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

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I. ABSTRACT

As petroleum prices continue to rise and the United States seeks to reduce its dependency on foreign oil, there is a renewed interest in the research and development of more efficient and alternative energy sources, such as fuel cells. One approach is to utilize processes that can produce long-chain hydrocarbons from other sources. One such reaction is Fischer-Tropsch synthesis. Fischer-Tropsch synthesis is a process by which syngas (CO and H_2) is converted to higher molecular weight hydrocarbons. The reaction involves a complex set of bond-breaking and bond-making reactions, such as CO and H_2 activation, hydrocarbon hydrogenation reactions, and hydrocarbon coupling reactions. This report details our initial construction of an ab initio based kinetic Monte Carlo code that can be used to begin to simulate Fischer-Tropsch synthesis over model Co(0001) surfaces.   The code is based on a stochastic kinetic formalism that allows us to explicitly track the transformation of all reactants, intermediates and products. The intrinsic kinetics for the simulations were derived from the ab initio results that we reported in previous year summaries.

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III. INTRODUCTION

Fischer-Tropsch synthesis is a catalytic process that converts syngas, CO and H_2, to long-chain hydrocarbons, which are more useful commercially. The reaction is used by Sasol in South Africa to produce diesel from syngas produced from natural gas and coal feedstock. In Malaysia, Shell Oil Company uses the Fischer-Tropsch reaction to produce 14,700 bbl/day of higher molecular weight products from natural gas syngas. The Fischer-Tropsch synthesis produces very high purity hydrocarbons that can be used as fuels and feedstock for other processes, depending on the molecular weight range that is distilled. The products are virtually free of sulfur, nitrogen and metallic contaminants, which makes them environmentally friendly.

In the more than 80 years since Fischer and Tropsch discovered this process, a large number of studies have been conducted to elucidate the mechanism and to determine the optimum operating conditions to maximize the desired products.[1-8] Most of these studies are focused on the synthesis and characterization of different catalysts. Although these studies provide essential information about catalyst development for industrial reactor design, there is remains a need to understand the Fischer-Tropsch reaction at a molecular level and to understand how atomistic-scale features of the catalysts control the elementary reactions.

The overall Fischer-Tropsch reaction is a complex network of bond-making and bond-breaking elementary steps, some of which are shown in Figure 1. They include the activation of 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 CO*. However, the products, namely surface C* and

surface O*, are so tightly bound to the surface that they are inactive for subsequent

hydrogenation reactions and coupling reactions. On the other hand, C* and O* on the transition

metals to the right side of the periodic table readily undergo hydrogenation and coupling

reactions. However, the barrier to CO* dissociation is prohibitively high.[9, 10] Clearly, a

catalyst which readily dissociates CO* but which binds C* and O* weakly would be a desirable

to facilitate the Fischer-Tropsch reaction. In addition, an ideal catalyst would have the proper

balance of hydrogenation and carbon-carbon coupling reactions to promote high molecular

weight hydrocarbon products.
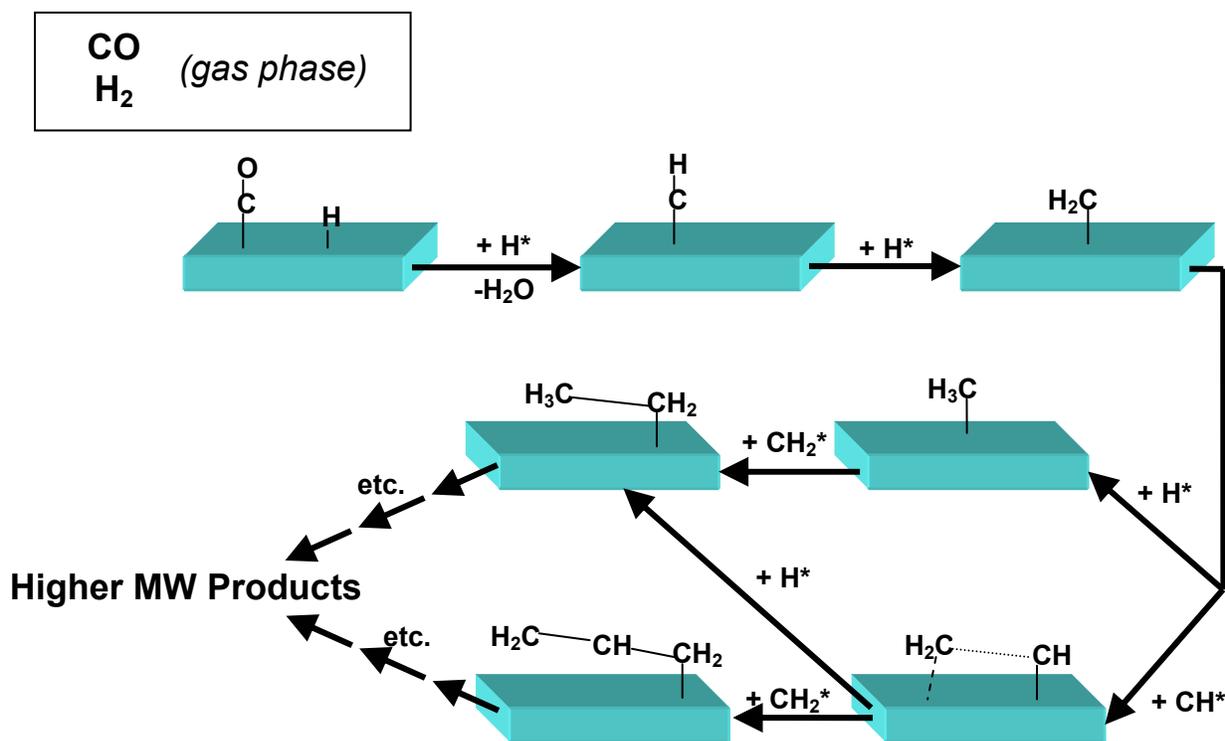
Figure 1. Schematic of some elementary reaction steps in the Fischer-Tropsch synthesis

In our previous efforts, we have examined several key elementary steps over different catalyst surfaces. We used ab initio density functional theoretical calculations to determine the adsorption energies for a range of different reactants, intermediates and products together with the overall energies and activation barriers for the most important elementary steps which include:

1) CO activation over Co(0001) surfaces

2) CO activation over over the Co($10\overline{1}2$), Co($11\overline{2}0$) and Co($11\overline{2}4$) to model the influence of steps.

3) CH_2* and CH* coupling reactions over Co(0001) and Ru(0001) surfaces.

4) Hydrogrenation of CHx* intermediates over Pt(111), Co(0001), and Ru(0001) surfaces.

Over this past year our efforts have focused on the development of an ab initio based kinetic Monte Carlo method which can be used to explicitly track individual molecular transformations for Fischer Tropsch catalysis as a function of time and processing conditions. The simulation uses the previous ab initio results for the elementary steps in Fischer Tropsch synthesis as an input database for the kinetics. While the model has been completed, we are currently just beginning to test it.

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. The Fischer-Tropsch synthesis involves a complex set of bond breaking and bond making reactions, and the balance between these steps dictates the 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 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. Over the past two years we have used ab initio density functional theory to calculate the adsorption energies, and activation barriers for the relevant elementary steps for Fischer Tropsch synthesis including CO activation, CH_x hydrogenation, and CH_x coupling reactions. The effort in this past year has focused on development of an ab initio based kinetic Monte Carlo method to begin to simulate the initial kinetics involved in Fischer-Tropsch synthesis over the model Co(0001) surface. The kinetic Monte Carlo methodology developed here begins to provide a link between the ideal calculated energetics and the more realistic kinetics by incorporating surface coverage effects on the product distributions. In addition, it 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. Much of the effort over this past year has been in the development of this code. The features of the code are described herein. We are currently in the process of testing it.

V. COMPUTATIONAL METHODS

Over this past year our efforts have focused on the development and modification of kinetic Monte Carlo scheme which can be used to explicitly track individual molecular transformations for Fischer Tropsch catalysis as a function of time and processing conditions. This was an extension from a previous method developed in our group to simulate ethylene hydrogenation and NO activation.[11-17]

The basic input to the simulation can be divided into three main areas: 1) the lattice (size and structure), 2) molecular data on the all of the reactants, intermediates and products (geometric structure, atomization energies, etc.), and 3) intrinsic kinetic data (activation barriers, pre-exponential constants, adsorption energies, overall reaction energies).

The current code was developed to simulate the initial steps for Fischer Tropsch synthesis over (111) as well as (100) surfaces. The catalytic surface is described in the simulation by a periodic MxM lattice where M defines the number of atoms along each edge of the repeating cell. The simulations can explicitly track atop, bridge, and higher-fold coordination sites. The lattice is atomically explicit to enable us to fully capture the influence of the local reaction environment on the kinetics. The user can specify the size of the grid. Computational constraints typically limit grid sizes to 100x100 or 200x2000. We usually run a grid of at least 24x24 and average over several replicates. The results match up reasonably well with higher grid sizes.

The molecular or species input data refers to a set of general molecular properties for all of the possible reactants, intermediates and products within the simulation. This includes the molecules

binding energy of the adsorbate at specific sites, van der Waals radius (physical size), gas phase dissociation energies and geometric structure.

Lastly, the intrinsic kinetic database is compiled from the ab initio results that have been developed in the first few years of the program on CO activation, CH_x hydrogenation and coupling reactions over the Co(0001) surface. The current reaction database will be extended over the next two years to provide for a complete description of not just the Co(0001) surface but other surfaces and the influence of steps and defect sites.

The input data is subsequently used to construct a surface simulation model that incorporates the intrinsic reaction kinetics along with adsorbate-adsorbate interactions that occur on the surface via through-surface and through-space lateral interactions. This enables us to explicitly treat the effects of the reaction environment on the kinetics. These models of the surface, molecules and intermediates, and reaction kinetics and environment comprise the basic modules of the simulation.

The Kinetic Monte Carlo Engine

At the heart of the simulation is a dynamic Monte Carlo algorithm which follows individual molecular transformation over the Co(0001) surface as a function of time and processing conditions. After initialization, all of the sites on the surface are examined in order to determine all possible kinetic processes which might occur at the specific site. This includes adsorption, diffusion, desorption, and surface reaction steps. The reaction site along with its environment is interrogated in order to determine appropriate intrinsic reaction kinetics along with the influence

of the local reaction environment. Each site can take on many different reaction events. The kinetics for all sites and all of their events are subsequently collected in order to construct a cumulative reaction probability distribution (CRPD). The CRPD outlines all of the possible kinetic events that might occur at a given instant in time. The events considered depend on the specific site of the event along with their specific reaction environment. For surface reaction events, we calculate the binding energies of reactants as well as the possible product states in order to determine the overall energetics and the influence of reaction environment. The activation barriers for each step are calculated from the DFT results along with estimates from our through-surface and through-space interaction models to treat higher coverage situations. These interaction models are described below.

The general framework for our Monte Carlo code has been described in earlier papers.[11-17] We have adopted it herein to the simulation of FT synthesis. At any instant in time, t_i, the rates for all possible events are added up in order to determine the total rate. The total rate of all possible surface events is calculated by summing all of the possible surface reaction rates. This is accomplished by examining all interacting pairs within a cutoff distance sufficiently far from the reaction site to be sure to fully capture the environment. For each surface adsorbate pair, all the possible reactions are tested. If the reaction event is possible, the rate constant for this event is computed and stored. All recombinative (pairwise) reaction rates are normalized by a factor of one half.

The total rate, Σr_i, is subsequently used along with the variable time-step equation given as Eq. 1 to determine the time at which the next event on the surface happens. The time step is calculated by drawing a random number and substituting into the following equation

$$\Delta t_v = \frac{-\ln(RN)}{\displaystyle\sum_i r_i} \tag{1}$$

where Δt_v is the variable time step and RN is a random number between 0 and 1. The specific reaction that occurs within the calculated time step interval is chosen based on the cumulative reaction probability distribution derived from Eq. 2.

$$S_i = \frac{r_i}{\displaystyle\sum_i r_i} \tag{2}$$

Diffusion is monitored by using a fixed-time kinetic Monte Carlo algorithm. An overall fixed time-step for diffusion is chosen to correspond with the previous reaction dynamics of the system. We calculate the overall diffusion time step as the average over the previous n reaction steps within the variable time simulation:

$$\Delta t_{diff} = \frac{\displaystyle\sum_{i=1}^{n} \Delta t_{rxn}}{n} \tag{3}$$

We used a value of n equal to five. Increasing n to a large value pushes the limit of fast (equilibrated diffusion) between each reaction step. We scan the surface and test for the movement of all possible intermediates on the surface within the time step Δt_f. Time is therefore

advanced by a series of fixed time increments. The probability for a specific diffusion event to occur within the time step is give by Eq. 4 which is overall energy for an intermediate at site i to move to j.

$$P_{i-j} = \exp\left(\frac{-\Delta\left[\left(Q_i + \sum_i Q_{i,neighbors} \right) - \left(Q_j + \sum_j Q_{j,neighbors} \right) \right]}{RT} \right) \tag{4}$$

We have made two approximations here: the first is that Δt_{fix} is sufficiently small to reduce any errors associated with multiple steps that occur within a given Δt. The second is that the change in energy to hop from site i to site j provides a reasonable estimate (or is proportional to) the activation barrier for diffusion. Diffusion is therefore treated by a hopping mechanism. The approach is not exact but does allow us to begin to treat reaction and diffusion by approximately separating time scales. In this system, the apparent rate constants for diffusion are about two to three orders of magnitude higher than those for reaction. We therefore were able to provide a series of test simulations whereby we treated diffusion simultaneously with surface reaction in a full variable time approach. The results showed very little differences between the approximate approach outlined here and the full reaction/diffusion simulation.

The overall simulation procedure is outlined in Figure 1. The simulation can be used to simulate various different experimental protocol. We can simulate temperature programmed desorption (TPD) for different reactants or intermediates, temperature programmed reaction (TPR), initial surface dynamics or steady state catalytic operation. TPD and TPR simply requires that the

surface be equilibrated at a finite temperature allowing only for the adsorption, desorption and diffusion of the molecules of interest. The system is then started at t=0 whereby all adsorption, desorpion, diffusion and surface reaction steps are all allowed.   The surface is then ramped at some temperature interval β over time.
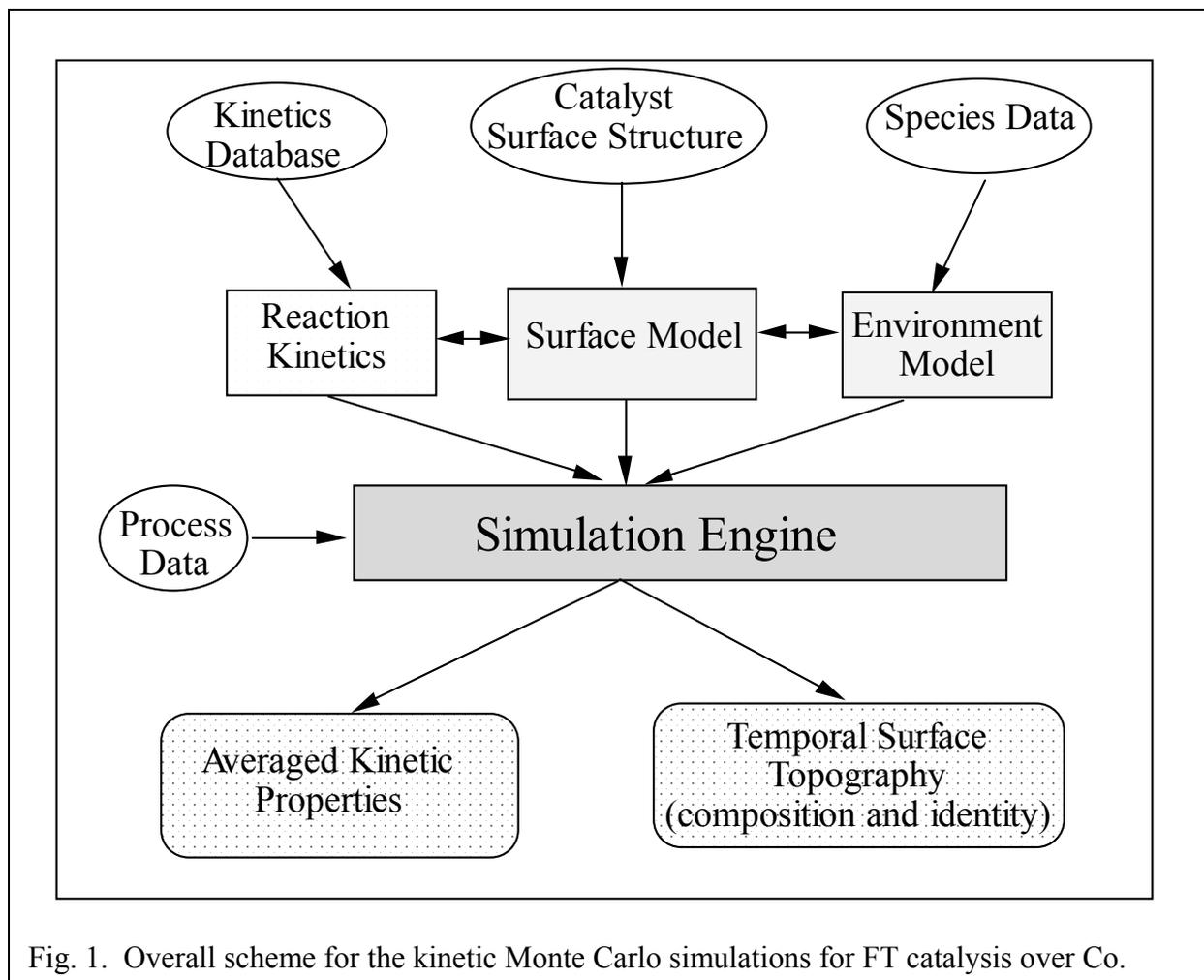
Fig. 1. Overall scheme for the kinetic Monte Carlo simulations for FT catalysis over Co.

state kinetics, we first equilibrate the surface based on the known gas phase composition. The equilibration allows for all diffusion, adsorption and desorption steps. Once the surface is equilibrated we then let the reactions begin to occur. A variable time step approach is used to follow the sequence of reaction, adsorption, and desorption steps for some length of time. A

fixed time step is subsequently constructed as moving average of the previous n variable time steps (where n=5). If the variable time step becomes extraordinarily large, the occurrence of an event is not guaranteed. The probability for reaction is instead calculated within the fixed time step algorithm, where the probability of i reacting to j is:

$$P_{i \to j} = 1 - \exp\left(-k_{i \to j} \cdot \Delta t_f\right) \qquad (5)$$

where $k_{i \to j}$ is the pseudo first order reaction for i to react to j. $k_{i \to j}$ can be used to model any given reaction rate regardless of its dependency on concentration, by writing it as $\frac{r_{i \to j}}{C_i}$ where $r_{i \to j}$ is the rate of i reacting to j and C_i is the concentration of component i. A random number is then checked against this event probability. If an event occurs, the simulation proceeds to determine the event as in the variable time step interval. If there is no event, the total simulation time is simply updated by the fixed time step and the simulation proceeds forward to equilibrate the surface by diffusion and repeat this process again. This approach is necessary here to circumvent any non-reactive surface states that are artifacts that arise from the separation of reaction and diffusion. For example, it is possible that the simulation can end up where no surface events are possible simply because of the proximity of the reactants. If reaction and diffusion were treated within the same construct, the system could simply undergo a series of diffusion steps which might then provide the right positioning of species to allow them to possibly react. By allowing a series of diffusion events on the surface we can begin to find reactive pairs.

We have examined a series of simulations over different grid sizes to establish the grid size effect. The results do not change when we go to grids larger than a 24x24. We explicitly count atop, bridge and hollow sites and therefore the 32x32 grid used here examines up to 32,768 active reaction sites. Generally there are more than 1000 different reactions that can occur on a particular site during the equilibrium stage.

The outcome from the simulation includes the detailed structure and composition of the adlayer as a function of time and processing conditions. This temporal and spatial resolution of the surface enables us to compute a range of properties included either molecular or site explicit TOFs, activation barriers, surface coverages, as well as overall averaged properties.

Interaction Model

The reaction energies are specifically influenced by the local environment around the reaction site. The intrinsic kinetic database was calculated at low coverages in order to minimize the interaction between adsorbates. Subsequent calculations at higher coverages were carried out to appropriately model the influence of the local environment on the reaction kinetics. The results were used to parameterize more coarse-grained models that are called upon internally within the simulation to provide estimates of the adsorbate-adsorbate interactions, thus providing a more quantitative analysis of the influence of the reaction environment. We classify adsorbate-adsorbate interactions at the surface into two general categories: *through-space* and *through-surface*. *Through-space* interactions are the result of direct steric interactions or longer range interactions between different surface intermediates. The *through-space* interactions are calculated "in-situ" in the simulation by using the van der Waals interaction term from the Merck

Molecular Force Field (MMFF) model [18, 19]. *Through-surface* interactions arise from metal-atom sharing or adsorbate-bond sharing and are estimated by using a DFT-scaled bond order conservation(BOC) model[11,13, 14, 15,17] developed previously. The BOC model was parameterized against DFT results carried out at different coverages. One should note that any longer range electronic interactions would be implicitly incorporated in the BOC model since it was regressed against different coverage DFT values. The MMFF model treats the cooperative van der Waal interactions that might exist through longer range adsorbate networks. This was described in more detail in previous publications [11,13,14, 15,17]

Reaction Rates

   The DFT derived energetics/kinetics database for FT was subsequently used to calculate reaction rates. The reaction rate for each elementary step is calculated using transition state theory, where the rate is given by:

$$r_i = \nu_i \, exp\left(\frac{-\Delta E_i}{RT}\right)$$

(10)

where ν_i is the pre-exponential factor, R is the gas constant, T is the temperature, and ΔE_i is the activation energy barrier for the elementary reaction i. The pre-exponential factor ν_i can be calculated directly from density functional theory calculations or from statistical mechanics estimates. The barriers for individual elementary steps were determined by DFT calculations. The pre-exponential factors, ν_i, were chosen herein to be standard statistical mechanical estimates for surface processes. For unimolecular surface reactions and (immobile) bimolecular reactions, the pre-exponential factors were calculated to be $10^{13} s^{-1}$ [12]. The pre-exponential factors for desorption were also estimated from statistical mechanical estimates to be on the order of 10^{13}.

The calculation of the adsorption rate is characteristically different from the surface elementary reaction rate calculations. The adsorption rate for species *i* is defined as [11,13, 14,15,17]

$$r_{ad,i} = s_0 \cdot P_i \cdot A_s \cdot \left(2\pi \cdot MW_i \cdot RT\right)^{-0.5} \cdot \exp\left(\frac{-\Delta E_i}{RT}\right)$$

(11)

where s_0 is the sticking coefficient, P_i is the partial pressure of species i, A_s is the area of one surface site, and MW_i is the molecular weight of species i.

VI. RESULTS AND DISCUSSIONS

The simulation that was constructed was written in C++ and is based on our previous algorithms which run on Linux or in a graphical environment on an SGI. The windowing environment allows the user to easily specify the lattice, operating conditions, the species involved, the reactions to use, the actual simulation to perform (TPD, TPR, catalytic kinetics), the operating conditions. The species window which is shown in Fig. 2A details all of the reactant, intermediates and products in the simulation. The reaction window which is shown in Fig. 2B is provides a graphical user interface that enables the user to specifically toggle on and off particular reactions directly within the simulation. The binding energies can be calculated for any of the species at any given site on the surface using a specific graphic interface that enables the user to actually place specific molecules at sites on the surface. Both the apparent binding energy as well as the lateral interaction energy at that particular site can be calculated as is shown in Fig. 3C. The activation barrier for a particular reaction can be calculated via the interactive reaction window shown in Fig. 3A. The type of simulation and the time and temperature for the simulation are included in the simulations window as shown in Fig. 3C.

A)

Application
Color

-
Co
Pt
CO
H2
C
O
H
OH
O2
H2O
CO2
CH
CH2
CH3
CH4

B)

Surfaces

Application

☐ $O^* + O^* - O2$

☐ $O2 - O^* + O^*$

☐ $CO2^* - CO2$

☐ $CO2 - CO2^*$

☐ $H^* + H^* = H2$

☐ $H2 = H^* + H^*$

☐ $H2O^* = H2O$

☐ $H2O - H2O^*$

☐ $CO^* - CO$

☐ $CO - CO^*$

☐ $CH4^* - CH4$

☐ $CH4 = CH4^*$

☐ $OH^* = O^* + H^*$

☐ $O^* + H^* - OH^*$

☐ $H2O^* + O^* - OH^* + OH^*$

☐ $OH^* + OH^* - H2O^* + O^*$

☐ $H2O^* - OH^* + H^*$

☐ $OH^* + H^* = H2O^*$

☐ $CH^* = C^* + H^*$

☐ $C^* + H^* = CH^*$

☐ $CH2^* - CH^* + H^*$

☐ $CH^* + H^* - CH2^*$

☐ $CH3^* - CH2^* + H^*$

☐ $CH2^* + H^* - CH3^*$

☐ $CH4^* = CH3^* + H^*$

☐ $CH3^* + H^* = CH4^*$

☐ $C^* + O^* = CO^*$
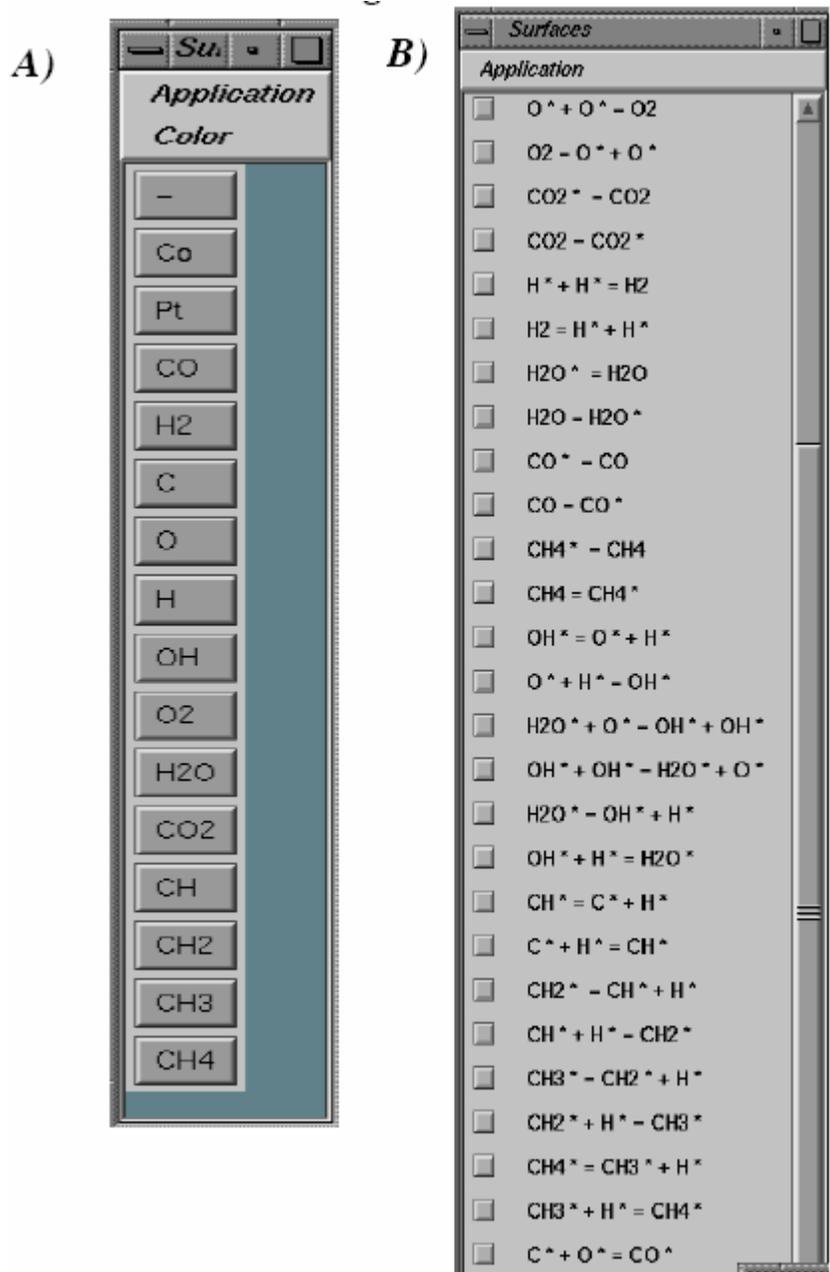
Figure 2.   KMC interface for that defines: A) the molecular species and the metal as well as B) the reaction. The user can select species as well as reactions to carry out on the surface.

A)

Surfaces

Application

Activation Energy

Forward : 0.
Reverse : 0.
Equilibrium : 0.
Distance : 0.

B)

Surfaces

Application   Run

500.0

Start Temperature (K)

.0

Beta (K/s)

600.0

Simulation Run Time (s)

C)

Surfaces

Application   Model

Binding Energy

0.00

Interaction Energy

0
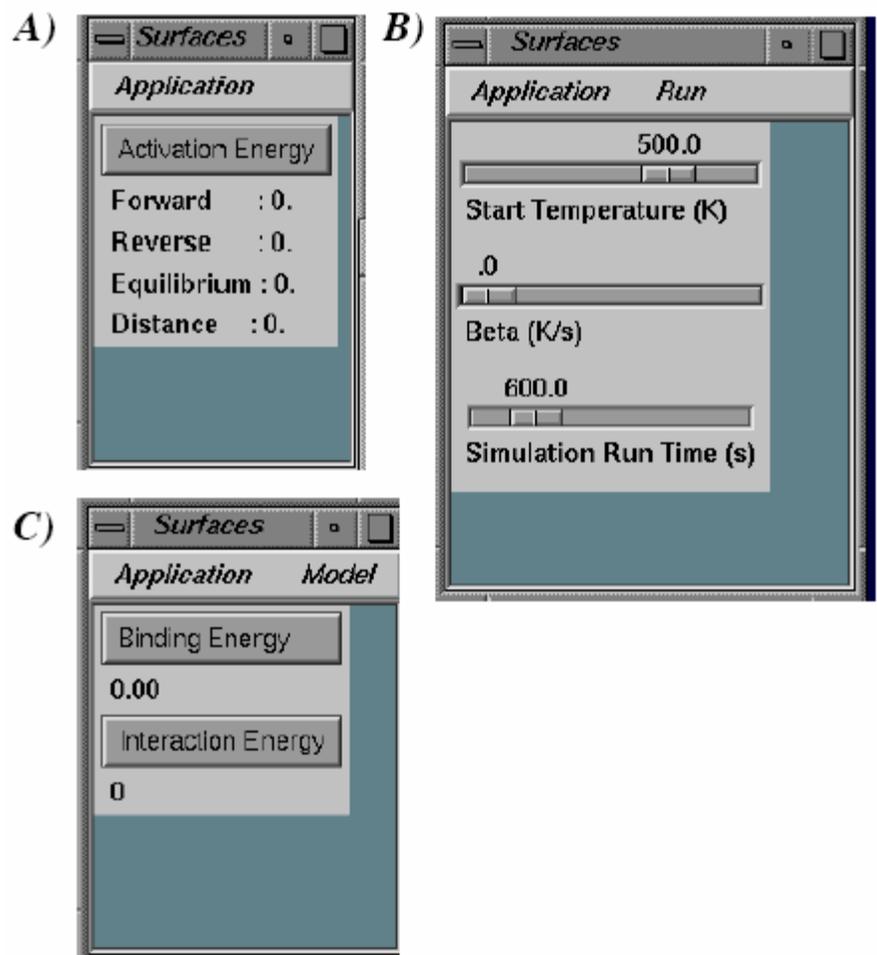
Figure 3.   KMC interface for that enables the user to A) calculate the activation barriers, B) determine the binding and interaction energies and C) set the temperature, time and heating ramp.

Simulations proceed by first initializing the surface that is to be examined. The Co(0001) surface used is constructed and is shown in Fig. 4A. As the reaction proceeds the simulation monitors, all of the adsorbed surface intermediates and their specific site locations on the surface, the kinetics for each step, the time, the change in the gas phase populations, the overall reaction rate as well as surface averaged, and gas phased averaged concentrations. This data is stored in output files that can be opened up into spreadsheets for plotting. In addition, we can explicitly watch individual molecular transformations that occur on the surface via a real-time movie. In Fig. 4B we present just a single snapshot of the surface at some point shortly after the simulation began to simulate the steady state catalytic reaction of CO with H_2 over Co(0001). The results in Fig. 4B show the surface is comprised of hydrogen, molecular CO, and dissociated carbon and oxygen adatoms. As time proceeds in the simulation, the surface becomes covered with CO (at least for the current conditions examined). CO begins to drive hydrogen and other species from the surface. Since it doe not like to dissociate over Co(0001) it mainly acts to block the surface as is seen in Fig. 5. The in-activation of CO on the ideal Co(0001) is well know. The barrier to dissociate CO on pure Co(0001) single crystal is quite high which is consistent with our DFT calculations. By artificially assuming that a few sites are step sites or surface defect sites ultimately leads to much higher CO activation rates with more dissociated C-O on the surface. This leads to higher carbon and oxygen surface coverages.

These simulations help to demonstrate that the code is up and working as well as the power of the code in terms of examining molecular level transformations. We are now beginning to run the simulations to understand the surface chemistry for the initial stages of Fischer Tropsch synthesis.
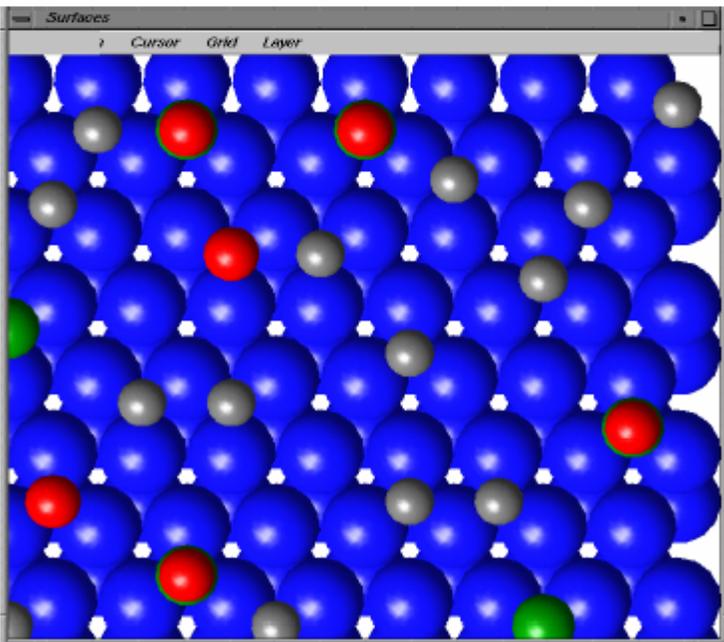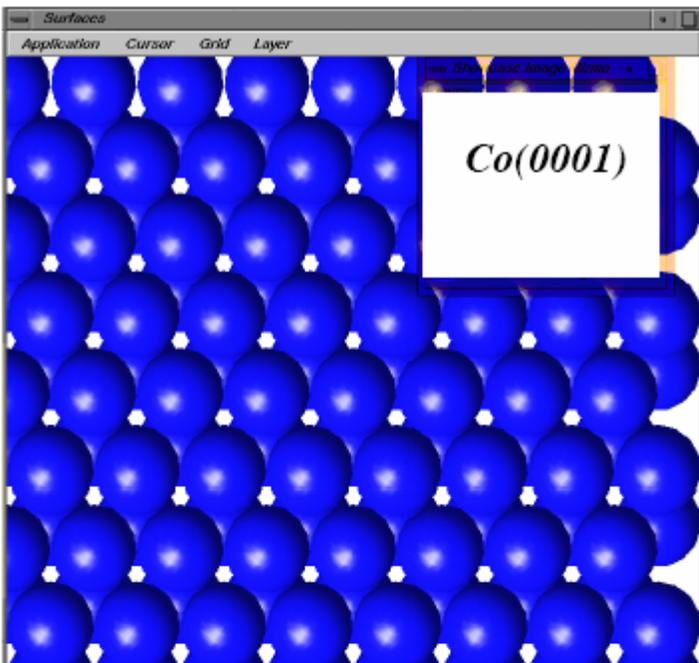
Figure 4.   Snapshot taken of: A) the initial Co(0001) surface, and B) the covered surface taken at a short time after the reaction began. (Red spheres are oxygen atoms, green spheres are carbon, and gray spheres are hydrogen atoms.
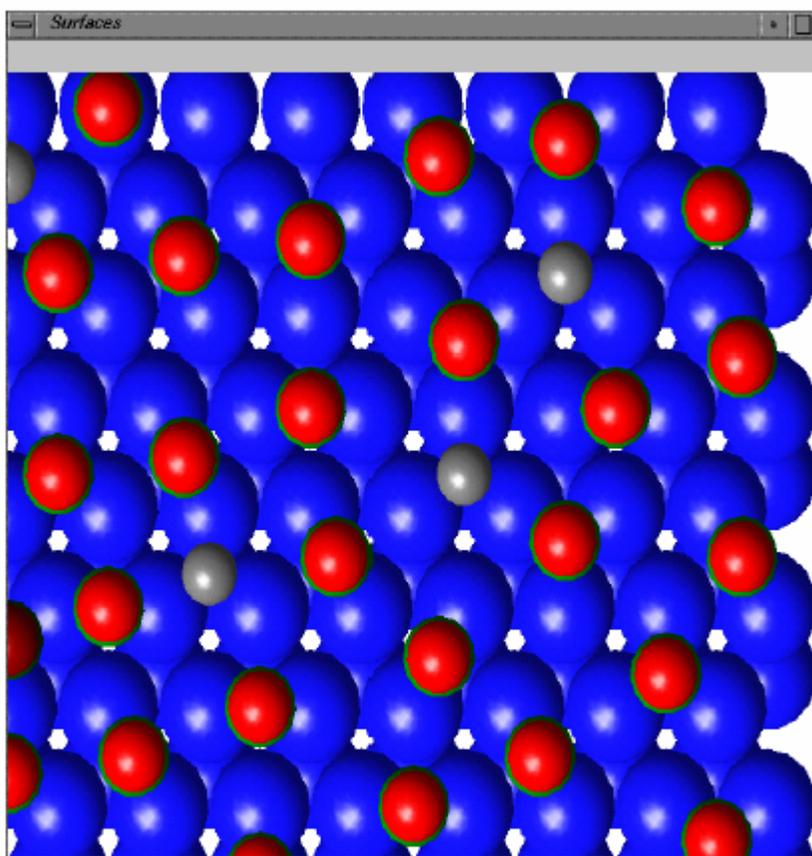
Figure 5.   Snapshot taken at longer times in the simulation whereby CO begins to poison the surface.

VII. CONCLUSION AND FUTURE EFFORTS

Over this past year we have developed an ab initio based kinetic Monte Carlo approach to simulate Fischer Tropsch synthesis. The code is based on a hybrid fixed-time step and variable time step method which enables us to treat the disparate time scales associated with reaction and diffusion. The simulations follow individual molecular transformations as a function of time and processing conditions. The kinetics and overall energetics for the simulation are based on the ab initio DFT calculations performed in the previous years of this grant. The code can be used to

simulate a variety of different experimental protocol such as temperature programmed desorption, temperature programmed reaction, and transient and steady state catalytic kinetics. The simulations provide a user-friendly graphical input that can be used in an interactive mode to calculate binding energies, lateral interaction energies, activation barriers as a function of different surface structures. The simulations follow the molecular transformations and thus allowing us to capture potential changes in the surface adlayer as a function of time and conditions. In addition, one can average out over the different states in order to provide more macroscopic information such as the surface coverages and the gas phase product compositions.

Our efforts over the next year will be to use the code to simulate various conditions for Fischer Tropsch catalysis over Co at various conditions and examine how changes in the temperature, partial pressures of CO, H_2 and H_2O influence the initial activation of CO, overall FT activity, and the production of longer hydrocarbons as well as methane.

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