First principles based design of a Ni catalyst with improved stability

Xu Jing, Mark Saeys

Department of Chemical and Biomolecular Engineering, National University of Singapore

Ni catalysts are commonly used for hydrocarbon processes such as steam methane reforming and (de)hydrogenation reactions. Deactivation by carbon deposition is a common challenge in many catalytic processes over Ni-based catalysts involving hydrocarbons, such as steam reforming of methane and heavier hydrocarbons [1]. To the design Ni catalysts with improved stability, first principles Density Functional Theory (DFT) calculations were combined with experimental investigations.

To develop a molecular level understanding of the coking mechanism on Ni catalysts, the stability of different forms of carbon that can exist on Ni catalyst and the kinetics of carbon diffusion were studied using first principles calculations. Calculated binding energies are summarized in Table 1. On-surface carbon atoms are relatively unstable with binding energies of around −660 kJ/mol. Extended graphene islands were found to be the most stable form of carbon on a Ni catalyst, with a carbon binding energy of −760 kJ/mol. However, the formation of graphene islands resembles a nucleation process and requires critical islands of about 15-20 carbon atoms [2]. Surface carbon atoms have a strong affinity for step sites, and step sites act as nucleation sites for graphene formation. Subsurface octahedral sites are also more stable than on-surface sites, and first principles calculations indicate that the formation of a thin carbide film by the diffusion of surface carbon to the octahedral sites in the first subsurface layer is both

kinetically and thermodynamically likely [3]. The presence of subsurface carbon significantly decreases the activity of Ni catalysts and increases the calculated methane activation energy from 80 kJ/mol to about 140 kJ/mol.

Calculations indicate that boron atoms preferentially bind at the step sites and at octahedral sites just below the surface [2] (Table 1). Boron and carbon atoms hence show similar a relative binding preference, and boron is proposed to selectively block both step and subsurface sites and hence prevent coking. In addition, subsurface boron atoms were found to restructure the Ni(111) surface and slightly lower the calculated methane dissociation barrier from 80 kJ/mol to 64 kJ/mol. Hence, boron atoms are believed to both enhance the catalyst stability and slightly increase the catalyst activity.

To validate the theoretical predictions, 15 wt% Ni/γ-Al$_2$O$_3$ catalysts, promoted with 0.5 and 1.0 wt% B were synthesized, characterized and tested during steam methane reforming. Experiments, summarized in Figure 1, at 800 ºC and at a GHSV of 330,000 cm3/hr.g$_{cat}$ demonstrate that promotion with 1.0 wt% B not only reduces the first order deactivation rate coefficient by a factor of 3, but also enhances the initial conversion from 56% to 61%. A temperature programmed oxidation and scanning electron microscopy study of the catalysts after 450 min on stream further confirms that boron assists in preventing carbon buildup.

Table 1. Calculated binding energies (kJ/mol) for carbon and boron atoms on Ni surfaces.

Site	Carbon	Boron
On-surface hcp[a]	−662	−572
Subsurface octahedral	−707[a] −611[b]	−620[a] −639[b]
Bulk octahedral[c]	−686	−570
Step 5-fold hollow[d]	−752	−672
Graphene	−760	

Details about the DFT calculations can be found in [2,3]; [a]Ni(111)-p(2x2) unit cell; [b]Ni(111)-p(1x1) unit cell; [c]C/B:Ni ratio = 1:8; [d]Ni(211)-(1x2) unit cell.
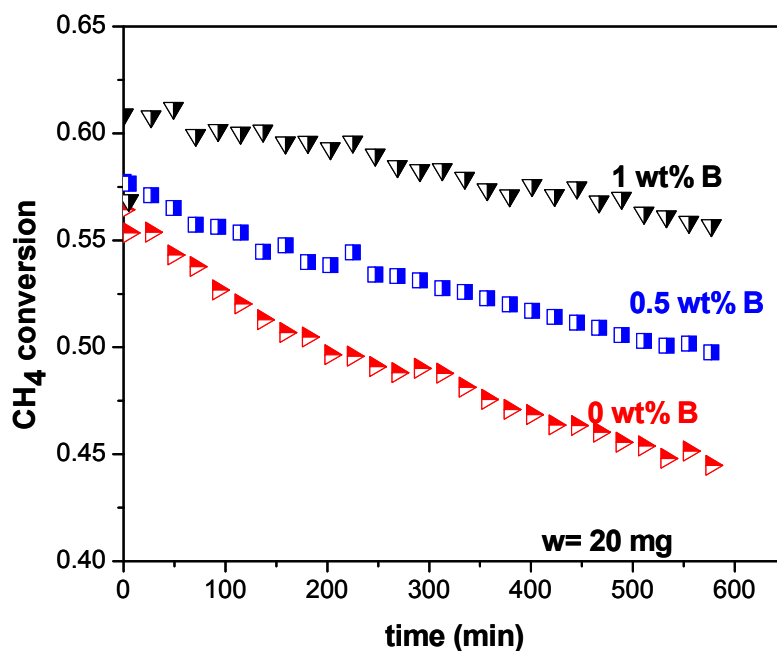

Figure 1. Methane conversion as a function of time on stream. Reaction conditions: T=800 ℃, P=1 atm, $CH_4:H_2O:N_2$=10:10:1, methane flowrate= 50 Nml/min, catalyst weight = 20 mg, and GHSV = 330,000 cm^3/hr.g_{cat}.

References

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