390e Coking Mechanism and Promoter Design for Ni-Based Catalysts: a First Principles Study

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Introduction

Because of their good catalytic activity Ni-based catalysts are widely used in chemical processes such as hydrocarbon hydrogenation and dehydrogenation, stream reforming and catalytic partial oxidation of methane. Ni is also often a component of high temperature steels which are used as construction materials for the tubular reactors in the steam cracker and in the steam reformer. The relatively low price as compared to Pt, Pd and Rh makes Ni a very attractive catalyst material. However, carbon deposition, so-called coking, is especially severe for nickel based catalyst and can lead to catalyst deactivation. Also in steam cracking, coking of the reactor walls is catalyzed by the Ni in the construction material and is an important challenge, leading to regular shutdowns and production losses.

To better understand the coking mechanism of Ni-based catalysts and materials, we have used first principles density functional theory (DFT) to study the relative stability of the various possible forms of carbon on Ni. Such molecular level understanding might help to find a promoter to prevent or reduce coking of Ni catalysts. Experimental studies of the coking mechanism have suggested the following steps are involved: initially carbon atoms deposit on the catalyst surface, next the carbon atoms start to dissolve into the Ni bulk, until the bulk is saturated. At this point graphitic carbon starts to precipitate, often in the form of carbon nanotubes. Other studies suggest that adsorbed carbon atoms form a graphene overlayer, i.e. a single layer of graphite, on the Ni surface. The different mechanisms are illustrated in Figure 1.

Method

Carbon chemisorption energies were calculated using periodic spin-polarized density functional theory as implemented in the Vienna Ab initio Simulation Package (VASP)[1] with the Perdew Wang 91 functional and projector-augmented-wave (PAW) pseudopotentials to describe the inner shell electrons. The Ni catalyst was modeled as four-layered slabs, separated by 12 Å vacuum layers. Depending on the coverage, (3x3x1) and (5x5x1) *k*-point grid were used for the surface Brillouin zone integrations.

Results and discussion

Carbon chemisorption on the Ni(111) surface was studied for coverages varying from 0.125 to 1.0 ML. For the entire coverage range, the hollow hcp site was found to be preferred, with a strongly coverage dependent binding energy ranging from –660 to –487 kJ/mol. The fcc site was slight less stable by about 7 kJ/mol. Interestingly, subsurface chemisorption in the octahedral sites of the first subsurface layer (Figure 1, mechanism 4) was found to be preferred over surface chemisorption by 40 to 120 kJ/mol for the entire range of coverages. Also bulk chemisorption was found to be more preferred than on-surface chemisorption up to a bulk C:Ni molratio of about 1:2. The bulk chemisorption energy was found to vary strongly with concentration, ranging from –698 kJ/mol at molratios below 1:8 to –550 kJ/mol for equimolar ratios. Alternatively, the stability of a graphene overlayer was studied (Figure 1, mechanism 3). Different adsorption sites were distinguished. For the preferred adsorption mode with an adsorption energy of –41 kJ/mol per carbon atom, the carbon atoms are located at the top and the hcp sites. The binding energy of carbon in chemisorbed graphene is –760 kJ/mol and is more stable than the other forms of carbon, i.e. chemisorbed carbon, subsurface carbon and bulk carbon. From the relative stabilities, the following mechanism can be envisioned (Figure 1). First the hydrocarbon reactant decomposes on the Ni surface, to form chemisorbed carbon at the hcp sites (mechanism 1 in Figure 1). Next, the on-surface carbon has 3 options. The first option is to react with co-adsorbed hydrogen or oxygen to form products which can desorb (mechanism 2). Hence, surface carbon can be labeled active carbon because it can be removed from surface and does not lead to catalyst deactivation. The second option is for the surface carbon atom to penetrate into the first subsurface layer, and then diffuse further to the Ni bulk until the bulk is saturated with carbon (mechanism 4). It is thermodynamically favorable for surface carbon to dissolve into the Ni bulk. Once the carbon molfraction in the bulk reaches a value where low coverage surface chemisorption becomes thermodynamically favorable, i.e. for a Ni:C ratio of about 2:1, any additional carbon will stay on the surface. This surface carbon can possible accumulate to reach a coverage where the formation of a graphene overlayer becomes possible (mechanism 5). The third option corresponds to the formation of a graphene overlayer (mechanism 3). Although an extended graphene layer is more stable than bulk carbon, this mechanism requires high coverages of surface carbon since the formation of graphene follows a higher order reaction. Hence, this mechanism is more likely for high carbon deposition rates and low oxygen or hydrogen surface concentrations. Both the bulk carbon and graphene are considered inactive carbon and might lead to catalyst deactivation. Hence, both forms of carbon deposition need to be prevented to avoid catalyst deactivation. Some studies have proposed alloying the Ni surface layer with gold atoms or blocking the most active sites with sulfur, to reduce the surface diffusion rate of carbon and to slow down the formation of a graphene overlayer[2]. This method will be most effective for high carbon coverages. Alternatively, one might try to prevent carbon from dissolving into the Ni bulk. Our DFT studies indicate that boron might effectively block the octahedral subsurface sites and hence compete with carbon for these sites. The binding energy for B, about –660 kJ/mol, is similar to the value for carbon. Similar to carbon, B strongly prefers the subsurface octahedral sites by about 100 kJ/mol and is unlikely to precipitate to the surface. Hence a new way to prevent Ni catalyst deactivation might be by adding B as a promoter. The boron blocks the subsurface sites and prevents carbon from diffusing into the bulk of the catalyst (mechanism 4, Figure 1), forcing the carbon atoms to stay on the surface, available for reaction along mechanism 2 (Figure 1). Experimental tests indeed indicate that B can effectively reduce coking of Ni based catalysts during the catalytic partial oxidation of methane[3].

Conclusions

Ab initio density functional calculations were performed to analyze the relative stability of three types of carbon on a Ni catalyst: chemisorbed carbon, bulk carbon and graphene. Bulk carbon was found to be preferred over on-surface adsorption up to bulk C:Ni molfractions of 1:2. The build-up of bulk carbon will affect the catalytic properties of Ni and might lead to catalyst deactivation. At sufficiently high coverages, graphene is more stable than bulk carbon. However, the formation of a graphene overlayer follows higher order kinetics and might require higher carbon surface coverages. Ab initio calculations indicate that boron effectively blocks the subsurface sites and might prevent carbon from diffusing into the bulk of the catalyst, hence forcing the carbon atoms to stay on the surface, available for reaction. This effect is thought to be responsible for the improved coking resistance observed experimentally for boron promoted Ni catalysts. **References**

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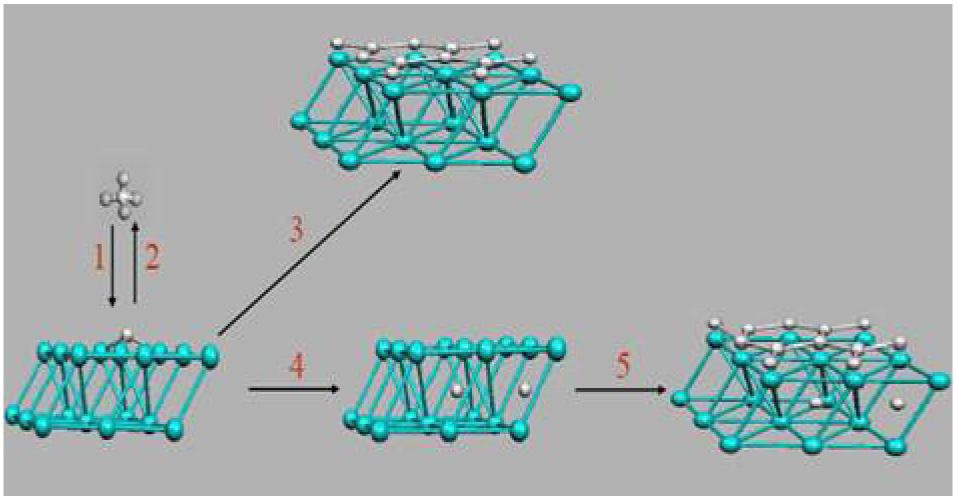

Figure 1. Different possible reaction paths for carbon deposition on a Ni catalyst.