

Improving Carbon Tolerance of Ni Catalysts and Electrocatalysts

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Introduction

Steam reforming is a process that converts hydrocarbon fuels into hydrogen and oxygenated carbon species. This process is important for catalytic hydrogen production and for direct electrochemical reforming of hydrocarbons over high temperature fuel cells, such as Solid Oxide Fuel Cells (SOFCs). One of the main problems associated with the process is that conventional reforming (electro)catalysts, such as Ni supported on oxides, deactivate due to carbon poisoning.

We have utilized Density Functional Theory (DFT) calculations to study carbon chemistry on Ni and Ni-containing alloys.[1-3] The DFT calculations showed that a number of Ni surface alloys had lower tendencies towards carbon poisoning compared to monometallic Ni. The identified alloy catalysts were tested in steam reforming of methane, propane, isooctane, and other hydrocarbon fuels. These catalysts were also tested as anodes in SOFCs. The alloy (electro)catalysts showed significantly improved performance compared to monometallic Ni.[1-3]

We will also discuss the underlying physical characteristics of the alloy catalysts that are associated with the improved performance of the alloy catalysts. In this discussion we will focus on the analysis of the electronic structure of the alloy catalysts, and we will relate the alloy electronic structure to the performance.

Materials and Methods

DFT calculations were performed with the Dacapo pseudo-potentials plane wave code [www.fysik.dtu.dk/CAMPOS]. The density of valence electrons was determined self-consistently by iterative diagonalization of Kohn-Sham Hamiltonians. The plane wave basis set used to describe the one-electron states was cut off at 350 eV. An electronic temperature ($k_B T$) of 0.1 was used during calculations with the final results extrapolated to 0 K. The forces were minimized to 0.05 eV/Å. Relevant transition states were identified via Nudged Elastic Bend (NEB) method.

The Ni-YSZ and Ni-alloy/YSZ catalysts were synthesized using either incipient wetness or ball milling approaches.

Results and Discussion

We have utilized DFT calculations to study carbon chemistry on Ni and Ni alloys. DFT calculations showed that the formations of carbon deposits on Ni can be suppressed by identifying Ni-alloys that: (i) compared to monometallic Ni, preferentially oxidize carbon atoms and (ii) offer lower thermodynamic driving force for the nucleation of carbon deposits on the low-coordinated Ni sites. The DFT calculations were further utilized to identify a family of alloys as potential reforming catalyst with improved carbon tolerance with respect to monometallic Ni.

The alloy catalysts were synthesized using the incipient wetness technique. The Ni and alloy catalysts were tested in steam reforming of methane, propane and isooctane, see Fig.

1a. The reactor studies showed that the alloy catalysts are more stable than monometallic Ni. Post reaction characterization studies identified extended carbon structures on monometallic Ni as the main source of the deactivation of the Ni catalyst (for example, Fig 1b). We have also tested the alloy catalysts as anodes in the direct utilization of various hydrocarbon fuels in SOFCs. These studies also showed that the alloy catalysts exhibit superior carbon-tolerance compared to pure Ni.

We have also measured the near Fermi level electronic structure of Ni alloy catalysts and compared it to the electronic structure of pure monometallic Ni. Our measurements showed that there are unique features in the alloy electronic structure that significantly change the chemical activity of alloys compared to pure Ni. Based on the analysis of the electronic structure we have developed a simple physically transparent framework for predicting the shifts in the electronic structure and chemical activity in response to alloying.

Significance

This work represents an example where the detailed understanding of the mechanisms of elementary steps that govern the poisoning of the catalyst was used to identify a family of alloy catalysts that are more stable than conventional monometallic catalysts. Furthermore, measurements of the catalyst electronic structure were used to identify critical electronic features which can be related to the enhanced carbon-tolerance of the alloy catalysts. We have also developed a simple physically transparent framework for predicting the shifts in the electronic structure and chemical activity in response to alloying.

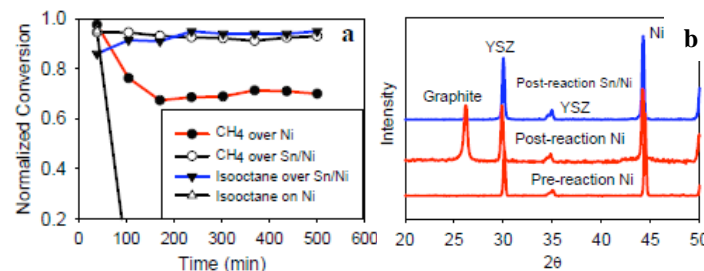


Figure 1. (a) Normalized conversion, calculated as the ratio of measured conversion to the highest conversion of methane and isooctane over Ni/YSZ and Sn/Ni/YSZ, is recorded as a function of time on stream. Steam to carbon ratio was 0.5 and 1.5 for methane and isooctane, respectively. (b) XRD spectra show the presence of graphite on the Ni catalyst.

References

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