

Hybrid Experimental/Theoretical Approach aimed at the Development of Carbon Tolerant Catalysts

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Introduction

Steam reforming is used to convert hydrocarbon fuels into hydrogen and oxygenated carbon species.[1] This process is important not only for the catalytic hydrogen production but also for direct electrochemical reforming over high temperature fuel cells such as Solid Oxide Fuel Cells (SOFCs). [2] One of the main problems associated with the process is that the commonly used anode reforming catalysts, such as Ni supported on oxides, deactivate due to carbon poisoning. The rapid carbon-induced deactivation of the catalysts is an important obstacle for the development of robust SOFC anodes for internal hydrocarbon utilization. The extent of carbon poisoning can be suppressed by increasing the feed steam concentration. However, this approach is not viable for SOFCs since it lowers the energy density of the products and diminishes the power density. [3]

We have utilized Density Functional Theory (DFT) calculations to study carbon chemistry on Ni and Ni-containing alloys. The main objective of these studies was to develop molecular insights regarding carbon poisoning on Ni and to utilize this molecular information to identify possible carbon-tolerant alternatives to Ni. The DFT calculations showed that Sn/Ni alloy has lower tendencies towards carbon poisoning compared to monometallic Ni. The alloy and monometallic Ni catalysts were tested in steam reforming of methane, propane and isooctane. These tests showed that Sn/Ni is much more carbon-tolerant than Ni.

Materials and Methods

DFT calculations we 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 0.05eV/Å. Relevant transition states were identified via Nudged Elastic Bend (NEB) method.

Ytria-stabilized zirconia (8mol%) was prepared via the standard co-precipitation method. The Ni-YSZ catalyst was synthesized by ball milling a mixture of NiO (Alfa Aesar) and YSZ in methanol for 24 hours. Once dried, the powder was pressed into 13mm diameter pellets at 5000psi. The pellets were then sintered at 1400°C for 4 hours at a ramping rate of 2°C/min. The Sn was introduced using SnCl₄ via the incipient wetness technique. The catalyst was characterized utilizing various spectroscopy and microscopy techniques.

Results and Discussion

We have utilized DFT to study carbon chemistry on Ni and Ni alloys. DFT calculations showed that the formations of carbon deposits on Ni can be suppressed by (i)

identifying Ni-alloys with higher rates of C oxidation and lower rates of C-C bond formation compared to pure Ni and (ii) lower the thermodynamic driving force associated with the nucleation of carbon deposits on the low-coordinated Ni sites. [4] The DFT calculations were further utilized to identify Sn/Ni alloy as a potential reforming catalyst with improved carbon tolerance with respect to monometallic Ni. Furthermore, we also established that Sn/Ni surface alloy is the thermodynamically stable phase of Sn/Ni in the limit of low Sn concentration.

The Sn/Ni catalyst was synthesized in our laboratory using the incipient wetness technique. By utilizing various characterization techniques we were able to confirm the formation of a Sn/Ni surface alloy. The Ni and Sn/Ni catalysts were tested for steam reforming of methane (S/C=0.5), propane and isooctane (S/C=1.5). It was observed that the Ni/YSZ catalyst deactivated rapidly, while the Sn/Ni surface alloy was stable for as long as it was kept on stream. Post reaction characterization of the catalysts identified extended carbon structures on monometallic Ni, and no signs of carbon formation on the 1wt% Sn/Ni catalyst, see Figure 1.

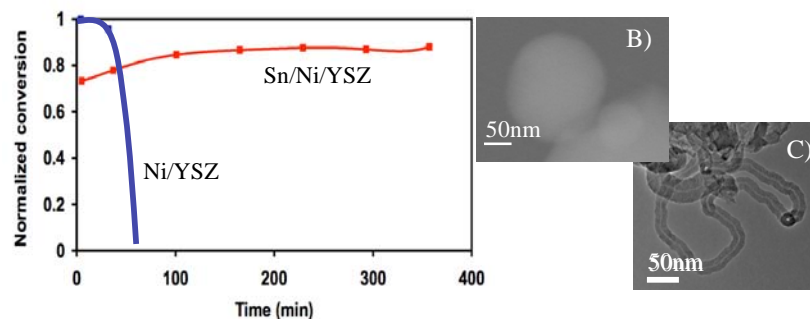


Figure 1. A) Normalized steam reforming conversion of isooctane at S/C=1.5. B) TEM image of the Sn/Ni catalytic particle after isooctane steam reforming. C) TEM image of the Ni catalyst after isooctane steam reforming.

Significance

Development of carbon-tolerant catalysts is crucial for hydrogen production from hydrocarbons and for SOFCs that convert hydrocarbon directly into electricity.

References

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