
IV.B.8 Hybrid Experimental/Theoretical Approach Aimed at the Development of Carbon Tolerant Alloy Catalyst

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Objectives

- Utilize quantum density functional theory (DFT) calculations and various state-of-the-art experimental tools to identify carbon-tolerant hydrocarbon reforming catalysts and solid oxide fuel cell (SOFC) anodes.
- Test the potential carbon-tolerant catalysts in steam reforming of various fuels.
- Implement these catalysts as SOFC anodes.
- Utilize various tools of spectroscopy and microscopy to characterize the tested catalysts.

Accomplishments

- In our first principles DFT calculation, we have established that the carbon-tolerance of Ni can be improved by formulated Ni-containing surface alloys that, compared to Ni, preferentially oxidize C atoms rather than form C-C bonds and/or that have lower thermodynamic driving force associated with carbon nucleation on the low-coordinated sites.
- Based on the molecular insights, we have identified a number of surface alloys that satisfy the above described criteria.
- We have tested these surface alloys in steam reforming of various hydrocarbon fuels.
- We have also utilized the surface alloy as a SOFC anode catalyst.

Introduction

The development of clean, efficient, and environmentally friendly energy generation systems will require major advances in catalysis. Among others,

improved hydrocarbon reforming catalysts and electro-catalysts need to be formulated and synthesized. These catalysts need to perform the desired reactions with utmost efficiencies, at reduced costs, and with improved durability.

One of the main issues associated with the catalytic and electro-catalytic reforming of hydrocarbon fuels is that current catalysts, such as Ni supported on oxides, deactivate due to the formation of carbon deposits formed in the process of hydrocarbon activation. In this document we describe a hybrid experimental/theoretical effort aimed towards a bottom-up, knowledge-based formulation of carbon-tolerant reforming alloy catalysts that can be used as potential anode electro-catalysts for SOFCs.

Our objective was to utilize quantum DFT calculations and various state-of-the-art experimental tools to study the factors that govern the stability of Ni-based reforming catalysts. We demonstrate that monometallic Ni deactivates due to the high rates of C-C bond formation and the high thermodynamic driving force associated with the nucleation and growth of extended sp² carbon structures. We have identified Ni surface alloys as potential carbon tolerant catalysts [1-3]. The utility of these catalysts was demonstrated in multiple reactor tests in the reforming of various fuels.

Approach

We have employed quantum DFT calculations as well as catalyst synthesis, testing, and characterization studies to identify carbon-tolerant alloy catalysts.

DFT calculations allow us to obtain, from first principle and with high accuracy, the ground state geometries and energies of relevant reactants, products, and transition states involved in elementary chemical reactions on catalyst surfaces [4]. Reactor experiments and various characterization techniques were applied to test the predictions of DFT calculations. The alloy catalysts were also tested as potential SOFC anodes.

Results

A critical issue with catalytic hydrocarbon reforming and on-cell reforming in SOFCs is that traditional catalysts, such as Ni supported on oxides, facilitate the formation of extended carbon deposits which deactivate the catalyst or electro-catalyst, see Figure 1a. The formation of carbon deposits can be partially suppressed by an introduction of steam (steam reforming). This approach is problematic for SOFCs since (i) the

presence of steam results in low power densities, (ii) significant energy is required to heat the steam to the desired temperature, and (iii) the storage of steam requires additional cell components, making the cell design more complex. It is imperative to design carbon-tolerant reforming electro-catalysts that can operate with minimal steam concentrations.

The elementary-step mechanism for hydrocarbon reforming on Ni involves the hydrocarbon activation and fragmentation into H and C adsorbates. The strongly bound carbon atoms or fragments are removed from the Ni surface in C-oxidation reactions yielding adsorbed CO, which further reacts in the water-gas shift reaction to form gas-phase CO_2 . The oxidizing agents, O and OH, are formed on the catalyst surface in the process of steam activation. In addition to reacting to form CO and CO_2 , the C atoms and fragments also react with each other to form extended sp² carbon networks such as graphene sheets or nanotubes. It has been shown that the extended carbon deposits nucleate at low-coordinated sites on Ni [5]. The formation of extended carbon networks leads to the loss of catalyst activity. Figure 1b shows the DFT-calculated reaction energies for various elementary steps involved in methane steam reforming on Ni(111). The calculations in Figure 1b support the mechanism discussed above.

Figure 1b also suggests that the catalyst lifetime can be prolonged by formulating catalysts that (i) preferentially oxidize C atoms rather than from C-C bonds or (ii) suppress the nucleation and growth of carbon deposits. We have utilized the above discussed molecular mechanistic information to identify Ni-containing surface alloy catalysts that are promising carbon-tolerant alternatives to monometallic Ni [1-3]. For example, our quantum DFT calculations have shown that a small amount of Sn alloyed into the Ni surface layer enhances the rates of C-oxidation compared to the rate of C-C bond formation [1,2]. In addition, our DFT studies also showed that the nucleation of carbon deposits can also be suppressed with the introduction of Sn [3]. This is illustrated in Figure 2b which shows the calculated adsorption energies for various carbon nucleation centers on low-coordinated step sites of Ni and Sn/Ni. The calculated adsorption energies are a measure of the thermodynamic driving force to form these structures on the catalyst surface. Figure 2a shows that the driving force to nucleate the carbon centers on Ni is significantly larger than the driving force on Sn/Ni. For example, the DFT calculated adsorption energies for a C_8 carbon cluster (8 sp² carbon atoms) and a graphene chain on Ni(211) are by 0.23 eV and 0.15 eV per carbon atom respectively more exothermic than for Sn/Ni(211), see Figure 2a. The reason for the Sn-induced change in the thermodynamic driving force to form the carbon nucleation centers is that Sn disrupts the connectivity of the low-coordinated Ni sites which bind carbon very strongly.

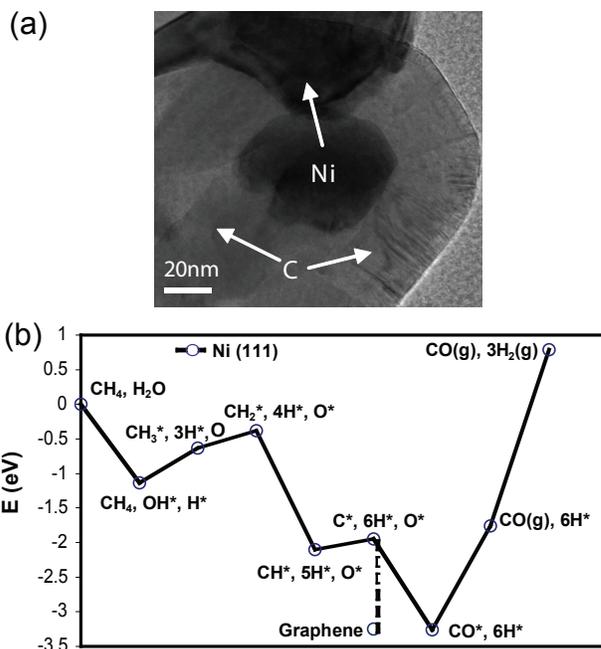


FIGURE 1. a) Transmission electron micrographs of the Ni particles covered by carbon deposits. The carbon deposits are formed in the process of propane steam reforming at 1,073 K and a steam-to-carbon ratio of 1.5. b) Reaction energies for various elementary steps in steam reforming of methane on Ni(111).

In addition to the investigation of the chemistry of carbon on Ni and Ni alloys described above, we have also utilized DFT calculations to assess the thermodynamic stability of Sn/Ni surface alloys [3]. In these studies, we have calculated the formation energies of various Sn/Ni structures including: (i) Sn/Ni surface alloys, (ii) Sn/Ni bulk alloys, (iii) Sn adsorbed on Ni substrate, and (iv) separated Sn and Ni. The calculated formation energies are shown in Figure 2b. Figure 2b demonstrates that Sn/Ni surface alloys have the lowest formation energies out of all examined structures and that the surface alloys should be stable under typical reforming conditions.

To test the predictions of the DFT calculations, we have synthesized and characterized Sn/Ni alloys. Various characterization techniques including scanning electron microscopy (STEM), electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS), and temperature programmed reduction (TPR) demonstrated that the synthesized material was the Sn/Ni surface alloy [3]. The performance of the alloy catalysts was examined in a reactor setup in steam reforming of methane, propane, and iso-octane at moderate steam-to-carbon ratios (between 1 and 2). In all experiments, the Sn/Ni catalyst shows no significant deactivation while the Ni catalyst deactivated rapidly. The characterization studies on used catalysts (SEM, transmission electron microscopy [TEM], X-ray

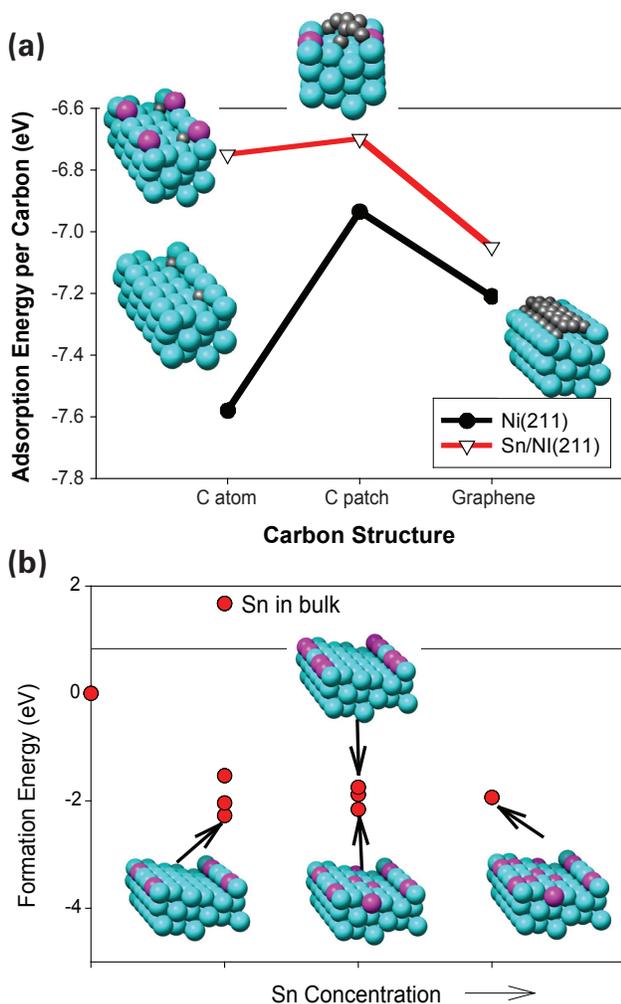


FIGURE 2. a) The DFT calculated adsorption energies per carbon atom for a C atom, C_8 cluster, and a graphene chain adsorbed on Ni(211) and Sn/Ni(211). The surface alloy is characterized by replacing every third Ni atom on the edge by the Sn atoms. b) Formation energy for various Sn/Ni configurations is plotted as a function of Sn concentration. The structure with the lowest energy is the thermodynamically most stable structure for a given Sn concentration.

photoelectron spectroscopy [XPS] and X-ray diffraction [XRD]) showed no signs of carbon formation on Sn/Ni. On the other hand, the Ni catalysts were completely poisoned by graphitic carbon deposits.

We have also implemented the Sn/Ni surface alloy catalyst as a SOFC anode electro-catalyst for on-cell utilization of hydrocarbons. The anode was composed of a mixture of the Sn/Ni catalyst and YSZ. The electrolyte was made of a thin layer (~20 microns) of YSZ and the cathode was composed of a mixture of LSM and YSZ. Our preliminary results indicate that when isoctane is used as a fuel, the Ni/YSZ/LSM SOFC degrades significantly over time due to carbon poisoning which leads to the cell fractures. On the

other hand, the Sn/Ni/YSZ/LSM SOFC shows a higher resistance to carbon than the Ni SOFC under identical conditions. One issue worth mentioning is that the formation of carbon deposits in gas-phase (before the fuel comes in contact with the anode) presented a problem for the life span of both the Sn/Ni and Ni electrocatalysts. The formation of these carbon deposits over time puts a significant strain on the seal. The strain results in the fuel cell damage. For example, in the case of the Sn/Ni surface alloy anode, the triple phase boundary was free of carbon, as demonstrated by the elemental mapping of the interface, but the large carbon deposits on the wall of the cell-reactor resulted in the failure of the seal over time.

Conclusions and Future Directions

- We have utilized DFT quantum calculations to develop molecular insights into the mechanism of carbon poisoning of Ni.
- We have determined that the long-term stability of reforming electro-catalysts is governed by their capacity to (1) selectively oxidize carbon atoms, while preventing the formation of C-C bonds and (2) suppress the C nucleation on the low coordinated catalyst sites.
- DFT studies demonstrated that Sn/Ni favored the C-oxidation reaction over C-C bond formation and hindered the nucleation of carbon at the low coordinated sites.
- The reactor studies showed that the Sn/Ni catalyst was more stable than monometallic Ni in steam reforming of various hydrocarbons at moderate steam-to-carbon ratios.
- Sn/Ni alloys also showed promising preliminary results as potential anodes for on-cell utilization of hydrocarbons.

Special Recognitions & Awards/Patents Issued

1. Best Paper Presentation, "Experimental/Theoretical Studies Aimed at the Development of Carbon-Tolerant Catalysts", Michigan Catalysis Society Annual Meeting 2006, Dow Chemicals, Midland, MI, May 2006.
2. Best Poster, "Controlling Carbon Chemistry via alloying: Hybrid Experimental/theoretical Approach", University of Michigan Engineering Competition 2006, Ann Arbor, MI, March 2006.
3. Best Poster Award (Eranda Nikolla, fourth year Ph.D. student), Gordon Research Conference on Catalysis, 2006, New Hampshire. (The poster was selected, along with four others, among >100 posters presented by Ph.D. students and postdoctoral fellows.)

FY 2007 Publications/Presentations

1. Nikolla, E. Schwank, J. Linic, S., "Promotion of the Long-Term Stability of Reforming Catalysts by Surface Alloying", *Journal of Catalysis*, in press.
2. Nikolla, E. Holowinski, A. Schwank, J. Linic, S., "Controlling Carbon Surface Chemistry by Alloying: Carbon Tolerant Reforming Catalyst", *JACS*, 128 (35), 11354–11355, 2006.
3. Nikolla E., Schwank J., Linic S., "Development of Carbon Tolerant Anodes for Solid Oxide Fuel Cells", North American Catalysis Society Meeting, Houston, TX, May 2007.
4. Linic S, Nikolla E., "Controlling Carbon Surface Chemistry on Ni by Alloying: Carbon Tolerant Hydrocarbon Reforming Alloy Catalysts", American Chemical Society National Meeting, Chicago, IL, March 2007.
5. Nikolla E., Schwank J., Linic S., "Controlling Carbon Chemistry by Surface Alloying", AIChE Annual Meeting, San Francisco, CA, November 2006.
6. Nikolla E., Schwank J., Linic S., "Hybrid Theoretical/Experimental Approach Aimed at the Development of Carbon Tolerant Alloy Catalysts", Gordon Research Conference on Catalysis, New Hampshire, June 2006 (poster).
7. Nikolla E., Schwank J., Linic S., "Experimental/Theoretical Studies Aimed at Development of Carbon-Tolerant Catalysts", Michigan Catalysis Society Annual Symposium, Midland, MI, May 2006.

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