

# First-principles investigations of the Ni<sub>3</sub>Sn alloy at steam reforming conditions

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## Introduction

Catalytic carbon deposition on Ni nanoparticles and surfaces is the first step towards coking of steam reforming Ni catalysts and carbon-induced corrosion, i.e., metal dusting corrosion, on Ni-based alloy surfaces [1,2]. The fundamental processes at the atomic scale are essentially the same. Therefore an atomistic understanding of how the gas-phase components influence carbon deposition and nucleation is very valuable for the understanding of metal dusting and avoid this degradation. The growth of graphene on the Ni surface is a necessary step in both processes. Recent ETEM [3] and DFT [4] studies have shown that steps on the metal surface act as growth centers for graphene.

Several strategies to modify these growth centers and thus avoid carbon growth can be pursued by: alloying Ni with metals less reactive towards carbon [5,6], applying protective coatings [7,8], and selective poisoning of the active surface sites by sulfur and alkali metals [1,9]. Alloying Ni with noble metals, to increase its stability towards carbon formation has been suggested [6]. In this work the effect of Sn, a much cheaper metal than the noble ones, is investigated as an alloying element to Ni, extending previous experimental [9,10] and theoretical [11] work. It is here focused on the Ni<sub>3</sub>Sn alloy phase and gas-induced segregation. In this contribution a theoretical study of the Ni<sub>3</sub>Sn alloy surface chemistry is presented. It is shown that Sn perturbs the growth centers rather than blocking them. Mechanism for graphene growth will also be discussed.

## Materials and Methods

Density Functional Theory (DFT) is used as implemented in the computer code ultra-soft pseudo potentials plane-wave code DACAPO using the RPBE exchange correlation functional [12] and a plane-wave basis set.

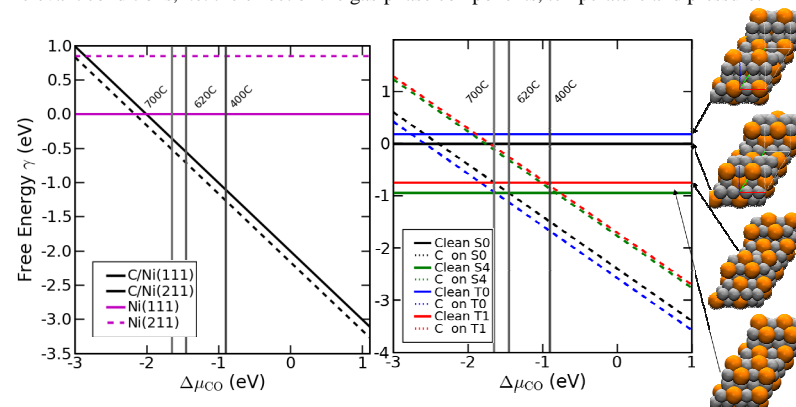
## Results and Discussion

It is found that the equilibrium surface termination is different from the bulk termination, and is dependent on the conditions and gas composition. This surface rearrangement causes carbon deposition to be less favorable on Ni<sub>3</sub>Sn than on pure Ni. The chemisorption energies of CO, C, OH and H were calculated for both the flat and stepped Ni<sub>3</sub>Sn surface. The results were extrapolated to realistic conditions by varying the gas-phase chemical potential. The analysis showed that the surface is predominantly covered by CO and C. When taking segregation effects into account it is shown that the stepped surface is stabilized by CO (Figure 1.) and C. Comparing this result to pure Ni it is seen that CO binds weaker on the most stable Ni<sub>3</sub>Sn site than on pure Ni.

The Brønsted-Evans-Polanyi [14] principle suggests that the barrier for dissociation and thus C deposition must be higher than on pure Ni. This is consistent with previous work by Linic et al. [9].

## Significance

The present work elucidates the surface composition of the Ni<sub>3</sub>Sn alloys during experimentally relevant conditions, i.e. the effect of the gas-phase components, temperature and pressure.



**Figure1.** The free energy of CO chemisorption on the most stable site of the 4 most stable terminations compared to pure Ni. The horizontal line shows the clean surface and the dashed the CO covered one as a function of the CO chemical potential. The conditions from [9] are plotted as the vertical lines. Ni<sub>3</sub>Sn will start adsorbing CO at chemical potentials above -1.7 eV. For pure Ni the CO starts binding at chemical potentials above -2.1 eV.

## References

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