

Ab Initio Studies of Coke Formation on Ni Catalysts During Methane Reforming

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Reforming of methane with either water (steam reforming) or CO₂ (dry reforming) to produce syngas is a significant pathway for converting natural gas into more versatile chemical feedstocks. A significant difficulty with practical use of Ni as a catalyst for methane reforming is the formation of surface carbon (coke), which leads to catalyst deactivation. We have used quantum chemistry calculations, specifically, plane wave Density Functional Theory (DFT), to elucidate the atomic-scale mechanisms for the initial stages of carbon deposition on Ni surfaces. One important elementary reaction leading to the net formation of surface carbon is the disproportionation of adsorbed CO. We have used DFT to examine the adsorption of CO, C, and O on a set of Ni surfaces chosen to represent both the atomically flat low Miller index surfaces likely to exist on practical catalysts and also surface defect sites that are created by surface steps. Specifically, we have examined Ni(111), Ni(110), Ni(210), and Ni(531). The latter two surfaces are stepped surfaces which, in their ideally terminated structure, are well suited for representing general classes of surface defects within the limitations of plane wave DFT.

Our calculations for adsorbed CO yield structural data in excellent agreement with experimental results where these are available. More importantly, our results confirm earlier experimental calorimetry data that indicated that the adsorption energy of CO on Ni is not surface sensitive. That is, the binding energies on a range of flat and stepped surfaces are quite similar. The adsorption of the relevant atomic species, C and O, however, is found to be structure sensitive, with adsorption of these species near surface steps being considerably more favorable than on flat surfaces. This observation points to surface defects as potentially playing a key role in the initial nucleation of surface carbides on Ni catalysts.

While understanding the thermochemistry of adsorbed species gives some insight into surface reaction mechanisms, a much more complete picture can be obtained by rigorously determining the transition states between reactants and products for reactions of interest. Estimates of the energy of the transition state for CO disproportionation were obtained using the semi-empirical unity bond index-quadratic exponential potential (UBI QEP) method. This method estimates transition state energies using only information about the reactant and product states. These estimates suggest that CO disproportionation is quite unfavorable on flat Ni surfaces relative to molecular desorption of CO, but that disproportionation is more likely to occur on stepped surfaces. To understand the accuracy of these estimates, calculations have been performed to rigorously locate the

transition states related to CO disproportionation on Ni(111). Our calculations show that the C and O atoms move through a series of local minima separated by transition states as the atoms become separated on the surface until the limit of well separated atoms used as the final state in the UBI-QEP estimate is reached. Significantly, the true transition state for this process is substantially higher in energy than the UBI-QEP estimate. In the future we aim to determine the true transition states for the same disproportionation reaction on the two stepped Ni surfaces we have studied, Ni(210) and Ni(531), to provide an accurate assessment of the rate of this reaction on these surfaces.

During methane reforming on Ni catalysts, species containing C, O, and H are all simultaneously present on the catalyst surface. Even for the small molecules relevant to this process, the number of distinct elementary reactions that needs to be considered to completely describe practical catalysis is enormous. To move towards a more complete description of these systems, we have begun to use DFT to examine the adsorption of H on the same Ni surface mentioned above. Atomic H can adsorb both on top of metal surfaces and also in subsurface interstitial sites, so both modes of adsorption are being considered in our calculations.