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Catalysis Today 50 (1999) 445–450

CATALYSIS TODAY

Preface: Advances and Applications of Quantum Chemistry and Molecular Simulation to Heterogeneous Catalysis

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The developments of new computational methods coupled with the tremendous increases in CPU have led to a number of major advances in modeling heterogeneous catalysis. In the past decade we have seen the transformation of first-principle quantum mechanical methods and molecular simulation algorithms into useful tools that begin to partner with experiment in understanding the elementary chemical transformations that occur on catalytic surfaces. We can now begin to move beyond very simple models of the active site and simulate larger models of the catalytic surface. In addition, we can begin to model the reaction environment and account for the dynamic changes in surface structure.

The growing excitement in this field convinced us of the timely need to organize a symposium on the latest developments and applications of first-principle methods and molecular simulation techniques for modeling catalytic reaction systems. The papers presented herein are the product of the 1996 American Chemical Society symposium on the Advances and Applications of Computational Chemical Modeling to Heterogeneous Catalysis that was held in San Francisco CA. A broad range of different catalytic materials was covered.

The papers in this issue are organized into the following seven sections: I. Current and Future Directions for Heterogeneous and Homogeneous Reaction Systems, II. Zeolites, III. Metal Oxides, IV. Metals, V. Metal Sulfides, VI. Developments in Molecular Simulation, and VII. Homogeneous Systems.

I. Current and Future Directions

Newsam and his colleagues from MSI outline the major impacts that have occurred in the application of molecular modeling to heterogeneous catalysis over the past decade and project some of the likely advances that will occur over the next few years. They review a host of different catalytic materials including zeolites and metals, and also present a short summary of some of the current computational methods. In particular, they discuss developments and opportunities in parametrizing structure-property relationships, building structural models for accelerated experimental screening, predicting local and extended structure, discerning reaction mechanism, and computing process simulation data. As a community we are still at the initial development stages. Continued efforts will rapidly increase what we can compute and the success of the methods.

Woo, Margl, Deng, Cavallo and Ziegler provide an excellent synopsis of the state-of-the- art methods for modeling homogeneous catalysis and project area where advances in this field are likely to occur over the next decade. They clearly show how combined ab initio molecular dynamics (AIMD), and ab initio molecular mechanics methods (QM/MM) are making it possible to examine larger and more realistic model

0920-5861/99/$ – see front matter
PII: S0920-5861(99)00091-7

systems that include the active catalytic site as well as the surrounding environment. They discuss the application of QM/MM methods to complex homogeneous systems. They focus on modeling the Brookhart's Ni(II) diimine olefin polymerization catalyst. The active site includes the Ni ion along with different ligand substituents. The nature of bulky ligand intermediates is described by molecular mechanics. They discuss the difficulties in accurately modeling the interface between the QM and MM regions. Their QM/MM model predictions of the activation barriers are in excellent agreement with known experimental barriers for insertion, branching and termination reaction steps. This is in contrast to the results predicted by using quantum mechanics with a simple truncated ligand environment.

They also demonstrate the application of ab initio molecular dynamics (AIMD) simulation for modeling homogeneous catalytic systems. In AIMD, the forces are determined in-situ of the full electronic structure calculations and used to simulate the dynamics. Much of the current emphasis in the literature has focused on the application of the plane-wave Car Parrinello type methods that work very well for condensed phase systems. Homogeneous catalysts however are molecular entities that are much more amenable to atom-centered basis sets rather than plane-wave methods. The authors use the Projector Augmented Wave Car-Parrinello AIMD program that was developed by Blöchl. The PAW method uses plane-waves that are then augmented with atomic-like functions near the core of the nuclei. They demonstrate the approach by computing a series of relative free energies for reaction of constrained metallocene olefin polymerization catalysts. Dynamics were used to follow reaction trajectories for hydrogen transfer, olefin σ-bond metathesis and alkyl σ-bond metathesis. In a concluding section the authors illustrate future, by combining both QM/MM and ab initio MD simulation in an effort to reexamine the Brookhart Ni-diimine catalyst.

II. Zeolites

In heterogeneous catalysis, quantum mechanical methods have likely had one of the greatest impacts in the area of zeolite catalysis. The well-defined structure of the zeolite as well as the detailed understanding of the active sites that has emerged from the experimental community provides theoreticians with an excellent model for computational studies. Theory has generally become an accepted tool for predicting structure, energetics and spectroscopic trends for zeolitic systems. In the first paper of this section, Schwarz, Nusterer, and Blöchl demonstrate how first-principle molecular dynamics simulations can be extended from homogeneous to heterogeneous catalysis to model adsorption in zeolites. In particular, they examine water and methanol in sodalite and chabazite zeolites. They develop the augmented plane wave (PAW) MD approach and use it to assign infrared bands and predict adsorption energies. The periodic unit cell model is defined such that it accounts for the full primary zeolite structure. First- principle simulations of the dynamics allow for the explicit accounting of time-dependent relaxation of the zeolite structure on chemisorption properties. It can also be used to follow the IR spectral shifts. The results indicate that both methanol and water do not protonate at low temperatures and coverages. At higher coverage, both form adsorbed carbenium ion complexes that can undergo further catalytic chemistry.

In the second paper, Van Santen provides a succinct overview of the application of theory towards understanding protonation and proton activation processes that occur in zeolites. He discusses the application of first-principle methods to predict infrared and NMR spectroscopic data, adsorption and activation energies for different intermediates. He extends these efforts along with classical molecular simulations to the development of microscopic kinetic models. A complete set of pathways that analyze the activation barriers for dehydrogenation of ethane, cracking of ethane and hydride transfer mechanisms for methane and methoxide species is presented. He discusses how spectroscopy was used to convincingly identify the true nature of the adsorbed methanol complex. The splitting of bands in the experimental spectrum was found to be due to band bleaching from Fermi-resonance. In addition, heats of adsorption for hydrocarbons in zeolites were simulated using Configurationally Biased Monte Carlo methods in an effort to show how we can begin to follow longer time and length scales.

The contribution by Hay, Redondo, and Guo examines the cracking of alkane and alkene over zeolites. Cracking is thought to involve a cycle in which the hydrocarbon adsorbs at an acid site to form a carbenium ion intermediate. This is followed by the scission of the bond β to the location of the ion that was formed. The product fragment then desorbs back into the gas phase. The authors use both Hartree Fock (HF) and density functional theory (DFT) cluster calculations to compute the energies for pentene adsorption and cracking over a three-T site model of the acid center in faujasite. They examined pentene as well as 4 methyl-2-pentene to establish the effects of the formation of both primary as well as secondary product formation. The substituted pentene had a barrier that was 6 kcal/mol lower than that for n-pentene. The overall reaction energy was found to be endothermic by 19 kcal/mol. Their results indicate that kinetics rather than thermodynamics may control the cracking product distribution.

In the final paper on QM applications to zeolite catalysis, Gale uses periodic DFT calculations to examine the adsorption of methanol within the zeolite. This is an important topic that has been intensely debated in the literature over the past several years. Methanol is physisorbed when introduced at monolayer coverages for many of the zeolitic systems examined. Proton exchange, however, is possible. At higher coverages, the methoxonium intermediate forms through proton transfer to neighboring intermediates. The zeolite appears to behave as a Brönsted acid as well as a solvent. The potential energy surface has a large number of potential energy minimum. Dynamic simulation enabled a more appropriate sampling of this complex potential energy surface. The overall energetics for the series of steps to take adsorbed methanol to dimethyl ether were also worked out.

III. Metals

The application of first-principle quantum chemical calculations to chemistry on metals has, for the most part, been limited to cluster and periodic slab models of well-defined single crystal surfaces. Although the advances in spectroscopy have brought us closer toward understanding the nature of the active surface, it still cannot provide us with the atomic resolution necessary for direct input into quantum chemical calculations. Much of the theoretical efforts have therefore focused on well-defined single crystals in an effort to compare the computational results with detailed experimental results.

In the first paper of this section, Whitten and Yang provide a detailed analysis of the thermal and photo dissociation paths for alkane decomposition. Their results indicate that the thermal C–H bond activation of adsorbed ethyl on the Ni(100) surface involves a β-hydrogen transfer step. The process is governed by the tilting of the ethyl group toward the surface. The barrier was found to be +17 kcal/mol, which is consistent with known experimental studies. The photo activation of methane over Pt(100) was also examined. The model used here was a ring of Pt atoms. Methane is thought to absorb a photon to become CH_4^-, which is then attracted to the surface image charge. Dissociation of the excited state, however, required a significant C–H stretch and therefore did not occur. Methane appears to dissociate only from the ground state surface.

F. Illas, A. Clotet and J.M. Richart present detailed ab initio calculations on model metal clusters in order to understand the binding of atomic oxygen and sulfur to Pt(111). Hartree-Fock theory is used along with correlated wave functions to predict bond lengths, interaction energies, and vibrational frequencies. The results indicate that the structural predictions are in good agreement with known experiments. The energetics, however, are strongly dependent upon the level of configuration interaction that is included in the calculation. Constrained space orbital variation analysis is used to elucidate the nature of covalent versus ionic bonding. They find that many common electron correlation functionals fail at predicting the correct bonding. Multireference MP2 and MRCI provide much better estimates of electron correlation and therefore provide more consistent binding energies.

The cluster approach was also used by Chen, Friend, and Van Santen to analyze the adsorption of a methyl fragment on Rh(111) model surfaces. Density functional methods were carried out on larger and more realistic metal clusters. They find that the methyl group binds most favorably at the three-fold fcc site. The methyl group is tilted by an angle of 20° from the surface normal thus suggesting an interaction of the surface and the C–H bonds from methane. This is consistent with their HREELS experiments which demonstrate a shift in the C–H stretch mode to lower wave numbers. Crystal orbital overlap population analysis is subsequently used to show that the C–H antibonding states become occupied upon adsorption via their interaction with the surface metal d-orbitals. They also discuss the limitations of the cluster approach whereby edge effects can skew the reactivity of outside edge sites.

Venkataraman and Neurock extend the DFT cluster approach to model chemisorption as well as surface reactivity of maleic anhydride and its reactive intermediates over Pd(111) surfaces. Their results indicate that adsorption energies can be predicted within about 5 kcal/mol of corresponding experimental UHV studies provided that the cluster is large enough to accommodate the adsorbate. At low surface coverages maleic anhydride was found to bind most favorably in the di-σ configuration. By carrying out a series of different reaction coordinate calculations they were also able to determine the activation barrier for the hydrogenation of maleic to maleic anhydryl intermediate. Subsequent hydrogenation steps were all found to be exothermic leading to succinic anhydride, γ-butyrolactone and tetetrahydrofuran. In addition to the selective hydrogenation paths that lead to tetrahydrofuran, maleic anhydride can also undergo ring open reactions. DFT calculations indicate that the barrier over Pd is quite high at 186 kJ/mol and highly endothermic. On Re however, the barrier is reduced to 80 kJ/mol and the reaction is exothermic. The results agree quite well with experimental data.

IV. Metal Oxides

Although the bulk structure for a number of metal oxides is well known, the geometric as well as the electronic structure of the surface can be quite complex leading to a variety of different active sites for both chemisorption and reactivity. Oxide surfaces display a full range of behavior including a distribution of acid as well as base sites, both of which can catalyze different chemistries.

Pacchioni and Ferrari use a series of small molecules such as CO and O_2 to probe the electronic effects of vacancy sites on MgO(100). They analyze adsorbate-surface bonding through Hartree-Fock theory. Both CO and O_2 strongly interact with Fs defect centers at the surface. Radical anions such as O_2^- and CO^- are readily formed at these defect sites. This is in contrast to the idealized MgO(l00) surface which is unreactive. The interactions of both O_2 and CO are dominated by electrostatic forces. This is governed by a strong coulomb potential that forms in the cavity due to trapped electronic charge.

Ahdjoudj, Makovits and Minot also examine the reactivity of MgO. In addition, they move from this basic oxide to TiO_2 that is known to have both acid and basic properties. They probe the acid and base sites on both surface by adsorbing NH_3, water and CO_2. Periodic Hartree-Fock slab calculations were used to assess the interactions. The Ti(4+) sites were found to be rather basic. The strength of interaction with different adsorbates was correlated with the proton affinity of the adsorbate. Dissociation of these species over the surface was found to correlate with gas phase dissociation energies. MgO was shown to be much more basic than TiO_2 and was found to be inactive in the dissociation of NH_3. The interaction with CO_2, which is a much softer base, was significantly stronger than that with NH_3. Water dissociation leads to surface hydroxyl groups that can form hydrogen bonding networks with polar adsorbates. The acid and base character of different sites along with the hardness and softness of the adsorbate appeared to correlate with the strength of interaction and whether or not dissociation was possible. Coverage effects were also found to be quite important in predicting the chemisorption on metal oxide surfaces.

Cheng, Reiser, and Dean extend the ideas of chemisorption to the reactivity of metal oxide surfaces. In particular, they performed a comprehensive set of DFT cluster calculations on a model FeO surface to examine the Boudouard reaction. Boudouard chemistry is thought to control deleterious metal dusting which involves the corrosion of the metal oxide interface by reaction with CO. The interaction of CO and the pristine FeO(100) surface was found to be quite weak. The barrier for CO to extract oxygen from the surface was found to be very high. These results indicate that the Boudouard reaction on FeO(l00) is unfavorable. The reaction occurs much more readily at defect sites. They suggest that a pitting mechanism is therefore more likely to dominate.

Both vanadium and molybdenum oxides are known to be active as oxidation catalysts. MoO_3 is also known to catalyze a series of other chemistries including isomerization, cracking, hydrogenation, and dehydrogenation. Hermann, Witko and Michalak analyze chemical bonding on model MoO_3 surfaces with DFT cluster calculations. They perform a series of calculations on different Mo_xOH_y clusters to model the features of both the (010) and (100) faces of MoO_3. Both ionic and covalent metal-oxygen bonding was found to be present. The terminal and bridging oxygen sites were found to have very different properties. The selective oxidation of propene to acrolein was examined by 1) computing the binding energies of H and OH groups to the oxide cluster, 2) following the initial reaction steps involved in the formation of surface allyl groups and 3) simulating its subsequent reaction to acrolein.

Analyses on how the total energy changes as a function of bringing both H+ and OH intermediates toward particular surface sites provided a glimpse of the detailed potential energy surface for these important intermediates. The results for the interaction of allyl intermediates with $MoOH_x$ clusters begin to demonstrate the structural features of the (010) and (100) surfaces lead to differences in reactivity.

Witko, Hermann, and Tokarz follow up this work with a second study on V_2O_5. Both DFT and semiempirical UNDO calculations were used to examine the binding of H and H+ as well as CH_3 and OH intermediates on model clusters of the V_2O_5(0l0) surface. Their results show a difference in electronic properties of the different bridging oxygen species on this surface. The strongest bonding occurs at oxygen bridge sites that connect two bare vanadium atoms. They follow the formation of a C–O bond that forms at the bridge site as propene or toluene approach the surface. Vanadium appears to be distinctly different than Mo in that it only exhibits oxidation functionality. Mo has both oxidation as well as acid sites. The bridging oxygen sites on the vanadium oxide clusters were found to be much more negatively charged than the terminal vanadyl sites. Bridging OH groups that form are more weakly bound than the OH groups that form at terminal sites. There is likely to be increased reactivity of electrophilic reactants at the bridge sites. ZINDO semiempirical methods enable the authors to examine a much larger cluster and begin to probe the adsorption and reactivity of propene and toluene.

V. Metal-Sulfides

The reactivity of metal-sulfide catalysts for hydrodesulfurization and other hydroprocessing reaction chemistries has been suggested to be tied to an optimal balance of the metal-sulfur bond strength. The application of the well-known Sabatier's principle for HDS would suggest that there is an optimal M–S bond strength for which the metal-sulfur bond is strong enough to adsorb thiophenic hydrocarbon intermediates yet weak enough to release H_2S to regenerate the active site. Toulhoat, Raybaud, Kasztelan, Kresse, and Hafner build on this premise by performing first-principle M_xS_y slab calculations to determine the metal-sulfur bond strength for a number of different transition metal sulfides that span across the periodic table. They develop a more consistent definition of the metal-sulfur bond strength and use these values to organize the experimental measurements of activity into a volcano plot. The emerging plot nicely demonstrates Sabatier's principle.

VI. Insights from Homogeneous Catalysis

Doren, Konecny, and Theopold use first-principle DFT calculations to predict the geometric and electronic structures for a series of organometallic cobalt complexes which involve the Tp (tris(pyrazoly borate)) ligand which induces strain about the Co center. Their theoretical results for bond lengths and angles compare very well to their experimental results. They also examine the activation of molecular oxygen over these complexes to begin to understand the factors that control O_2 activation. They show how simple Extended-Hückel theory can be used to understand the essential features that guide the geometric structure.

VII. From QM to Molecular Simulation

The ability to bridge ab initio electronic structure calculations and macroscopic chemistry will undoubtedly involve molecular simulation. While first-principle quantum chemical calculations can be used to begin to predict the adsorbate/surface interactions, the ability to simulate process chemistry will require modeling more realistic environments and simulating extrinsic features such as coverage, mass transfer, and thermodynamic issues. Molecular dynamics, Monte Carlo and coarse-graining models will likely play a pivotal role in modeling longer time and length scales to capture some of these features. The development and application of these methods to heterogeneous catalysis has been growing at a rapid pace. Most of these efforts have focused on simulating the equilibrium behavior, adsorption, and diffusion of guest molecules in zeolites. This is due to fact that the zeolite structure is well-defined and reasonable interatomic potentials exist.

Keil, Hinderer and Garayh, develop and apply a range of different algorithms to analyze combined diffusion and reaction of hydrocarbon intermediates in composite catalyst particles. A dusty gas model, Monte-Carlo simulation, and Molecular Dynamics were used to compute multicomponent diffusivities and simulate reaction and diffusion processes that occur within ZSM-5 for the Methanol-To-Olefin synthesis. The simulated diffusivities compare quite favorably with experimental values. In addition, they were able to follow the changes in diffusivities due to multicomponent behavior. While the present work deals with constrained lattices, the authors are currently working on lattice relaxation effects.

Inorganic membranes offer the hope of achieving very high permaselectivities with high throughputs. The design of these materials, for the most part has been trial and error. Computational chemistry offers the hope of design of the molecular properties of these membranes for separations. Takaba, Mizuhami, Oumi, Kubo, Chatterjee, Fahmi, and Miyamoto use molecular dynamics to evaluate the Knudsen diffusivities and the flow through permeable inorganic membranes such as MgO. The flux of isobutane and n-butanes through ZSM-5 silicate membranes was examined via molecular dynamics. n-butane was found to readily pass through the membrane, isobutane however would not penetrate the membrane due to steric interactions. The affinity of the membrane for CO_2 is also presented.

In the final paper, Guliants, Mulhaupt, Newsam, Gorman, and Freeman use molecular dynamics to predict the location of non-framework ions in zeolites. They apply a new grid-based algorithm to simulate equilibrium as well as dynamic behavior of these ions in the zeolite. The cation locations in various dehydrated zeolite forms such as Na88X, Ca48X and 3A(K60Na56A) and Cu-mordenite are predicted. MD and MC methods are used to show the docking of benzene in the supercage of zeolite Ca48X. Sodium and calcium were found to sit at numerous sites in the six ring and β cages as well as at the 4R edges. The site location as well as the unit cell occupancies appear to agree well with experimental measurements.

Collectively these papers provide just a snapshot of the exiting work that is currently being carried out to simulate homogeneous and heterogeneous catalytic systems. With breakthrough advances in both hardware and computational methods, we expect to see many more exciting developments over the next decade.