Reactivity of CO on clean and carbon covered cobalt surfaces in Fischer-Tropsch synthesis

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The increasing demand for liquid transportation fuels on the one hand, and the high prices for petroleum oil on the other, raised the interest for alternative hydrocarbon feedstock, such as natural gas, biomass and coal. In the promising Gas-To-Liquid process, Fischer-Tropsch Synthesis (FTS) is used to convert syngas (a mixture of CO and H_2) to long-chain hydrocarbons on a cobalt catalyst.

Different mechanisms deactivate the cobalt surface during FTS[1]. Carbon deposition is one of the main deactivation mechanisms but is extremely difficult to observe experimentally, due to the presence of wax-like hydrocarbons on the surface and in the pores of the catalyst. Understanding the deactivation mechanism at a molecular level is crucial for developing efficient cobalt-based FTS catalysts with high activity, selectivity and stability.

In our computational study, the influence of carbon deposits on CO adsorption and dissociation on cobalt is modeled. CO dissociation is taken as a model reaction as it is the first step in the carbene mechanism and has to proceed fast enough in order to produce long carbon chains[2]. Both on-surface and subsurface carbon species are considered and both the Co(0001) and the Co($11\bar{2}1$) surface are taken into account. Studying two surface allows us to investigate the influence of the topology of the active site[3].

Our calculations show that carbon species increase the reaction barrier and energy for CO dissociation. The reaction is slowed down and is also thermodynamically less likely to proceed. The subsurface carbon species have the largest influence. We conclude that carbon deposition is indeed a significant mechanism for deactivation. It is thus necessary to keep carbon fouling under control in industrial reactors.

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