

IMPROVING THE STABILITY OF COBALT FISCHER-TROPSCH CATALYSTS THROUGH BORON PROMOTION

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Supported Co catalysts exhibit good activity and selectivity for Fischer-Tropsch synthesis, but deactivate slowly. To explore the possibility of deactivation by carbon deposition, the stability of various forms of deposited carbon was evaluated using density functional theory. Carbon diffusion into step sites, initiating a p4g clock reconstruction, and carbon growth out of step sites, forming graphene islands, were calculated to be thermodynamically very favorable. Two forms of deposited carbon could also be distinguished experimentally. Based on this mechanistic insight, boron was proposed as a promoter to enhance the stability of Co catalysts. DFT calculations indicate that boron displays binding preferences comparable to carbon, and boron can be used to destabilize carbon deposits. To evaluate the theoretical predictions, supported 20 wt% Co catalysts were promoted with 0.5 wt% boron and tested under realistic FTS conditions. Boron promotion was found to reduce the deactivation rate six-fold, without affecting selectivity and activity.

Keywords: Fischer-Tropsch Synthesis, boron promotion, deactivation mechanism

Introduction.

Fischer-Tropsch synthesis (FTS) converts synthesis gas, a mixture of CO and H₂ to various hydrocarbons. Its flexibility to utilize biomass, natural gas, as well as coal as a raw material contributes to the growing importance of FTS.¹ Supported Co catalysts are the preferred choice for FTS because of their high hydrocarbon selectivity and low water gas shift activity.^{1,2} Nevertheless, supported Co catalysts deactivate slowly under realistic FTS conditions² and it is therefore desirable to improve their stability.

To evaluate the mechanism of deactivation by carbon deposition, the stability of different forms of carbon was calculated using Density Functional Theory (DFT) and studied experimentally using XPS and TPH. Previously, we proposed boron as a promoter to enhance the stability of Ni catalysts during steam reforming.³ Boron is calculated to mimic the site preference of carbon, and can hence be used to selectively block nucleation sites for carbon deposition.

Results and Discussion

The thermodynamic stability of different forms of deposited carbon relative to a gas phase of CO, H₂, and H₂O was calculated using periodic DFT-PBE as implemented in the Vienna Ab initio Simulation Package.⁴ Carbon adsorption at step sites is thermodynamically very favorable at 20 atm and 500 K (Table 1). Carbon formed at step sites can subsequently diffuse into the steps and induce a p4g clock reconstruction (Fig. 1). The p4g clock structure is -96 kJ/mol more stable than the syngas reactants. Alternatively, carbon can grow out of the steps to form hydrogen terminated graphene islands. This is -80 kJ/mol favorable. Experimentally, after 200 hours of reaction, two types of deposited carbon could be identified using XPS and graphene-like carbon sheets were observed in TEM (Fig. 2).

Next, boron was calculated to exhibit a binding preference similar to carbon, and was also able to induce a p4g clock reconstruction. The

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presence of boron was calculated to significantly reduce the thermodynamic driving force to deposit carbon near step and clock sites (Table 1), hence possibly preventing the formation of carbon deposits.

Table 1. Effect of boron on the ΔG_{rxn} for the formation of carbon at step and clock sites from CO and H₂ under typical FTS conditions.

Site	Gibbs free energy of reaction (kJ/mol)	
	Without boron	With boron
Step	-70	+110
Graphene island	-80	n.a.
p4g clock	-96	+76

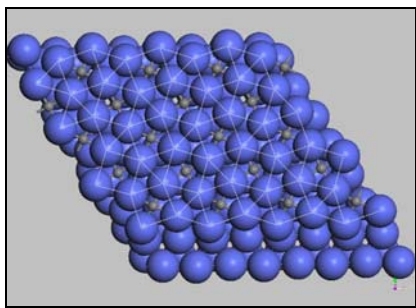


Figure 1. Carbon adsorption at p4g clock sites

The effect of 0.5 wt% boron on the stability, activity and selectivity of a 20 wt% Co/ γ -Al₂O₃ catalyst was evaluated in a micro fixed bed reactor under typical FTS conditions (240 °C, 20 bar, 7.5 g_{cat} hr/mol) (Fig. 2). The unpromoted catalyst deactivates with a first order rate coefficient of $-1.7 \times 10^{-3} \text{ hr}^{-1}$, comparable to literature values.² Boron promotion was found to reduce the deactivation rate six-fold to $-2.7 \times 10^{-4} \text{ hr}^{-1}$, without affecting the activity or the C₅₊ selectivity.

XPS characterization of the promoted catalyst catalysts indicates the formation of a thin cobalt boride film after reduction, consistent with the theoretical model. TEM characterization of the catalyst after reaction indicates the presence of sheet-like carbon deposits (Fig. 2) on the unpromoted catalyst but not on the promoted catalyst.

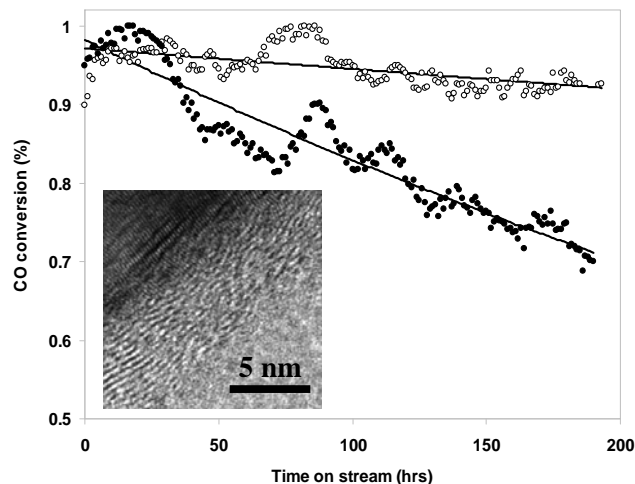


Figure 2. CO conversion for promoted (○, 0.5 wt% boron) and unpromoted (●) Co catalysts. Insert: TEM image of an unpromoted Co catalyst after 200 hrs, showing sheet-like carbon deposits.

Conclusions.

DFT calculations were performed to evaluate the relative stability of different forms of deposited carbon on Co catalysts. The formation of extended graphene islands and a p4g clock reconstruction was calculated to be favorable under FTS conditions. Based on this mechanistic insight, boron was proposed as a promoter to destabilize these carbon deposits. Promotion of a supported 20 wt% Co catalyst with 0.5 wt% boron indeed reduced the deactivation rate coefficient six-fold, without affecting the activity and C₅₊ selectivity in a 200 hr experiment.

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