

Narrative Progress Report PRF#: 57589-ND5

Effect of P-Block Modifier and Element Ratio in Transition Metal Intermetallic Alloy Catalysts for Semi-Hydrogenation

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1 Quantum Chemical Study of Element Selection and Element Ratio Effects

To systematically understand the effect of p-block element selection on the control of surface and catalytic chemistry of IMCs, we have performed a computational surface science study over Ni+B-group IMCs (NiB, NiAl, NiGa, NiIn, and NiTi) in the context of the semi-hydrogenation of acetylene (published in *Journal of Catalysis*) [1]. A kinetic rate constant analysis was performed to understand the kinetic preference for each catalyst for the selective production of ethylene, unselective overhydrogenation to ethane, oligomerization via $\text{HCCH} + \text{HCCH}_2$ coupling, and coke formation. The most favorable reaction pathway for each material has been isolated. Considering adsorption probes as surface reactivity makers, general changes in surface reactivity as a function of p-block element agreed well with observed reaction pathway preference, but some critical deviations are present over NiAl and NiGa. Acetylene, ethylene, and dissociative H_2 adsorption follow a rough volcano-like trend with NiAl and NiGa exhibiting the lowest reactivity towards the adsorbates (see Figure 1a, 1b, and 1c). The reduced surface reactivity of NiAl and NiGa correlate well with improved orbital overlap where the element sizes match. Whereas, for smaller (B) or larger (In or Ti) p-block elements where a size mismatch occurs with Ni, greatly elevated surface reactivity is encountered.

The correlations between activity and surface chemical reactivity markers were investigated via Sabatier analysis. Sabatier correlations for hydrogenation of acetylene to ethylene, hydrogenation of ethylene to ethane, and oligomerization of acetylene to butadiene are shown in Figure 1d, 1e, and 1f, respectively. Significant changes in surface chemical reactivity of the suite of IMCs towards intermediates and reactants as a function of p-block element produces an equally significant range of relative activities in each reaction pathway. The lack of systematic and localized linear trends that were a function of only one surface chemical reactivity marker, as commonly encountered over monometallic surfaces, further suggests significant ensemble or electronic effects in the Ni+B-group IMC surface and catalytic chemistry [2–7]. As all Ni+B-group IMCs are isoelectronic, the changes in surface chemistry are driven predominantly by changes in orbital-orbital overlap, electronegativity differences between Ni and the p-element, and a minor ensemble effect (three-fold to two-fold Ni reaction sites, where applicable).

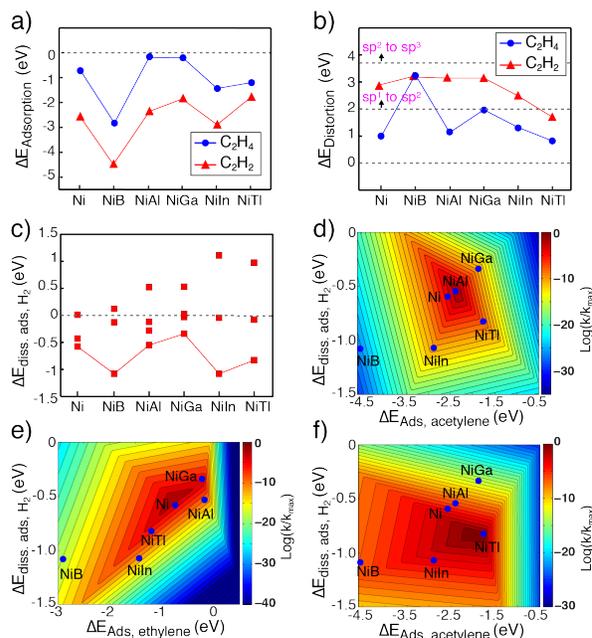


Figure 1

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2 Experimental Synthesis and Performance Studies of Ni+Ga IMC Systems

Experimental efforts to bring computational predictions to reality have focused considerably on developing synthesis techniques for oxide supported IMC nanoparticles of phase pure bulk and controlled particle surface composition. At this time, oxide and carbon-supported nanoparticles of IMCs with pure bulk phase and bulk-like or modified surface composition have been successfully synthesized by investigating the effect of salt choice, support choice, reduction conditions, and annealing conditions on bulk and surface composition, particle size, and overall stability of supported nanoparticle IMCs. One of the major issues in the synthesis is the availability of TM and p-elements on the support surface, which is dictated by salt reduction kinetics and the diffusion of the reduced-elements across the support. In the choice of precursor, we find that nitrates most often allow for rapid and complete reduction of the precursors within a tight temperature range (see Figure 2a). Choice of silica oxide support, with its low surface reactivity, enabled element diffusion as well as rapid reduction. When utilizing alumina, HR-EDS analysis showed that pTM element diffusion was inhibited leading to sub-stoichiometric IMC particles with unused pTM elements distributed across the support (see Figure 2d and 2e). Use of other more reactive oxide supports amplified this effect. In addition, high H_2 chemical potential can drive the formation of pure bulk phase by weakening the interaction between element and support surface.

Despite these advances, it is also necessary to have well-defined surface composition of the IMCs such that surface and catalytic chemistry may be connected. Preliminary studies have determined that utilizing H_2 as a reducing agent can pull either TM or p-block elements to the surface leading to core-shell structure. For example, Ni-rich surface terminated Ni_3Ga and In-rich surface terminated Ni_2In_3 were produced after reduction pretreatment with pure H_2 . However, this effect can be really countered by employing high temperature annealing to reorganize the elements in the particles. HS-LEIS of as-reduced and after-annealing samples of Ni_3Ga show the transformation from nickel-rich surface to bulk-like surface (see Figure 2c). HS-LEIS data shown in Figure 2c also indicated successful synthesis of Ni+Ga and Co+Ga at 1:1 with bulk-like surface composition. Our established fundamental understanding of IMC formation enables us to produce a larger range of IMC compositions to be used. Our recent publications focused on the development of highly selective and stable Ni+Ga IMC catalysts for the direct dehydrogenation of alkanes illustrates how IMC surface composition and catalytic chemistry can be manipulated [8, 9].

3 Impact of Research on the Career of the PI and Graduate Students

This ACS PRF funding jumpstarted the PI's career in the study of IMC catalysts. This compositional space was under-explored, most notably the non-noble metal IMCs. The PI ultimately was awarded an NSF CAREER award for his work in IMC catalysts, which was made possible through this grant. Two graduate students, Yuanjun Song and Yang He were partially trained through this funding in many aspects of IMC surface and catalytic science. Both students have published 2+ papers each on the research performed in this project.

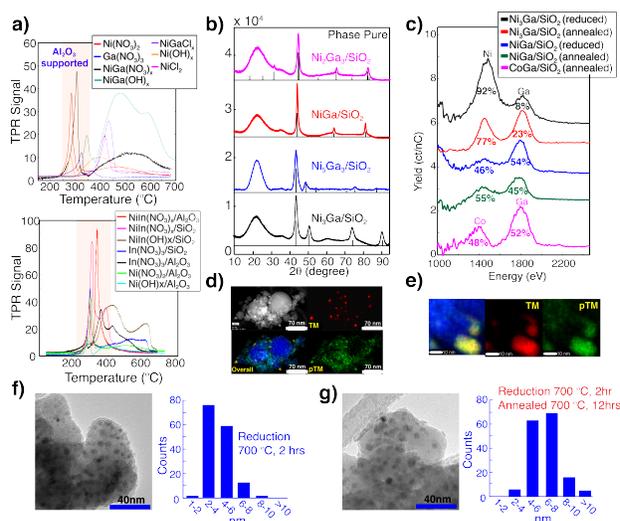


Figure 2

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