

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 25 - Session HC+SS-TuA

Advances in Theoretical Models and Simulations of Heterogeneously Catalyzed Reactions

Moderator: Xiaofeng Feng, University of Central Florida

2:20pm **HC+SS-TuA-1 Hindered Translator/Rotor Models for Calculating the Entropy of Adsorbed Species for Improved Micro Kinetic Models Based on Density Functional Theory Calculations**, *Liney Arnadottir, L Sprowl*, Oregon State University; *C Campbell*, University of Washington

INVITED

With the recent explosion in computational catalysis and related microkinetic modeling, the need for a fast, yet accurate, way to predict equilibrium and rate constants for surface reactions has become more important. Here a method to calculate partition functions and entropy of adsorbed species and equilibrium constants is presented. Instead of using the vibrational frequencies estimated from DFT and the harmonic oscillator approximation to calculate all modes of motion in the partition function, we use a hindered translator and hindered rotor model for the three modes of motion parallel to the surface, one for each of the two translations in the directions parallel to the surface and one for rotation about the axis perpendicular to the surface. This hindered translator and hindered rotor model joins the two limiting cases for adsorbates on a surface, the 2D ideal lattice gas (harmonic oscillator) model and the 2D ideal gas (free translator) model, making it valid over large temperature range. At the limit of low temperature, or high energy barrier, only vibrations are present and this model is the same as the harmonic oscillator approximation, while at high temperature, or low energy barrier, translations and rotations readily occur and this model becomes identical to the 2D ideal gas model for translations or the 1D free rotor model for rotations. The transition between the 2D ideal lattice gas (harmonic oscillator) model and the 2D ideal gas (free translator) model is surprisingly sharp, but modeled very closely by the hindered translator/rotor model. To verify this model, density functional theory was used to calculate adsorbate entropies of four different adsorbate species and found to agree well with experimental results.

3:00pm **HC+SS-TuA-3 CO₂ Dynamics as a Product of Formate Decomposition on Cu(111)**, *Fahdzi Muttaqien, H Oshima, Y Hamamoto, K Inagaki, I Hamada, Y Morikawa*, Osaka University, Japan

Formate (HCOO) synthesis has been experimentally clarified to occur by the Eley-Rideal (ER) mechanism,¹ which suggests that the reaction rate depends on the initial energy of impinging CO₂. Since HCOO synthesis and decomposition are reversible reactions, the energy of impinging CO₂ must be related to the energy states of desorbed CO₂ from formate decomposition. Therefore, elucidation of HCOO decomposition dynamics is important to deduce optimal conditions for catalytic HCOO synthesis.

We performed ab initio molecular dynamics analysis to elucidate the dynamics of CO₂ from HCOO decomposition on Cu(111). We first investigated the translational energy of desorbed CO₂ from the velocity of center of mass of CO₂. The calculated translational energy (shown in Fig. 1 of Supp. Info) using PBE, PBE-D2, vdW-DF1, rev-vdW-DF2, and optB86b-vdW are 0.30 eV, 0.05 eV, 0.18 eV, 0.16 eV, and 0.11 eV, respectively. Those calculated CO₂ translational energy using PBE-D2 and vdW-DFs are in reasonable agreement with the experimental estimation (0.10 eV),² while PBE fails in predicting this energy.

We then explored the rotational and vibrational energies of CO₂ from HCOO decomposition. The rotational energy of CO₂ was calculated from its moment of inertia and angular momentum. We obtained that calculated CO₂ rotational energy varies between 0.08–0.11 eV. The CO₂ vibrational energies are evaluated based on the time evolution of the bond angle, C–O bond length, and difference between two C–O bond lengths of desorbed CO₂ (shown in Fig. 2 of Supp. Info). The vibrational energy of bending, symmetric stretching, and antisymmetric stretching modes are 0.25 eV, 0.11 eV, and 0.0015 eV, respectively. The vibrational energy of desorbed CO₂ bending mode is close to the third excitation energy of the vibrational energy of bending of isolated CO₂.

In summary, the vibrational energy of desorbed CO₂ bending mode is twice larger than the translational energy. Since HCOO synthesis from CO₂ and H₂, reverse reaction of the HCOO decomposition, is experimentally

suggested to occur by the ER mechanism, our results indicate that the reaction rate of formate synthesis can be enhanced if the bending vibrational mode of CO₂ is excited rather than the translational, rotational, and/or stretching modes. These results are in contrast to the case of CO₂ dissociation, in which the CO₂ symmetric and antisymmetric stretching modes are more important to increase the dissociation rate.^{3,4}

References:

1. H. Nakano *et al.*, *J. Phys. Chem. B* **105**, 1355 (2001).
2. J. Quan *et al.*, *Angew. Chem. Int. Ed.* **56**, 3496 (2017).
3. T. Yamanaka, *Phys. Chem. Chem. Phys.* **10**, 5429 (2008).
4. B. Jiang and H. Guo, *J. Chem. Phys.* **144**, 091101 (2016).

4:20pm **HC+SS-TuA-7 Reaction Mechanisms and Nature of Active Sites on Alloy Catalysts: Combining First-principles, Microkinetic Modeling, and Reaction Kinetics Experiments**, *Manos Mavrikakis*, University of Wisconsin - Madison

INVITED

Using a combination of first-principles calculations, microkinetic modeling, and reactivity experiments, we establish a rigorous framework for developing a fundamental mechanistic understanding of chemical reactions catalyzed by heterogeneous catalysts. First, and through an iterative process between these three components of our research, we demonstrate unique insights derived on the nature of the active site. Then, based on that understanding, and insights derived for the importance of atomic-scale structure sensitivity, we show how we can provide guidance to inorganic synthesis for preparing alloys, which are predicted to hold promise for improved activity and selectivity for the reactions of interest.

5:00pm **HC+SS-TuA-9 CO₂ Hydrogenation on Defect-Laden Hexagonal Boron Nitride**, *Tao Jiang, T Rawal, D Le, R Blair, T Rahman*, University of Central Florida

Defect-laden hexagonal boron nitride (*dh*-BN) has recently been shown [1] to be an excellent metal-free hydrogenation catalyst. Here, we employ density functional theory based calculations, including van der Waals interaction, to examine the reactivity of single layer *dh*-BN with N vacancy (V_N) or N substitution by B (B_N), toward the CO₂ hydrogenation to alcohols. To begin with, we find that CO₂ binds strongly at the B sites (near the vacancy) with binding energy of 1.66 eV. Next, we find that formic acid, an important reaction intermediate, chemisorbs molecularly on *dh*-BN with these defects (V_N and B_N) with adsorption energy of -1.82 eV and -0.83 eV, respectively. Through detailed comparison of the adsorption geometries and energetics of the various reactants and intermediates, we conclude that *dh*-BN with V_N defect, rather than B_N , is more suitable a catalyst for purposes here. The potential energy for the decomposition of formic acid (HCOOH → HCO + OH) on *dh*-BN with V_N is found to be -1.12 eV, indicating an exothermic reaction. The activation barrier for this reaction turns out to be 0.39 eV. We present the reaction pathways and their energetics for further hydrogenation of formic acid to form methanol or to dissociate into CO and H₂O. Reaction rates and turn over frequencies are next calculated using kinetic Monte Carlo simulations to obtain evaluate the propensity of *dh*-BN to serve as a catalyst for CO₂ hydrogenation.

[1] D. Nash *et al.*, *ACS Omega*, **1**, 1343 (2016).

Work supported in part by NSF grant CHE-1465105.

5:20pm **HC+SS-TuA-10 Interaction of Atomic Oxygen with Ag(111) and Ag(110) Surfaces: Oxygen Adsorption and Kinetics at Surface versus Subsurface**, *Sara Isbill, S Roy*, University of Tennessee

Transition metals are commonly used to catalyze transformations of small organic compounds, but the mechanisms of these catalytic reactions are not yet completely understood. Silver surfaces are important industrial catalysts for the partial oxidation of ethylene to ethylene oxide and methane to methanol. While significant strides have been taken towards revealing the complex chemical pathways of oxidation reactions on silver surfaces, the role of subsurface oxygen (oxygen adsorbed just beneath the surface) in surface reconstruction and oxidative catalysis by silver has yet to be elucidated. Does subsurface oxygen affect catalysis by changing the electronic and geometric properties of silver, or does it emerge to the surface to directly interact with reactants? Does it initiate or promote surface reconstructions of silver? Does the participation of subsurface oxygen change with reaction conditions, such as surface structure, surface temperature, and oxygen coverage? Answers to such questions will promote a deeper mechanistic understanding of heterogeneous catalysis by silver, and help to design more effective industrial catalysts. In the present study, density functional theory (DFT) was used to probe the interactions of atomic oxygen with the surface and subsurface of Ag(111) and Ag(110) surfaces. The goal was to investigate the adsorption and

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kinetics of surface and subsurface oxygen at different coverages on the metal surfaces, and examine their effects on the structural and catalytic properties of silver. On the Ag(111) surface, it was found that both surface and subsurface adsorption energies decreased with oxygen coverage, but surface adsorption weakened more drastically than subsurface adsorption, resulting in oxygen binding more strongly to the subsurface than to the surface at coverages above 0.5 ML. In contrast, surface adsorption remained stronger than subsurface adsorption at higher coverages on the Ag(110) surface. Calculations also show that kinetic barriers for formation of subsurface oxygen or its emergence into the surface are strongly dependent on coverage, indicating that the direct participation of subsurface oxygen in catalysis might strongly depend on coverage. Overall, our results provide valuable insight into the competition between adsorption and kinetics of oxygen on different facets of the silver surface, the importance of charge transfer in the binding and motion of atomic oxygen on silver, and the role of subsurface oxygen in catalysis by silver.

5:40pm **HC+SS-TuA-11 Electronic Structure and Catalytic Properties of Au/h-BN Composite System**, *Takat Rawal, T Jiang, D Le*, University of Central Florida; *P Dowben*, University of Nebraska - Lincoln; *T Rahman*, University of Central Florida

Rational designing of functionalized materials owning superior properties than those of their constituents is of great importance for potential applications. Herein, we study the electronic structure and catalytic properties of subnanometer sized gold nanoparticle (Au_{13}) supported on hexagonal boron nitride (h-BN) with single boron vacancy, employing density functional theory including van der Waals (vdW) interaction. The electronic interaction between Au_{13} and h-BN is strongly facilitated by the formation of covalent bonds between an Au atom and three N atoms (the first-nearest neighbors of B vacancy), giving rise to the frontier states (near Fermi energy), which spatially distribute around the corner Au atoms as well as the Au atom that occupies the B vacancy site. We examine CO oxidation, as a prototype reaction, on $Au_{13}/h-BN$ via the peroxy-type (OOCO) reaction path. Our results reveal that the highly active sites for CO activation are the corner Au atoms where the frontier states are localized. The strong affinity of CO to bind at those sites, with binding energy of 0.84 eV, can also be understood in terms of the negatively charged Au atoms. The reaction energy and the activation barriers for the reaction $OOCO^* \rightarrow CO_2(g) + O^*$, are found to be -2.28 eV and 0.10 eV, respectively whereas they are -1.89 eV and 0.12 eV for the reaction $CO^* + O^* \rightarrow CO_2(g)$. These results suggest that Au/h-BN composite can catalyze the CO oxidation even at the low temperature.

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