Final Report

TITLE PAGE

Development of Sulfur and Carbon Tolerant Reforming Alloy Catalysts Aided by Fundamental Atomistic Insights

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Abstract

Current hydrocarbon reforming catalysts suffer from rapid carbon and sulfur poisoning. Even though there is a tremendous incentive to develop more efficient catalysts, these materials are currently formulated using inefficient trial and error experimental approaches. We have utilized a hybrid experimental/theoretical approach, combining quantum Density Functional Theory (DFT) calculations and various state-of-the-art experimental tools, to formulate carbon tolerant reforming catalysts. We have employed DFT calculations to develop molecular insights into the elementary chemical transformations that lead to carbon poisoning of Ni catalysts. Based on the obtained molecular insights, we have identified, using DFT quantum calculation, various Ni alloy catalysts as potential carbon tolerant reforming catalysts. The alloy catalysts were synthesized and tested in steam reforming and partial oxidation of methane, propane, and isooctane. We demonstrated that the alloy catalysts are much more carbon-tolerant than monometallic Ni catalysts under nearly stoichiometric steam-to-carbon ratios. Under these conditions, monometallic Ni is rapidly poisoned by sp^2 carbon deposits. The research approach is distinguished by two characteristics: (a) knowledge-based, bottom-up approach, compared to the traditional trial and error approach, allows for a more efficient and systematic discovery of improved catalysts. (b) the focus is on exploring alloy materials which have been largely unexplored as potential reforming catalysts.

Executive Summary

The envisioned shift to hydrogen economy driven by rapidly evolving fuel cell technology will require energetically feasible and environmentally friendly conversion of fossil, synthetic, and bio-renewable fuels into hydrogen. To realize this vision, major advances in catalysis are required. Improved hydrocarbon reforming, water gas shift (WGS), and preferential CO oxidation (PROX) 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. Even though there is a tremendous incentive to develop more efficient catalysts, these materials are currently formulated using inefficient trial and error experimental approaches. In this project we utilize a hybrid experimental/theoretical approach aimed towards a bottom-up, knowledge-based formulation of carbon-tolerant reforming alloy catalysts.

Unlike current state-of-the-art reforming catalysts, which are often monometallic metal particles (Ni is often used) adsorbed on oxide supports, we focus on oxide-supported metallic alloy catalysts. These catalysts would be utilized for hydrogen production from hydrocarbons and as robust anodes for direct electro-catalytic reforming over Solid Oxide Fuel Cells (SOFC).

The main results of the project are:

1. We have demonstrated that monometallic Ni deactivates due to the high rates of C-C bond formation and a high thermodynamic driving force associated with the nucleation and growth of extended sp² carbon structures.
2. Density Functional Theory (DFT) calculations have shown that Sn/Ni surface alloys, with small amount of Sn alloyed into the Ni surface layers, should be more carbon tolerant than monometallic Ni.
3. Furthermore, our DFT calculations have illustrated that, in the limit of low Sn concentrations, the formation energy of the Sn/Ni surface alloy is lower than the formation energy associated with the bulk mixing of Sn and Ni and with the separate Sn and Ni phases. This suggests that there is a large thermodynamic driving force to synthesize Sn/Ni surface alloys and the surface alloy will be stable under high-T reaction conditions.

4. The predictions of the DFT calculations have been supported by reactor tests, performed under the conditions similar to those associated with the internal on-cell reforming over SOFC anodes. These tests established that the carbon-tolerance of reforming Ni catalysts can be dramatically improved when these Ni catalysts are doped with small amount of Sn.
5. We have also performed various catalyst characterization studies, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), energy dispersive x-ray spectroscopy (EDS), x-ray diffraction (XRD), and x-ray photoelectron spectroscopy (XPS). These studies have reaffirmed the formation of Sn/Ni surface alloys and have further corroborated the results of the studies performed in our reactor set-up which showed that the formation of carbon deposits is halted on Sn/Ni surface alloys.
6. In addition to the above described studies which mainly focused on the synthesis of large Ni and Ni-alloy particles, typical of SOFCs, we have also synthesized smaller particles of Ni and Ni-alloys. These smaller particles can be used for hydrocarbon steam reforming, where in contrast to SOFC electro-catalysts the requirements of electron conductivity does not need to be satisfied. We have also characterized these surface alloy nano-particles. The characterization experiments included a number of electron and photon microscopies and spectroscopies.
7. We demonstrated that for a wide range of the particle diameter the performance of Sn/Ni was superior to pure Ni catalysts.
8. In addition to the Sn/Ni alloy catalysts, we have also identified Au/Ni and Ag/Ni as catalysts that might offer an improved carbon tolerance compared to monometallic Ni
9. We have synthesized these catalytic materials and tested them in the steam reforming of iso-octane at moderate steam-to-carbon ratios. These reactor tests corroborated the predictions of the calculations and demonstrating the superior potential of the alloy catalysts compared to monometallic Ni.
10. We have also studied the performance of the alloy catalysts in partial oxidation of hydrocarbon and C/O ratio of ~ 1 . These reactors tests also showed that the Sn/Ni

alloy is superior to monometallic Ni with respect to the carbon-induced catalyst deactivation in partial oxidation of isooctane at C/O ratio of 1.

11. We also characterized extensively the alloy catalysts identifying unique electronic feature that differentiate these catalysts from monometallic Ni catalysts and that are one of the main reasons for the enhanced carbon tolerance of the alloy catalysts.
12. We also performed thorough kinetic studies showing that methane activation is the rate controlling step in steam reforming of methane of each tested catalysts, and that under steady-state conditions, the catalyst surface is fairly free of adsorbates.

Methodology:

We have employed a hybrid experimental/theoretical approach – the approach combines quantum Density Functional Theory (DFT) calculations, catalyst synthesis, catalysts testing, and catalysts characterization – to identify potential carbon-tolerant reforming bimetallic catalysts. We were interested in the formulation of carbon-tolerant reforming catalysts since: (i) these catalysts are crucial for efficient H₂ production from renewable and fossil hydrocarbon fuels, (ii) the catalyst could be employed as anodes for direct internal hydrocarbon utilizations over Solid Oxide Fuel Cells (SOFC).

Below, we discuss the theoretical and experimental methodologies as well as the results of DFT quantum calculations, reactor testing, and catalyst characterization. This is followed by a conclusion section.

2. Theoretical and Experimental Methods

In this section we outline theoretical and experimental methodology. We first describe DFT quantum chemical calculations. This is followed by the description of catalyst synthesis methods and the reactor test-station. Lastly, we briefly describe various microscopic and spectroscopic tools that were employed to characterize the mechanism of carbon poisoning and also to characterize our alloy catalysts.

2.1. Density Functional Theory (DFT) Methodology

DFT is a methodology that is employed to efficiently solve the quantum Schrodinger equation with high accuracy.^{1,2,3} Due to its accuracy and computational efficiency DFT has become, within the last ten years, the quantum computational tool of choice in solid state physics and surface chemistry.⁴ These tools have already had a significant impact on the discovery of efficient solid-state catalysts as corroborated by the DFT-driven discovery of novel ethylene epoxidation and ammonia synthesis catalysts.^{5,4}

DFT calculations allow us to obtain, from first principles and with high accuracy, the ground state geometries^{6,7,8} and energies^{6,7,8} of relevant reactants, products, and transition states involved in elementary chemical reactions on catalyst surfaces. For example, DFT was utilized to investigate elementary chemical reactions of carbon atom metal surfaces. We have calculated the carbon atom diffusion and elementary surface reactions over various reforming catalysts such as pure Ni and various alloys. This information can be obtained easily using DFT calculations while it is almost impossible to accurately acquire

via other computational or experimental means. The DFT calculations were also utilized to identify promising carbon-tolerant alloy catalysts. We further elaborate on the DFT studies below.

Along with DFT calculations we have employed various experimental tools to synthesize, test, and characterize the reforming catalysts.^{5, 9,10,6,7,8}

2.2. Catalyst Synthesis

As emphasized above, an important objective of our research was to assess the predictions of DFT calculations by synthesizing and testing the promising alloy catalysts, identified in our DFT studies.^{5,11} In order to synthesize these alloys we have utilized standard wet impregnation methods and less conventional sequential ionic layer deposition (SILD) and atomic layer deposition (ALD). These synthesis methods allow for high control over the atomic structure and composition of catalysts.

Wet impregnation methods are based on liquid-phase impregnation of soluble salts on a support. The support is usually a metal oxide compound. Our steam reforming catalysts are supported on Ytria-Stabilized Zirconia (YSZ) The catalyst/support system is then calcined and reduced at elevated temperatures.

The SILD method is based on solution surface chemistry.^{12,13,14} Generally, SILD consists of successive treatments of a substrate surface with various solutions of salts, anions, and cations.^{12,13,14} Controlled surface reactions between these solution-stabilized ions and substrates yield well-defined materials. The advantage of this approach is that complex materials such as metal alloys can be synthesized with high control over their atomic structure and morphology.^{12,13}

Another synthesis technique that has been used recently to create various multi-component layered structures with atomic precision is ALD. ALD is based on standard chemical vapor deposition (CVD) technologies. In the ALD, a binary reaction is split into two half-reactions that occur on the surface of a substrate, i.e., the substrate actively participates in chemical reactions.^{15,16,17} Understanding of the relevant surface chemical reactions allows one to control precisely the structures of materials produced via ALD. This technique has been used to create well-defined oxide layers on metal particles, and layers of one metal on other metals.¹⁵

2.3. Reactor Setup

The promising catalysts identified in our DFT calculations and synthesized using the above described methods were evaluated under steady state conditions in a reactor test-station.⁵ The reactor test-station consisted of a 20 mm I.D. quartz tube encased in a vertical tube furnace. We tested the catalyst in methane, propane, and iso-octane steam reforming and partial oxidation. In the experiments we have systematically varied the concentration of steam and fuel. Analysis of the product gas stream was performed by in-line gas chromatography which utilizes thermal conductivity and flame ionization detectors.

2.4. Catalyst Characterization: Microscopy and Spectroscopy

As stated above we have also characterized fresh and used catalysts with various characterization techniques. We have employed transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), x-ray photoelectron spectroscopy (XPS), and x-ray diffraction (XRD). These techniques allowed us to determine the morphology and atomic composition of the catalytic particles as well as the nature of carbon deposits that deactivate the catalysts. Below we describe the equipment and the information that can be acquired with these tools.

A Jeol 2010F electron microscope was used for EDS, STEM, and TEM studies. The instrument operates under vacuum conditions of 1.5×10^{-7} torr. The instrument utilizes a zirconated tungsten (100) thermal field emission tip filament. The EDS measurements were obtained via Ametek EDAX system in spot and scanning modes. The lens conditions were set for a probe size of 0.5 nm to obtain adequate probe current. To minimize the effect of specimen drift, a drift correction mode was used during elemental mapping. For each sample we have analyzed several particles from several different areas.

SEM was employed to investigate the morphology and size of catalytic particles that are larger than ~50 nm. SEM detects secondary electrons that are created after primary electrons interact with a sample surface. SEM is employed to image fairly large (compared to TEM) areas of a sample. TEM is a transmission electron-based microscopy that is employed to image catalytic particles with atomic resolution. TEM is based on the detection of the primary electrons that are transmitted through the sample. TEM and SEM are usually used in tandem with the energy dispersive x-ray spectroscopy (EDS), which

analyzes the x-rays that are emitted in the process of the electron-sample collisions. The emitted x-rays provide the element-specific fingerprint of catalytic particles. Coupling EDS with scanning mode TEM allows one to obtain the atomic information about the arrangement of different atoms in catalytic particles. These atom-specific insights are particularly useful when working with alloys where the information about the mixing of the alloy constitutive elements is crucial.

We have also utilized XPS, a photon-based spectroscopy, to analyze the electronic structure and the elemental composition of our catalysts. The advantage of XPS is that it is a surface sensitive technique. We have employed Kratos Axis Ultra XPS with 150 W Al (Mono) X-ray gun. This instrument was operated ex-situ under pressure of 5×10^{-9} torr. The analyzed samples were left under vacuum over night before taking data. The runs were conducted using pass energy of 40 eV. The charge neutralizer was utilized to prevent sample charging. The instrument was calibrated with respect to Au 4f_{7/2} at 84 eV.

The X-ray diffraction (XRD) measurements were conducted with a Cu-K α source using a Philips XRG5000 3 kW x-ray generator with crystal alignment stage and Rigaku thin film camera. The spectrum was analyzed using Jade v.7 software. XRD was employed to obtain the structural information about the catalysts and carbon deposits that are formed during the reforming process.

3. Results and Discussion

3.1 Experimental Studies of Carbon Poisoning

Critical issue in hydrocarbon reforming is that conventional reforming catalysts such as Ni facilitate the formation of carbon structures which deactivate the catalyst.^{18,19,20,21,22,23} The formation of carbon deposits can be partially suppressed by an introduction of steam (steam reforming) which oxidizes and removes the deposited carbon atoms therefore preserving the catalyst surface.²⁴ Steam reforming is an endothermic process which requires high operating temperatures.

Steam reforming:
$$C_nH_m + n H_2O \rightarrow (n+m/2) H_2 + n CO$$

Metallic Ni is often used as the catalyst for steam reforming and generally very high concentrations of steam are required to prevent carbon poisoning of Ni. However, high

steam concentration is not desirable since it lowers the energy density of the products. For example, when H_2 is produced by direct steam reforming in SOFCs, the low density of H_2 leads to low SOFC current density and low power output.^{25,26} It is imperative to design carbon-tolerant reforming catalysts that can operate with low steam concentrations.^{27,28} Optimal catalysts would utilize one H_2O molecule per one carbon atom in a hydrocarbon, i.e., these catalysts would operate at the steam-to-carbon ratio of one. Current reforming catalysts such as Ni are rapidly poisoned by carbon deposits at this steam to carbon ratio.

To illustrate the problem of carbon poisoning, in Figure 1 we show the results of our experimental studies where the deactivation of Ni catalyst supported on YSZ during CH_4 steam reforming was investigated.

Figure 1: (a) Methane conversion over Ni/YSZ (Ni supported on YSZ) catalyst as a function of the time on stream. Steam to carbon ration was 0.5. (b) TEM studies show that thick graphitic carbon deposits are formed on the Ni catalyst during methane reforming process.

It is observed that the catalyst activity decreases as a function of the time on stream. The deactivation is a consequence of the formation of large deposits of sp^2 -carbon networks. TEM, EDS, and XRD experiments were also utilized to detect the graphitic carbon on Ni catalyst. We note that we have observed even more dramatic poisoning of Ni catalysts for heavier hydrocarbon fuels.

We have investigated, using quantum DFT calculations, the underlying molecular processes that lead to carbon poisoning. The goal of these DFT studies was to develop molecular insights into the mechanisms that govern the catalyst poisoning and to

formulate a rational approach towards the design of carbon-tolerant steam reforming catalysts. The results of these calculations are outlined in the next sections.

3.2 Quantum DFT Studies of Carbon/Ni interactions and Carbon Poisoning

We have utilized DFT calculations to calculate, from first principles, the elementary step reaction energies associated for methane steam reforming on Ni(111), see Figure 2. It is important to note that DFT allows us to obtain the reaction energies accurately and efficiently. This information is difficult to acquire via other means.

Figure 2: DFT-calculated reaction coordinate for steam reforming of methane over Ni(111). The figure demonstrates that the thermodynamically stable state of carbon is graphene. To prevent the catalyst poisoning, the formation of the graphitic sheets needs to be prevented

The DFT-calculated reaction coordinate clearly demonstrates that thermodynamically the most stable state of carbon on Ni(111) is a graphene sheet adsorbed on the surface. For example, we calculate that the adsorption energy for a carbon atom in a graphite sheet on Ni(111) is by ~2 eV more exothermic than the adsorption energy for individual carbon atoms adsorbed on Ni(111) at $\frac{1}{4}$ ML (one monolayer (ML) corresponds to all surface Ni atoms covered with C atoms) coverage. Clearly, there is a strong thermodynamic driving force for carbon atoms to form deposits of sp²-carbon. The tendency to form sp² carbon structures is the main reason for the rapid deactivation of Ni catalysts.

Furthermore, Figure 2 also demonstrates that carbon atoms, created in the process of hydrocarbon decomposition on Ni, can be removed from the surface by their oxidation and the formation of CO. Oxygen that oxidizes carbon atoms is formed by the splitting of water (steam) on Ni. The DFT studies suggest that the long term stability of reforming catalysts is governed by their ability to selectively oxidize carbon (form C-O bonds) and

remove it from the surface, while preventing the formation of C-C bonds as shown in Scheme 1.

Scheme 1: Carbon atoms can either react with each other to form sp²-carbon deposits which deactivate the catalyst, or they are oxidized to form CO which desorbs from the surface.

Motivated by these insights, we have further utilized DFT to investigate the elementary steps associated with C-C and C-O bond formation on Ni. In order for C-C bonds to form on a catalyst surface, C atoms need to diffuse on the surface and collide with each other²⁹. Similarly, oxidation of carbon atoms requires collisions between C and O atoms on the surface. We have employed DFT to calculate activation barriers for C and O atoms diffusion and the activation barriers for C-O and C-C bond formation.

Figure 3 (dark line) depicts the potential energy surface associated with C atom diffusion and subsequent C-C bond formation on Ni(111). We observe that the activation barrier for C atom diffusion on Ni(111) is ~ 0.5 eV (50 kJ/mol), suggesting that C atoms are very mobile on the surface. We also calculate that the activation barrier for the formation of C-C bonds is fairly low ~ 0.92 eV. The high rate of C atom diffusion and the low activation barrier for C-C bond formation result in the rapid formation of extended sp²-carbon deposits, ultimately leading to Ni deactivation.^{23,24,30}

Figure 3 also depicts the potential energy surface for C-O bond formation on Ni(111) (dotted red line). The Figure demonstrates that on Ni(111) the chemical pathways leading to C atom oxidation (C-O bond formation) have comparable overall activation barriers as those for the C-C bond formation. Similar activation barriers associated with the C-O and C-C bond formation on Ni suggest that this is not an ideal reforming catalyst. Simply stated, the rate of C-C bond formation is too high to ensure the long lifetime of Ni catalysts.

Figure 3: DFT calculated energies for C and O atom diffusion and C-O and C-C bond formation on Ni(111). Full dark lines represent the energy landscape associated with the C-C bond formation, while red dotted lines represent the energy for C-O bond formation. $C-C^\ddagger$ represents the DFT calculated energy for the transition state for C-C bond formation, while $C-O^\ddagger$ depicts the transition state for C-O bond formation. Inserts show the lowest energy pathways for C-C (right panel) and C-O (left panel) bond formation on Ni(111) surface. The pathways consists of C (dark atom, right panel) or O (red atom, left panel) atom diffusion over the surfaces and subsequent formation of C-C and C-O bonds respectively.

3.3 Quantum DFT identification of novel carbon-resistant reforming alloy catalysts

We have further utilized DFT calculations to investigate C-O and C-C bond formation on various Ni-containing alloys. The objective of these studies was to identify alloy catalysts that might be more carbon-tolerant than monometallic Ni. Optimal catalysts will, relative to monometallic Ni, favor carbon oxidation (C-O bond formation) over C-C bond formation. In our DFT calculations we have determined that Au/Ni, Ag/Ni and Sn/Ni alloy catalysts are good candidates for carbon-tolerant reforming. The alloy material that emerged as the most promising in the DFT studies was Sn/Ni. The results of the DFT calculations for Sn/Ni are shown in Figure 4.

Figure 4: DFT calculated energies for C and O atom diffusion followed by the respective C-C and C-O bond formation on Sn/Ni(111). Full dark lines represent the energy landscape associated with the C-C bond formation, while red dotted lines represent the energy for C-O bond formation. Inserts show the lowest energy pathways for C-C (right panel) and C-O (left panel) bond formation on Sn/Ni(111) surface. The pathways consists of C (dark atom, right panel) or O (red atom, left panel) atom diffusion over the surfaces and subsequent formation of C-C and C-O bonds respectively. Notice that the activation barrier for C-C bond formation is much larger than the one for C-O bond formation. Sn atoms are large red spheres, Ni atoms are large light blue spheres.

The DFT calculations presented in Figure 4 show that on Sn/Ni surface alloy – characterized by Sn displacing Ni atoms from the top Ni(111) layer – the relative kinetics

of C-O and C-C bond formation is significantly different than on Ni. For example the kinetic barriers for C (full dark lines) and O (dotted red lines) atom diffusion on Sn/Ni(111) surface are 1.9 and 1.2 eV larger than the respective kinetic barriers on Ni(111). The dramatic Sn-induced increase in the diffusion barriers suggests that over Sn/Ni, C and O atom diffusion becomes kinetically-limiting for the respective C-C and C-O bond formation. The DFT calculations suggest that on the alloy surface the rate of C-oxidation is much greater than the rate of C-C bond formation. We note that on Ni(111), the rates of C-O and C-C bond formation were similar to each other, see Figure 3. The DFT studies imply that the growth of carbon deposits should be suppressed by alloying Sn into the Ni lattice since carbon atoms will preferentially react with oxygen forming CO rather than react with other carbon atoms.

Furthermore, our DFT calculations also showed that the formation energy of Sn/Ni surface alloy is lower than the formation energy of Sn/Ni bulk alloys or the formation energy corresponding to separate, pure Sn and Ni phases. We calculate an alloy formation energy as:

$$E = E(\text{Ni/Sn_slab}) - E(\text{Ni_slab}) - \mu(\text{Sn}) + \mu(\text{Ni})$$

where $E(\text{Ni/Sn_slab})$ is the DFT calculated energy of a 3x3x4 alloy slab with an Sn atom displacing a Ni atom either in surface or bulk, $E(\text{Ni_slab})$ is the DFT calculated energy of a 3x3x4 Ni slab, while $\mu(\text{Sn})$ and $\mu(\text{Ni})$ are chemical potentials of Sn and Ni atoms respectively. $\mu(\text{Sn})$ and $\mu(\text{Ni})$ were obtained in DFT calculations as energies per atom associated with bulk Sn and bulk Ni respectively. The bulk calculations were performed for fcc Ni and cubic Sn lattices.

The above formulation of the formation energy sets up a pure Ni_slab as the reference state with the formation energy of zero. The formation energy associated with Sn/Ni surface alloy (one Sn atom replaces one Ni atom in the Ni top layer) was -2.044 eV/A², while the bulk alloy (one Sn atom in the second layer) has the positive energy of 1.67 eV/A². We note that we report the formation energy in the units of energy per unit area, i.e., the energy has been normalized to the area of the unit cell. Since we utilize 3x3x4 unit cell in all calculations, this does not have any impact on our conclusions.

The observation that Sn/Ni surface alloy has lower formation energy than the bulk alloy or the configuration corresponding to separate Sn and Ni phases is important since it suggests that there is a strong thermodynamic driving force to form and sustain Sn/Ni surface alloy. We have also calculated that aside from the formation of Sn/Ni surface alloy, there is a favorable thermodynamic driving force for Sn to displace Ni atoms from the step-edge sites or to decorate the step-edge sites on Ni substrate. In these configurations the Sn atoms, adsorbed in or on the edge sites, effectively repel C atoms from the low-coordinated step sites. Since low-coordinated step sites have been proposed to play an important role in the nucleation and growth of carbon deposits over Ni, this arrangement of Sn atoms would further lower the propensity of the alloys to form carbon deposits.

According to the above presented DFT calculations a small amount of Sn alloyed into a Ni catalyst surface should improve the stability of the catalyst by increasing the activation barrier for C-C bond formation, therefore preventing the formation of the deposits of sp²-carbon.

To summarize, the main conclusions of our DFT calculations are:

1. Carbon atoms, formed in the process of hydrocarbon decomposition on a reforming catalyst, react either with other carbon atoms, forming sp² carbon networks, or with oxygen, forming CO which desorbs into the gas phase.
2. The main problem with monometallic Ni catalyst is that the rate of C-C bond formation is high, yielding extended sp²-carbon structures, which deactivate the catalyst.
3. Carbon-tolerant reforming catalysts should preferentially oxidize carbon atoms (promote C-O bond formation) and suppress the formation of extended carbon networks (suppress C-C bond formation).
4. We have identified Sn/Ni alloy as potential carbon-tolerant reforming catalyst. The main advantage of Sn/Ni with respect to monometallic Ni is that the activation barrier for C-O bond formation is much lower than the barrier for C-C bond formation. We note that on pure Ni, the activation barriers for C-O and C-C bond formation are comparable.

The predictions of these calculations were examined in our experimental studies where pure Ni and Sn/Ni alloy catalysts were tested in a reactor setup in the steam reforming and partial oxidation of methane, propane, and isooctane.

3.3 Reactor testing and characterization of Sn/Ni alloy catalysts

Pure Ni catalysts were prepared using the wet impregnation technique, with Ni nitrate salt and ethanol as the solvent. The catalytic particles were supported on yttria-stabilized-zirconia (YSZ). The dried precursor was thermally reduced at 600 °C in a calcination furnace for approximately 4 hours. The Ni weight loading for these catalysts was approximately 25%. We use YSZ support and the high weight loading of Ni since these catalysts could possibly be utilized as SOFC anodes where ion-conducting supports and high metal loading are required to achieve acceptable electron and ion conductivity. For Sn/Ni alloy catalysts, Sn was added (0.5-3 % by weight with respect to Ni loading) in the aqueous form as a Sn-chloride salt, to the reduced Ni catalyst via wet impregnation. Following the addition of the Sn salt, the catalyst was dried for 12 hours at 100 °C and then reduced at 900 °C for 2 hr.

All catalysts were evaluated at steady state conditions in a flow reactor using gas flows of a hydrocarbon, H₂O, and N₂ or argon. The reactor consisted of a 20 mm I.D. quartz tube encased in a vertical tube furnace. Analysis of the product gas stream was performed by in-line gas chromatography. The gas chromatograph utilized thermal conductivity and flame ionization detectors to give quantitative analysis of all gaseous products.

The results of steam reforming of methane and isooctane over Ni and Sn/Ni catalyst are shown Figure 5. Sn/Ni alloy catalyst contained 1% Sn by weight with respect to Ni loading. The methane reforming experiments were performed with steam-to-methane ratio of 0.5, while isooctane reforming was performed at steam-to-carbon ratio of 1.5. Figure 5 illustrates that Sn/Ni is much more stable than monometallic Ni. For example, we observe that in isooctane steam reforming monometallic Ni catalyst deactivates within a few minutes. Similar results were obtained in the reforming of propane. The deactivation is accompanied by a large pressure drop across the reactor which is a consequence of a rapid buildup of carbon deposits.

X-ray Photoelectron Spectroscopy (XPS) for monometallic Ni catalyst performed after steam reforming of iso-octane, shown in Figure 5b, demonstrates that the catalyst is completely covered by carbon deposits. While Ni electronic signal was not detected, we observed C 1s signals at 284.5 eV, indicative of sp² carbon, and 283.1 eV, which we assign to C atoms in intimate contact with the metal. In post-reaction XPS analysis of Sn/Ni, Ni 2p_{3/2} signal was detected at 253 eV corresponding to metallic Ni, while C electronic fingerprint was not measured. These results are consistent with the thesis that carbon deposits did not accumulate on the Sn/Ni catalyst.

Figure 5: (a) H₂ yield obtained in steam reforming of isooctane over Sn/Ni alloy catalyst supported on YSZ at the steam-to-carbon ratio of 1.5. Pure Ni supported on YSZ rapidly deactivates under these conditions, while Sn/Ni is very stable. (b) XPS spectra in the energy range corresponding to Ni signal. Ni signal is very strong for the used Sn/Ni alloy supported on YSZ catalyst. On the other hand, Ni signal could not be detected for monometallic Ni supported on YSZ catalyst. The reason for this was that Ni catalyst is covered by carbon deposits as is illustrated in the insert where the XPS spectrum corresponding to carbon peak was collected for pure Ni catalyst. The carbon XPS spectrum suggests that Ni catalyst is completely covered with carbon deposits.

As suggested above the main reason for the exhibited robustness of Sn/Ni alloy catalyst is its resistance to the formation of extended carbon structures, as had been predicted in our DFT calculations. This is further corroborated by the XRD (x-ray diffraction) studies, shown in Figure 6(a) and STEM imaging shown in Figure 6(b). The XRD experiments showed that YSZ-supported Ni catalyst yields graphitic carbon in the reforming of all tested fuels, while Sn/Ni catalyst supported on YSZ does not produce any graphitic carbon structures, see Figure 6.

Figure 6(b) shows post-reaction STEM images of Ni and Sn/Ni catalysts. Elemental analysis (EDS) coupled with the STEM studies confirmed that Sn/Ni alloy catalyst did not form carbon deposits on catalyst surface while pure Ni catalyst is completely poisoned with carbon deposits.

Figure 6. (a) XRD results for catalyst before and after isooctane reforming. XRD spectra for post- and pre-reaction Ni catalyst and post-reaction Sn/Ni catalyst are shown. Graphite peak is observed over Ni catalyst. (b) Post-isooctane reforming STEM spectra of Ni and Sn/Ni. Ni particles are completely covered with carbon deposits while Sn/Ni is carbon-free. Furthermore, elemental mapping of Sn/Ni particles via EDS suggests Sn surface alloying. Sn pixels are colored yellow, while Ni is blue. (c) SEM micrographs of Sn/Ni catalyst and Ni catalyst after isooctane steam reforming. Ni is completely covered by carbon deposits.

In addition to the steam reforming reactions, we also showed that the alloy catalyst was superior to monometallic Ni in isooctane partial oxidation. The partial oxidation reactions were carried out over Ni and Sn/Ni catalysts at temperatures above 550 °C, the C/O molar ratio of 1, and a space velocity of 50,000 h⁻¹. Under these conditions the dominant products were CO and H₂. Our experiments showed that the catalytic activity,

measured in terms of the *iso*-octane conversion, was not significantly affected by small amounts of Sn loadings (up to 1 wt % with respect to Ni). Our testing showed that, similar to the steam reforming process, the Sn/Ni catalysts were more resistant to carbon deposition than monometallic Ni catalysts. For example, temperature programmed oxidation and XPS studies, performed after partial oxidation reaction was run for 6 hours, showed two orders of magnitude higher concentration of deposited carbon on monometallic Ni compared to the Sn/Ni catalysts.

The studies presented above demonstrate that Sn/Ni alloy formulated in the first principles DFT calculations is a very promising carbon-tolerant steam reforming and partial oxidation catalyst that is robust under fairly low oxygen-to-carbon ratios. This catalyst is far superior to monometallic Ni catalyst which rapidly deactivates during hydrocarbon reforming.

3.4 Kinetic studies: Reaction mechanisms on Ni and Ni alloy catalysts

In order to learn about the mechanism of reforming reactions on alloys we have also performed detailed kinetics studies of methane steam reforming on Ni and Sn/Ni catalysts. The reaction orders with respect to methane and water for methane steam reforming on Sn/Ni/YSZ and Ni/YSZ were determined by measuring the response of the forward rate to a change in the respective partial pressures of CH₄ and H₂O while keeping everything else in the system constant. Figures 7 a and c show that there is a linear increase in the forward rate for both Ni and Sn/Ni catalysts as the partial pressure of methane is increased. In these experiments, the partial pressure of methane was varied from 0.2 - 0.6 atm, while the partial pressure of water was kept constant at 0.39 atm. The feed was balanced by argon to reach the total pressure of 1 atm. Figures 8 b and d show that the forward reaction rate is not affected by a change in the partial pressure of water from 0.2 to 0.6 atm for a constant methane partial pressure of 0.39 atm. The behavior was consistently observed over a temperature range between 973 and 1073 K for Ni/YSZ and 1013 and 1123 K for Sn/Ni/YSZ.

Our results also show that as we varied the methane conversion from 1 – 10 % by changing the reactor temperature for a give flowrate, the order of the forward rate with respect to H₂O and CH₄ did not change on either catalyst. Since higher CH₄ conversion would lead to higher partial pressures of the reaction products, these observations imply

that the forward reaction rate is not sensitive to the changes in the partial pressure of the reaction products for either catalyst, and that the steady state coverage of product species (or surface intermediates which are precursors for the reaction products) on active sites does not change significantly. If this was not the case we would have seen a deviation in the reaction orders as a function of the change in conversion. Identical conclusions were made when small amount of product species were added to the inlet stream (up to 10 mol % with respect to methane). These conclusions are consistent with the results of our DFT calculations, which showed that at the relevant conditions ($T \sim 1000$ K) the adsorption energy of CO, H₂O, CO₂, and H₂ in its lowest energy configurations (e.g., dissociated or molecular) on under-coordinated sites of the Ni(211) surface are -164, -135, 19.2, and -77.2 kJ/mol, respectively. The adsorption energies are even lower for close packed Ni surfaces and for all sites on the Sn/Ni surfaces. These adsorption energies are insufficient to keep these species on the surface in significant concentrations under the high temperature conditions ($T > 973$ K), i.e. the Gibbs free energy of adsorption is positive. Based on the presented experimental results and the results of DFT calculations, we suggest that for both catalysts, the catalyst surface is approximately free of adsorbates under steady state conditions, and the overall rate is controlled only by the rate of the dissociation of CH₄. Similar observations were made previously for Ni/MgO catalysts.

Figure 7: a) A plot of reaction rate as a function of the partial pressure of methane (P_{CH_4}) for a Sn/Ni/YSZ catalyst at 1073 K and a constant water partial pressure of 0.39 atm diluted in argon. Total pressure was 1 atm. b) A plot of reaction rate as a function of $P_{\text{H}_2\text{O}}$ for a Sn/Ni/YSZ catalyst at 1073 K and a constant methane partial pressure of 0.39 atm diluted in argon. Total pressure was 1 atm. c) Same as in a) for Ni/YSZ and at 1013 K d) Same as b) for Ni/YSZ and at 1013 K.

The apparent activation energy for methane steam reforming, defined in terms of the response of the forward rate to changes in operating temperature, was determined in an identical reactor setup. Prior to each measurement, the absence of mass transport limitations was verified. Figure 8 shows an Arrhenius plot for methane steam reforming on the Ni/YSZ and Sn/Ni/YSZ catalysts for 0.39 atm of methane, 0.39 atm of water diluted in 0.22 atm of argon. The apparent activation barrier was determined to be $\sim 101 \pm 4$ and 132 ± 4 kJ/mol for the Ni and Sn/Ni catalysts, respectively. Further analysis of Fig. 8 suggests that the overall pre-exponential factor, calculated from the y-axis intercept in the Arrhenius plot, is ~ 10 -15 times larger for the Sn/Ni catalyst compared to the Ni catalyst. It is important to note that the overall pre-exponential factors were calculated

from our experimental turnover frequencies based on the total number of surface sites, which are approximately identical for the Sn/Ni and Ni catalysts, i.e., it was not based on the number of active sites since it is almost impossible to count the active sites. This means that if the numbers of active surface sites (the sites that participate in the most frequent reaction channels) on Ni and Sn/Ni are different from each other, the overall pre-exponential factors will, in addition to describing the pre-exponential factor associated with the elementary step that controls the overall rate, also reflect this difference

Figure 8: A plot of the turnover frequency of methane steam reforming as a function of the inverse temperature for 1wt% Sn/Ni/YSZ and Ni/YSZ catalysts when exposed to 0.39 atm of methane, 0.39 atm of water diluted in argon. The total pressure was 1 atm.

If one accepts that under the relevant conditions the surfaces of both catalysts are nearly free of adsorbates and that the rate is controlled by the dissociation of CH_4 , then the difference in the overall activation barrier and pre-exponential factors between Ni and Sn/Ni is a consequence of the change in the nature of surface sites that dominate the catalytic process. It appears that on pure monometallic Ni the active sites (i.e., the sites responsible for the dominant reaction channel) are different in their chemical activity and relative abundance compared to the Sn/Ni alloy catalyst.

CH_4/CD_4 kinetic isotope labeling studies

The analysis presented in the previous sections suggested that the rate controlling step in methane steam reforming on Ni and Sn/Ni is the activation of C-H bonds in methane. To independently verify our conclusions regarding the nature of the rate-controlling elementary step we have studied the kinetics of the process using labeled methane (CD_4). In these experiments, the reaction rates were measured in an identical differential reactor setup, free of mass transport limitations and artifacts due to reverse rates. Figure 9 shows plots of the measured forward reaction rates as a function of time for Ni/YSZ and Sn/Ni/YSZ catalysts as the feed was switched from CH_4 to CD_4 and back to CH_4 . Figure 9 shows that as the feed is switched from CH_4 to CD_4 , the forward rate decreases for both catalysts. Quantitative analysis of the reactions rates shows that the drop in forward rate is approximately equal on both catalysts for a given reaction temperature. The observed kinetic isotope effect demonstrates that the overall rate is controlled to a similar degree by the rate of C-H bond dissociation on both catalysts. Similar observations were made by others for supported monometallic Ni catalysts. We note that the measured kinetic isotope effect of ~ 1.6 is slightly lower than the isotope effect predicted based on the transition state theory, assuming that the rate-controlling step involves the C-H and C-D vibration with a frequency identical to those measured in the gas-phase for CH_4 and CD_4 , respectively. The reasons for this discrepancy might be in slightly different vibrational frequencies of normal modes involved in the reaction coordinate on two surfaces compared to the normal modes associated with gas-phase CH_4 and CD_4 .

Figure 9: The rate of steam reforming is measured for CH_4 and CD_4 reactants as a function of time on a) Ni/YSZ at 973 K and b) Sn/Ni/YSZ at 1033 K. The dark lines depict points in time when the reactant is switched from CH_4 to CD_4 and back to CH_4 .

4. Conclusions

We have utilized DFT quantum calculations to develop molecular insights into the mechanism of carbon poisoning. The results of the DFT calculations were supported by various microscopic (TEM, EDX, SEM, XRD), and spectroscopic (XPS, EDS) studies. We have identified carbon-atom diffusion and carbon-carbon bond formation as two critical elementary processes that lead to the formation of extended sp²-carbon networks which deactivate Ni catalysts. We have also determined that the long-term stability of steam reforming catalysts is governed by their capacity to selectively oxidize carbon atoms while suppressing C-C bond formation.

DFT calculations were further utilized to identify from first principles alloy materials which, as compared to monometallic Ni, have lower activation barrier for C-O bond formation and higher activation barriers for C-C bond formation. These DFT studies showed that Sn/Ni is more efficient in oxidizing and removing carbon atoms than Ni. The predictions of DFT calculations were tested in a reactor test station.

We have synthesized YSZ-supported Sn/Ni and Ni catalysts and tested these catalysts in steam reforming of methane, propane, and isooctane. The steam-to-carbon ratio in these experiments ranged from 0.5 for methane to 1.5 for isooctane and propane. The reactor studies conclusively demonstrated that Sn/Ni catalyst is much more robust than monometallic Ni for all fuels. For example, we find that Ni catalyst is rapidly poisoned by carbon deposits in the steam reforming and partial oxidation of propane and isooctane within a few minutes. On the other hand, Sn/Ni alloy is stable for as long as it was kept on stream. Our experimental characterization studies combining SEM, TEM, EDX, XPS, and XRD supported the predictions of DFT calculations and demonstrated that the main reason for the robustness of the alloy catalyst is that its resistance to the formation of sp² carbon networks.

5.1 Relevancy and future:

The work outlined above is distinguished by a few characteristics:

- (a) It represents a rare example where molecular level information was utilized directly to formulate an improved solid state catalyst. This is very important for further development of the field and it suggests that similar knowledge-based, as

opposed to trial and error, approaches could be employed to address many issues related to hydrogen economy. Particularly intriguing is the research approach that combines state-of-the-art experiments and theory towards formulating more efficient solid state catalysts. It is our belief that alloy materials provides exciting opportunity for novel, active, selective, and stable catalysts.

- (b) The developed alloy catalysts are also excellent anode electro-catalysts for direct electro-chemical oxidation of hydrocarbons on Solid Oxide Fuel Cells (SOFCs)

6.1 Special Recognitions & Awards/Patents Issued

- 1. Young Scientist Award of ICC 2008**, International Congress on Catalysis, Seoul, Korea, 2008 (Eranda Nikolla, the PhD student working on the project)
- 2. Walter J. Weber Jr. Award in Environmental and Energy Sustainability**, University of Michigan, 2007 (Eranda Nikolla, the PhD student working on the project)
- 3. Rackham Predoctoral Fellowship**, Horace H. Rackham School of graduate Studies, U of M, 2007-2008 (Eranda Nikolla, the PhD student working on the project)
- 4. Best Paper Presentations**, “Experimental/Theoretical Studies Aimed at the Development of Carbon-Tolerant Catalysts”, Michigan Catalysis Society Annual Meeting 2006, Dow Chemicals, Midland, MI, May 2006 (Eranda Nikolla, the PhD student working on the project)
- 5. Best Poster**, “Controlling Carbon Chemistry via alloying: Hybrid Experimental/theoretical Approach”, University of Michigan Blue and Green Engineering Competition 2006, Ann Arbor, MI, March 2006 (Eranda Nikolla, the PhD student working on the project)
- 6. Best Poster Award, Gordon Research Conference on Catalysis, 2006, New Hampshire.** (The poster was selected, along with 4 others, among >100 posters presented by Ph.D. students and postdoctoral fellows) (Eranda Nikolla, the PhD student working on the project)

6.2 Publications/Presentations

- Eranda Nikolla, Johannes Schwank and Suljo Linic, Measuring and Relating the Electronic Structures of Nonmodel Supported Catalytic Materials to Their Performance, *J. Am. Chem. Soc.*, **2009**, *131* (7), pp 2747–2754

2. Eranda Nikolla, Johannes W. Schwank, and Suljo Linic, "Comparative study of the kinetics of methane steam reforming on supported Ni and Sn/Ni alloy catalysts: the impact of the formation of Ni alloy on chemistry", *Journal of Catalysis*(in press)
3. Eranda Nikolla, Johannes W. Schwank, and Suljo Linic, "Hydrocarbon steam reforming on Ni alloys at solid oxide fuel cell operating conditions", *Catalysis Today* 136(3-4): 243-248, 2008
4. Nikolla E., Schwank J., Linic S., "Promotion of the long-term stability of reforming catalysts by surface alloying", *Journal of Catalysis*, 250 (1), 85-93, 2007
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6. Nikolla E., Linic. S, "Controlling carbon chemistry on Ni surfaces by alloying: First principles approaches toward carbon-tolerant alloy catalysts and electrocatalysts" ACS Spring Meeting, New Orleans, LA, Apr 2008
7. Nikolla E., Schwank J., Linic. S, "Development of carbon tolerant anodes for Solid Oxide Fuel Cells", AIChE Annual Meeting, Salt Lake City, UT, Nov 2007
8. Nikolla E., Schwank J., Linic. S, "Formulation of Novel Steam Reforming Catalysts Guided by Molecular Insights", American Chemical Society National Meeting, Boston, MA, Aug 2007
9. Nikolla E., Schwank J., Linic. S, "Development of carbon tolerant anodes for Solid Oxide Fuel Cells", North American Catalysis Society Meeting, Huston, TX, May 2007
10. 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
11. Nikolla E., Schwank J., Linic. S., "Controlling Carbon chemistry by surface alloying", AIChE Annual Meeting, San Francisco, Ca, Nov 2006
12. 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, Jun 2006 (poster).
13. 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

Acronyms

SOFC - Solid Oxide Fuel Cell

DFT - Density Functional Theory

C-O - Carbon/oxygen bond

C-C - Carbon/carbon bond

S/C - Steam-to-carbon ratio

CO - carbon monoxide

TEM - Transmission Electron Microscopy

STEM – Scanning Electron Microscopy

EDS - Energy Dispersive X-ray Spectroscopy

XRD - X-ray Diffraction

EELS – Electron Energy Loss Spectroscopy

Sn - tin

Ni - nickel

XPS – X-ray Photoelectron Spectroscopy

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