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Letter

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The Origin of the Special Surface and Catalytic Chemistry of Ga-Rich Ni_3Ga in the Direct Dehydrogenation of Ethane

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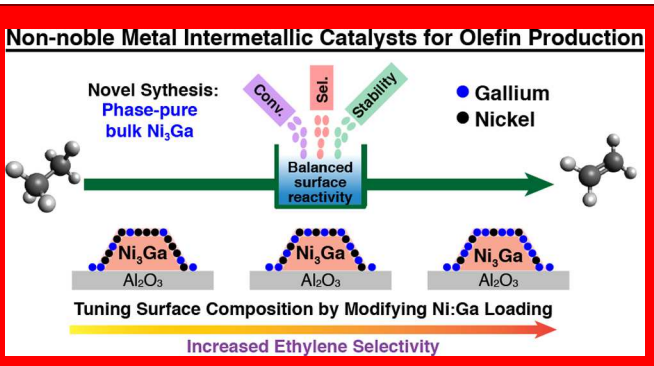
Supporting Information

Synthesis of kinetically trapped, alumina-supported Ni_3Ga nanoparticles with particle surface composition partially controlled by off-stoichiometric Ni:Ga loading ratios enabled active, highly selective, and stable catalysts to be developed for the direct dehydrogenation of ethane to ethylene. Experimental studies indicated a direct correlation between superstoichiometric Ga loading and ethylene selectivity yet an inverse correlation with ethane conversion. A catalyst with a 1:1 Ni:Ga loading ratio exhibited a good balance between activity (TOF 5.0 × 10^{-2} s^{-1}), selectivity (94%), and stability (94 to 90% over the 32-h test). The catalyst could also be easily regenerated using an oxidation and reduction cycle. DFT calculations and in situ DRIFTS CO adsorption confirm that surface reactivity is attenuated as Ga concentration at the particle surface increased.



C−H activation, C−C activation, transition metal solid compounds, non-noble metal catalysts, rational design

Unsaturated hydrocarbons (olefins and aromatics) are important building blocks for a wide range of products including plastics, solvent, fuel additives, and chemical intermediates.[1−4] Efficient production of unsaturated hydrocarbons still remains a challenge due to the large difference in the reactivity between reactant and product.[3,5−7] Appropriate surface chemistry toward C and H must be able to drive dehydrogenation to initiate the reaction. However, appropriately low surface reactivity toward C═C is needed to limit olefin decomposition and coke formation to maintain selectivity and catalyst activity. Pt-group noble metals (PGMs) promoted by a selection of p-block elements, namely Sn, Ga, In, and Zn, have been extensively utilized in alkane transformation toward olefin production.[3,8,9] The addition of p-block elements to PGMs enhanced both selectivity and stability in many direct alkane dehydrogenation reactions with the effect explained by evoking ensemble and electronic effects.[3,10,11] Unfortunately, these catalysts are still composed of expensive noble metals, may suffer from sintering, and often require co-fed H_2 to maintain selectivity and stability.[3,10,12] A handful of non-noble metal oxides, such as CrO_x, VO_x, MoO_x, GaO_x, etc., have also been reported to show considerable activity and selectivity in alkane dehydrogenation reactions.[3,13−15] However, these materials suffer from the loss of oxygen under reaction conditions, rapid deactivation, and requirement for frequent regeneration treatments.[3,14−16] Because of the rapid increase in olefin demand in the near future, more economic, noble-metal-free catalytic materials are needed. Further improvement of rate and selectivity are also still needed as well as enhanced understanding of how to control surface reactivity toward C and H.

In this report, we present a stable and selective alumina-supported Ni+Ga catalyst consisting of nearly phase-pure Ni_3Ga particles with off-stoichiometric loading of Ni and Ga of a 1:1 ratio. The Ni:Ga loading ratios of 3:1, 1:1 (basecase), and 1:2 were systematically studied in the reaction to ascertain how the surface active sites were modified by Ni:Ga loadings and how they affect catalytic activity and selectivity. Our prior study in propane dehydrogenation to propylene determined that relatively phase-pure Ni_3Ga could be kinetically trapped using lower temperatures during the precatalyst reduction step over a relatively large range of Ni:Ga loading ratios (e.g., 3:1, 1:1, and 1:2 Ni:Ga).[17] However, the origin of the changes in surface reactivity were not fully determined. It is hypothesized that the surface Ga concentration can be elevated as Ga loading increased, which may lead to a decrease in surface reactivity. The findings of this study suggest that both the ensemble size of Ni sites and surface reactivity decreased when superstoichiometric amounts of Ga were used to produce the catalyst. These novel findings are supported by the systematic performance studies, in situ ethylene and CO DRIFTS studies, and quantum chemical modeling calculations. Energy-dispersive X-ray spectroscopy (EDX) suggested that a portion of the extra Ga loaded was atomically dispersed on the alumina support and was not detectable by XRD investigations (Figure

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S1 and S2). Particle size (10 wt % total metal loading for all catalysts) was quantified by TEM (Figure S3 and Table S1). ICP-OES measurements confirmed actual loadings were within a few percent of nominal loadings (Table S2).

Performance tests of the main catalyst of the study, Ni_3Ga/Al_2O_3 with 1:1 Ni:Ga loading ratio, indicated excellent selectivity toward ethylene production (~94%) using only ethane in an Ar diluent gas. The catalyst was treated under 10% propane balanced with Ar at 600 °C for 6 h before switching to ethane dehydrogenation reaction to poison over-reactive sites. Stability toward ethylene selectivity was appreciable with minor deactivation detected after extended operation of 30+ hours at 600 °C (from ~94% to ~90%). Conversion of ethane was also quite stable at approximately 10% early in the reaction and fell to a value of 6% at the end of the 30+ hr test. In addition to ethylene, methane was the only other product observed besides H_2 (Figure 1). The in situ

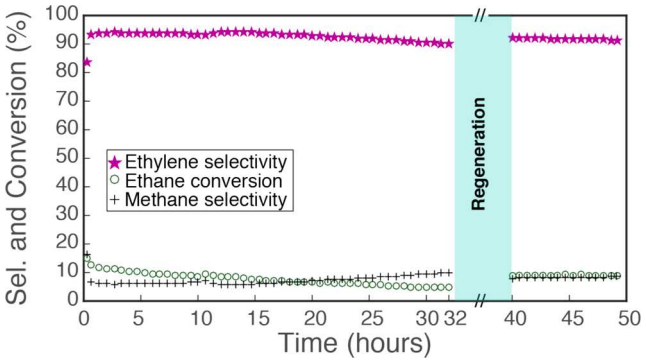

Figure 1. Catalytic activity, stability, and regenerability of Al_2O_3-supported Ni_3Ga with 1:1 Ni:Ga loading ratio.

regeneration of the catalyst with an oxidative/reductive cycle using only O_2 and H_2 and then another propane treatment showed the catalyst stability could be greatly improved. Both initial selectivity and conversion were restored after the regeneration cycle and the stability of conversion and selectivity was nearly ideal. Comparison of catalytic performance with published CrO_x and noble-metal-based intermetallic compound (IMC) catalysts showed that our catalyst exhibited comparable or even better results regardless of the various reaction conditions (Table S3). It is also noted that these catalysts are noble-metal free and do not require co-fed H_2. Tests of a Ga/Al_2O_3 catalyst without Ni added showed high ethylene selectivity (98%) but with a very low level of conversion (<2%) and suggested that Ni was required to enhance conversion and sustain high selectivity (Figure S4 and S5).

To further understand how extra Ga loaded on Ni_3Ga/Al_2O_3 influenced the surface chemistry of the Ni_3Ga IMC particles, a systematic study was conducted using catalysts that consisted of Ni:Ga of 3:1, 1:1 (the basecase), and 1:2 loading ratios. A systematic and monotonic increase in ethylene selectivity was found as the Ga loading increased (Figure 2a). With 3:1 Ni:Ga loading ratio, the catalyst showed appreciable selectivity toward ethylene, ~80%. As the Ga loading increased, selectivity increased monotonically to ~94% (1:1 Ni:Ga) and to a limit of ~96% (1:2 Ni:Ga loading). Interestingly, more aggressive deactivation was found over the catalyst with 1:2 Ni:Ga loading ratio in comparison to the other two catalysts (Figure S6).

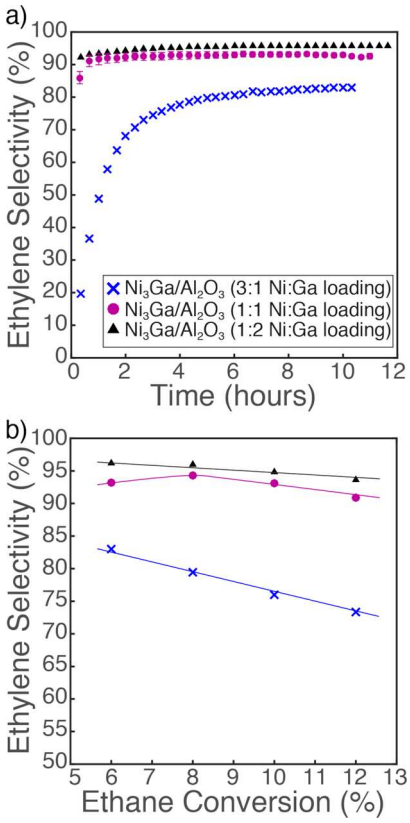

Figure 2. Catalytic performance of ethane dehydrogenation over Ni_3Ga/Al_2O_3 with a range of Ni:Ga loading ratios.

The results suggested a systematic decrease in surface reactivity toward carbon when Ga loading increased as well as ensemble and electronic effects in the surface chemistry. A similar systematic reduction in overly reactive sites was encountered by others and ourselves using noble and transition metal IMC catalysts (e.g., Pt+Sn, Pd+In, and Ni+Ga).[17−19] Surface science studies of Pt+Sn and Pd+Sn have demonstrated that reactivity toward unsaturated HCs could be attenuated systematically as p-element-rich surface compositions were employed.[20,21] Trends in ethane TOF also tracked with the Ga loading illustrating ensemble and potentially marked electronic effects that modify surface reaction energetics (Figure S7). It is worth noting that the presented ethane TOFs are based on H_2 chemisorption on as-prepared catalysts that have not had over-reactive sites poisoned by propane pretreatment. Therefore, they are expected to be lower than TOFs calculated if accurate H_2 chemisorption was possible over a catalyst treated with propane and brought to initial steady-state activity. This study was, unfortunately, not possible. The catalytic performances suggested that both surface reactivity and reaction sites can be attenuated by elevating Ga loading and an appropriate amount of Ni needed to be presented on the surface to achieve elevated selectivity, stability, and ethane conversion. The effect of conversion vs selectivity was investigated by modifying the catalyst loading (Figure 2b). The results showed that the selectivity of the 3:1 Ni:Ga-loaded catalyst was affected by conversion. However, the selectivity of the catalysts with 1:1 and 1:2 Ni:Ga loading ratios was not a strong function of conversion. This further indicated that the elevated selectivity observed could not simply be attributed to lower conversion.

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Characterization of postreaction catalysts (3:1, 1:1, and 1:2 Ni:Ga loading ratios) indicated that the IMC nanoparticles were surprisingly stable. TEM particle size analysis suggested little change in particle size or morphology (avg of 9.8 vs 11.9 nm, 11.2 vs 12.5 nm, and 9.0 vs 12.2 nm before and after reaction over 3:1, 1:1, and 1:2 Ni:Ga loading ratios, respectively). XRD showed that the phase-purity of Ni_3Ga persisted over all three materials during reaction process (Figure S11). Coke formation occurred over all three catalysts (Figure S12), which was potentially driven by the over-reactive surface sites. Further study is needed to understand if the superstoichiometric Ga loading is able to suppress coke formation or not.

To further understand the origin of the elevated selectivity of the catalyst with 1:1 Ni:Ga loading ratio, ethylene temperature-programmed desorption (TPD) was investigated over as-prepared catalyst using in situ diffuse reflectance infrared fourier transform spectroscopy (DRIFTS). Ethylene was adsorbed at room temperature and then tracked with DRIFTS as the catalyst temperature was ramped to 100, 200, and 300 °C (Figure 3). Over as-prepared catalyst, ethylene

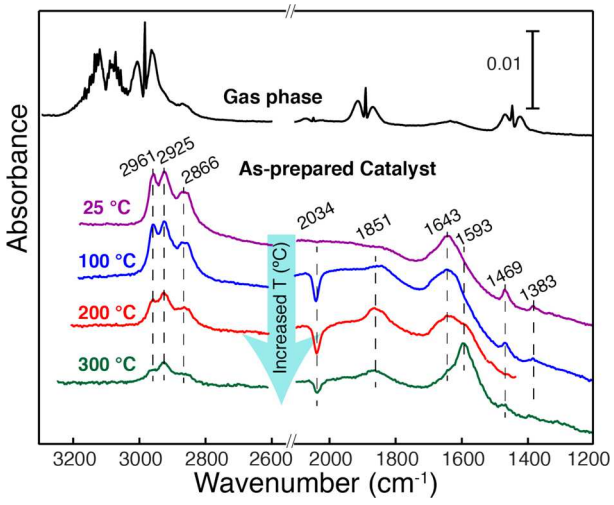

Figure 3. Ethylene adsorption over the Ni_3Ga/Al_2O_3 with 1:1 Ni:Ga catalyst at room temperature and desorption under inert sweep gas at elevated temperature tracked by in situ DRIFTS. See the Supporting Information for more details of peak assignment.

adsorption leads to further dehydrogenation and ethylidyne production at temperatures between 25 and 200 °C. This was evidenced by the absorption peaks at 2925, 2866, and 1383 cm^{-1} and similar spectra recorded for ethylene adsorption over Pt, Rh, Pd, and Ir.[22−24] The vibrations at 2961, 1626, and 1469 cm^{-1} suggested that molecular ethylene could adsorb intact on the catalyst surface similar to other adsorption studies.[25−27] The vibration at 1593 cm^{-1} observed after heating to 300 °C suggests coke formation in the form of polyaromatic carbon species.[28,29] This study suggested the presence of over-reactive surface sites in the as-prepared catalysts, which may be poisoned and made to be catalytically inert through the propane pretreatment. Unfortunately, propane-treated catalysts could not be reasonably analyzed by DRIFTS due to coke deposition making the catalyst opaque.

The nature of the reaction sites on the catalyst were investigated by in situ CO adsorption and desorption DRIFTS experiments. All three catalysts (3:1, 1:1, and 1:2 Ni:Ga loading ratios) were prepared ex situ and passivated. All passivated catalysts were reduced in situ but not contacted with propane before CO adsorption. Spectra were taken after dosing 1% CO/Ar for 10 min at room temperature (Figure 4a). A systematic suppression of CO adsorption was found as

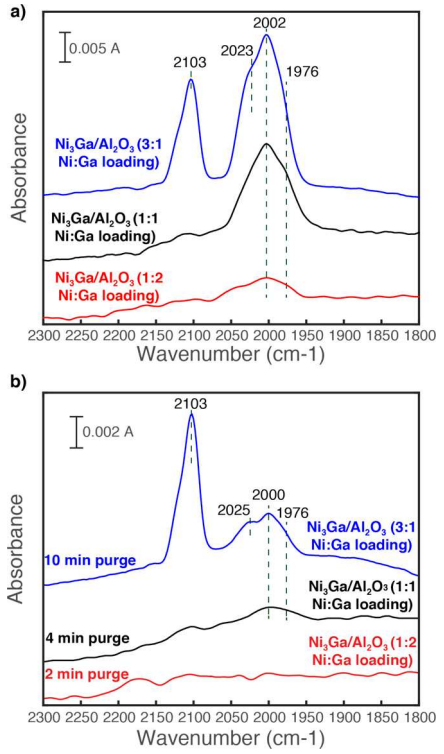

Figure 4. In situ CO DRIFTS studies over Ni_3Ga/Al_2O_3 with respect to the Ni:Ga actual loadings of 3:1 (blue), 1:1 (black), and 1:2 (red) before (a) and after (b) purging process. A gas-phase CO background was subtracted from each data set in plot (a).

the actual Ga loading increased. This may be attributed to the reduction of surface reactivity through an electronic effect or a Ni ensemble-size effect. Over 3:1 Ni:Ga actual loading, CO adsorbed at Ni−Ni bridge sites (1976 cm^{-1}), Ni atop sites (2002 and 2023 cm^{-1}), and atop Ni with multiple CO bound (2103 cm^{-1}) were all detected. The vibrational signatures and assignment are in agreement with prior studies by others.[30−32] As Ga loading increased, bridge and singular-CO adsorption atop Ni were diminished and nearly absent at a loading of 1:2 Ni:Ga. Desorption by purging at room temperature showed surface reactivity was affected by Ga loading in addition to ensemble effects. CO remained adsorbed over the 3:1 Ni:Ga sample but desorbed readily from the 1:1 and 1:2 Ni:Ga catalysts. The same effect was reproduced with DFT calculations over Ni_3Ga surfaces with varied surface Ni:Ga ratios of 3:1 (−1.92 eV), 1:1 (−1.06 eV), and 1:3 (−0.52 eV) (Figure S15). This phenomenon was also found in CO adsorption over Pt+Sn and Pd+In catalysts as a function of p-block element concentration suggesting catalytically important tunability and IMC composition spaces useful for catalysis.[30,32] The electronic effect of Ga on Ni as a function of surface composition on Ni_3Ga was also investigated. See the calculation section in the Supporting Information for details.

A reaction mechanism study of ethane transformation toward ethylene by DFT calculations were carried out to ascertain the role of surface Ga concentration on Ni_3Ga in the

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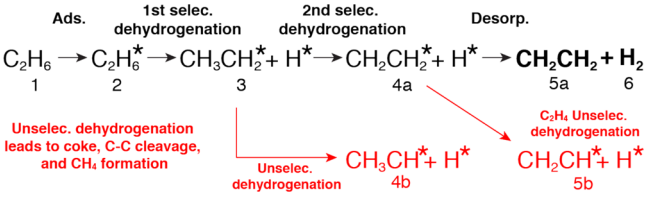
reaction. The first layer of Ni_3Ga model surface was modified to exhibit the Ga concentrations of 25% (stoichiometric), 50%, and 75% (Figure S16). The conversion of ethane toward ethylene and H_2 was achieved via two consecutive selective dehydrogenation steps (Scheme 1). Additionally, unselective

Scheme 1. Partial Reaction Mechanism Network for the Direct Dehydrogenation of Ethane to Ethylene[a]



[a]Critical unselective reaction steps that could affect catalytic activity and selectivity were also included (4b and 5b). See Figure S18 for the model figures of transition states.

dehydrogenation reaction paths, such as the dehydrogenation of the alpha-carbon group after the first dehydrogenation step or after ethylene is produced were also investigated (Scheme 1). These two steps are critical to dictate the formation of coke, C−C cleavage, and unselective CH_4 production. Calculations (Figure S17 and Table S4) indicated a systematic increase in the kinetic barriers for both selective and unselective dehydrogenation steps as surface Ga concentration increased. The analysis of reaction rate constant estimations over Ni_3Ga with the stoichiometrically terminated surface (25% Ga, Table S4) showed that the two unselective dehydrogenation reactions steps were either competitive or faster than the selective dehydrogenation and desorption steps (2.53×10^{10} vs 4.85×10^{11} s^{-1} for 3 → 4b vs 3 → 4a and 9.51×10^{9} vs 5.80×10^{3} s^{-1} for 4a → 5b vs 4a → 5a). This suggested that stoichiometrically terminated Ni_3Ga catalyst exhibited an aggressive surface reactivity that could promote the unselective decomposition reaction paths toward the formation of coke and saturated hydrocarbon. Therefore, the stoichiometrically terminated Ni_3Ga would likely result in a reduced ethylene selectivity. On the other hand, the unselective dehydrogenation steps were drastically inhibited as surface Ga concentration increased to 50%, and the selective dehydrogenation reaction path appeared to dominate the reaction at 75% Ga (Figure S17 and Table S4), which could enhance the selectivity toward ethylene. DFT calculations clearly showed that the surface reactivity could be attenuated by increasing surface Ga concentration on Ni_3Ga catalyst, which correlated well with dramatic selectivity increases toward ethylene production. This result is crucial in understanding the effect of additional Ga in the experimental catalysts since more exact surface composition measurements were not possible even with ion-scattering techniques.

In summary, an Al_2O_3-supported Ni_3Ga catalyst has been isolated that exhibits excellent tunability with respect to its surface chemistry and high selectivity toward ethylene in the direct dehydrogenation of ethane at 600 °C. A kinetically trapped Ni_3Ga phase could be achieved despite super-stoichiometric Ga loading. This allowed Ni and Ga loading ratio to manipulate surface composition of the Ni_3Ga nanoparticles. Conversion decreased and selectivity increased as Ga loading was increased from 3:1 to 1:2 Ni:Ga. The catalyst made by 1:1 Ni:Ga loading ratio presented the best balance of activity and selectivity as well as excellent stability and regenerability. Propane treatment of the catalyst was critical to react away over-reactive sites, likely rich in Ni. This study demonstrates that non-noble metal IMC catalysts provide a relatively new compositional space for the community for classic and contemporary reactions as surface chemical needs change. Molecular level investigations suggested that a combination of ensemble and electronic effects manipulated surface chemistry and could be tuned to promote selective ethylene production at appreciable rates over non-noble metal IMC catalysts.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b03402.

Experimental details, including synthesis, reactor test, TEM, pXRD, ICP-OES, and H_2 chemisorption (PDF)

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Notes

The authors declare no competing financial interest.

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