Environmental TEM Study of $NiMoO_4$ Nanorods Undergoing Thermal Reduction: Observing the Formation of a Ni–Mo Alloy@oxide Core-shell Catalyst

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Catalyst composites containing nickel and molybdenum are widely used in hydrotreating processes and in electrocatalytic reactions associated with water electrolysis (e.g., for hydrogen fuel or chemical feedstocks)[1-3]. These types of composites can be synthesized from mixed oxide precursors that are broadly classified as nickel molybdates (i.e., $NiMoO_4$), but in fact comprise a wide range of compositions and crystal structures.[4] Moreover, the way that these oxides are generated and processed (e.g., thermal treatments, deposition on catalyst supports) can substantially impact their ultimate catalytic activity.

We are studying Ni–Mo alloy catalysts for their electrochemical activity toward hydrogen production from aqueous alkaline electrolytes[5]. These alloys can be synthesized via thermal reduction of nickel molybdate precursors in a hydrogen environment[6]. However, we recently found that Ni–Mo catalysts synthesized in this way are not pure-phase alloys; instead, they exhibit a mixed-phase composition comprising Ni-rich alloy nanoparticles encapsulated in a Mo-rich oxide shell[5]. The natural conversion of a compositionally homogeneous precursor into a core-shell product in a single reduction step is intriguing and suggests broader opportunities to control structure-function relationships in these catalysts. Tailoring synthesis first requires understanding the complex transformation process occurring. This cannot be accomplished by *post mortem* analysis alone. The environmental transmission electron microscope (ETEM) is an ideal tool to investigate this question, as it enables direct observation of structural and compositional dynamics at sub-nm spatial resolutions under relevant synthetic conditions.

In this work, we present an *in situ* ETEM study – correlated with temperature-programmed reaction (TPR) – of the compositional and morphological evolution of $NiMoO_4$ nanorod precursors as they undergo thermal reduction to form the desired catalyst structure. The highly uniform $NiMoO_4$ nanorod samples were synthesized using a previously reported hydrothermal method[7]. Briefly, an aqueous solution of nickel nitrate and sodium molybdate was heated in an autoclave reactor at 160 °C for 6 hours. The resulting green precipitate was characterized further for its reactivity toward thermal reduction. X-ray diffraction from the nanorods matched a known phase of $NiMoO_4$ [7], and energy-dispersive X-ray spectroscopy (EDXS) measured a 60/40 ratio of Ni to Mo. TPR experiments involved heating the nanorods at a rate of 1 °C/min under a 15% H_2 atmosphere to observe the temperatures associated with reduction events. We used a Hitachi H9500 ETEM (operated at 100 keV) equipped a homebuilt multi-species gas injection system and a double-tilt heating holder to examine the structural transformation of the nanorods under a 0.1 Pa H_2 reducing environment while heating up to 550 °C in 50 °C increments. The specimen was held at each temperature until no further changes were observed.

The TPR measurement (Fig 1a) exhibited two clear reduction events (indicated by minima in the first derivative of the mass vs temperature data) at 330 and 465 °C. The structural changes occurring at these two points were revealed by the *in situ* TEM reduction (Fig 1b), wherein two distinct transformations were observed. Upon reaching 350 °C, Ni uniformly migrated out of the nanorods, nucleating (mostly) 4-12 nm Ni-rich particles on the exterior and near-surface interior, and leaving behind a porous Mo-rich oxide shell. This process effectively halted once a ~5-10 nm depth below the nanorod surface was evacuated in this manner. The Ni-Mo material in the nanorod core remained intact until reaching 450 °C, at which point it transformed into larger (~10-25 nm) Ni-rich nanoparticles that remained inside the oxide shell. The hollows produced were also notable larger than the small-scale porosity of the shell. Subsequent heating, up to 550 °C, induced significant sintering of the nanoparticles and structural alternation of the oxide shell, corresponding to the measured drop in catalytic performance. Additional *in situ* TEM reduction experiments are underway to probe for a temperature/time-dependence of the final structure and use electron energy-loss spectroscopy to quantify the compositions and – catalytically impactful – oxidation states of the various metal and oxide structures formed at each stage. This work has provided insight into the formation of these core-shell-type structures, and the knowledge gained from these studies will enhance our ability to tailor the synthesis of these materials to optimize their catalytic performance [8].

References:
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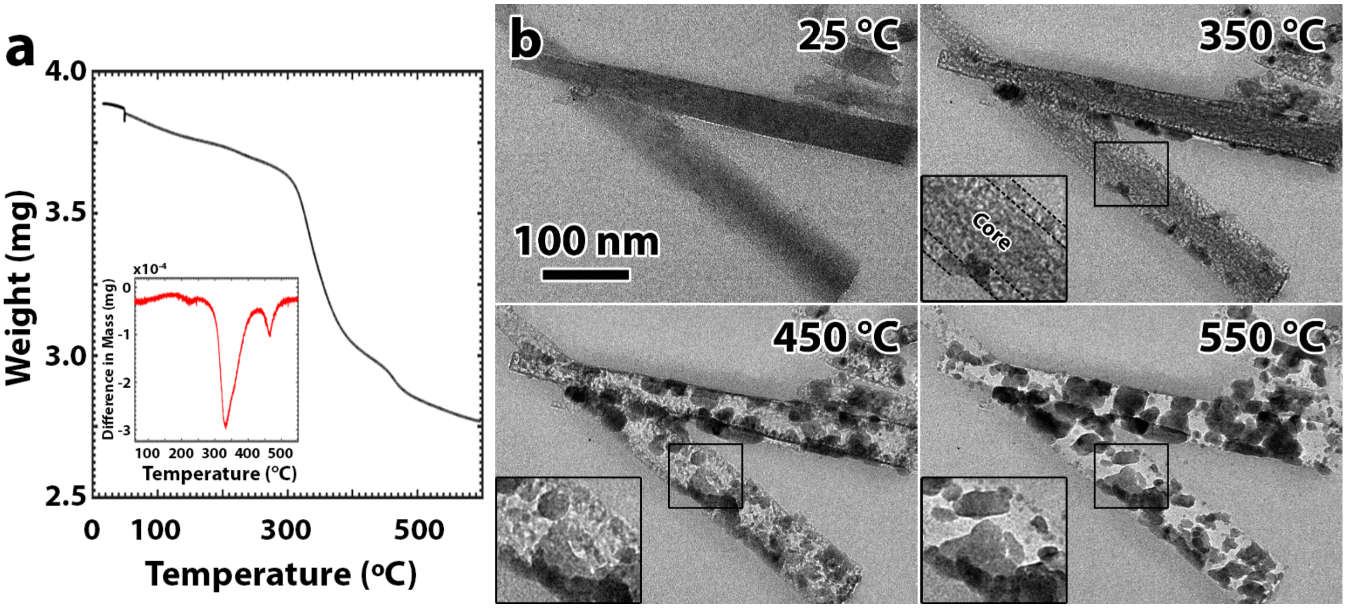

Figure 1. (a) TPR analysis of the $NiMoO_4$ nanorod reduction. The inset shows the first derivative of the data, to more clearly visualize the inflection points, (b) Micrographs from the *in situ* TEM reduction in H_2 showing the corresponding structures formed at the key transformation temperatures. The dashed lines in the inset bound the Ni-depleted layers.