

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

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The past decade has witnessed a renewed interest in Fischer-Tropsch (FT) synthesis as a process critical in the conversion of methane to liquid fuels and the clean processing of coal to chemicals and energy. Fischer-Tropsch synthesis involves a complex but tightly balanced scheme of bond making and breaking processes including the activation of CO and H<sub>2</sub>, the hydrogenation of hydrocarbon fragments, the coupling of hydrocarbon surface intermediates, and desorption of longer chain hydrocarbon products. The ideal catalysts for FT synthesis would be those metals that can promote CO activation, along with a balanced degree of surface hydrogenation and hydrocarbon coupling in order to produce longer chain hydrocarbon products. An understanding of the elementary steps involved in the reaction is therefore important in the search for the best catalysts and the optimal operating conditions. Despite years of research, the fundamental understanding of the how the atomic surface structure of the catalyst controls the elementary molecular transformations in FT catalysis is still poorly understood.

We have used *ab initio* quantum mechanical methods to analyze the elementary surface steps over model transition metal surface in order to help elucidate reaction mechanisms. In the first year of this project, we analyzed in detail the activation of CO over Co(0001) and stepped Co single crystal surfaces to establish the influence of the surface corrugation and openness on the energetics. In addition, we probed the effect of coverage on the calculated energetics. Both surface structure as well as coverage were found to have a significant effect. In year two of the project we focused on relevant CH<sub>x</sub> hydrocarbon coupling pathways. Our results suggest that both CH<sub>2</sub> and CH may be kinetically important intermediates.

### **Accomplishments in the Past Year.**

In this past year we have examined in detail the decomposition of methane to CH<sub>x</sub> intermediates and the reverse process, the hydrogenation of CH<sub>x</sub> intermediates to methane. We have calculated the reaction energies and activation barriers for both C-H bond breaking and bond making for all of the C<sub>1</sub>H<sub>x</sub> intermediates over model Ru, Co and Pt closed packed surfaces in order to elucidate periodic trends. In addition to the intrinsic energetics, we have also explored the effect that surface carbon has on each of these CH<sub>x</sub> hydrogenation steps on Pt(111) and Ru(0001) surfaces.

We focus here on a comparison of the energies for the activation of methane on Pt(111) and Ru(0001) surfaces in both the absence and the presence of adsorbed surface carbon. This is simply the reverse of the hydrogenation reaction necessary for FT. Recent results from Iglesia indicate that methane activation occurs more readily on metals further to the right in the periodic table. This is inconsistent with simple ideas based on d-band filling and surface reactivity. Our results show that the overall reaction energies as well as the activation barriers for methane activation are higher on metals that lie to the right (Pt) in the periodic table. The values for the

overall reaction energies however on the ideal surfaces Pt(111) and Ru(0001) surfaces at low coverages are +1 Pt (-6 Ru), +24 Pt (-11 Ru), -23 Pt (-56 Ru), and +38 (-21 Ru). This behaves according to simple d-band filling model which suggests that the reaction should become more exothermic (less endothermic) in moving from right to left in the periodic table. We show similar results for a plot of the activation energies. . This, however, is inconsistent with the experimental results by Iglesia. One possible explanation is that Ru may be so active that it can actually form a carbidic overlayer which should reduce its reactivity. Subsequent methane activation steps were carried out over a surface which was covered with 0.25 ML of preadsorbed carbon atoms. The overall reaction energies for  $\text{CH}_4 \rightarrow \text{CH}_{3-x} + \text{H}_x$  were -1 Pt (0 Ru), 49 Pt (45 Ru), +49 Pt (+41 Ru), 113 (19 Ru), 141 (+19 Ru) and 261 Pt (81 Ru) kJ/mol respectively. The overall energies are clearly more endothermic than those on the bare surfaces. Ru(0001) however still appears to be more active than Pt. A comparison of the activation barriers shows similar trends.

The emerging picture is that Ru may be so active that it initially readily activates  $\text{CH}_4$  into CH or C intermediates which are difficult to remove and thus poison the surface. On Pt, methane dissociates but subsequent hydrocarbon coupling reactions act to remove the surface carbon.

## 2. A List of Published Journal Articles, Completed Presentations and Students Receiving Support from the Grant

This grant was used to support Dr. Qingfeng Ge and Mr. Siddharth Chopra an M.S. Chemical Engineering candidate.

### Papers

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