Trends in the Reactivity of CO and Light Oxygenates on Subnanometer Metal Clusters: A Density Functional Study

Jeffrey P. Greeley[1*], Faisal Mehmood[2], Daniel Torres[1], Paul C. Redfern[2], Peter Zapol[2,3], Stefan Vajda[1,3], and L. A. Curtiss[1,2,3]

[1]*Center for Nanoscale Materials, Argonne National Laboratory,*
[2]*Materials Science Division, Argonne National Laboratory,*
[3]*Chemical Sciences and Engineering Division, Argonne National Laboratory,*
Argonne, IL 60439 (USA)
*jgreeley@anl.gov

Introduction

Subnanometer catalysts are an emerging class of materials whose properties are often intermediate between those of traditional, nanoparticle-based heterogeneous catalysts (with diameters of >2 nm) and ligated homogeneous catalysts. Recently developed atom-by-atom synthetic techniques allow the clusters to be produced with exquisite size control (±1 atom) [1], and the highly undercoordinated nature of the metal atoms in the clusters can lead to unusual reactivity properties for these materials[2]. This important combination of synthetic precision and superior catalytic properties holds forth the promise that subnanometer metal catalysts will provide an important alternative to traditional catalysts for reactions ranging from CO cleanup in reformate feed streams to the production of hydrogen from cellulose and lighter oxygenates.

In this contribution, we present a systematic, Density Function Theory (DFT)-based study of the decomposition and reforming of methanol, together with the methanation of carbon monoxide, on subnanometer clusters of 4-8 metal atoms. We consider multiple transition metals for each class of reactions, and we present detailed potential energy diagrams for the various reaction networks. For selected calculations, we rigorously analyze the impact of alumina supports on the energetics of the various reactions, and we describe important trends that emerge from our analysis, including the existence of kinetic/thermodynamic correlations, the effect of supports on the cluster reactivity, and the change in the clusters' activity at different points in the periodic table.

Materials and Methods

Periodic, planewave DFT calculations are performed for all reaction pathways. Both the VASP and Dacapo codes are employed, and the PW91 and RPBE functionals are used; excellent consistency is found between the two codes for all reactions. Planewave cutoffs of 25 Ry are used. Cluster shapes and adsorbate geometries are fully optimized according the Hellman-Feynman forces acting on the systems, and the optimized spin structures of the clusters, as a function of the adsorbate coverages, are determined. For the alumina surfaces, the (010) surface of theta alumina is used. All transition states are determined using a variation on the Nudged Elastic Band algorithm[3], and reaction rates are estimated using standard transition state rate theory.

Results and Discussion

Our results indicate that methanol decomposition on Pd_4 will proceed preferentially through either C-H or O-H bond scission; C-O scission, in contrast, has a prohibitively high barrier at typical reaction conditions (~200°C), and no evidence is found that dimethyl ether (a reaction product that is occiasionally observed in studies of methanol activation on supported Pd catalysts) will be formed on unsupported clusters. Activation barrier differences of ~0.1 eV are found for most elementary reaction steps when the cluster size is increased from 4 to 8 atoms, and similar differences are determined when the clusters are supported on (010) theta alumina. Co_4 clusters are found to show enhanced exothermicity than Pd for methanol decomposition. On both metals, and for all cluster sizes, however, the thermodynamic driving force for formation of adsorbed CO is high, implying that high CO coverages will be found on the clusters and that high temperatures are required to avoid CO poisoning under realistic reaction conditions.

For CO hydrogenation to methane on subnanometer Ni_4, Co_4, and Fe_4 clusters, cleavage of the C-O bond (either through C-O itself or through a C-OH intermediate) is the rate-determining step, and all reaction intermediates are bound less strongly on Co and Fe than on Ni.

Finally, for all elementary reactions associated with both methanol decomposition and CO hydrogenation, clear correlations between the kinetics and thermodynamics of the various elementary steps are found. These correlations are expected to reduce the need to explicitly calculate transition state structures on other clusters of interest and, thereby, to greatly facilitate the rapid development of potential energy surfaces on such clusters.

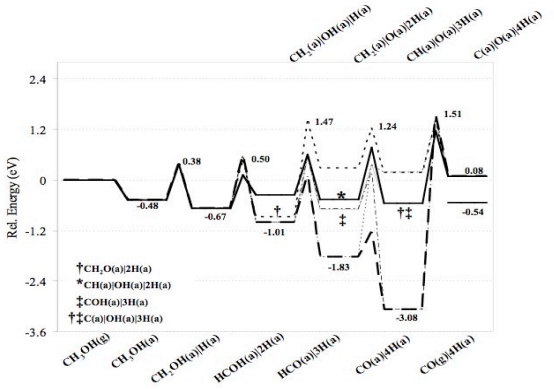

Figure 1. Decomposition of methanol through initial C-H bond scission on Pd_4 clusters.

References

1. Vajda et al., *Top. Catal.* **2006**, *39,* 161.
2. Vajda et al., *Ang. Chem. Int. Ed.* **2008**, *accepted.*
3. Henkelman, G., Jonsson, H., *J. Chem. Phys.* **2000**, *113*, 9901.

This work was supported by the U. S. Department of Energy, Basic Energy Sciences, under contract DE-AC02-06CH11357.