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14. ABSTRACT
The project personnel have performed a number of density functional calculations aimed at understanding why small Au clusters are catalytically active and why small Ag clusters have different catalytic chemistry than large ones. In addition they used advanced quantum chemistry method to test whether density functional theory is capable of providing accurate results for adsorption of oxygen, hydrogen, and propene on gold clusters. Finally they developed new methods for solving problems in quantum mechanics by using a basis set that is as efficient as plane waves (i.e. Fourier transforms) but does not automatically impose periodic boundary conditions.

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I. Summary of accomplishments

1. Adsorption of small Au and Ag clusters

Experiments have shown recently that small Au clusters catalyze a number of reactions even though the bulk gold is chemically inert. We have shown[1], by performing a number of "computer experiments" that the activity is invariably connected to surface roughness. Recently we have refined this picture[2] to show that it is the geometry of the LUMO or HOMO that controls activity, not the geometry of the cluster. We have studied adsorption of Au on stoichiometric TiO_2 and on a TiO_2 surface having oxygen vacancies. We have shown that the electrons left behind when a vacancy is formed are delocalized around the vacancy and not localized on the Ti atoms. Recent STM work by Makki (ECOSS meeting, Berlin, 2005) confirms this picture. We have also shown that addition of Au to the vacancy results in charge transfer to the Au atom and this causes a change in its chemical activity. It is very strange that the small Au_n clusters are planar and we performed high-level calculations[4] to determine the value of n for which a three-dimensional cluster is most stable.

2. How accurate are the DFT calculations?

Density functional theory is the only quantum chemical method used to perform calculations on systems of interest to catalysis. We need to know what kind of accuracy we can expect from such calculations. Since it is very difficult to characterize precisely experimentally catalytic systems, it is difficult to validate DFT by comparison with experiment. We have chosen to evaluate the accuracy of DFT by applying it to small clusters for which we can perform accurate quantum chemical calculations. We found that the results are qualitatively correct for oxygen adsorption on small Au clusters[5], but they are accurate[6] for H_2 and propene adsorption[7]. In the latter case the DFT calculations also agree with accurate measurements of binding energy to gas-phase clusters, performed in Professor Bowers's laboratory.

3. The electronic properties of linear metal clusters deposited on a metal surface

Wilson Ho has performed several spectacular experiments whose results could be interpreted very accurately by using a one-dimensional model. Unfortunately, while the data was fitted well, the model violated Pauli principle. Our theoretical analysis[8] showed that the one must use a three-dimensional model which satisfied Pauli principle and also explained why the experimental result behaved as if the system was one-dimensional.

4. Qualitative rules explaining the binding of molecule to Au and Ag clusters

We have developed an extremely simple model which showed that the results of the density functional calculations, for binding of several molecules (CO, O_2, propene) to Au and Ag clusters, can be predicted by examining the shape and the energy or either the LUMO or the HOMO orbitals[9-11]. These rules have been used recently in Bowers group to determine the structure of gas-phase metal clusters.

5. A proposal of a new system for catalytic oxidation

We performed density functional calculations to show that doped oxides might provide a new class of oxidation catalysts. A paper on this subject was accepted by *Catalysis Letters*[12] and two others are being prepared.

6. A new method for solving scattering and bound state problems in quantum mechanics

Plane wave basis set and Fourier transforms are extensively used in quantum mechanics for solving eigenvalue and dynamics problems. The use of this basis set has several advantages: accurate representation of the wave function and rapid and very accurate evaluation of derivative and Coulomb integrals. Unfortunately, these methods automatically make the system periodic and sometimes this causes artifacts in the physics of the system. We have shown[13-15] that a basis set of Chebyshev polynomials has all the good properties of the plane waves, but do not impose periodicity. We have also shown that this basis set is particularly useful when one intends to use the values of the wave function on a spatial grid as the unknown quantities in the calculation.

7. Is phenomenological kinetics applicable to catalysis problems?

Phenomenological kinetics, of the kind taught in the introductory physical chemistry courses, is extensively used to analyze the kinetics of the catalytic reactions. The results of such analysis are extensively used in industry for reactor design and in science for determining the reaction mechanism. Recently the kinetics of the catalytic reaction has been analyzed by using the kinetic Monte Carlo method, which is capable to treat realistically all the microscopic events taking place during a reaction: adsorption, migration on the surface, adsorbate morphology, reaction and product desorption. We have performed[16] extensive comparisons between the kinetic Monte Carlo results and the phenomenological theory, for the reaction of CO oxidation by Ru. We have shown that the phenomenological theory is qualitatively correct but it is not quantitatively accurate. We have explained and analyzed the reasons for the failure of the phenomenological approach.

II. Personnel associated with the research effort

Prof. Horia Metiu, Dr. Greg Mills, Ms. Burçin Temel, Dr. Bing Wang

III. Publications resulting from the research effort

1. Oxygen adsorption on Au clusters and a rough Au(111) surface: the role of surface flatness, electron confinement, excess electrons, and band gap, Greg Mills, Mark S. Gordon, and Horia Metiu, *J. Chem. Phys. 118,* 4198-4205 (2003)

2. Why is gold chemically active: geometric roughness or orbital roughness?, Steeve Chrétien and Horia Metiu, in preparation

3. Adsorption of gold on stoichiometric and reduced rutile $TiO_2(110)$ surfaces,

Amrendra Vijay, Greg Mills, and Horia Metiu, *J. Chem. Phys. 118*, 6536-6551 (2003)

4.   Where does the planar-to-nonplanar turnover occur in small gold clusters?, Ryan M. Olson, Sergey Varganov, Mark S. Gordon, Horia Metiu, Steeve Chrétien, Piotr Piecuch, Karol Kowalski, Stanislaw A. Kucharski, and Monika Musial, *J. Am. Chem. Soc. 127*, 1049-1052 (2005)

5.   The Interaction of oxygen with small gold clusters, Sergey Varganov, Greg Mills, Mark S. Gordon, and Horia Metiu, *J. Chem. Phys. 119,* 2531-2537 (2003)

6.   A study of the reactions of molecular hydrogen with small gold clusters, Sergey A. Varganov, Ryan M. Olson, Mark S. Gordon, Greg Mills, and Horia Metiu, *J. Chem. Phys. 120,* 5169-5175 (2004)

7.   The binding of the noble metal cations Au^+ and Ag^+ to propene, Ryan Olson, Sergei Varganov, Mark S. Gordon, and Horia Metiu, *Chem. Phys. Lett. 412*, 416-419 (2005)

8.   Electronic states of linear Au clusters supported on metal surfaces: Why are they like those of a particle in a box?, Greg Mills, Bing Wang, Wilson Ho, and Horia Metiu, *J. Chem. Phys. 120,* 7738-7740 (2004)

9.   Binding of propene on small gold clusters and on Au(111): simple rules for binding sites and relative binding energies, Steeve Chrétien, Mark S. Gordon, and Horia Metiu, *J. Chem. Phys. 121,* 3756-3766 (2004)

10. Density functional study of the adsorption of propene on silver clusters, Ag^q_m (m = 1 – 5; q = 0, +1), Steeve Chrétien, Mark S. Gordon, and Horia Metiu, *J. Chem. Phys. 121*, 9925-9930 (2004)

11. Density functional study of the adsorption of propene on mixed gold-silver clusters, Au_nAg_m: propensity rules for binding, Steeve Chrétien, Mark S. Gordon, and Horia Metiu, *J. Chem. Phys. 121*, 9931-9937 (2004)

12   Density functional study of the CO oxidation on a doped rutile TiO_2(110): effect of ionic Au in catalysis, Steeve Chrétien and Horia Metiu, *Catalysis Letters*, to appear

13. The minimum-error method for scattering problems in quantum mechanics: two stable and efficient implementations. Burcin Temel, Greg Mills and Horia Metiu, submitted to *J. Chem. Phys.*

14. Inelastic scattering by minimum-error method, Burcin Temel and Horia Metiu, in preparation

15. The use of Chebyshev basis set to solve eigenvalue problems: a variational method in the coordinate representation, Burcin Temel, Greg Mills, Bing Wang, and Horia Metiu, in preparation

16. A test of the accuracy of the phenomenological kinetics for the study of a catalytic system, Burcin Temel, Karsten Reuter, Matthias Scheffler, and Horia Metiu, in preparation