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

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I. ABSTRACT

One of the greatest societal challenges over the next decade is the production of cheap, renewable energy for the 10 billion people that inhabit the earth. This will require the development of various different energy sources potentially including fuels derived from methane, coal, and biomass and alternatives sources such as solar, wind and nuclear energy. One approach will be to synthesize gasoline and other fuels from simpler hydrocarbons such as CO derived from methane or other U.S. based sources such as coal. Syngas (CO and H_2) can be readily converted into higher molecular weight hydrocarbons through Fischer-Tropsch synthesis. Fischer-Trosch synthesis involves the initiation or activation of CO and H_2 bonds, the subsequent propagation steps including hydrogenation and carbon-carbon coupling, followed by chain termination reactions. Commercially viable catalysts include supported Co and Co-alloys. Over the first two years of this project we have used ab initio methods to determine the adsorption energies for all reactants, intermediates, and products along with the overall reaction energies and their corresponding activation barriers over the Co(0001) surface. Over the third year of the project we developed and advanced an ab initio-based kinetic Monte Carlo simulation code to simulate Fischer Tropsch synthesis.

This report details our work over the last year which has focused on the derivation of kinetic parameters for the elementary steps involved in FT synthesis from ab initio density functional theoretical calculations and the application of the kinetic Monte Carlo algorithm to simulate the initial rates of reaction for FT over the ideal Co(0001) surface. The results from our simulations over Co(0001) indicate the importance of stepped surfaces for the activation of adsorbed CO. In addition, they demonstrate that the dominant CH_x* surface intermediate under steady state conditions is CH*. This strongly suggests that hydrocarbon coupling occurs through reaction with the adsorbed CH*.

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III. INTRODUCTION

Fischer-Tropsch (FT) synthesis involves the catalytic conversion of CO and H_2 into long-chain hydrocarbons, which can be used to produce a variety of different commercially relevant fuels and products including diesel, heating oil, and higher hydrocarbons. Both Sasol as well as Shell have commercial ventures based on FT synthesis technology. The demand for cheaper more prevalent energy sources have made FT synthesis quite attractive as it can produce very high purity hydrocarbons that can be readily converted into high purity fuels. The products are virtually free of sulfur, nitrogen and metallic contaminants, which makes them much more environmentally friendly.

Despite the tremendous number of studies reported in the literature the mechanism for this reaction and the optimal catalysts are still not very well understood [1-8] Most of these studies have focused on the synthesis and characterization of different catalysts with little emphasis on the mechanism or the elementary kinetics. Advances in current catalyst technology will likely require a more complete understanding of the elementary molecular level transformations involved in FT synthesis along and the atomistic-scale features of the catalyst that control these elementary processes.

The overall Fischer-Tropsch reaction is comprised of a complex network of bond-making and bond-breaking elementary steps, which are highlighted in Figure 1.
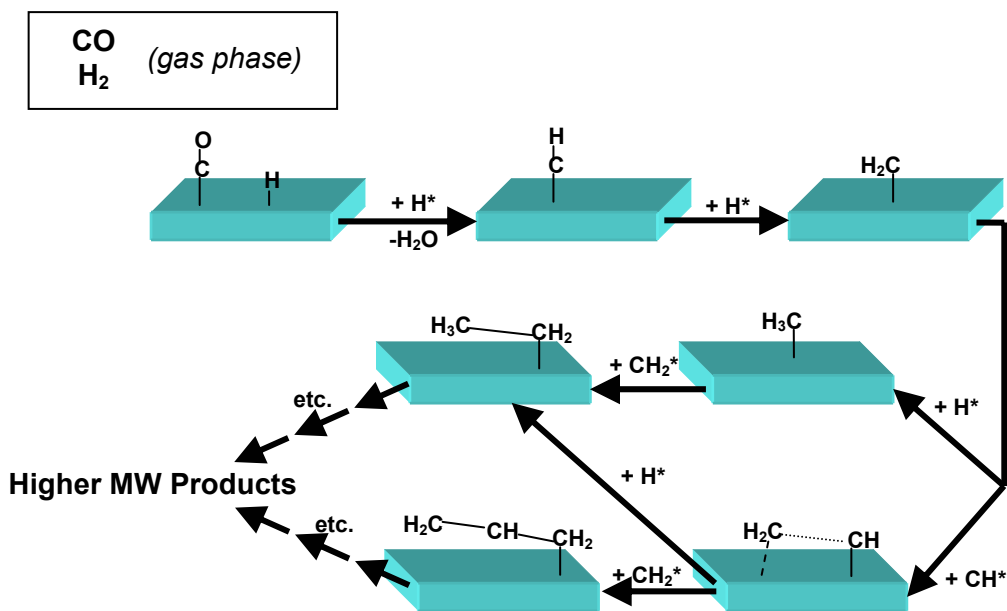
Figure 1. Schematic of some elementary reaction steps in the Fischer-Tropsch synthesis

These include the activation of adsorbed CO and H_2, the hydrogenation of carbon-containing surface intermediates, and carbon-carbon coupling reactions. The balance between the rates of these reactions is what controls the reactivity and selectivity of the process. For example, it is known that transition metals to the left side of the periodic table will readily dissociate adsorbed CO. However, the products, namely surface chemisorbed carbon (C*) and oxygen (O*) can strongly inhibit the rate of hydrogenation reactions and hydrocarbon coupling reactions. On the other hand, C* and O* on the transition metals to the right side of the periodic table can readily undergo hydrogenation and coupling reactions. The barrier to CO activation, however, is prohibitively high.[9, 10] The optimal material should readily dissociate CO* yet not be poisoned by strongly adsorbed carbon or oxygen. In addition, an ideal catalyst would have the proper balance of hydrogenation and carbon-carbon coupling reactions to promote high molecular weight hydrocarbon products. The products that form under reaction conditions may, to a large extent, be controlled by the species present at the surface as the reaction proceeds.

Various speculations as to the dominant surface intermediate have been proposed but there are no clear in-situ or operondo spectroscopic data or firm theoretical predictions on what the nature of the surface is as a function of time or reaction conditions.

In the first two years of this grant, we have examined several key elementary steps over different catalyst surfaces. *Ab initio* density functional theoretical calculations were carried out to determine the activation barriers for CO* dissociation over Co(0001) surfaces. We examined in some detail the adsorption of CO at various different sites on different surfaces including Co($10\bar{1}2$), Co($11\bar{2}0$) and Co($11\bar{2}4$) in order to elucidate the role of step defect sites on CO activation. In addition, we calculated the overall reaction and activation energies for a number of different carbon-carbon coupling reactions over the model Co(0001) and Ru(0001) surfaces. We also examined the binding energies and hydrogenation reactions of CH_x over the model Co(0001), Pt(111) and Ru(0001) surfaces. In addition, we explored the effect of surface coverage of C* on the individual hydrogenation reactions.

In the third year we developed a general kinetic Monte Carlo method to simulate FT synthesis over model Co surfaces. In the past year, we have focused on understanding the relationship and the kinetics between the elementary reactions on the model surface of Co(0001) to better understand the mechanism of the Fischer-Tropsch reaction at an atomic level. We have completed the kinetic Monte Carlo (started in year 3) to simulate the molecular transformations of individual molecule for FT, and their behavior as a function of time as well as reaction conditions. We used the binding energies and reaction barriers from our DFT calculations as the input to the kinetic Monte Carlo simulations. We analyzed the surface coverage of the CH_x

species as a function of time in the absence of carbon-carbon coupling reactions. Finally we have started to include some of the carbon-carbon coupling reactions to better understand the chain growth mechanism.

IV. EXECUTIVE SUMMARY

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. Fischer-Tropsch synthesis involves a complex set of bond breaking and bond making reactions. The balance between these steps dictates the ultimate product distribution. These reactions include the activation of CO and H_2, the hydrogenation of hydrocarbon surface intermediates, the coupling of hydrocarbon intermediates, and the desorption of products. A key aspect of Fischer-Tropsch catalysts is that they 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. While this reaction has been studied for many years, there is still a rather poor fundamental understanding of how the atomic surface structure influences catalytic performance.

Fischer-Tropsch synthesis involves the activation of CO and hydrogen, the hydrogenation of different CH_x intermediates, the coupling of different CH_x intermediates and finally the termination of the growing hydrocarbon chain. Ultimately, the products that form desorb from the surface. There is a delicate balance between the hydrogenation reactions, carbon-carbon coupling reactions, and desorption reactions that determines the size and composition of the molecular product distribution. In order to examine this system in detail, we have used ab initio quantum mechanical calculations to determine the kinetics for elementary steps and kinetic Monte Carlo simulation to track the changes in the surface and product distribution to changes in the surface structure as well as changes in the operating conditions.

Density functional theoretical calculations were performed to determine the binding energies for various different intermediates at different sites on idealized Co substrates such Co(0001), and calculate overall reaction energies and activation barriers. We have 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.

We have also examined the reaction energies and activation barriers for the hydrogenation of different CH_x intermediates over Ru, Co, and Pt closed packed surfaces to establish periodic trends. The barriers for hydrogenation are higher for metals that lie to the left in the periodic table due to the difficulty associated with breaking the metal-carbon and metal-hydrogen bonds. These calculations were also carried out at different coverages in order to establish the influence of the interaction of intermediates that takes place at the higher coverages. Our studies of the hydrocarbon coupling reactions over Co(0001) suggest that both CH_2 and CH may be kinetically important intermediates.

Over this past year, we have developed a kinetic Monte Carlo algorithm to simulate the initial kinetics involved in Fischer-Tropsch synthesis over Co(0001) as well as other ideal surfaces. Kinetic Monte Carlo simulations begin to provide a link between the idealized theoretical calculations which are typically carried out at low surface coverage conditions and more realistic operating conditions by embedding models that describe the nature of lateral interactions

between coadsorbed molecules that take place at higher coverages and are the result of more realistic higher pressures conditions. The simulations can thus be used to carry out "virtual experiments" to probe the sensitivity of different reactions and or kinetics to the resulting catalytic performance. In addition, they can be used to provide insight into the relative importance of different reaction pathways. This can be performed by turning on and off specific reactions or adjusting their calculated rate constants. This also provides insight into the governing reaction mechanisms.

The results from the simulations indicate that CO does not dissociate on the terrace sites of the Co(0001) surface under typical operating conditions. CO ultimately blocks the surface and begins to drive hydrogen off of the surface. CO activation, however, is much more prevalent at step sites as was suggested by the DFT results. The KMC simulations that use the barriers for CO dissociation at step sites show that the dissociation of CO happens on the time scales which are on the order of other reaction steps. The simulation results indicate that there is an initial build-up of hydrogen on the surface since H_2 has a much lower barrier for activation than CO. At longer times, however, some of the hydrogen is still driven off the surface 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 $CO_2(g)$. A fraction of the adsorbed oxygen atoms react to form hydroxides or water (which desorbs). This suggests that our hydrogenation rates maybe too slow or that CO activation should occur at even higher rates since water should be the primary oxygenated product. At steady state, the surface concentration of CO reaches a coverage of 0.45 ML. The surface coverage of CH* at steady-state reaches a value of 0.12 ML. Small amounts of CH_2* are also present on the surface. The hydrogenation of CH_2* to CH_3* is more difficult. In addition, any CH_3* that forms readily dehydrogenate back to CH_2* and H*. The dominant carbon-carbon coupling reactions then are CH* + CH* or CH* + CH_2*.

V. COMPUTATIONAL METHODS

All of the ab initio calculations reported herein were carried out using gradient-corrected plane-wave density functional theoretical methods as implemented in the Vienna *ab initio* Simulation Package (VASP) developed by Kresse and coworkers.[11-15] Ultra-soft pseudopotentials with a plane-wave cutoff energy of 287 eV were used for all of the calculations.[16] The Perdew-Wang (PW91) form of the generalized gradient approximation was used to calculate the exchange and correlation energies.[17] Surfaces were modeled using 2x2 supercells with four metal atom layers, and the Monkhorst-Pack mesh was used to sample the first Brillouin zone.[18] Transition states were located using the Nudged Elastic Band technique as implemented in VASP.[19]

The kinetic Monte Carlo simulations were carried out using the basic algorithms developed for this project last year and in addition previous models and subroutines developed earlier [20]. The current algorithm uses a variable-time approach that simulates the temporal changes of the adsorbate layer, using a surface with periodic boundary conditions. A fairly comprehensive database was constructed from DFT-calculated binding energies for H, O, C, CH, CH_2, CH_3, CH_4 and C_2H_x intermediates, and overall reaction and activation energies for CO and H_2 activation, CH_x hydrogenation, and CH_x coupling reactions. This resulting database is considered the zero-coverage limit for the reactions considered. Lateral interactions, defined as either through-surface or through space, were modeled by using more coarse-grained models. Through-surface interactions are described as changes in the adsorption energies and reaction energies that arise from electronic interactions that take place through the metal surface as the result of coadsorption. We have shown previously that these interactions strongly depend on the

number of metal atoms in the adsorption complex that have bonds to other adsorbates. They can be weakly attractive for cases where adsorbate do not share metal atoms but remain nearby or highly repulsive for adsorbates which share one or more metal atoms. These interactions typically follow the bond order conservation principles. Bond Order Conservation (BOC) methods therefore have proven to be quite useful for modeling through-surface interactions.[21-24] Through-space interactions are those that occur through space. These are typically steric type interactions that can be modeled by the inclusion of the electrostatic and van der Waals interactions. We have shown that these interactions can be modeled reasonably well by using force field models. We have successfully used the Merck Molecular Force Field (MMFF94) in previous studies and therefore this approach is adopted herein.[25, 26] Both the BOC algorithm as well as the MMFF algorithm can be called upon internal within the simulation to explicitly account for the effects of the local surface coverage.

For each time step, the barriers for all possible adsorption, desorption and surface reactions are computed. Using an Arrhenius relationship, the rate for each possible reaction can be calculated. The next reaction to occur in the system is chosen by comparing a randomly chosen number with a cumulative probability distribution for all of the possible events. The probability of choosing a specific reaction is proportional to its rate reaction verses the overall rate which is taken as the sum of the rates for all events at that particular instant in time. The time is advanced by choosing a second random number, and is inversely proportional to the total rate calculated, so that surfaces with larger total rates of reactions will be incremented by smaller time steps than surfaces with smaller total rates of reactions. The simulations follow a hybrid variable-time step and fixed-time step approach. The reactions are ascribed to variable time steps. A number of

fixed time steps are subsequently carried out between each successive variable time step in order to simulate diffusion. This approach enables us to simulate both reaction events together with diffusion events without having to resort to neglecting diffusion or assuming that the reaction is fully equilibrated.

VI. RESULTS AND DISCUSSION

Fischer-Tropsch synthesis can be viewed as three separate sets of reactions: initiation, propagation, and termination. The initiation reactions consist of the adsorption of gas phase CO and H_2 and their subsequent dissociation to generate the hydrocarbon precursors, C*, O* and H*. The second set of reactions are referred to as the propagation reactions. They consist of hydrogenation reactions and carbon-carbon coupling reactions. In the hydrogenation reactions, surface hydrocarbons react with surface hydrogen atoms ($C_xH_y* + H^* \rightarrow C_xH_{y+1}*$). In the carbon-carbon coupling reactions, two surface hydrocarbon species react to form a larger surface hydrocarbon species ($C_xH_y* + C_aH_b* \rightarrow C_{x+a}H_{y+b}*$). The carbon-carbon coupling reactions are therefore chain growth reactions which increase the size and molecular weight of the surface intermediates. The hydrogenation reactions and the coupling reactions can produce either strongly adsorbed radical-like intermediate hydrocarbons or result in the formation of more weakly bound closed-shell hydrocarbon products. The later process is typically referred to as termination. The close-shell species can desorb from the surface. The balance between all of these reactions is what determines the product distribution.

1. Initiation Reactions

We have previously calculated the barrier to dissociate CO* on the model Co(0001) surface at 140 kJ/mol for a 1/9 ML coverage. The barrier rises significantly to about 230 kJ/mol for a 1/4 ML coverage. Using this barrier for dissociation, the simulations showed essentially no dissociation of adsorbed CO at realistic operating conditions. The increased barrier is the result of lateral repulsive surface interactions together with a lack of availability of sites.

In addition to CO* dissociation barriers over the Co(0001) surface, we have also calculated the dissociation barrier over the model stepped surfaces including the Co($10\overline{1}2$), Co($11\overline{2}0$), and Co($11\overline{2}4$) surfaces shown in Figure 2. On the Co($10\overline{1}2$) surface the dissociation of CO* was calculated to be exothermic. This same reaction, however, was calculated to be endothermic on the other three surfaces examined (including the Co(0001) surface). In addition, the CO* activation barrier (110 kJ/mol) over the Co($10\overline{1}2$) surface is also significantly smaller than those of the other four surfaces. By using this barrier in the simulations, the coverage of CO* drops from about 0.5 ML to about 0.4 ML. More significantly, the dissociation of CO* becomes quite facile, and CO*, C*, and O* are all present on the surface. From this, we conclude that surface corrugation (i.e. steps or kinks) is essential for CO* dissociation to take place in quantities sufficient to generate products to any appreciable degree. In addition, because the dissociation of CO* over the stepped surfaces is so much faster than CO* dissociation over the Co(0001) surface, it is likely that only a small fraction of the total surface needs to be the steps in order for there to be a sufficient quantity of C* present on the surface.
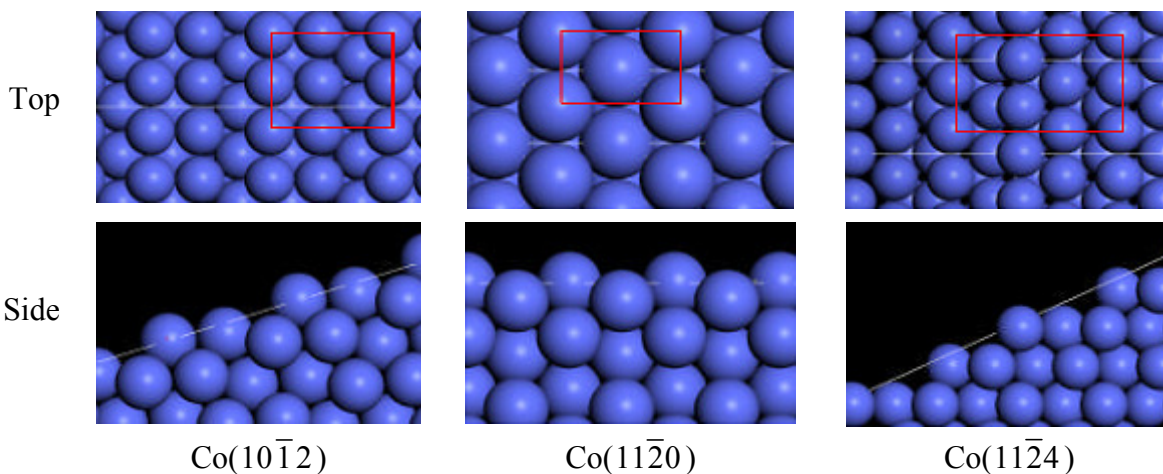
Figure 2. Top and side view of the Co surfaces. The red box is the minimum unit cell size.

The dissociative adsorption of $H_2(g)$ was set to have a barrier of 40 kJ/mol in order simply test the code. This reaction is typically very fast so that even at these relatively high barriers, the reaction occurs frequently enough that H* is in equilibrium with gas phase H_2.

The DFT barriers and overall energies were collectively used with lateral interaction models to simulate various different initial kinetics. The initial simulations of CO and H_2 activation show that there is a fast build-up of H* in about the first 10^{-8} of a second to establish a surface coverage of about 0.1 ML. CO then begins to dissociate. The C*, O* and initial (CH*) hydrogenation products begin to appear and drive adsorbed hydrogen from the surface. The surface coverage of H* drops down to about 0.02ML, where it stays fairly constant for the rest of the simulation. The surface O* also goes through an initial build-up period. The surface coverage of O* peaks at about 10^{-7} seconds at a value of about 0.1 ML. It then begins a steady decline towards it steady-state value of 0.02 ML, which it reaches by about 10^{-6} seconds.

2. Propagation Reactions: Hydrogenation Reactions

The hydrogenation reactions over the model Co(0001) surface were calculated using VASP. The hydrogenation reaction energies and reaction barriers for CH_x* are shown in Figure 3. From the figure, it is clear that the energetically most favorable surface species is CH*. At equilibrium, we would therefore expect to have surface coverages in the following order:

CH* > CH_3* > CH_2*, C*.
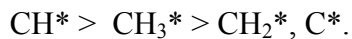
The formation of $CH_4(g)$ is also energetically favorable as it compares with the energy to form CH_3*.

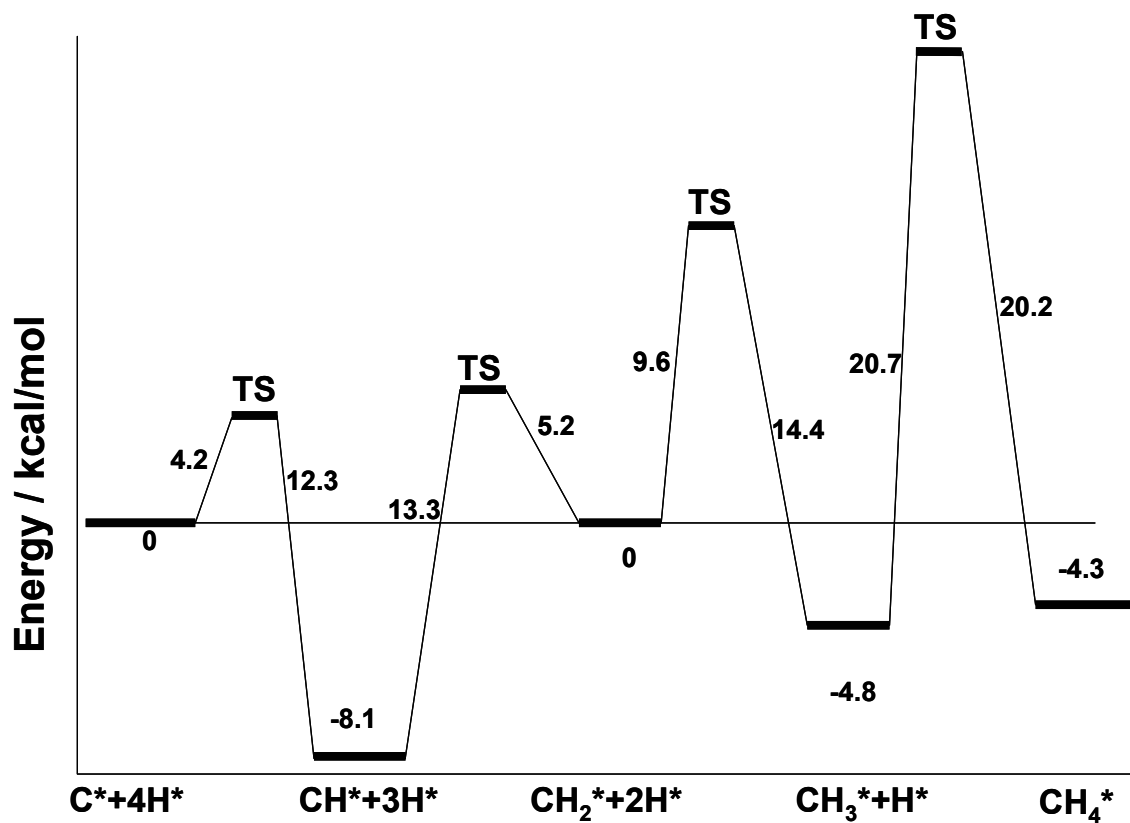## Activation Barriers and Adsorption Energies on Co(0001)

Figure 3. The hydrogenation of CH_x* intermediates over Co(0001).

The kinetic Monte Carlo simulations which include the hydrogenation reactions reveal interesting results. After the surface coverage of H* begins to decrease (starting at about 10^{-8} seconds), CH* becomes the dominant species (rather than CO*). CH* reaches a surface coverage of a little less than 0.1 ML by 10^{-7} seconds, which is the time that H* has predominantly disappeared from the surface. Figure 4 shows surface coverages of the most abundant surface species.
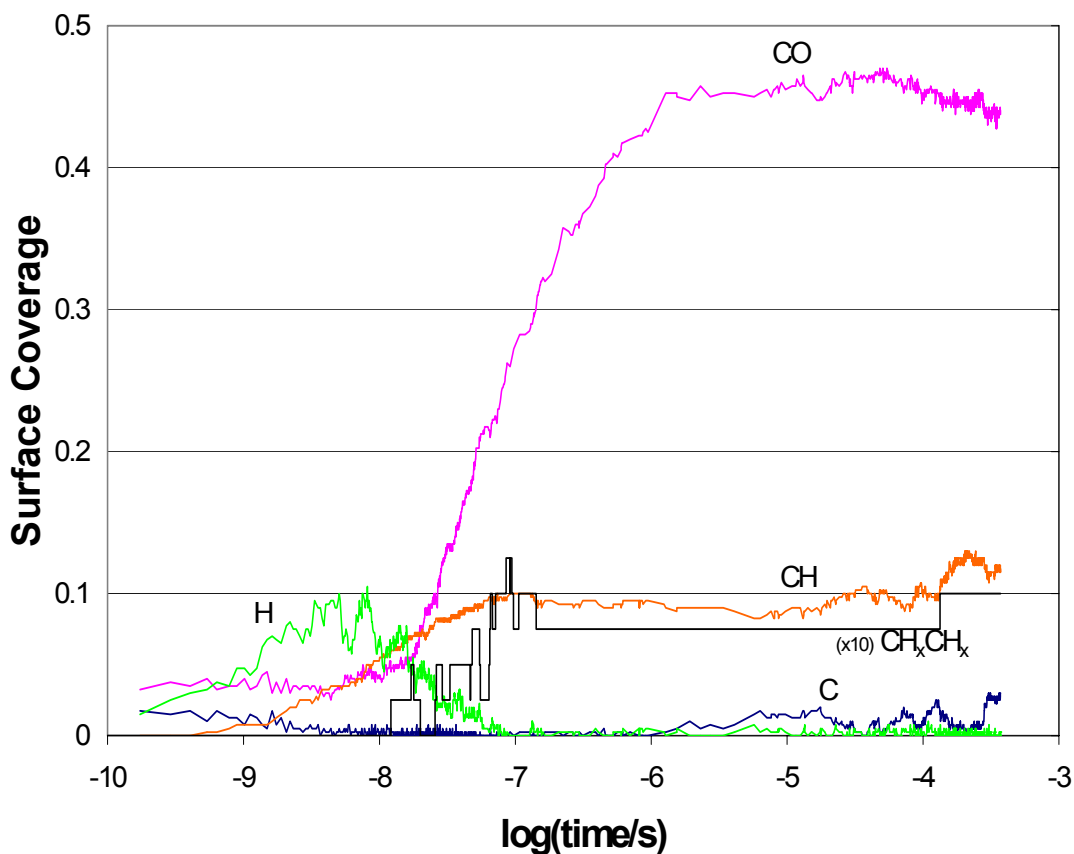

Figure 4. Kinetic Monte Carlo Surface Coverages.

Unlike what would be predicted from the pure thermodynamic reaction energies, CH_3^* is not the next most abundant CH_x^* species on the surface. The simulations demonstrate that CH^* is the most abundant CH_x surface intermediate. The coverages of C^* and CH_2^* follow that of CH^* but only have surface coverage of about 0.005 ML and 0.02 ML respectively. This can be understood from the kinetics of the hydrogenation reactions, seen in Figure 3. There is only a small barrier to hydrogenate C^* to form CH^*. The barrier to hydrogenate CH^* to form CH_2^* is roughly the same as the barrier to dehydrogenate CH^* to form C^* and H^*. Thus, it is not too surprising to find that those two species are present in small amounts and at a lower surface coverage than CH^*.

The barrier to form CH_3^* from CH_2^* and H^* is roughly similar to the barrier to form CH_2^* from CH^* and H^*. However, because the surface coverage of CH_2^* is significantly lower than the coverage of CH^*, we find that the surface coverage of CH_3^* is much smaller. The rates of course are controlled not only by the barriers but by the surface coverages. Finally, the barrier to form CH_4 from CH_3^* and H^* is significantly higher than the other hydrogenation barriers. The high barriers, combined with the lower surface coverage of CH_3^* ultimately results in the lack of production of CH_4 in the simulations.

3. Propagation Reactions: Carbon-Carbon Coupling Reactions

We have calculated the carbon-carbon coupling reaction energies and reaction barriers from *ab initio* Density Functional Theory calculations. We found that the barrier for the reaction of $CH_2^* + CH_2^*$ to form $CH_2CH_2^*$ is 7.2 kJ/mol. The barrier for the reaction of $CH^* + CH_2^*$ to form $CHCH_2^*$ is significantly higher at 55.9 kJ/mol. This is due to the fact that the CH^* group is

much more strongly bound to the surface than the CH_2* group. We have not yet included any coupling reactions to form $C_{3+}H_x$* species in the simulations as we first wanted to establish the initial C_2H_x formation paths.

Kinetic Monte Carlo simulations of the system shows that some C_2H_x* species is formed on the surface. Although we did not calculate the barrier for the reaction of CH* + CH_3* to form $CHCH_3$*, bond order conservation estimated that reaction barrier to be around 46 kJ/mol. In addition, the coverage effects changed the CH* + CH_2* reaction barrier to be 50-300 kJ/mol, depending on the local coverage. The reactions of CH* + CH_2* and CH* + CH_3* were the only carbon-carbon coupling reactions seen. In fact, the CH_2* coverage was low enough that CH_2* + CH_2* was not even a common *possible* reaction. Once C_2H_x* species were formed, they typically underwent hydrogenation reaction and dehydrogenation reactions to lead to the formation of chain terminating products. Some underwent decoupling reactions to form CH_x* + CH_y* species, although this was less common. This will be an area of focus over the next year or two.

VII. CONCLUSION AND FUTURE EFFORTS

We have completed an ab initio-based kinetic Monte Carlo algorithm developed in the previous year and applied it to simulate kinetics of the initial catalytic reaction paths for Fischer-Tropsch synthesis over model Co(0001) substrates. The results from *ab initio* Density Functional Theoretical calculations carried out in this grant were used within these kinetic Monte Carlo simulations to show that CO* dissociation on the Co(0001) surface is too large to produce the required surface coverages of C* for Fischer-Tropsch to occur. The dissociation of CO over the

stepped surface was found to have a much lower barrier, and thus occurring at time scales such as those reported in the literature. This step edges or defect sites are responsible for activating CO to produce surface carbon. However, the number of steps can be a small fraction of the total surface. Initial simulations indicate that the dominant surface intermediate is CH*, although small amounts of CH_2* and very small amounts of CH_3* are present. The surface coverage of CH_2* is so low, however, that the CH_2* + CH_2* reaction is seldom possible in the simulations and that chain coupling appears to proceed through the reaction of the most abundant CH* intermediate on the surface.

Future efforts will include further calculations on the carbon-carbon coupling reaction barriers so that we can simulate more of the chain growth on the ideal (0001) terraces as well as at stepped defect sites. We will include $C_{3+}H_x$* species in the kinetic Monte Carlo simulations in order to examine coupling to form higher hydrocarbons. In addition, we have previously calculated some of the binding energies and reaction barriers on Pt(111) and Ru(0001) surfaces, which will allow us to investigate alloys using our Monte Carlo code.

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