

An *Ab Initio* Approach Towards Engineering Fischer-Tropsch Surface Chemistry

David A. Walthall, Siddharth Chopra, and Matthew Neurock

Department of Chemical Engineering

University of Virginia

102 Engineers' Way

P. O. Box 400741

Charlottesville, VA 22904-4741

Phone: (434) 924-6248

Fax: (434) 982-2658

mn4n@virginia.edu

DOE Grant DE-FG26-01NT41275

OBJECTIVE:

In recent years, there has been an increased interest in the Fischer-Tropsch synthesis as an alternative source of liquid hydrocarbon fuels from sources such as methane and coal. The Fischer-Tropsch synthesis involves a complex set of bond breaking and bond making reactions, and the balance between these dictates the product distribution. These reactions include the activation of CO and H₂, the hydrogenation of hydrocarbon surface intermediates, the coupling of hydrocarbon intermediates, and the desorption of products. A key aspect of a Fischer-Tropsch catalyst is that it must promote CO activation. In addition, a careful balance of surface species hydrogenation reactions and hydrocarbon coupling reactions is crucial to produce longer chain hydrocarbon products. Although this reaction has been studied for many years, the fundamental understanding of how the atomic surface structure of the catalyst affects the elementary reaction steps in the Fischer-Tropsch synthesis is still not well understood.

The Fischer-Tropsch synthesis can be conceptualized as several separate sets of reactions. The first set of reactions is the initiation reactions, involving the activation of CO and H₂ to form the C* and H* (as well as O*) surface species. The second set of reactions is the hydrogenation reactions, in which surface hydrocarbon species are hydrogenated ($C_xH_y^* + H^* \rightarrow C_xH_{y+1}^*$). When the products of hydrogenation are stable close-shelled species, they can desorb, yielding the product alkanes and alkenes. The third set of reactions is the carbon-carbon coupling reactions. These reactions increase the chain length and molecular weight of the intermediates and products. It is the balance between these sets of reactions that determines the product distribution.

ACCOMPLISHMENTS TO DATE:

We used *ab initio* quantum mechanical methods to analyze the elementary surface steps over model catalytic surfaces to better understand the reaction mechanisms. We studied in detail the activation of CO over Co(0001) and stepped Co surfaces to better understand the role of surface corrugation and openness on the energetics. In addition, we examined the effect of different coverages on the calculated reaction energies, and we found that both the surface structure and the coverage have significant effects on the energetics.

Our studies of the hydrocarbon coupling reactions over Co(0001) suggest that both CH₂ and CH may be kinetically important intermediates. We also studied the reaction energies and activation barriers for CH_x hydrogenation over Ru, Co, and Pt closed packed surfaces to elucidate periodic trends. We found that the reaction energies and activation barriers for the hydrogenation reactions are lower for metals that lie to the right on the periodic table, such as Pt.

We have developed a kinetic Monte Carlo method to simulate the initial kinetics involved in Fischer-Tropsch synthesis over Co(0001). Kinetic Monte Carlo simulations begin to provide a link between the ideal calculated energetics and the more realistic kinetics by incorporating surface coverages effects on the product distributions. In addition, they can be used to provide insight into the relative importance of different reaction pathways. The ability to study one set of reactions in detail while turning off other reactions can provide insight into a complex reaction mechanism.

The results from our kinetic Monte Carlo simulations suggest that the CO does not dissociate on the terrace sites of the Co(0001) surface under typical operating conditions. The activation of CO is much more prevalent at step sites as calculated DFT. The simulations therefore use the barriers for CO dissociation at steps to describe the initial dissociation of CO* into surface C* and O*. The simulations show that there is an initial build-up time during which H* dominates the surface with about 0.1 ML coverage. Hydrogen is quickly driven off by CO*, C*, and O*. As the surface concentration of CO* continues to rise, most of the O* reacts with CO* and desorbs from the surface as CO₂(g). A fraction of the adsorbed oxygen atoms react to form hydroxides or water (which desorbs). The CO* concentration reaches a steady-state at about 0.45 ML, and the CH* concentration reaches a steady-state value of about 0.12 ML. A small amount of CH₂* is present on the surface. Hydrogenation to form CH₃* is more difficult, and most CH₃* dehydrogenates quickly to form CH₂* and H*. Thus, we expect the dominant carbon-carbon coupling reactions to be either CH* + CH* or CH* + CH₂*.

FUTURE WORK:

In the future, we plan to further explore the different carbon-carbon coupling reactions on Co(0001). The reactions appear to occur more readily at steps, and so we plan to do *ab initio* calculations to examine the reaction barriers. In addition, we plan to simulate the reactions over different metal surfaces and different alloys to elucidate the effects these have on the products of the Fischer-Tropsch synthesis.

This grant was used to support Dr. David Walthall, Dr. Qingfeng Ge and Mr. Siddharth Chopra.

LIST OF PUBLICATIONS:

Matthew Neurock "Perspectives on the First Principles Elucidation and Design of Active Sites", J. Catal., 216, 2003, 73-88