{\AA}$ -scale. However, for inherently dynamic processes like materials synthesis or catalytic reactions, the dynamic state of the materials cannot generally be inferred from *post mortem* examination alone. Transient structures, for example, would be entirely missed, and correlating structural changes with specific performance behavior is challenging when those structural changes can only be inferred and not directly observed.

This study focuses on the use of environmental TEM (ETEM), in which the microscope column^{39,40} and/or the sample holder^{41,42} have been modified to allow for the introduction of gaseous or liquid environments around the sample. Additional external stimuli—such as heat,^{43–45} electrical biasing,⁴⁶ light,^{47,48} and mechanical stresses^{49,50}—can then be applied through the use of specialized sample holders, enabling examination of materials in real time under relevant reaction conditions. These capabilities have rendered *in situ* ETEM indispensable for understanding the fundamental reaction mechanisms and structural dynamics occurring during catalysis,^{51–54} oxidation and corrosion,^{55,56} and nano-synthesis.^{57–59} It is to this end that we employed ETEM in our study of the transformation of Ni–Mo oxides into complex, multiphase electrocatalysts.

Experimental

Nickel molybdate nanorods were synthesized via a hydrothermal reaction between aqueous Ni and Mo salts, following several prior reports.^{24,60–68} In a representative synthesis, 0.15 g of nickel nitrate hexahydrate (98%, Alfa Aesar) and 0.12 g of sodium molybdate dihydrate (99.5%, Alfa Aesar) were added to 15 mL of deionized water (purified using a Millipore Advantage A10 system) and dissolved by sonication in an ultrasonic bath (Branson M1800). Ni gauze (Alfa Aesar, 100 mesh, 100 mm dia wire) was cut into several 3x8 cm strips and cleaned by ultrasonication for 5-10 minutes in 2 M hydrochloric acid (99.5%, Fisher Scientific), followed by rinsing in ethanol (99.5%, Decon laboratories) and de-ionized water. Several strips were then vertically oriented against the interior walls of a polytetrafluoroethylene (PTFE) lined acid digestion reactor (Parr 4744). The reactor was finally loaded with the aqueous Ni+Mo precursor mixture, sealed, and placed in a preheated muffle furnace (Lindberg/Blue M Moldatherm) at 160°C for 6 hours. The reactor was allowed to cool to room temperature passively for several hours prior to opening. The Ni gauze, which had become matte green in color, was then removed from the reactor and sonicated for 30 minutes to remove the green

solid. The resulting suspension was dried at 60 °C overnight.

Reduced Ni–Mo composites were generated by heating the NiMoO₄-coated Ni gauze samples in a tube furnace (Lindberg/Blue M Mini Mite) under an atmosphere containing 5% H₂ and 95% Ar (Matheson). The reduction temperatures were varied from 200 to 600 °C for a total of 1 hour. After reduction, the mesh was sonicated in isopropanol to suspend the Ni–Mo catalyst composite. The mass of catalyst in the suspension was obtained by dropcasting a known amount of the solution on a borosilicate glass microscope slide and weighing it on an ultramicrobalance. A final suspension was then prepared with 1 mg/mL of Ni–Mo in isopropanol along with 1 mg/mL of 20 wt% Nafion solution.

Reaction products were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). A Bruker D8 system with Cu K α radiation ($\lambda=1.54$ Å) was used for XRD. The diffraction angle was varied from $2\theta = 10^\circ$ to 80° with an increment of 0.02° . The data collection time at each increment was modified empirically to obtain adequate signal to noise. SEM analysis made use of Zeiss Sigma 500 VP microscope, wherein a small amount of powder was supported on a carbon tape substrate. Micrographs were collected using secondary electron detector at an accelerating voltage of 10 keV. TGA was carried out using a TA Instruments SDTQ600 thermogravimetric analyzer. He gas was flowed continuously throughout the experiment at a rate of 100 sccm. The sample was loaded into an alumina pan and equilibrated under 20 sccm of Ar gas flow inside the chamber. Then the Ar flow was replaced by 15 sccm of H₂ and the temperature was ramped from ambient to 600 °C at a rate of 2 °C/min.

Specimens for TEM examination were prepared by drop-casting colloidal suspensions diluted in isopropanol onto 400 mesh ultrathin carbon-coated Cu TEM grids (Ted Pella Inc.) or, for *in situ* experiments, 5-nm thick SiN_x membrane grids (SiMPore Inc.). High-resolution TEM (HRTEM) and scanning TEM (STEM) imaging, selected-area electron diffraction (SAED), and energy-dispersive X-ray spectroscopy (EDS) mapping were performed using

a JEOL JEM-2100F S/TEM operated at 200 kV and equipped with an Oxford X-Max^N 80T energy-dispersive X-ray spectrometer.

Additional TEM imaging, electron diffraction, and *in situ* thermal reduction were carried out using a Hitachi H-9500 ETEM, operated at 100–300 kV. The *in situ* experiments were performed at a 100 kV operating voltage; at this voltage the NiMoO₄ was fully stable under the electron beam, even at lattice resolution. Above this voltage, voids were observed in the oxide after extended high-resolution observation (see Supporting Information). The H-9500 was equipped with a home-built, computer-controllable gas manifold for introducing gases and vapors directly into the sample chamber. Heating of the sample was accomplished through a Hitachi double-tilt furnace-style heating holder.

Ex situ high-angle annular dark-field (HAADF) STEM imaging and EDS mapping following the ETEM experiment was performed using a Thermo-Fisher Scientific/FEI Titan Themis G2 200 probe-corrected S/TEM operated at 200 kV and equipped with a Super-X 0.7 sr quad-EDS detector system. No appreciable changes in the specimens were observed during TEM analysis, even during the extended EDS mapping, indicating that beam-damage did not result in sample modifications under the conditions employed. The observed morphologies were consistent across all microscopes and imaging modes.

A Gamry Reference 1000 potentiostat/galvanostat was used for all electrochemical analysis. The electrolyte was 0.1 M aqueous KOH (ACS reagent grade), which was freshly prepared prior to each measurement and pre-saturated with H₂ (99.999%, Matheson) at atmospheric pressure. HER measurements were carried out using a rotating disk electrode (Pine MSR) apparatus, wherein a known quantity of catalyst was deposited onto a glassy carbon substrate (Pine Changedisk). A large-area Ni foil (5 mil thickness, ≥99%) was used as a counter electrode and Ag/AgCl (Thermo Scientific) was used as a reference electrode. The reference electrode was further calibrated to the reversible hydrogen electrode (RHE) potential using commercial Pt/C catalyst (Johnson Matthey HiSPEC) after experiments with Ni-based catalyst were complete. Cyclic voltammograms were collected over a voltage

range bracketing the equilibrium potential for the hydrogen evolution reaction at a scan rate of 10 mV/s. Solution resistance was measured via electrochemical impedance spectroscopy using a high-frequency AC waveform superimposed on a DC bias of 0 V vs. RHE and was compensated by subtracting the iR drop from the observed current versus overpotential data after experiments were complete. The measured solution resistance was generally found to be in the range of 40 to 50 Ω , which agrees well with the expected value based on the electrolyte composition and cell geometry.⁶⁹

Results and Discussion

To evaluate structural and morphological changes in the NiMoO_4 nanorods, we combined temperature-programmed reaction experiments with *ex situ* SEM, TEM and XRD measurements. The structural and compositional analysis of as-synthesized oxide are compiled in Figure 1. The prominent phases identified by XRD were α - and β - NiMoO_4 with the possible addition of residual NaNO_3 from the synthesis mixture. Energy dispersive spectroscopy analysis in SEM gave 60:40 ratio of Ni:Mo. The stability of β - NiMoO_4 phase at room temperature is attributed to the presence of excess Ni, as has been reported elsewhere.^{15–17,70,71} The NiMoO_4 particles were predominately rods that were up to a few hundred nm in diameter and several μm in length (Figure 1b), although a small fraction of spherical particles were also observed (see Supporting Information). TEM examination confirmed the nanorods to be crystalline NiMoO_4 with a high density of planar faults running parallel to the rod axis.

Figure 2 depicts representative diffraction, SEM, and TPR data for the thermal reduction of NiMoO_4 nanorods. Reduction at 300 °C resulted in a marked decrease in long-range crystalline order, as evidenced by the loss of discernible XRD features. After reduction at 400 °C, the XRD shows peaks corresponding to unreduced NiMoO_4 and comparatively broad features at $2\theta = 44, 52, \text{ and } 76^\circ$ (Figure 2a), which we assigned to a Ni-rich fcc $\text{Ni}_x\text{Mo}_{1-x}$ alloy. A lattice constant of $3.56 \pm 0.01 \text{ \AA}$ was extracted from these peaks. The Mo content

Figure 1: (a) XRD pattern of as-synthesized Ni–Mo oxide nanowires with the corresponding standard diffraction pattern obtained from ICDD database. (b) SEM image of the as-synthesized oxide. (c) TEM micrograph of a representative nanorod. (d) HRTEM of a representative nanorod showing planar faults running parallel to the rod axis, seen in the lattice shifts (examples indicated with dashed lines). These faults also manifest as the stripes in the contrast of (c). (e) Representative SAED pattern of the nanorod in (c) indexed to α -NiMoO₄; the pattern also displays characteristic streaking (perpendicular to the rod axis) and extra spots associated with planar faults.

Figure 2: Characterization of NiMoO_4 nanorods after thermal reduction: (a) Empirical XRD patterns at 300, 400, and 500 $^\circ\text{C}$ along with standard patterns obtained from the ICDD database. (b) Representative SEM image of the product upon reduction at 400 $^\circ\text{C}$. (c) Temperature programmed reduction data showing percent weight loss and the first derivative of the weight loss over the full temperature range of interest.

in the reduced alloy was calculated from the shift relative to that of pure Ni and found to be 9.86 ± 1.99 mol%.⁷² Increasing the reduction temperature to 500 °C resulted in a significant decrease in the intensity of the fcc peaks relative to several new features below $2\theta = 25^\circ$, which we were unable to successfully index to known phases containing Ni and/or Mo.

SEM imaging of the Ni–Mo composite after reduction at 400 °C (Figure 2b shows that the rod structure remained intact alongside a modest population of isotropic particles. The temperature programmed reduction data in Figure 2c indicate a monotonic decrease in mass with an increase in temperature under H₂, consistent with thermal reduction of NiMoO₄ to metallic and/or suboxide products.²⁵ The first-derivative of the weight loss curve gives three minima at 240, 340, and 460 °C. This suggests multiple distinct chemical transformations occur over the temperature range from 25 to 600 °C.

Figure 3 compiles XPS data for as-synthesized NiMoO₄ and the composite obtained after reduction at 400 °C. Prominent peaks identified in the survey spectra were Mo 3d, C 1s, N 1s, O 1s, Ni 2p and Na 1s. We attribute the presence of Na and N to NaNO₃, the water soluble product of the salt metathesis reaction that may remain entrained within NiMoO₄.

High resolution XP spectra for the Ni 2p and Mo 3d regions were also collected. Nickel peaks in the oxide are consistent with Ni²⁺, and upon reduction there emerged evidence for metallic Ni. The relatively low intensity of this metallic feature is consistent with considerable oxidized Ni on the surface of the catalyst composite, which may result from incomplete reduction or re-oxidation of Ni in the alloy phase upon sample handling in air. Similarly, the Mo region in the oxide phase shows only features corresponding to Mo⁶⁺, while the final product shows a clear evidence for partially reduced Mo⁵⁺ and Mo⁴⁺ and a tentative evidence for Mo⁰.

The observed changes in composition and morphology can be directly correlated with catalytic activity towards the alkaline hydrogen evolution reaction. Figure 4 collects representative polarization data (normalized to electrode area) and hydrogen evolution activity at 200 mV overpotential as a function of reduction temperature in 0.1 M KOH.

Figure 3: Representative XP spectra and fits for NiMoO_4 oxide before and after reduction at 400 °C: (a) survey scans; (b) Ni 2p region; (c) Mo 3d region.

Figure 4: Representative polarization curves (a) along with geometric and mass activity data (b) for NiMoO₄ nanorods that were thermally reduced over a range of temperatures. Measurements were performed in H₂-saturated 0.1 M KOH using a catalyst mass loading of 50 $\mu\text{g}/\text{cm}^2$ at 10 mV/s scan rate.

A catalyst mass loading of $50 \mu\text{g}/\text{cm}^2$ was used throughout these measurements to minimize the confounding effects of electrical resistance associated with thicker films containing significant residual oxide.²⁵ The catalytic activity increased initially up to 400°C and then decreased significantly at higher reduction temperatures. This trend is consistent with the TPR measurements, where two distinct chemical transformations were observed below and above 400°C .

These activity measurements combined with the characterization results suggest that NiMoO_4 reduction is a multi-step process, and only the product obtained at moderate reduction temperatures is a competent HER catalyst. The as-synthesized oxide and the products obtained on reduction at $\leq 200^\circ\text{C}$ display activity that is not significantly greater than the glassy carbon background (see Supporting Information). At 240°C , a slight mass loss in the TPR data does not result in any apparent change in composition (see Supporting Information); hence, we attribute this feature to be loss of surface water. The HER activity begins to increase discernibly at 300°C , which also coincides with initial XRD evidence for formation of the fcc Ni–Mo alloy, suggesting nucleation of the active catalyst species. At 400°C , XRD data clearly indicate the formation of an alloy phase, but the high XPS intensities for Ni and Mo oxides suggest incomplete reduction of the initial oxide. Nonetheless, the HER catalytic activity is maximized at this treatment temperature, which further suggests that the active catalyst requires both metallic and oxidized components.

The decrease in activity at 450°C corresponds well to the TPR data showing the onset of a third chemical transformation near this temperature. Additional analysis by XRD and *ex situ* TEM (see Supporting Information) do not give a clear indication of the nature of this chemical transformation. Furthermore, all of the materials analysis presented up to this point leave open the question of what is the nanoscale composition and morphology of the active form of the catalyst obtained around 400°C .

To provide further insight into the nanoscale structural changes occurring during the catalyst nucleation and growth processes, we performed TEM characterization *in situ* during

thermal reduction under hydrogen flow using an ETEM system. NiMoO_4 nanorod specimens were heated under 1.1×10^{-2} Pa of H_2 from 25 to 500 °C. Heating was performed in 25 °C steps, with the temperature held steady at each step until no further structural changes were observed. In addition to the nanorods followed continuously throughout this process, additional nanorods that were not continuously exposed to the electron beam were also briefly examined after each major transformation (see Supporting Information). The morphological changes we observed were consistent across all examined nanorods, confirming that these changes were not merely products of electron beam interaction.

Real-time ETEM analysis data were collected during thermal reduction as continuous videos, which are included as Supporting Information. Selected bright-field still images as well as selected-area electron diffraction (SAED) data over a range of temperatures (after cessation of the associated structural changes) are collected in Figure 5. Additional imaging and SAED data have also been included in the Supporting Information. Consistent with the TEM imaging data in Figure 1, the as-synthesized NiMoO_4 rods (Figure 5a,g,k) were highly crystalline with planar faults running parallel to the rod axis. This morphology remained unchanged until reaching 350 °C (Figure 5b,h,l), when small Ni-rich nanoparticles (mean of 4.5 ± 1.5 nm, Figure 6) were observed to nucleate in and on a porous Mo-rich oxide “skin.” The nanoparticles were evenly dispersed and, once nucleated, remained in place, growing via diffusion of Ni from the surrounding NiMoO_4 as it continued to react. As seen both in the image itself, as well as by the continued presence of the strong planar-faulted single-crystal diffraction pattern in Figure 5j, the core of the nanorods remained mostly intact.

Increasing the temperature to 375 °C (Figure 5c,i,m) produced more Ni-rich nanoparticles along with a coarsening of their overall size to 9.4 ± 3.1 nm (Figure 6) as the porous outer layer progressed deeper into the nanorods. Upon equilibration, the outermost layer of each nanorod had transformed into a porous Mo-rich oxide network, into and onto which was embedded metallic nanoparticles. Electron diffraction indicated these particles indeed showed the Ni fcc crystal structure; hence, they agree well with the XRD observations

Figure 5: TEM micrographs and SAED patterns for NiMoO_4 nanorods that were thermally reduced in the ETEM at selected temperatures. Images were collected after cessation of observable structural changes. (a-f) Images of the full region continuously followed during reduction. (g-j) Close-ups of a region of the thin nanorod indicated by the box in (a), at the indicated temperatures. The dashed lines in (i) delineate the boundary between the porous, Mo-rich outer oxide layer and the solid nanorod core. Dashed outlines in (j) indicate Mo-rich oxide and/or nitride flakes. (k-o) SAED patterns of the thin (leftmost in a-f) nanorod at each of the indicated temperatures. The pre-reduction diffraction pattern (k) indexes as $\alpha\text{-NiMoO}_4$ (Miller indices are annotated). The polycrystalline pattern in (n) is consistent with fcc Ni and several Mo-rich oxides/nitrides.

indicating formation of a Ni–Mo alloy containing $\sim 90\%$ Ni. For all the rods examined, this structural change halted at a depth of 20–30 nm below the original nanorod surface, leaving the nanorod core largely intact (Figure 5i,m).

Figure 6: Size distribution violin plots of the Ni-rich nanoparticles in the Ni–Mo composite after thermal reduction at 350, 375, and 425 °C. The nanoparticle populations were taken from the same region of the same nanorod at the given temperatures. The dashed lines indicate the median and the dotted lines indicate the quartiles. Total population sizes were $N = 64, 90, 125$, respectively. Only particles that were clearly resolvable were counted.

Upon heating to 425 °C, the second major reductive transformation began to occur. The previously intact core of the nanorod completely reacted, leading to a dramatic phase segregation into isotropic Ni-rich nanoparticles and large, angular Mo-rich oxide crystals (Figure 5d,j,n). The number and average size of the Ni-rich nanoparticles notably increased (14.1 ± 7.4 nm, Figure 6), and the size distribution also increased markedly, with the largest particles growing to nearly 100 nm in diameter. The coarsening of existing nanoparticles combined with a transition to a strongly lognormal overall distribution (see Supporting Information) indicates that both Oswald ripening and particle migration and coalescence were active at this stage. The Mo-rich oxide particles—with a mean diameter of 72 ± 38 nm and an observed range from 20 to 200 nm—formed by the reduction of the core

were predominantly flake- or rod-like, highly faceted crystals, as confirmed via HRTEM (see Supporting Info). This porous outer layer that had formed at 350-375 °C was also partially consumed into these crystals as they reduced further.

The overall process of NiMoO_4 chemical transformation and phase segregation was largely complete after equilibration at 425 °C, but slight coarsening and particle movement continued up until 500 °C (Figure 5f,o), where the experiment was terminated. The transformation trends were consistent in all rods observed, regardless of initial rod diameter or whether they were actively imaged during reduction (see Supporting Information). In fact, particle coarsening and phase separation were actually more pronounced in some rods that were only exposed to the electron beam before and after heating. This suggests that although even relatively light interaction with the electron beam may change some specific details of the morphology change (e.g., the exact size, number, and/or distribution of nucleated Ni-rich particles), the general observations and trends are the same.

Attempts to quantitatively identify the crystalline phases present in the fully reacted product via SAED were hindered by the near-equivalent plane spacings in several Mo-rich oxides as well as fcc Ni. Thus, for each of the observed diffraction rings we identified at least two possible phases. Nonetheless, the measured diffraction rings/spots are consistent with a Ni-rich fcc alloy and the expected Mo-rich oxides. Major diffraction peaks present in the SAED pattern of (Figure 5n) corresponding to the dominant phases observed by XRD have been indicated. There was also some evidence for Mo nitride in the final product; we speculate that this results from thermal reduction of residual nitrate from the synthesis mixture.

The phase segregation of the fcc Ni-rich alloy from the Mo-rich oxide was confirmed via HAADF-STEM imaging and EDS elemental mapping of the fully reduced nanorods (Figure 7). These data show that Ni is effectively localized entirely to the isotropic nanoparticles (brighter in the HAADF image), while the rods' outer shell and large interior crystals are comprised primarily of Mo, O, and N. Additional HAADF-STEM images and EDS maps

Figure 7: HAADF-STEM image (upper left) and the corresponding EDS elemental maps from a region of the thinnest (leftmost) rod in Figure 5 after thermal reduction at 500 °C.

from nanorods in the primary cluster and from a nanorod that had not been imaged at all before or during the *in situ* reduction are included in the Supporting Information. These observations collectively indicate that all of the Ni in the NiMoO_4 precursors that is accessible to the gas-phase H_2 reactant is fully reduced at ≤ 500 °C. By contrast, the vast majority of the Mo content of the precursor remains oxidized, which is consistent with prior reports showing that Mo-oxides are highly resistant to full reduction under H_2 at temperatures below 600 °C.^{31,32,73}

Upon consideration of the *in situ* and *ex situ* data together, the increase in alkaline HER activity beginning at 300 °C is consistent with the formation of catalytically active Ni-rich nanoparticles surrounded by porous Mo-rich oxide network. The highest activity was then achieved when a substantial number of small Ni-rich nanoparticles was formed while still being embedded within a Mo-rich oxide matrix. This leaves at least two plausible explanations for the observed HER performance. The first is that metallic $\text{Ni}_{0.9}\text{Mo}_{0.1}$ nanoparticles are the only catalytically competent species, and the narrow activity maximum at ~ 400 °C corresponds to point at which the exposed surface area of these particles is maximized.

The activity decrease above 400 °C then results from the decrease in surface area and loss of inter-particle connectivity due to nanorod pulverization. However, this explanation is complicated by the fact that XPS results show substantial Ni surface oxidation in samples that were handled in air after thermal reduction, as well as a significant increase in the total number of Ni-rich particles at temperatures above 400 °C.

Another possibility is that the HER catalytic performance of these materials in fact depends on the interaction between the metallic alloy particles and the residual oxide. Indeed, numerous recent reports have emerged indicating that alkaline HER electrocatalysts based on precious and nonprecious metals benefit from synergistic interactions between metallic and oxidized surface sites.^{74–78} We speculate that the active catalytic unit in these Ni–Mo composites may in fact be interfacial sites where Ni, MoO_x, and aqueous electrolyte coexist under HER reaction conditions. Accordingly, the decrease in activity at reduction temperatures above 400 °C would then be attributable to a significant decrease in metal–oxide contact area associated with sintering and consolidation of larger nanoparticles. Nonetheless, the multiphase and morphologically irregular nature of this catalyst makes it difficult to implicate any particular active site or reaction mechanism.

Conclusion

Using a series of *in situ* and *ex situ* characterization tools, we showed that the thermal reduction of NiMoO₄ nanorods proceeds via a series of distinct chemical and structural transformations. The reduction of crystalline oxide initiates with Ni-centered nucleation events and ultimately leads to phase segregation between Ni-rich alloy nanoparticles and Mo-rich oxides. The catalytic activity of this composite toward the HER was maximized only over a narrow range of reduction temperatures, which coincides with the formation of small Ni-rich nanoparticles in intimate contact with a Mo-rich oxide matrix whose overall morphology (rod-shaped) matches that of the precursor. While these compositional and

structural transformations were all clearly resolved using ETEM, the multiphase nature of the catalyst makes it difficult to identify the precise composition of the active site(s). Further work would be warranted to identify synthetic strategies for phase-pure, monodisperse Ni–Mo alloys and metal/oxide composites to further assess the active site(s) for hydrogen evolution and thermochemical hydrogenation reactions.

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