Perspectives on the first principles elucidation and the design of active sites

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Abstract

First principle quantum chemical methods and atomistic simulations are used to probe active sites, ensembles, and reaction environments and assist in their design for metal catalyzed reactions. Heterogeneous catalytic reactions which take place over one- or two-metal-atom centers such as hydrogenation and dehydrogenation resemble analogous homogeneous systems and tend to be structure insensitive. Alloys can be used in order to improve the selectivity of these reactions to specific products by shutting down unwanted paths that lead to byproduct formation. The activity for these reactions, however, does not change appreciably with changes in structure or surface composition. For hydrogenation, this is due to a balance between lower hydrogen surface coverages which decrease the rate and more weakly bound hydrocarbon intermediates which increase the rate. Reactions that require larger ensemble sizes such as N_2 activation, ethane hydrogenolysis, hydrocarbon coupling, and vinyl acetate synthesis are much more structure sensitive. Both the activity and the selectivity can be improved in these systems by the optimal design of the specific sites and bifunctional ensembles. An ab initio based kinetic Monte Carlo simulation scheme was developed and used to engineer Pd/Au alloys in order to improve the activity for vinyl acetate synthesis by about a factor of 2 and the selectivity by about 5%. Altering the properties of the solution phase offers a means to probe and manipulate part of the 3D atomic structure around the active sites. More specifically we examine the activation of water over Pt, PtRu, and Ru surfaces in the presence as well as the absence of solution. Our results show that Pt, Ru, and the water solution work together synergistically to provide a low energy heterolytic path for the activation of water to form $OH^*(^-)$, $H_5O_2^+(aq)$, and 1e-. Ab initio MD simulations were subsequently used and uncovered a new path for the diffusion of hydroxyl across the surface which involves a sequence of proton transfer reactions.

1. Introduction

Catalysis is controlled by a close synergy between the atomic assembly at the active site and the reaction environment that surrounds the active site. We can begin to elucidate information about active sites for supported metals by drawing analogies with the homogeneous catalysis literature. The atomic architecture of a homogeneous catalyst is usually very well defined and, in many cases, precisely known. The reactivity and selectivity of a homogeneous catalyst is controlled by the properties of the metal center along with the properties imparted by the ligand sphere. This includes the oxidation state of the metal, the metal coordination number and coordination geometry, as well as steric and electronic interactions between the ligand sphere and potential reactants [1]. Manipulating the design of the homogeneous system involves optimizing the active metal site along with its corresponding reaction environment (ligand sphere). The differences between homogeneous and heterogeneous systems quite often arises from the finer level of control that we have in the homogeneous system to manipulate its reactivity by tuning the metal center and the ligand framework. In addition, the differences between the single metal atom site for the homogeneous system and the metal ensemble for the heterogeneous system also can play an important role.

Enzymes and biocatalysts can push the envelope on activity and selectivity even further because they begin to relax the rigidity within the ligand sphere and create an ideal three-dimensional active environment. Nature can be highly specific offering enzymes which can actively convert reactants or substrates into a single product with selectivities

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that begin to approach 100%. The substrate "docks" to a specific site within the enzyme. The protein backbone is highly flexible and can readily close itself around the active site to form an active three-dimensional pocket or cavity. The shape of the cavity that forms is controlled by its interaction with the substrate. As the reaction proceeds the cavity can change its shape in order to fully stabilize the intermediates and active complexes that form as the reactant converts to products. This is regarded as a "hand-in-glove" scheme [2]. This flexibility of the cavity that forms ultimately dictates the enzyme activity and selectivity.

As we look toward the design of supported metal catalysts, we note a number of important differences between the heterogeneous catalyst and their analog enzyme counterparts. The classical supported metal system involves nanometer-sized metal clusters attached or embedded within the catalyst support. While the metal particles that form may take on three-dimensional architectures, the chemistry that occurs over these particles takes place only at the surface and is therefore really two-dimensional. In comparison with homogeneous and biocatalysts, these supported metal systems typically display lower selectivities and in a number of cases lower activities as well. They have numerous active sites which offer little differentiability between them and therefore often lead to suboptimal selectivities.

The activity and selectivity of the heterogeneous system is controlled by the activity of the reaction environment that is within the direct vicinity of the active site. This can include not only the metal, but also the support as well. Recent advances in templating nanoporous materials have shown promise in creating tailored three-dimensional structures which offer some degree of structural flexibility. The flexibility, however, is still much more limited than that of the organic enzyme. Inorganic materials, for example, currently cannot readily self-assemble as the reaction proceeds to form a dynamic 3D cavity as reactants convert to products. Supported metal systems, however, can be self-assembled to form 3D particles with active two-dimensional surface environments (ensembles) that will influence activity and selectivity. The active sites for supported metal catalysts are typically composed of a collection of metal atoms with a prescribed atomic architecture. Structure sensitive reactions show changes in the turnover frequency when the ensemble size or the explicit atomic arrangement within or around the ensemble changes [3,4]. For example, ammonia synthesis is thought to occur at specific C7 sites which are shown later in Fig. 8 [3,5–7]. On the other hand, structure insensitive reactions can occur over various sites with little differentiation between sites. Much of what is currently known about the active sites for supported metal catalysts has been inferred from experiments on actual catalysts or from ultra high vacuum single crystal studies.

By understanding the nature of the active site and the active reaction environment we can begin to probe design ideas. Structure–activity relationships are useful in the guided synthesis of new materials and can be established through either traditional experiments or high-throughput methods. The goal is to correlate specific structural or chemical features such as the metal, the support, the synthesis strategy, bimetallics, solution used, etc., to catalytic performance. Direct one-to-one correspondence between any one of these variables and their impact on catalytic performance is difficult, however, since it is nearly impossible to separate a number of these effects.

Theory and modeling, however, have reached the stage whereby they can offer a useful complement to experimental endeavors. Theory can explicitly tie the exact changes in the atomic structure to chemical properties and even catalytic performance. The problem with theory and simulation, however, is that this same useful characteristic of atomic specificity can also lead to the generation of an infinite number of conceivable configurations that could be active. Many of the assemblies offered via computation methods may, in fact, be unstable under the conditions of interest. A balance between theory, simulation, and experiment, therefore offers the best guide toward the design of new systems. In this paper, I tried to demonstrate how theory and simulation can be used to begin to identify and in some instances even begin to design activate sites, ensembles, and environments.

2. Theoretical and simulation methods

Molecular modeling of catalysis covers a broad range of different methods that can roughly be categorized into either quantum mechanical methods or atomistic simulations. We have previously reported in more depth on the methods used along with their applications to catalysis [8–10]. Herein we provide only a short synopsis of some of the methods. The ability to calculate the intrinsic catalytic reactivity of bond-breaking and bond-making events requires a full quantum mechanical description of these events. The simulation of structure or reaction kinetics, on the other hand, can be predicted via atomistic simulations provided the appropriate interatomic potentials or intrinsic kinetic data exist. Over the past decade, it has become possible to derive this data from ab initio calculations, thus providing a hierarchical approach to modeling.

2.1. Quantum chemical methods

There are a number of excellent reviews and discussions about the advances that have taken place in quantum mechanical methods and their ability to calculate a host of different materials and their corresponding properties [10–21]. The path taken over the past decade for most of the researchers modeling catalytic systems has been to move to more robust methods which provide some reliable degree of accuracy. While there is still work on developing semi-empirical potentials to more accurately describe transition metals, many of those modeling catalysis have abandoned
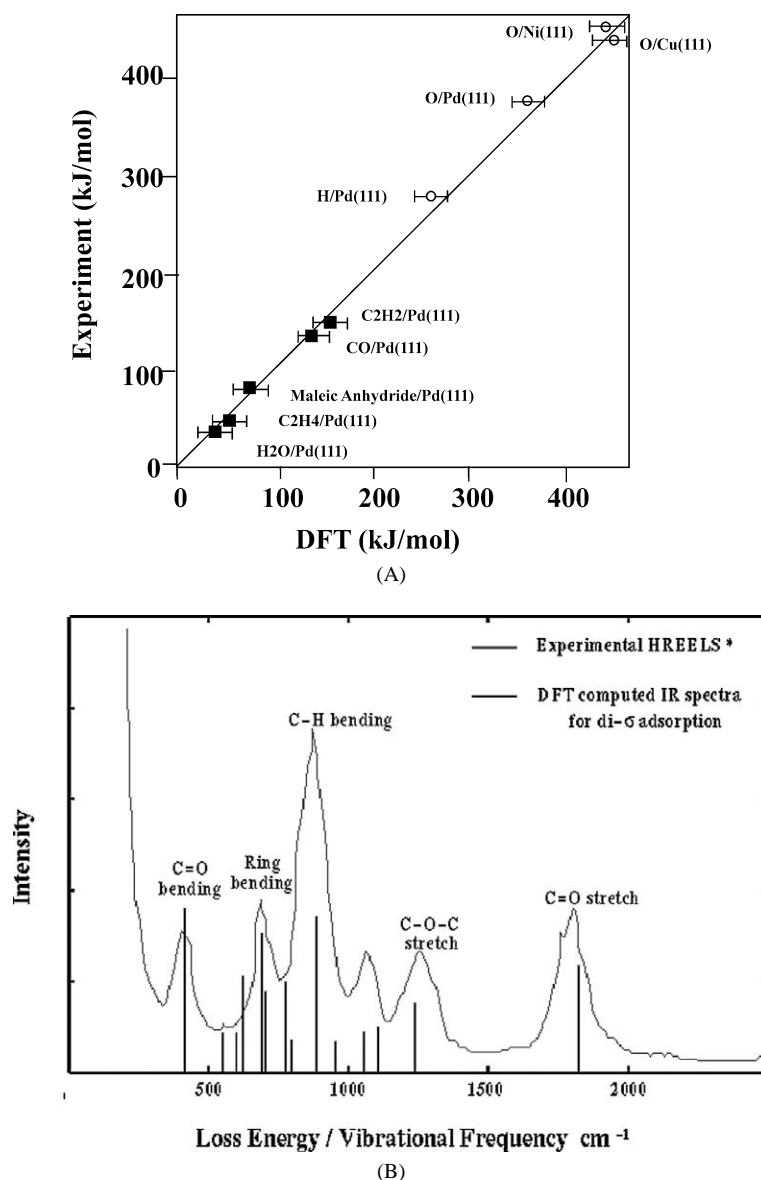
(A)

(B)

Fig. 1. (A) Comparison of calculated and experimental chemisorption energies for different adsorbates on different metal surfaces and (B) vibrational frequencies for surface adsorbates such as maleic anhydride bound to Pd(111) [23].

semiempirical methods for at least the near future for ab initio based methods. High level couple cluster wave function methods exist which can provide perhaps the highest level of intrinsic accuracy as they push close to the predictions of heats of formation to within 1 kcal/mol or less accuracy. They can only treat, however, systems with about 10 or fewer heavy atoms. This is prohibitively expensive. The size of the model used to represent the catalyst surface would then begin to take away from the desired level of accuracy. Most of the calculations for catalytic systems today use ab initio density functional methods. DFT is fairly robust and allows a first principles based treatment of complex metal and metal oxide systems whereby electron correlation is included at significantly reduced CPU cost. Density

functional theory can be used to calculate structural properties that are typically within 0.05 Å and 1–2°, overall adsorption and reaction energies that are typically within 5–7 kcal/mol and spectroscopic analyses to within a few percent of experimental data [9,10,22]. For example, a comparison between experimental adsorption energies for different adsorbates on different metal surfaces estimated from ultra high vacuum temperature-programmed desorption studies and those calculated using density functional theory is shown in Fig. 1A. Although this is a very useful first step, it is certainly not within the 1–2 kcal/mol engineering accuracy that one would like. Fig. 1B shows a comparison between high resolution electron energy loss spectroscopy and DFT calculated vibrational frequencies for maleic anhydride adsorbed to Pd(111) [23].
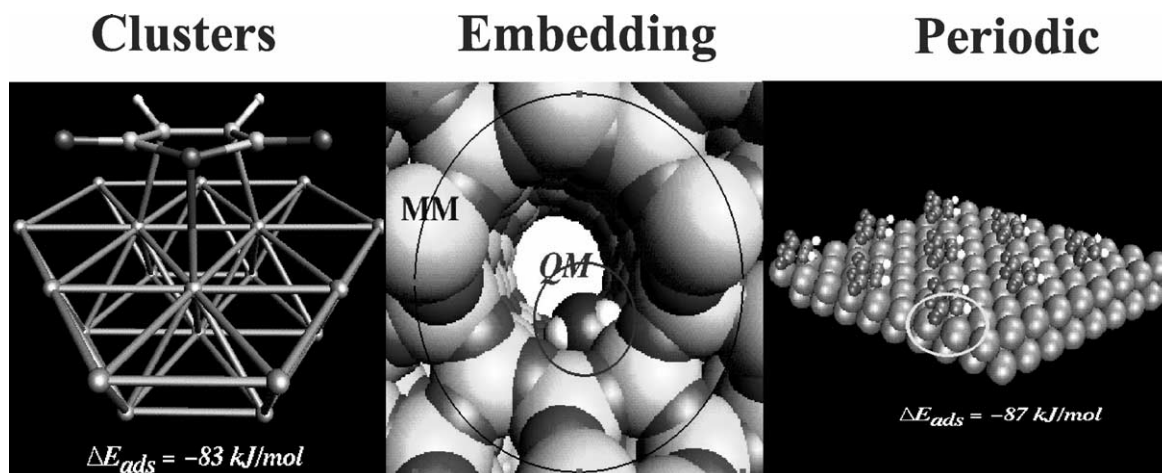
Fig. 2. Three approaches and examples for modeling chemisorption and reactivity on surfaces. (Left) cluster approach, maleic anhydride on Pd [19]; (center) embedding scheme: ammonia adsorption in a zeolite cage; (right) periodic slab model: maleic anhydride adsorption on Pd(111) [9].

2.2. Catalyst models

The success in modeling catalytic systems depends not only on the accuracy of the methods employed, but also on the reality of the model system that is studied. There are three different techniques that are currently used to model the structure at the active site. These are known as cluster [10,14,24], embedded cluster [19,21,25–27], and periodic methods [15–18,28]. Each method has its own set of advantages and disadvantages. Characteristic models for each of these systems are presented in Fig. 2.

In the cluster approach, a discrete number of atoms is used to represent the active site region. The basic premise is that chemisorption and reactivity are local phenomena, primarily affected only by the nearby surface structure. The embedded cluster model is an extension of the cluster approach whereby one treats the problems associated with the abrupt cluster termination by embedding the cluster into a lower level quantum mechanical or molecular mechanical model. In the embedded cluster approach, a rigorous QM method is used to model the local region about the active site. This primary cluster is then embedded into a much larger system in order to simulate the external electronic environment. The outer model employs a much simpler quantum mechanical treatment or an empirical force field to simulate the external environment. This minimizes cluster-size artifacts. The outer model can subsequently be embedded in yet a third model which is made of point charges to treat the Madelung potential. The last approach is the periodic slab method. In this method one defines a unit cell which comprises a large enough surface ensemble. Periodic boundary conditions are then used to expand the cell in x, y, and/or z directions, thus providing the electronic structure for linear, slab (surface), and bulk materials, respectively. Each of the methods described has its associated benefits as well as pitfalls, which are well described in the references already cited.

The work described herein was carried out by using periodic plane wave density functional theoretical slab calculations using both the VASP code from Kresse and Hafner [29–33] and the DACPO code from Hammer et al. [17,18,34]. The electron–ion interactions were described by ultra soft pseudopotentials using a plane wave cut-off energy of 320 Å. All calculations were performed using Perdew–Wang nonlocal gradient corrections for the exchange and correlation energies [35]. Various different cell sizes were used ranging from $\sqrt{3} \times \sqrt{3}$ to 3×3 in the analysis of the systems discussed along with various Monkhorst–Pack [36] meshes to sample the Brillouin zone. The calculations were carried out over metal slabs which were between three and five metal layers thick with a vacuum layer which was greater than 11 atomic layers. The outer most surface layer as well as the adsorbate surface structure were all optimized completely. Transition states were isolated using the nudged elastic band technique by Mills et al. [37].

2.3. Structural and kinetic methods

Ab initio quantum chemical methods can be used to calculate a range of relevant properties for homogeneous as well as heterogeneous catalysts. The size of the system that can be examined, however, is still quite small in comparison with the features that make up the actual system. Structural Monte Carlo simulations can explore significantly larger systems due to the fact that they only treat interatomic interactions with no focus on the electronic structure [38–41]. The interatomic potentials that are necessary for structural simulations can be derived either from experiment or from rigorous QM methods. Structural Monte Carlo as well as classical molecular dynamic methods can thus be used to simulate structure, sorption, and, in some cases, even diffusion in heterogeneous systems. Kinetic Monte Carlo simulation is characteristically different in that the simulations follow elementary kinetic surface processes which include adsorption, desorption, surface diffusion, and reactivity [42–54]. The elementary rate
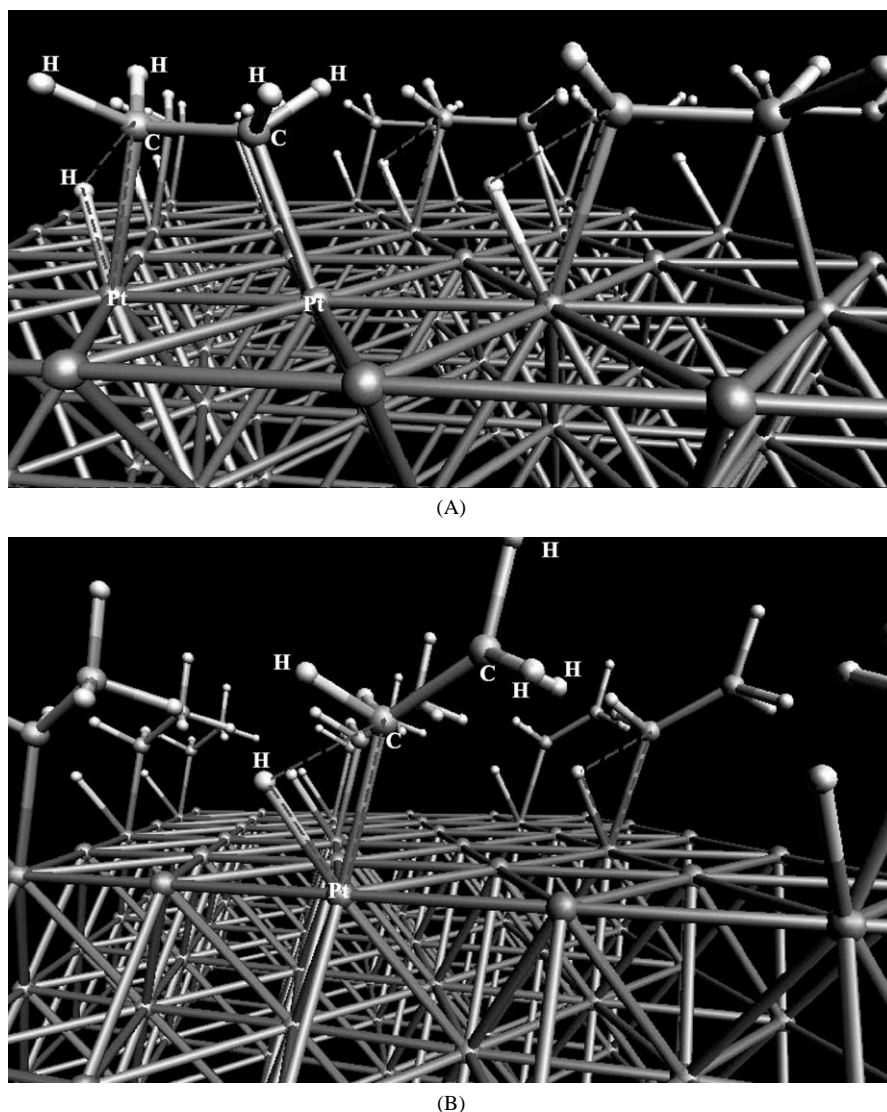
(A)

(B)

Fig. 3. Three-center (M–C–H) single site transition states for (A) ethylene and (B) ethyl hydrogenation.

constants for each of the elementary steps can be calculated from ab initio methods [51]. Simulations then proceed event by event. The surface structure as well as the time are updated after each event. As such, the simulations map out the temporal changes in the atomic structure that occur over time or with respect to processing conditions. More details on the methods used in simulating kinetics can be found in [48,51,55–57].

3. Active sites

3.1. Single centers

We start with the example of ethylene hydrogenation which is perhaps one of the most widely studied systems in all of catalysis. Ethylene is a useful probe molecule for the hydrogenation of olefins and aromatics of interest in the petrochemical industry as well as a structural moiety in a

number of oxygenate and nitrogen-containing intermediates found in pharmaceuticals and fine and agricultural chemicals. In addition, it is a reaction that we wish to prevent in order to selectively hydrogenate acetylene from ethylene feeds for the use in ethylene polymerization. It has been well established that ethylene hydrogenation is a structure insensitive reaction. We have performed a series of first principle quantum chemical calculations to help elucidate the nature of the active sites and establish the source of structure insensitivity.

The results indicate that the basic mechanism follows the ideas proposed by Horuiti and Polanyi [58]. At low or moderate coverages, hydrogen adds via a classical homogeneous catalyzed reductive-elimination step that involves hydrogen insertion into a metal carbon bond to subsequently form an ethyl intermediate [59,60]. The transition state involves the three-center M–C–H complex shown in Fig. 3A. The transition state is early along the reaction path whereby there is still a strong interaction between hydrogen and the metal
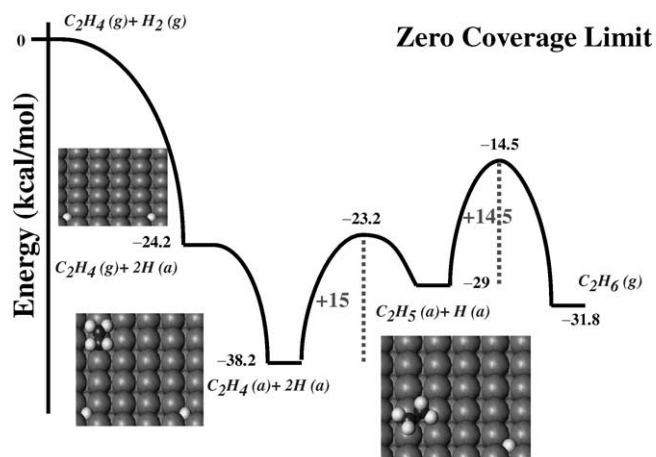
Fig. 4. DFT calculated potential energy diagram for ethylene hydrogenation over Pd(111) at low coverage.

as well as the carbon and the metal. The C–H bond is still quite long. The resulting transition state structure is consistent with results found for homogeneous catalyzed hydrogen steps [61–65].

The ethyl intermediate that forms reacts in a very similar way to yield ethane. The transition state to ethane, which is shown in Fig. 3B, is remarkably similar to that for ethyl. In fact, most of the hydrogenation reactions that have been examined in the literature are quite similar including benzene hydrogenation over Pt (Saeys et al., submitted for publication), CH_x hydrogenation over Ru [66], maleic anhydride hydrogenation over Pd [67], and CHO_x hydrogenation over Pd [68]. The important point here is that the active surface complex involves only one or perhaps two metal atoms. This is likely one of the reasons ethylene and

other hydrogenation reactions are structure insensitive. We performed subsequent calculations over the Pd(100) surfaces and found barriers similar to that on Pd(111).

The potential energy diagram for the overall reaction sequence is shown in Fig. 4. The activation barriers for ethylene and ethyl hydrogenation are quite similar at 15 and 14.5 kcal/mol, respectively. These calculated barriers are approximately 6 kcal/mol higher than those found experimentally [71]. The problem is that the intrinsic quantum mechanical calculations are performed at very low surface coverages. The actual experiments, however, are performed at much higher coverages. At higher surface coverages, the activation barriers for hydrogenation are reduced by the repulsive interactions between neighboring hydrocarbon and hydrogen intermediates. These interactions can lower the activation barrier by 5–6 kcal/mol [59,60]. In addition, higher coverages lead to the population of π-bound ethylene states that provide a second hydrogenation path which has a lower activation barrier [59,60]. The reaction from the π-bound state proceeds through a "slip-type" mechanism that was proposed in the homogeneous literature [62]. The only difference here is that the availability and participation of other surface metal atoms that can assist the reaction on the surface. The transition state, which is shown in Fig. 5, takes place over two metal atoms to form a five-center intermediate (M–C–C–H–M). The classical homogeneous slip mechanism takes place over one metal atom to form a four-center M–C–C–H complex.

Quantum mechanics provides critical information on the nature of the active site, bonding, and the relative energetics for individual steps. This, however, is only part of the picture with regard to catalytic performance. A more complete
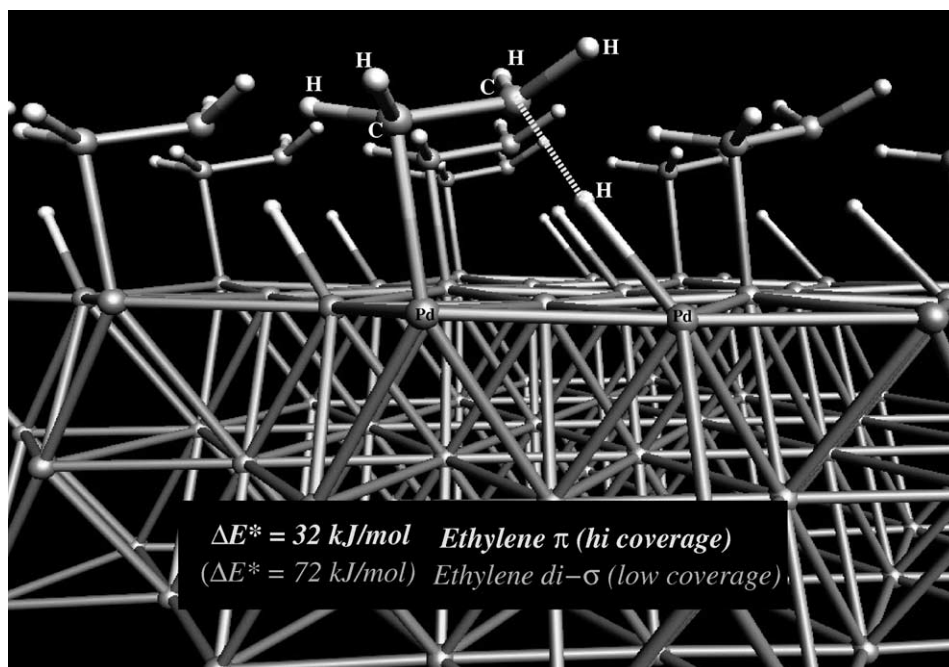

Fig. 5. π-bound transition state for ethylene hydrogenation occurs at higher surface coverages on Pd(111).
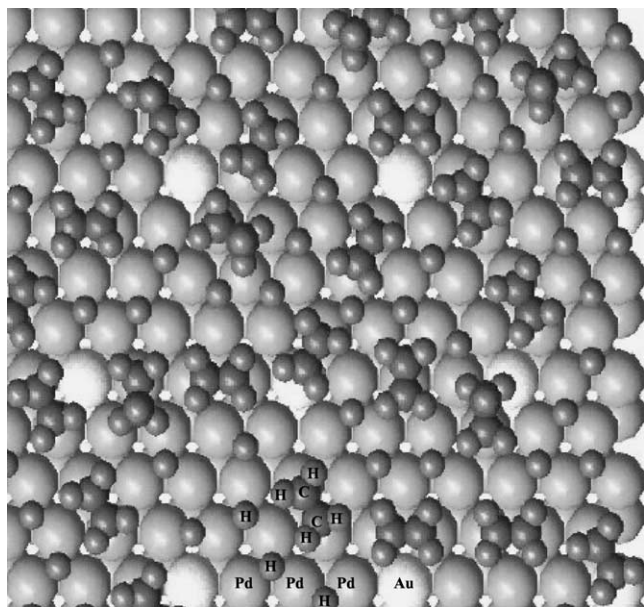
Fig. 6. Representative kinetic Monte Carlo simulation snapshot for ethylene hydrogenation over PdAu.

analysis requires elucidating the formation and consumption of all reactants, intermediates, and products along with simulating the full set of possible reaction steps to establish what actual controls the outcome. An ab initio based kinetic Monte Carlo simulation was developed which can follow a comprehensive set of adsorption, surface diffusion, desorption, and surface reaction steps in order to monitor the surface kinetics [51,55,56,69,70]. The adsorption energies, reaction energies, and intrinsic activation barriers used in these simulations were calculated from DFT methods [60]. The MC simulation enables us to explicitly include the atomic surface structure and track the dynamics associated with atomic transformations in the adsorbate surface layer including surface diffusion. A representative snapshot of the surface at some instant in time for ethylene hydrogenation over a PdAu alloy is shown in Fig. 6. The algorithm can be used to simulate the kinetics for various experimental systems such as TPD, TPR, and well-defined reactor systems. It can therefore be used as a virtual experiment. The simulation of ethylene hydrogenation over Pd in a continuous flow reactor system nicely matches those found experimentally. The apparent activation energy was calculated to be 9.5 kcal/mol which is within the range of 7–10 kcal/mol reported for fixed-bed experimental systems in the literature [71–76]. In addition, by changing the partial pressures of ethylene and hydrogen we find reaction orders for hydrogen to be 0.65 to 1.0 and reaction orders of ethylene to be −0.4 to 0.0. These are consistent with the experimental values of 0.5 to 1.0 for hydrogen and −0.5 to 1.0 for ethylene.

By calculating the adsorption energies, activation barriers and overall energies on model PdAu surfaces we were able to simulate the kinetics over different PdAu alloys and surface ensembles. The simulation results clearly demonstrate that the reaction is insensitive to the addition of gold regardless of the composition, and specific atomic arrangement of gold as is shown in Fig. 7. There is little change in the turnover frequency on a per palladium atom basis [77]. A more thorough analysis shows that gold reduces the number of sites to activate hydrogen. This decrease in the surface coverage of hydrogen will act to lower the rate. On the other hand, the presence of gold weakens the binding energy of ethylene which acts to increase the rate of reaction. These two factors offset one another and the activity remains essentially the same [77]. This is consistent with the experimental results by Davis and Boudart [71], who show that the TOF for ethylene hydrogenation was changed less than a factor of 2 by increasing Au to 40% in the Pd/Au alloy. *The two important points in this system are that the reaction occurs over one to two metal atom centers and that the reaction environment near the active site is important.*

Alkane activation reactions are simply the microscopic reverse path of that for olefin hydrogenation. The transition states are therefore identical. In this case, the path involves an oxidative addition of the alkane to the metal. The transition state is late with respect to the reactant (alkane). The C–H bond is stretched substantially in order to lower the σ^* orbital for backdonation of electron density from the metal. The three-center transition states reported in the literature on metal surfaces [66,78–80] are very similar to those found for the oxidative addition to homogeneous complexes [61,64]. The reaction involves just one or two metal atoms and is therefore not very sensitive to structure. This is consistent with experimental studies which show that alkane dehydrogenation is structure insensitive. For example, Sinfelt et al. [81] showed that the activity for cyclohexane dehydrogenation remained constant over a wide range of NiCu alloys from 5 to 90% Cu.

3.2. Active surface ensembles

3.2.1. N_2 activation

Nitrogen activation over Fe has been examined in great detail due to its use in ammonia synthesis. A number of experimental as well as theoretical studies have been carried out over this system to understand the nature of the active site and the controlling kinetics [5,6,82–85]. It has been well established that this reaction requires the presence of special C7 sites that can readily activate N_2. N_2 activation is considered the limiting step in ammonia synthesis over Fe. The C7 site is formed on the more open surfaces such as Fe(111) and Fe(211), which can expose sublayer Fe atoms. The C7 site on the Fe(111) surface is an Fe atom in the third layer, which has seven nearest Fe atom neighbors and yet is exposed to the gas phase. This site is highlighted in Fig. 8. The turnover frequencies for Fe(111) and the Fe(211) surfaces which contain these specific C7 sites were found to be at least five to six times greater than the turnover frequencies reported over the (100) and (210) surfaces which do not have C7
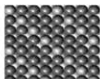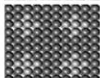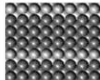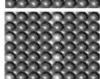
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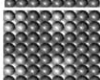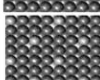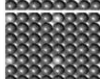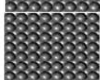
Surface Alloy Composition		Turnover Frequency	H* Coverage (ML)	E_{ads}(H*) (kcal/mol)	E_{ads}(C_2H_4*) (kcal/mol)	C_2H_4* Coverage (ML)
		0.10	0.15	60.0	10.7	0.1875
		0.10	0.27	61.6	9.7	0.176
		0.13	0.25	62.3	9.3	0.184
		0.11	0.29	61.3	8.5	0.179
		0.13	0.27	61.3	10.3	0.176
		0.15	0.28	61.2	9.1	0.18
		0.14	0.36	62.1	9.1	0.19
		0.14	0.42	62.5	9.1	0.182

Fig. 7. The effect of Au composition and ensemble size on the turnover frequencies for ethylene hydrogenation calculated from DFT-based KMC approach.

sites [5]. The reactivity on the (110) surface is essentially zero. This is consistent with the results for N_2 sticking probabilities, which show that the sticking probabilities vary with Fe(111) > Fe(100) > Fe(110) surfaces [82]. This is also consistent with studies over supported particles which show that larger Fe particles are more active than smaller particles.
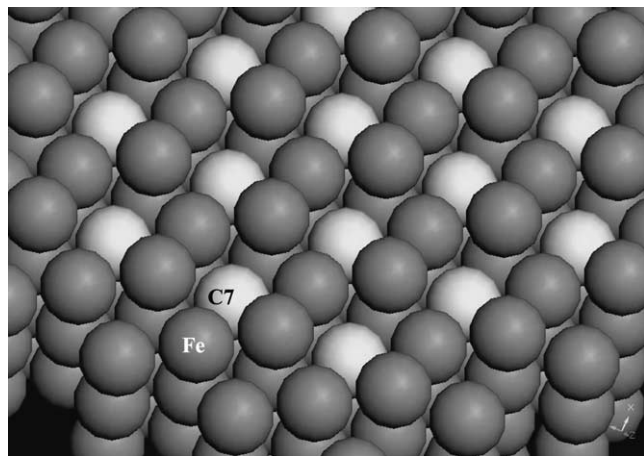

Fig. 8. Special C7 site of the Fe(111) surface, which is thought to be responsible for N2 activation and ammonia synthesis. The C7 sites are highlighted.

3.2.2. C–C bond activation and formation

The activation of a carbon–carbon bond is a second reaction system which is known to require larger surface ensembles. Ethane hydrogenolysis is a classic structure sensitive reaction. Dumesic et al. [86] have recently used ab initio DFT calculations to show that the active surface ensembles on Pt(111) and Pt(211) involve at least four metal atoms to activate various carbon–carbon bonds important for ethane hydrogenolysis. The active ensemble includes a single three-fold hollow site plus a neighboring atop, bridge, or three-fold hollow site. The authors provide a detailed study of the possible paths available for the activation of C_2H_y intermediates. The more hydrogenated ethyl and ethylidene surface species have the lowest barriers for activation. The activation barriers were found to be highly sensitive to the surface structure. The barriers on Pt(111) were significantly higher than those over the more open Pt(211) surface. The computational results were generally consistent with their experimental studies.

The reverse reaction involves hydrocarbon coupling which is a primary path for chain growth in Fischer–Tropsch synthesis. Microscopic reversibility helps to ensure that the transition states for C–C bond activation and C–C bond formation are the same. We found that the transition states require between four and six metal atoms for CH_2/CH_3 and CH/CH_2 coupling over both Ru(0001) and Co(0001) sur-
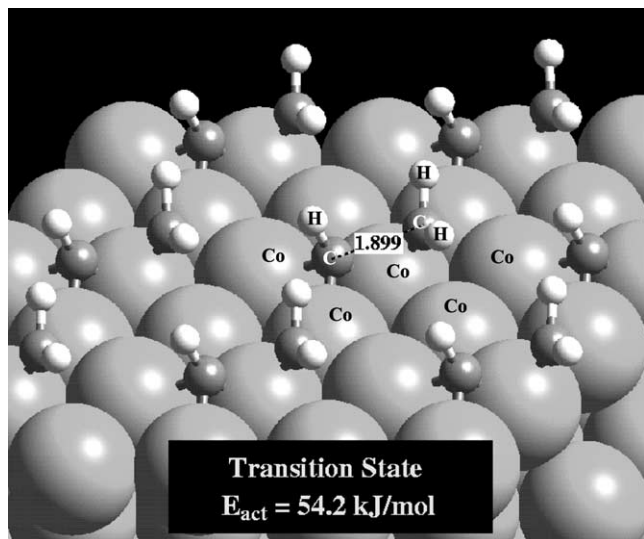
Fig. 9. Three- to six-atom surface ensembles are necessary for C–C coupling or C–C formation in FT synthesis.

faces [87]. The transition state for the coupling of CH and CH$_2$ over Co(0001) is shown in Fig. 9.

Although the ensemble size is important, the surface coverage and composition is just as critical. Reactions which have the lowest activation barrier need not be kinetically the fastest. The governing catalytic kinetics are controlled by the combination of the intrinsic rate constants as well as the relative surface concentrations of the reactants. It is important to note that the kinetics can change markedly as the surface coverage increases. In addition the local surface coverage and composition can change as a function of time. A better analysis of how all of this weighs out in terms of the apparent catalytic kinetics requires dynamic simulations of the surface physicochemical processes. We are currently examining this with kinetic Monte Carlo methods.

3.2.3. Vinyl acetate monomer synthesis

Vinyl acetate monomer (VAM) synthesis is a much more complicated system than the examples discussed so far. In VAM synthesis, a wide array of different surface intermediates can form. This results in a complex set of different possible reaction pathways that lead to VAM as well as to a host of unwanted side products. The controlling chemistry in this system has been debated for a number of years. Two different general reaction mechanisms have been presented in the literature to describe the acetoxylation of ethylene in the presence of oxygen. The first involves the adsorption and subsequent activation of ethylene to form vinyl [88–90]. Acetic acid coadsorbs and readily reacts to form acetate intermediates. The vinyl and acetate surface intermediates can subsequently couple to form vinyl acetate which desorbs as product. Oxygen either can be directly involved in the C–H activation steps or can simply provide a thermodynamic sink for any hydrogen that is produced. Regardless, the end result still involves the production of water. This first mechanism is regarded more as a classic Langmuir–Hinshelwood mechanism. Elucidating the nature of the active site requires an understanding of which steps control the overall mechanism. A plot of the potential energy surface for VAM synthesis via this Langmuir–Hinshelwood route which is shown in Fig. 10 indicates that ethylene activation to form vinyl and the coupling of vinyl and acetate to form VAM have the highest activation barriers and may be steps that control the rate. This is consistent with various speculations proposed in the literature about rate determining steps. A more detailed picture of the isolated transition states for both steps over Pd(111) is shown in Figs. 11 and 12. The activation of ethylene to vinyl requires at least a four-atom Pd ensemble (Fig. 11) in order to accommodate the vinyl and hydrogen surface product states. The oxygen-assisted activation of ethylene requires six-
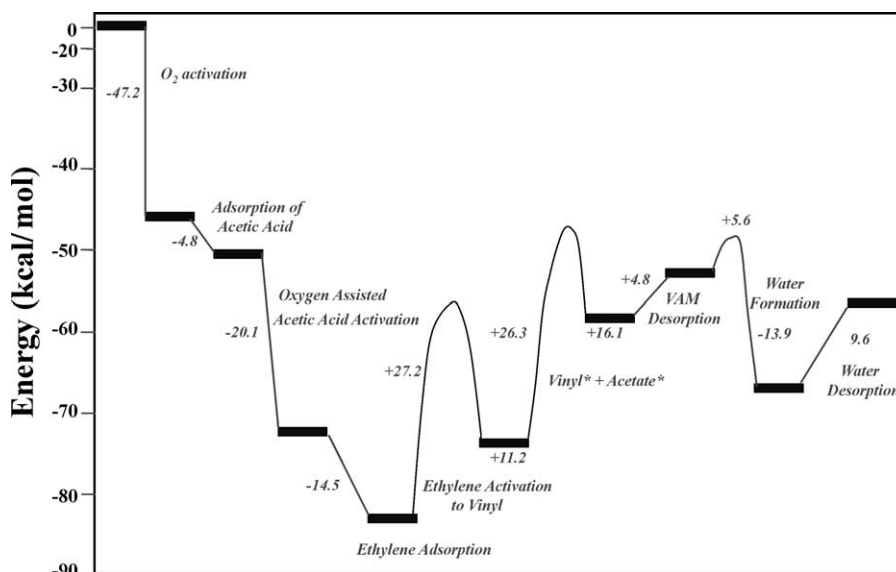

Fig. 10. DFT calculated potential energy diagram for ethylene acetoxolation.
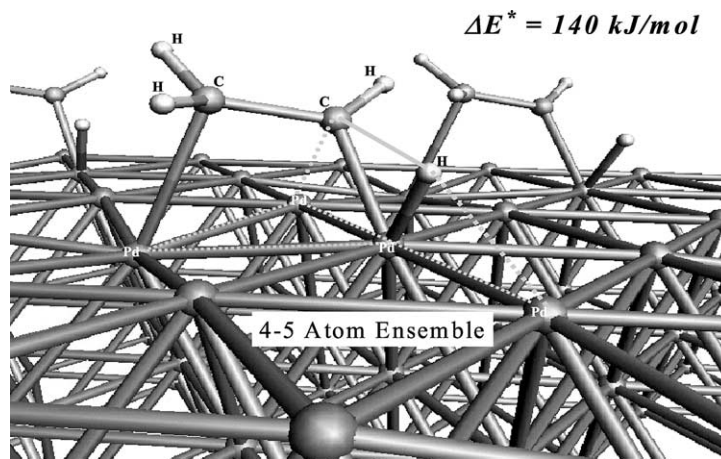
Fig. 11. The four/five metal atom ensemble required for the transition state for ethylene C–H activation to form vinyl.

atom ensembles. The ensemble size necessary for vinyl and acetate coupling is even larger at about six atoms (Fig. 12).

The second mechanism which was first proposed by Samonos et al. [91] follows more of a classic homogeneous nucleophilic addition step, whereby adsorbed ethylene is attacked by the adsorbed acetate nucleophile. The ethyl-acetate-like intermediate that forms then undergoes a β-CH elimination in order to produce VAM. The active site for the nucleophilic addition step here also requires an ensemble that ranges from four to six metal atoms. Both mechanisms are consistent in that the reaction requires a large ensemble of metal atoms and is therefore likely to be structure sensitive.

In addition to the selective pathways that lead to vinyl acetate, there are a number of unselective paths which lead to the formation of CO, CO_2, or surface carbon. Two of the most prominent unselective paths involve the decomposition

Fig. 12. DFT calculated transition state for the six-atom ensemble necessary for acetate and vinyl coupling.

of ethylene and acetic acid into CO, CO_2, and hydrocarbons. These paths require larger Pd ensembles to occur.

We have used first principle DFT calculations to map out the activation barriers and overall reaction energies for a fairly comprehensive set of reaction paths which include both mechanisms for VAM formation and the unselective paths. Overall the simulation monitors some 32 different surface reaction steps. In addition, we have used DFT calculations to estimate the overall energies and activation barriers for adsorption, desorption, and diffusion steps. The energies for all of these steps were calculated from first principles. The Arrhenius factors, however, were simply chosen based on traditional statistical mechanics.

The activation barriers, adsorption energies, overall reaction energies, lateral interaction energies, and rate constants were subsequently incorporated into the kinetic Monte Carlo simulation in order to evaluate the resulting kinetics [92]. The simulations follow the adsorption, desorption, diffusion and surface reaction steps over the ideal Pd(111) surface and explicitly monitor atop, bridge, and three-fold hollow sites on the surface. The simulations were run assuming an ideal continuous flow reactor system operating at constant temperature. We can monitor either the initial transient or the steady-state conditions. At moderate partial pressures of ethylene, the reaction is dominated by the ability for ethylene to adsorb or weakly coordinate to the surface. Fig. 13, for example, clearly shows that the surface is covered by acetate and oxygen intermediates which block active sites. This significantly lowers the activity since the availability of sites for ethylene to adsorb is very small. Snapshots from the simulation after it has achieved steady state primarily show only the diffusion of acetate and oxygen species on the surface. A representative snapshot is shown in Fig. 13. Increasing the partial pressure of ethylene allows ethylene to penetrate the surface adlayer. The yield, however, is still fairly low. Increasing the temperature helps to free up the surface sites, which enables ethylene to adsorb. Increased temperature and larger Pd surface ensembles, however, lead to an increase in the unselective decomposition routes and the formation of
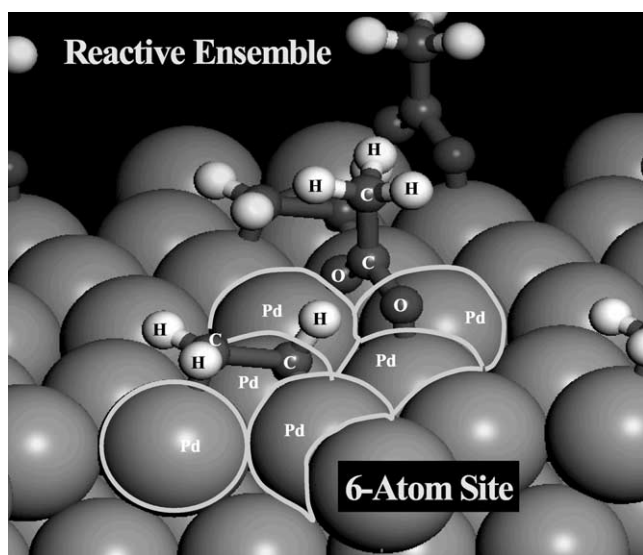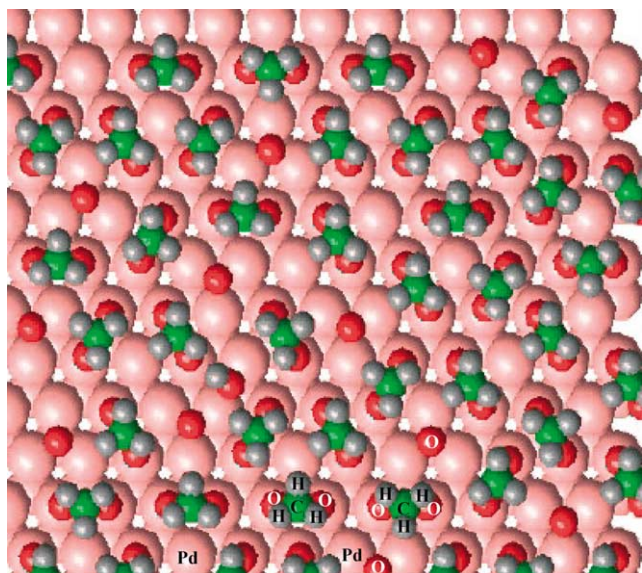
Fig. 13. Snapshot from the steady-state simulation of VAM synthesis over pure Pd(111).

Fig. 14. Simulation of surface coverage for vinyl acetate synthesis in the presence of PdAu alloys.

CO and CO_2 byproducts. The difficulty here is that while larger Pd ensembles are necessary for the main path, they enhance the unselective paths as well.

3.2.3.1. Addition of gold   It is well known that the addition of Au can improve the yield of VAM significantly [93]. Ab initio calculations indicate that the adsorption of ethylene on the Au(111) is 30 kJ/mol weaker than ethylene on Pd(111). The binding energy differences for oxygen and acetate on Au, however, are well over 100 kJ/mol lower than they are on Pd. Acetic acid and oxygen preferentially dissociate at Pd sites and remain bound to Pd. They can diffuse on the surface but prefer to move along paths which retain their interactions with Pd. The addition of Au into the Pd lattice, therefore, opens up sites where ethylene can preferentially adsorb and coexist with both acetate and oxygen. In addition, the presence of Au shuts down the active ensembles required for the unselective paths that lead to CO_2, CO, and carbon formation. Calculated barriers for C–H and C–C activation which are steps necessary for decomposition are substantially higher on alloyed surfaces. The gold sites by themselves are inactive for C–H and C–C activation. In addition, they impart both geometric and electronic effects that act to raise the C–H and C–C activation at neighboring sites.

Simulation over the PdAu surface alloys clearly shows the influence of Au on the nature of the adsorbed surface layer. Au provides "landing" sites for ethylene and as such influences the degree of contact between acetate and ethylene. We can therefore, begin to think about the design of the alloy to maximize the interactions between ethylene and acetate. The structure shown in Fig. 14 clearly shows that what we have done by alloying is to begin to create highly active sites whereby adsorbed ethylene is completely surrounded by acetate species. In addition, the presence of
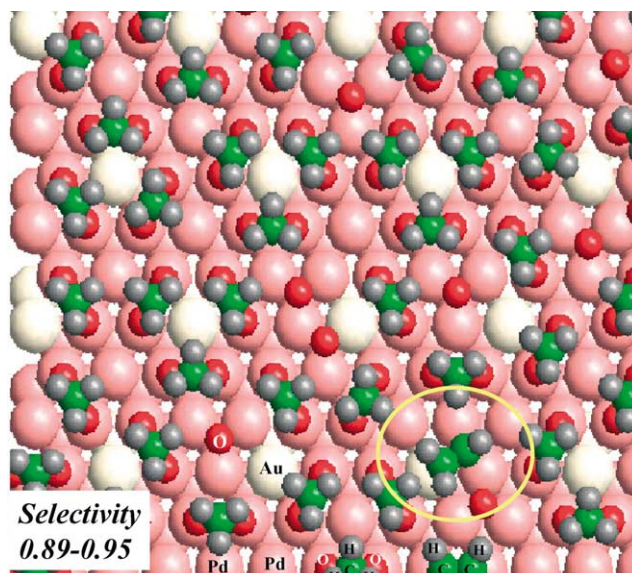
Au shuts down the larger Pd ensembles that were active for reactant decomposition. The simulations indicate that alloying Pd with Au improves the activity by a factor of 2 and the selectivity by about 5% from 89 to 94%. The results are consistent with temporal analysis of product studies over well-defined Pd, and PdAu particles, where the addition of Au improved both activity and selectivity [93].

To some extent, this is the 2D analog of the enzyme whereby the structure and composition of the alloy surface can be manipulated in order to fabricate the most active adsorbate environment. This, however, is still only a two-dimensional search for the active surface template. A future communication will discuss how the template which includes the two metals, the surface composition, and exact atomic arrangement for this system was manipulated to establish a surface that would be significantly more active and selective, according to the simulation results. Of course, there are a number of critically important questions that can be asked. For example, can one actually create an alloy with the specifically engineered atomic surface structure and composition? Even if this were possible, the next greatest hurdle would be the stability of the alloy under processing conditions. While these are major obstacles, it is important to note that one can begin to use theory and simulation in order to suggest systems that one can then try to synthesize and examine experimentally.

3.3. Active environments

While the active ensembles for metal systems can begin to take on some three dimensionality due to the presence of step edges, kink sites, surface promoters, and metal support interactions, the structural environment about the active site is still much more closely characterized as two-dimensional.
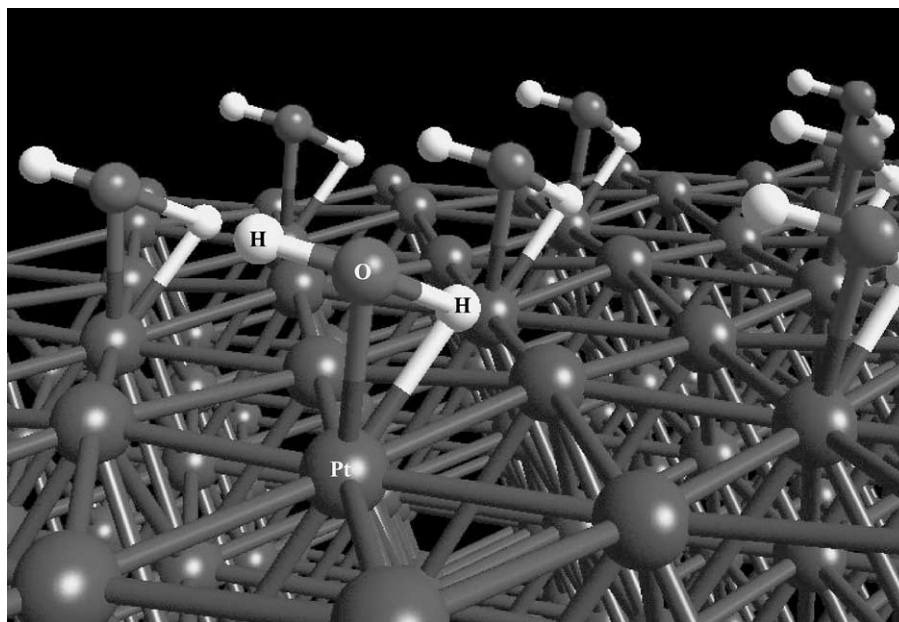
Fig. 15. DFT isolated transition state for the activation of water over Pt(111) surfaces.

The reaction occurs at the vapor/solid interface whereby the gas phase shows no specificity or ability to alter surface activity. The presence of a solution or solvent on the other hand can begin to provide a way in which we can begin to manipulate the third dimension in order to enhance particular reactions at the solution/metal interface. Polar solvents, for example, can stabilize surface catalyzed reactions that generate more charged-like intermediates or transition states by classical solvent effects. In addition, there is a growing number of examples including homogeneous and zeolite reactions whereby the presence of a solvent can directly participate in the catalytic sequence by involving solution molecules as part of the active ensemble. Water, for example, can be directly involved in catalytic chemistry by providing a medium for the shuttling protons. This is well known in enzyme- as well as in electrocatalysis. We have recently demonstrated that the participation of the reaction environment cannot only influence the reactivity, but also the nature of the reaction path taken (Desai et al., submitted for publication).

We discuss herein the results for the activation of water over bimetallic PtRu surfaces. Alloys of Pt are the most active and selective materials used in the catalytic oxidation that occur at the anode in both the reformate as well as the direct methanol fuel cells. Bimetallic PtRu systems are thought to actively catalyze a bifunctional route for the oxidative removal of CO which proceeds via the reactions shown in steps (1) and (2) below [94–97]. Pt is thought to be necessary for the adsorption and initial activation of CO. Ru, on the other hand, is thought to enhance the activation of water.

$$H_2O^* \rightarrow H^+ + OH^* + e^-, \tag{1}$$

$$CO^* + OH^* \rightarrow CO_2^* + H^+ + e^-. \tag{2}$$
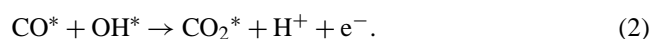
We have examined the activation of water over PtRu surfaces in both the vapor and the liquid phase for comparison purposes using ab initio density functional theoretical calculations. In the vapor phase, water weakly adsorbs on Pt(111). The calculations report an adsorption energy of -20 kJ/mol while the experimental value is somewhat higher at -40 kJ/mol. The differences may be due to hydrogen bonding in the experimental results. The reaction to form surface hydrogen and hydroxyl intermediates is endothermic by 97 kJ/mol. The barrier to activate water is high at 142 kJ/mol (Desai et al., submitted for publication). As the temperature is increased, water would much more likely to desorb than to react.

The activation of water over the Ru(0001) surface appears to be much more likely with an overall reaction energy (-3 kJ/mol) and the activation barrier ($+94$ kJ/mol). Interestingly, the results for water activation over various PtRu alloys indicate that the barriers and the overall reaction energies over $Pt_{66.6\%}Ru_{33.3\%}$ and other PtRu alloys were found to be rather similar to those reported over pure Ru. A closer examination of the active ensemble indicates that water activation occurs over a single metal atom site, where the metal atom inserts into the H–OH bond as shown in Fig. 15. Since the reaction occurs over a single metal atom site, it should not be very structure sensitive if carried out in the vapor phase.

We examined the effects of solution on the activation of water over the $Pt_{66.6\%}Ru_{33.3\%}$ alloy. In the presence of solution, the adsorption of water to the surface is weak since it can now begin to form hydrogen bonds with solution thus weakening its interaction with Pt. If we follow the same homolytic path shown above for the activation of water over PtRu in the vapor phase, we find that there is only a 15 kJ/mol reduction in the activation barrier and a
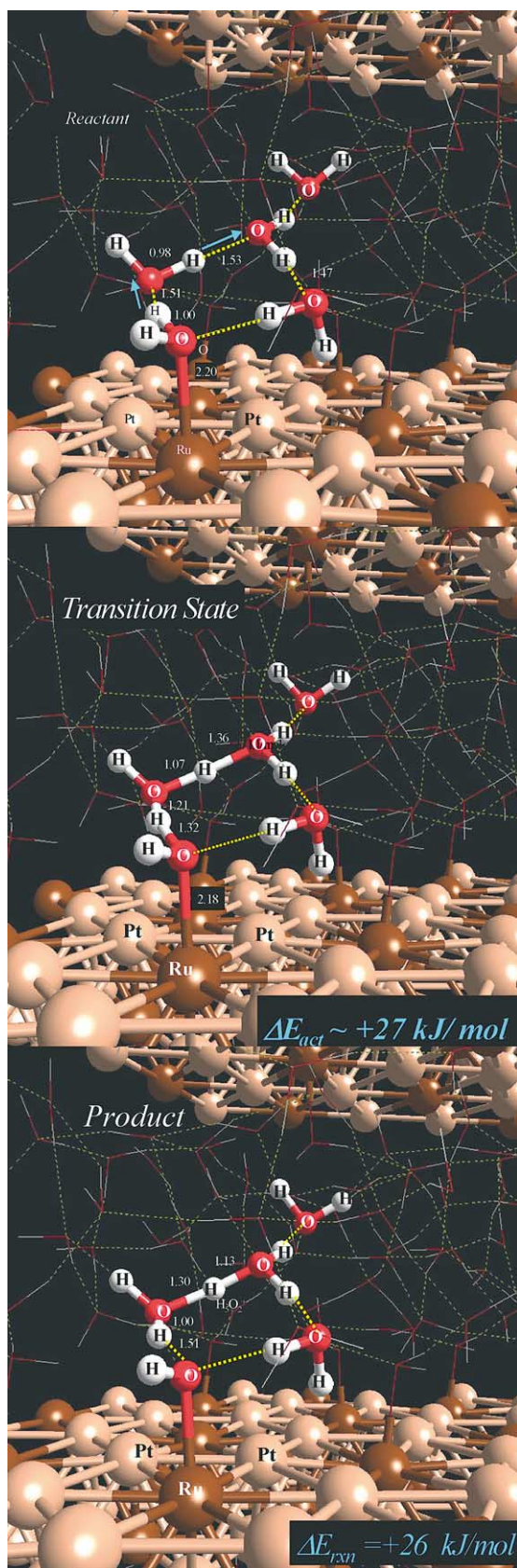
Fig. 16. The heterolytic activation of water in solution over the $Pt_{66.6\%}$ $Ru_{33.3\%}$ surface. There is a synergy between the Pt, Ru and solution which leads to the low activation barrier (Desai et al., submitted for publication).

10 kJ/mol reduction in the overall endothermicity due to the stabilization of the more polar transition state.

The presence of solution, however, opens up a heterolytic activation path which is greatly stabilized by the presence of solution (Desai et al., submitted for publication). Water preferentially binds to the Ru sites and dissociates there to form a surface bound hydroxide intermediate and a proton in the form an $H_5O_2^+$ intermediate. The end state is the well-known double layer from electrochemistry whereby a negative charge is delocalized across the hydroxide/Pt surface whereas the protons exist as $H_5O_2^+$ species that reside near to the negatively charged surface. The barrier for water activation is reduced to 27 kJ/mol which is within the range for the barriers involved in proton shuttling in solution (Desai et al., submitted for publication). The reactant, transition, and product states for this path are shown in Fig. 16.

A more detailed analysis of what drives this heterolytic cleavage indicates that there is a cooperative synergy between Pt, Ru, and the protic solution. We performed a series of calculations aimed at elucidating the possible states of atomic hydrogen on different metals in the presence of solution. On Pt, we find that hydrogen releases an electron to the surface thus forming $H_5O_2^+$ intermediates. This was also seen experimentally by Kizhakevariam and Stuve [98], who proposed that hydronium ions are likely to be formed on metal surfaces which have work functions that are greater than 4.88 eV. Simple calculations of the work function as well as more comprehensive calculations on the overall energy for adsorbed atomic hydrogen to release its electron to the surface and desorb into solution as H^+ indicate that hydronium ion formation can occur on Pt as well as $Pt_{66.6\%}Ru_{33.3\%}$ alloys but is not likely on Ru alone.

Ru appears to be responsible for the adsorption of water onto the surface and the initial activation of the H–OH bond. Pt aids electron transfer from H/Pt to $H^+(H_2O)_2/Pt + 1e^-$. The water solution acts to stabilize the formation of H^+ and OH^- intermediates. The reaction here is now much more structure sensitive, thus involving a three-dimensional-like environment between metal/adsorbate/solution. While the active site is still greatly removed from the 3D atomic architectures of the active sites in enzymes, we do begin to see some three dimensionality and cooperative synergy with the local environment which can significantly enhance catalytic performance.

This system also displays some very interesting physicochemical behavior that was captured by carrying out ab initio molecular dynamic simulations (Desai et al., submitted for publication). The simulations clearly show the heterolytic activation of water to form $OH^{(-)*}$ and $H_5O_2^{(+)}(aq)$ intermediates. The surface $OH^{(-)*}$ that is bound to Ru then induces the adsorption of water at a neighboring Pt site due to both through-surface electronic interactions and through-space hydrogen-bonding interactions. This sets up an ideal solution network to transfer a proton from the water adsorbed at the Pt site to the neighboring $OH^{(-)*}$ surface in-

termediate on Ru. This proton shuttling continues to other neighboring sites. The end result is the surface diffuse of the hydroxide intermediate which is mediated by proton shuttling. This may be of direct relevance to the CO oxidation at the anode of a working fuel cell since it is currently speculated that the rate of CO oxidation may be controlled by the ability to bring CO and OH groups together on the surface [94,99–101]. CO is thought to form islands on Pt whereas water dissociates over Ru and the reaction occurs solely at the edges of PtRu islands. More recent evidence, however, suggests that surface hydroxyl groups can migrate over onto the Pt islands [102]. Our results indicate that even though water activated on Ru is strongly bound to Ru, diffusion can occur onto Pt simply by proton shuttling. It is important to note, however, that the calculations described here are essentially for a system at zero potential charge.

4. Summary/conclusions

I have tried to show here that theory can be used to probe and even begin to design the nature of active sites, active ensembles, and active reaction environments for metal catalyzed systems. The models of the surface are admittedly overidealized simplifications of an actual working catalytic surface, which is quite complex and can change dynamically. Despite the simplifications, there are a number of ideas that result. Hydrogenation and dehydrogenation reactions typically require sites composed of just one or two metal atoms. This may be a factor which contributes to their lack of structure sensitivity since they do not require elaborate ensembles of metal atoms. They tend to have transition states very similar to analogous homogeneous catalysts. Engineering the design of these systems through alloying does not appear to change their activity but can markedly improve their selectivity. Reactions such as N_2 activation, ethane hydrogenolysis, and VAM synthesis, on the other hand, require larger and more specific atomic arrangements. They therefore tend to be more structure sensitive. These sites either offer unique structural elements within the ensemble as in the C7 sites for N_2 activation or provide for bifunctionality, such as the Pd and Au sites in VAM synthesis that enhance the activity and/or the selectivity. The design for these systems can lead to marked improvements not only in the selectivity, but also in the activity. Despite the fact that supported metal catalysis is primarily controlled by chemistry on two-dimensional surfaces, one can begin to probe and even manipulate the reaction environment to some extent by tailoring the nature of the metal–solution interface for cooperative effects. This was demonstrated with the results on simulating water activation over PtRu surfaces. The results suggest an important synergy between Pt, Ru, and the solution.

While theory provides a very useful probe of the active site for specific steps, its importance and impact on catalytic performance require full simulation of the kinetics. We have

shown here that by integrating ab initio DFT results into a dynamic Monte Carlo simulation we can begin to track temporal changes in the adlayer along with the governing catalytic kinetics. The simulations effectively show that the structure insensitivity for ethylene hydrogenation is due to a delicate balance or compensation between the relative hydrogen surface coverage and the binding energy of ethylene. The simulations for VAM synthesis clearly show that the calculated activation barriers cannot be used alone to assess the controlling steps. A full simulation of all adsorption, surface diffusion, and surface reaction steps is important in identifying what controls the chemistry.

4.1. Outlook

I have focused herein on the opportunities that theory and simulation have offered us over the past few years. I believe that theory will continue to advance our understanding and aid in directional discoveries when appropriately partnered with experiment. It is clear that even with the level of detail described herein that we are still dealing with very idealized model systems. We focused primarily on the intrinsic nature of the active sites for different systems and how we can model the effects of bimetallics, coverage, and solvation on the reaction environment about the active site. Defect sites, metal support interactions, promoters/poison effects, however, are just as important and any bridge between the electronic structure and microscale kinetics should include all of these features. There is now a growing effort in the area of computational catalysis to generally understand how these extrinsic features affect the chemistry at the active site.

In the future, we can likely expect to see significant advances in CPU processor speeds and random access memory. This will enable us to more routinely examine much larger system sizes that begin to approach more realistic reaction environments. The intrinsic accuracy of DFT, however, could likely still be an issue at least over the next few years. The functionals used to describe exchange and correlation are the limiting features. They are simply approximations and there is no clear way to improve upon their accuracy. The search for improved functionals is, therefore, quite slow.

Regardless of the exact level of accuracy one can expect to see theory and simulation partner more closely with experiment toward the design of the active site, ensembles, and environments. Much more effort will likely go into moving closer to the design of three-dimensional supported metal systems. This will likely include detailed analyses and optimization of surface modifiers that can begin to create more of a 3D architecture at the active site. For example, the addition of Cinchona-alkaloid modifier to Pt helps to form an active 3D-like ensemble that will effectively catalyze chiral hydrogenation. How does this system work and what can be done to improve the modifier?

Lastly, theory and simulation will begin to partner with high-throughput catalyst screening efforts [103,104]. The-

ory and simulation can be used to evaluate how changes in the metal, the support, bimetallics, modifiers, and processing conditions affect the nature of the active site and catalytic performance. They can, therefore, be used along with genetic searching strategies to begin to identify regions of active phase space for materials discovery [103,104]. The current turnaround time for theory, however, is significantly longer than that for laboratory HT screening. More approximate methods and faster CPUs will help decrease the analysis time. Despite this time lag, modeling will likely be an important contributor to future HT efforts.

Acknowledgments

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