DFT Calculations

The Dacapo pseudo-potentials plane wave code [www.fysik.dtu.dk/CAMPOS] was employed for all calculations. In performing calculations, one must make decisions about various parameters that affect both the absolute and relative accuracy of the results. Our approach was to find a set of parameters that ensured the relative convergence, i.e., the convergence in the respective energy among various structures reported in the contribution. With this set of parameters we have also been able to reproduce various properties (carbon atom adsorption energy, oxygen adsorption energies, graphene sheet adsorption energy on Ni(111), activation barrier for C-atom attachment to the graphite sheet over Ni(111)) reported previously by others (see Ref. 8 and A. Eichler et al. in Physical Review B 62(7) pg 4744).

All calculations were performed with 3x3 supercells with 4-layer slabs and 6 special Chadi-Cohen *k*-points. Six layers of vacuum separated the slabs, and a dipole-correction scheme was employed to electro-statically decouple the slabs. The GGA-PW91 functional for self-consistent spin-polarized electronic structure calculations was employed. The density of valence electrons was determined self-consistently by iterative diagonalization of Kohn-Sham Hamiltonian utilizing Pulay mixing of densities. The plane wave basis set used to describe the one-electron states was cut off at 350 eV. An electronic temperature (k_bT) of 0.1 was used during calculations with the final results extrapolated to 0 K. Vanderbilt pseudo-potentials were employed to describe core electrons. In geometry optimization calculations, the two top substrate layers and adsorbates were allowed to fully relax. The forces were minimized to 0.05eV/Å.

The first order transition states for diffusion were identified by probing the high-symmetry sites between reactor and product states. The diffusing atom (C or O) was fixed in x-y plane on these sites and it was allowed to relax in z-dir. Other atoms in the system were allowed to fully relax. Energies were calculated for all high symmetry sites and the potential energy surfaces were constructed, Figure 1. The identity of the first order transition states was validated by making sure that the forces acting on the system vanish at the transition state and that the force on the diffusing atom changes sign as it moves through the transition state from reactant to the product state. We have further validated the transition states by slightly moving the transition state toward the product or reactant geometry and allowing the system to fully relax into the respective product and reactant geometries. This establishes that the transition state energies are maximum along the reaction coordinate and minimum with respect to other degrees of freedom. The transition state calculations were performed in a 3x3 unit cell. The forces in these calculations were minimized to 0.05eV/Å. Transition states for C-O and C-C bond formation were identified using Climbing Nudged Elastic Band method as described on reference 8.

The theoretical lattice constant for Ni of 3.52 Å was utilized to model the fcc crystal structure.

Model System

We employed the (111) surface of pure Ni and Sn/Ni. The (111) surface has previously been utilized to investigate various aspects of hydrocarbon reforming from first principles (for example, see Ref (2) and Besenbacher et at, Science, 1998, Vol 279)
Sn/Ni surface alloy was modeled as Sn atoms dispersed in a Ni lattice. Justification for the choice of the model system is provided in the following section of this document, where the formation energies for various possible model systems were calculated. We also note that entropic driving

forces, in the limit of small Sn concentration, would favor this atomic arrangement, i.e., collections of Ni atoms broken up by Sn.
The choice of the model system is further supported by multiple experimental results (XPS, EDS, STEM), discussed in the text.

We focus on the (111) surface since recent in-situ TEM studies (Ref 2) argue that C atoms diffuse over terraces towards carbon nucleation centers, which are usually assembled at the interface of a catalytic particle and a sp2 carbon structure (growing nanotube, graphitic sheet, etc.). This implies that the diffusion over terraces (highly coordinated sites) is critical for the partitioning between C-C bond formation and C-oxidation. Simply stated, catalysts that prevent carbon atoms diffusion on terrace sites are excellent candidates since it is easier to oxidize these C atoms, before they reach the nucleation centers. Our model takes all these observations into account.

We also note that our catalytic particles are fairly large (0.1 – 1 micron in diameter) and one would expect that the ratio of terrace sites compared to the number of low-coordinated step sites is very large, which is reflected in our model system.

Alloy Formation Energy Calculations

In the text, we suggested that the formation energy of Sn/Ni surface alloy is lower than the formation energy of Sn/Ni bulk alloy and the energy associated with the separate Ni and Sn phases. We calculate the formation energy as

$$E = E(Ni/Sn\_slab) - E(Ni\_slab) - \mu(Sn) + \mu(Ni),$$

where E(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(Ni_slab) is the DFT calculated energy of 3x3x4 Ni slab, while $\mu(Sn)$ and $\mu(Ni)$ are the chemical potentials of Sn and Ni atoms respectively. $\mu(Sn)$ and $\mu(Ni)$ 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 lattice.

The above formulation of the formation energy results in Ni_slab having zero formation energy. 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/A^2, while the bulk alloy (one Sn atom in the second layer) has the energy of 1.67 eV/A^2. 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 calculation, this does not have any impact on our conclusions.

Catalyst Preparation

8mol% yttria-stabilized zirconia was prepared via the standard co-precipitation method where a mixture of yttrium nitrate and zirconyl chloride mixed in water was precipitated using ammonium hydroxide. After filtration and drying over night the precipitate was then filtered and calcined at 800°C for 2 hours. The resulting YSZ powder was characterized using single point BET and X-ray diffraction. Ni-YSZ powder was prepared by ball milling a mixture of NiO (Alfa Aesar) and 8mol% YSZ (synthesized in lab) 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 rate of 2°C/min. The catalyst was reduced at 900°C for 5 hours using 30% H_2/N_2.

Sn was introduced to the sintered pellets via impregnation with $SnCl_2*4H_2O$ to obtain the desired Sn loading on the catalyst. The pellets were dried over night at 150°C. The pellets were then crushed and reduced under 30% H_2/N_2 for 7 hours at 900°C. The reducing process was determined using TPR and XRD to ensure complete reduction of the catalyst.

Reactor Studies

The experiments were run isothermally at 800°C. Approximately 0.8g of catalyst (active material plus support) and a total inlet gas flowrate of 1400sccm were used. Gas feeds were delivered via mass flow controllers while liquid fuels and water were delivered via peristaltic pumps. The catalyst was tested using a standard flow reactor in line with a Varian gas chromatograph (Varian CP 3800) equipped with TCD detectors.

Microscopy and Spectroscopy

Jeol 2010F electron microscope was used for Energy Dispersive X-ray Spectroscopy (EDS), Scanning Transmission Electron Microscopy (STEM) and Transmission Electron Microscopy (TEM). The instrument operates at 200kV 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 the Ametec EDAX system both in spot and scanning mode. The lens conditions were set for a probe size of 0.5nm to obtain adequate probe current. The elemental scanning images were obtained using 512x512 pixels in a frame at a dwell time of 200 microseconds. 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.

For X-ray Photoelectron Spectroscopy (XPS) experiments we have utilized Kratos Axis Ultra XPS with 150W Al (Mono) X-ray gun. This instrument was operated ex-situ under a 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 40eV. The charge neutralizer was utilized to prevent sample charging. The instrument was calibrated with respect to Au 4f7/2 at 84 eV.

The X-ray Diffraction (XRD) experiments were conducted with a Cu-Kα source using a Philips XRG5000 3kw x-ray generator with crystal alignment stage and Rigaku thin film camera. The spectrum was analyzed using Jade v.7 software.