Catalytic Ethanol Decomposition: A Case Study in Reducing Brute-Force DFT Work for Surface Reactivity by Combining BEP and Scaling Relations.'

Peter A. Ferrin[1], Dante Simonetti, Shampa Kandoi[1], James A. Dumesic[1], Jens Nørskov[1,2], and Manos Mavrikakis[1]*
[1]University of Wisconsin-Madison, Madison, WI 53706
[2]Technical University of Denmark, Lyngby, Denmark,
*manos@engr.wisc.edu

Introduction

Ethanol is an important industrial chemical, both as a fuel and as a feedstock for other chemicals. Additionally, it can be used as a model molecule for selectivity of C-O and C-C bond cleavage, as it is the simplest molecule containing both types of bonds. The relative ease of cleavage of these two bonds determines the overall reaction product distribution. Previous work in our group has studied this reaction on the Pt (111) surface using density functional theory (DFT) [1]. There they found a Brønsted-Evans-Polanyi (BEP) relationship between the final state and the transition state for C-O and C-C cleavage. A second correlation (called the 'scaling relation) has also been recently developed by Abild-Pedersen, et al. [2] that relates the energy of adsorbates to the binding energy of the atoms through which they adsorb to transition metal surfaces. Our current work has a two-fold purpose. First, using the two correlations described above, extend the analysis of ethanol decomposition from a single metal to a generalized catalytic surface using very few inputs. Second, provide a simple kinetic model that predicts experimental trends in the activity and selectivity of ethanol decomposition, to establish the utility of the synthesis of the two correlations described above.

Materials and Methods

DFT calculations used in this study were performed using the DACAPO total energy program [3] with the PW91-GGA functional. Ionic cores were described by ultrasoft pseudopotentials. The (111) of fcc and (0001) facets of hcp metals were modeled using a 3x3 unit cell and periodic boundary conditions. Transition state calculations were made using the nudged-elastic-band method.

Experimental verification of the models developed in this study was done using activity tests of six transition-metal catalysts (Cu, Pt, Rh, Ru, Ir, and Pd). The catalysts were synthesized using incipient wetness impregnation of carbon black. The number of catalytic sites on these catalysts was calculated using CO chemisorption. Reaction kinetics measurements were taken at 523 K and 1 atm pressure in an apparatus described elsewhere[4]. The incoming ratio of H_2 and Ethanol was kept constant at 4:1. The effluent gas stream was analyzed using a gas chromatograph (GC) and TCD detector. The effluent liquid was condensed in a gas-liquid separator and drained for GC analysis.

Results and Discussion

First, we completed a set of ethanol decomposition calculations on Ru(0001) using a similar approach to that of reference [1]. We found that the BEP correlation for C-C and C-O cleavage on Ru was substantially similar to that found on Pt, suggesting its universality for the ethanol decomposition reaction. Combining the DFT data on Ru (0001) with the universal scaling relation of Abild-Pedersen, et al [5], we can then calculate the binding of intermediates for C-C and C-O bond cleavage of all $CH_xCH_yOH_z$ species on any transition metals using only four DFT-derived parameters: the binding energy of C, O, CO, and H on each metal surface. This information combined with the BEP relation allows for a description of the entire potential energy surface for ethanol decomposition on a generalized surface.

Using a simple kinetic model based on the correlation-derived potential energy surface, we can then predict the activity and selectivity of multiple catalysts for this reaction. While the absolute magnitude of the turnover frequency (TOF) for ethanol decomposition in our model differs from that of experiment by ~2 orders of magnitude, normalized TOF values show that trends are reasonably well described, with variation of less than ½ an order of magnitude. (See figure 1) Additionally, selectivity of C-C vs. C-O cleavage is also reasonably well predicted by the simple model employed.
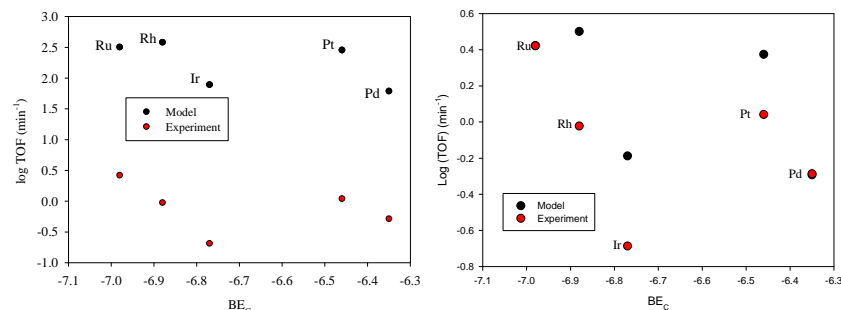

Figure 1: Model and experimental absolute (left) and normalized (right) log (TOF) for C-C bond cleavage on five transition metals vs. the C binding energy of each metal. Model and experimental TOF on Cu were very both low.

Significance

The work presented here illustrates the power of combining simple correlations to reduce the computational work necessary to predict reactivity trends across catalyst surfaces. While the model presented here is relatively simple, it is able to capture the relevant trends in reactivity across surfaces with only a few DFT-derived inputs. This allows an extension of computational resources to more complex reaction phenomena.

References
1. Alcala, R., Mavrikakis, M. Dumesic, J. A. *J. Catal.* 218, 178 (2003).
2. Abild-Pedersen, F., Greeley, J., Studt, F., Rossmeisl, J. Munter, T. R., Moses, P.G., Skulason, E., Bligaard, T, Nørskov, J. K. *Phys. Rev. Lett.* 99 (2007)
3. Hammer, B., Hansen, L. B., Nørskov, J. K.. *Phys. Rev. B* 59, 7413 (1999)
4. Spiewak, B. E. Shen, J., Dumesic, J. A. *J. Phys. Chem.* 99, 17640 (1995)