Progress Report

Research Period: January 15,1999 – January 14, 2002

First Principles Investigations and Simulations for Catalytic Properties of Bimetallic and Metal/Oxide Surfaces

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Principal Investigator:

Ruqian Wu

Professor of Physics

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I. Introduction

This report summarize our research accomplishments using funding by DOE grant (DE-FG03-99ER14948) for the period of January 15,1999 – 1/14, 2002. In the last three years, we have published 16 papers. My Postdoctoral Research Associates, my students and myself have presented our results at many conferences.

Specific Project Objectives.

Structural, kinetic, electronic, magnetic and optical properties for systems with up to 100+ atoms/cell can be determined through modern density functional approaches without any artificial parameters. Most of experimental phenomena can be reproduced with a satisfying accuracy and can be easily explained and understood in the most fundamental level from the wave functions, electronic interactions and band structures. In addition, many complex factors can be investigated separately in a controlled manner. These major advantages enable us to provide clear physical insights and clues for experimentalists to improve the performance of sophisticated catalysts.

We proposed to carry out first principles studies for various bimetallic, oxide and metal/oxide surface to improve the physical understanding in some important catalytic materials and processes. The highly precise full potentials linearized augmented plane wave (FLAPW) method was employed in our calculations. The FLAPW approach avoids the three basic approximations of the pseudopotential calculations, namely (1) the frozen core, (2) “pseudizing” the ionic potential, and thereby removing the near-nucleus wave function nodes, and (3) an approximate treatment (or complete neglect) of the nonlinearity of the core-valence exchange-correlation interaction. In addition, relativistic effects are invoked self-consistently in the FLAPW calculations.

II. Summary of progresses

a. Research accomplishments:

We began well-defined bulk crystals, perfect surfaces and pseudomorphic overlayers to address fundamental questions such as phase stability, surface relaxation, charge redistribution, surface/interface bonding mechanism and the subsequent changes in the chemical reactivity. We also calculated adsorption energies of small molecules on some of these surfaces. More recently, we shift our attention to problems with the surface defects (impurities or color centers) and nano-particles. For more direct comparison with experiments, we also developed new tools for the determination of nonlinear optical properties as second-harmonic generation (SHG) and sum-frequency generation (SFG) and have them tested on semiconductor bulks and surfaces.

Bimetallic surfaces:

To verify and explain the important correlation among chemical reactivity, adsorbate/adsorbent bonding energy and core level shift for bimetallic surfaces established by Goodman et al, we carried out FLAPW calculations for many systems with the Pd, Ni and Cu overlayers on the Ta(110), W(110), W(001), Re(0001), Ru(0001) and Rh(001) substrates. Most of theoretical results agree very well with the experiments, and the correlations established from the experimental data were nicely reproduced in the calculations (we used the value of density of states of the adlayer to represent the reactivity of the bimetallic surface). Physically, all these quantities (i.e., bonding energy, core level shift and surface reactivity) are governed by the height of an interfacial potential barrier established by pronounced charge polarizations.

Metal/oxide surface:

We have extensively studied catalytic properties of different oxide and metal/oxide surfaces, including effects of surface color centers. We have investigated properties of Au/MgO(001), Cu/MgO(001), Au/TiO_2(001) and Cu/SiO_2(0001).

The adsorption energies for adsorbates on MgO(001) are usually small using the generalized gradient approximation (GGA, PBE96) for the exchange-correlation interaction. Even when the coverage is reduced to 0.25, for example, the adsorption energy of Au/MgO(001) is still only –0.13 eV/adatom. The Au adatoms on the defected MgO(001), however, have an adsorption energy of -1.93 eV/atom. Therefore, the oxygen vacancy can strongly alter the chemical properties and appear to be essential for the adsorption of noble metals on MgO(001). The effect of O-vacancy appears to be long-ranged since the boning energy is still as large as 0.79 eV/adatom when Au is placed on the second neighbor O-site from the vacancy. Calculations to simulate the Au cluster formation around the O-vacancy are underway.

We found that the formation energy of a surface O-vacancy is 9.5 eV, a value which is quite close to its bulk counterpart 10.0 eV. In both cases, O-vacancy induces gap states at almost the same energy position, 1.8-3.3 eV above the MgO valence band. These states are strongly localized in the vacancy site and are responsible for the alternation of the surface chemistry of MgO(001). The calculated core level shifts and optical spectra were used for explanation of recent experimental results and provide means to identificatify the spatial location of the O-vacancies.

By contrast, the adsorption energy for Au on TiO_2(110) is as large as 1.48 eV/adatom. The Au/TiO_2(110) interaction is thus strong due to the smaller energy gap (1.8 eV in LDA calculations) and atomic roughness of TiO_2(110) [14]. Au is found to prefer the atop site above the 5-fold Ti surface atom. The calculated nearest Au-Ti bond length is 2.66 Å. The Au adsorbates are found not to significantly affect the atomic structure of the TiO_2(110) substrate (the Au-induced displacements of all the substrate atoms are smaller than 0.05 Å).

<u>CO and NO adsorption:</u>

Bonding mechanism, structural and electronic properties of CO adsorbates on oxide (MgO(001) and TiO_2(110)), noble metal (Au(001), Au(111), transition metal (Pt(111)) and metal oxide (Au/MgO(001)) have been investigated. For CO and NO on MgO(001),

the adsorption energies are extremely small and thus they provide ideal test cases for the accuracy and reliability of the density functional approaches to the catalysis problems.

The calculated adsorption energy sensitively depends on the choice of exchange correlation interaction approximations. The LDA adsorption energy for CO/MgO(001) is 6.0 kcal/mole, while its GGA counterpart is 3.0 kcal/mole. After long debating, it is believed now that the GGA result is closer to the truth, in general. To have a more conclusive answer for the (LDA vs GGA) debate, calculations is needed for CO and NO on NiO(001) for a direct comparison with the experiments of Wichtendahl and Freund et al. The C-O stretch frequency shows a blue-shift (33 cm^{-1} with LDA and 6 cm^{-1} with GGA).

On TiO_2(110) the CO adsorption energy obtained through GGA calculations is also unexpectedly small (4.2 kcal/mole), even though the band gap of the TiO_2(110) surface is much smaller than that of the MgO(001) surface. The calculated CO stretch frequency shows a red-shift of 23 cm^{-1} compared to that of a free CO molecule. This result agrees well with the experimentally determined value for one of the CO adsorption state (a red-shift of 28cm^{-1}). For both CO/MgO(001) and CO/TiO_2(110), the influence of CO on the atomic and electronic structures are very weak.

For CO on Au, repulsive potential barriers develop for large CO-Au distances in GGA calculations, a behavior which is very different from that on oxide substrates. Chemical interaction and hybridization prevail when $d_{C\text{-}Au}$ becomes smaller than 2.7 Å and attractive potential wells start to develop. The calculated adsorption energies are 0.2 kcal/mol, 4.1 kcal/mol and 1.3 kcal/mol for CO/Au(111), CO/Au(001) and CO/Au/MgO(001), respectively. The depths of their attractive potential wells measured from the peaks of their repulsive potential barriers, however, are 1.8 kcal/mole (for CO/Au(111)), 6.0 kcal/mole (for CO/Au(001)) and 6.1 kcal/mole (for CO/Au/MgO(001)).

Significant differences were found for the bonds between CO with metals (σ-donation and π-back donation) and with oxides (σ-covalent bonding). In addition, CO induce sizable core level shift for the Au-$4f_{7/2}$ state, despite the weakness of CO-Au interaction. Therefore, the calculated core level shifts for CO/Au(111) and CO/Au(001) are 0.20 eV and is somewhat smaller than that in (*ca.* 0.5 eV) . The calculated binding energy of the Au-$4f_{7/2}$ core state in CO/Au/MgO(001) is enhanced by 1.35 eV compared to that on the Au(001) clean surface.

Nonlinear optical properties:

We developed method and code to calculate the second harmonic generation (SHG) and now we are developing the formulism and code for the determination of sum-frequency generation based on the FLAPW method. We have studied SHG properties of various bulks (for benchmark comparisons) and surfaces as Ge/Si(001), H/Si(001), B/Si(001) and GaN(0001). For the first time, we revealed the microscopic mechanism of the strong quenching effect of H adatom on the second harmonic generation spectra of different surfaces. By contrast, Ge and B doping or coverage enhance the SHG signals of Si(001). The calculated results peak intensity, peak position and the adsorbate induce energy shift are in good agreement with experimental data available. It was found that the SHG signal is not very sensitive to the adsorbate-induced change in atomic structures, but rather depends on the surface chemistry. For GaN(0001) surface, we found that SHG signal for the N-terminated case is hundreds times stronger that that for the Ga-terminated geometry.

We recently extend the studies to H and OH/M (M=Pd. Pt and Cu) and found that these adsorbates quench the SHG signal of metal surfaces by a factor of 100 from the results for their clean cases. These results are very encouraging for detection/monitoring small atoms and molecules in chemical reactions.

S/Pt(111):

The adsorption of a sulfur atom and a sulfur molecule on the Pt(111) surface was investigated using the FLAPW method and first-principles pseudopotential CASTEP

calculations. Different sulfur coverage (1/4, 1/3 and 1 ML) and several adsorption geometries were considered. It was found that, for atomic sulfur, (i) the S-Pt bond is weakened with the increase of sulfur coverage, (ii) the most stable adsorption site changes from the fcc-hollow site to the atop site, (iii) the energies of the S-$2p_{1/2}$ and S-$2p_{3/2}$ core levels are very sensitive to the chemical environment and shift to higher binding energy with the increase of S coverage, (iv) compared to the Pt(111) clean surface, the Pt-$4f_{5/2}$ and Pt-$4f_{7/2}$ core levels are stabilized in energy upon S adsorption, (v) at small sulfur coverages the net charge transfer from Pt to S is minimal but there is a substantial shift in the Pt-4f levels, and (vi) S adsorption induces significant decreases in the density of Pt-5d states near the Fermi energy. For the case of adsorption of the the S_2 molecule, the S-S bond length is 2.1 Å with one atom near an atop position and the other on a mixed hollow-bridge site. The adsorption energy is close to 44 kcal/mol.

b. Project personnel:

Student:

We have one student, Albert Lee, participated in this research program, partially supported by the DOE fund and partially supported from the other sources. He finished his Master degree in physics on "Adsorption of Cu on the perfect and defected MgO(001)" and joined the Ph. D program in Ohio State University in 2000.

Postdoctoral Research Associate:

Dr. Z.X. Yang has been working on this project in the last two and half years. Dr. V. Gavrilenko, supported from other sources, was also involved in developing the SHG method and code.

Collaborations:

Although there is no co-PI nor subcontractor for this project, we have active collaborations with other scientists. These informal collaborations are very constructive for the quality and relevance of our theoretical work and have generated exciting science. A list of co-authors on papers acknowledging the DOE support from 1999 onward is given below.

D.W. Goodman	Texas A&M University
M. Downer	University of Texas, Austin
J.A. Rodriguez	Brookhaven National Lab
W. Weber	Ford Research Lab
Q.M. Zhang	University of Texas, Arlington

III. Ongoing research

In the following cases, most calculations are in the final stage and papers will be ready shortly.

Lithium doped MgO:

That is, Li "catalyzes" the formation of F-centers. The key question is the relative roles of the [Li^+O^-] and F-centers in controlling the reactivity of MgO. FLAPW studies of the Li-doped MgO(001) surface and the doping-effect on the vacancy formation and other chemical properties are in progress. On a Li-doped MgO(001) surface, Li and its O neighbors relax in opposite directions, in agreement with experimental results. Li impurity induces energy shifts for the MgO valence band (creating holes) in a large spatial area.

Ti doped Al_2O_3:

The diffusion/relaxation/segregation mechanisms of metal impurities are expected to vary with the openness of the surface structure and its ionicity and thus alter the surface chemical properties of oxides. This needs large unit cell and extensive structural optimization and we thus employed the CASTEP and SeQUEST (written by P.A.Schultz

in Sandia Natl Labs). We use a 90-atom cell to simulate the surface doping and found that Ti buckles largely out of the Al_2O_3 plane.

O_2 dissociation on Ag(110):

To study the dissociation pathway of an O atom or O2 molecule on Ag(110) , we are calculating the potential energy surface of O on Ag(110). A large unit cell [p(3x2)] is used to minimized the interaction among adjacent O atom/molecule.

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B. Presentations (DOE)

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"Bonding mechanism and adsorption energy of CO on Au and Au/MgO(001) surfaces", 16th NAM, Boston, (1999).

"First principles study on the adsorption of CO on TiO_2(110)", APS March Meeting (2000).

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