DFT modeling of selective reduction of acetic acid to acetaldehyde on Pt-based bimetallic catalysts

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Introduction

Carboxylic acids are the most widely used precursors for the production of aldehydes because they are less expensive and easy to synthesize. Studies have been done successfully for the reduction of carboxylic acids without any α-hydrogen atoms. A significant amount of work has also been performed to study the use of iron oxides as catalysts for the selective reduction of acetic acid. It has been found that high selectivity toward the production of acetaldehyde can be obtained over Fe_2O_3, Pt/Fe_2O_3, and Pd/Fe_2O_3 catalysts[1,2].

The main objective of the current research project is to study the performance of Pt-based bimetallic catalysts for the selective reduction of acetic acid to acetaldehyde. Hydrogenation of acetic acid to ethanol has been studied using Density Functional Theory (DFT) on Pd(111), Re(0001) and PdRe alloy surfaces[3]. In this work, a plausible mechanism for acetic acid hydrogenation to ethanol has been stated, according to which, acetic acid dissociates to form an acetyl surface intermediate. Rachmady and Vannice have formulated a similar mechanism on Pt(111) surface based on experimental studies[4]. The Pt/Ni bimetallic catalyst is an excellent model system to determine the effect of bimetallic formation on the catalytic activity and selectivity. The bimetallic surfaces show significantly different catalytic properties, and work done in our group has shown that these properties can be correlated to the values of the surface d-band center[5-8]. Hence, we plan to study the kinetics of this mechanism initially on Pt and Pt/Ni bimetallic surfaces and then expand these studies to other bimetallic systems.

Materials and Methods

Self-consistent periodic slab calculations were carried out based on gradient corrected DFT to produce the theoretical results. These DFT calculations were carried out using the plane-wave pseudopotentials program VASP (Vienna *ab inito* Simulation Package) developed at the Technical University of Vienna. The PW91 functional was used to describe the exchange correlation term. The Vanderbilt ultrasoft pseudopotentials were used to describe the core electrons and the nuclei of the atoms. A plane-wave cutoff energy of 396 eV was used for the calculations. Electronic energies were calculated using a 3 x 3 x 1 *k*-point grid mesh. The adsorption of adsorbates was studied using 3×3 super cells. Four atomic layers were used, with the top two layers allowed to relax in each case.

Results and Discussion

As mentioned before, Pt(111) and Pt/Ni bimetallic surfaces were chosen as the initial model surfaces to study the partial reduction of acetic acid. DFT calculations were used to study the modes and energies of adsorption of the involved intermediates along with the overall reaction energies for the elementary steps. DFT calculations on acetic cid, acetaldehyde

and ethanol showed that the binding energy (B.E.) of the molecules decreases as the surface d-band center shifts away from the Fermi level. Figure 1 clearly shows that ethanol binds strongly than acetaldehyde on Pt(111) as well as the subsurface Ni on Pt (Pt-Ni-Pt) surface, but the trend reverses when Ni is on top of Pt (Ni-Pt-Pt). It is apparent from Figure 2 that this change in B.E. affected the overall heat of reaction for ethoxy going to ethanol, making it highly exothermic on Pt(111) and Pt-Ni-Pt surfaces, while it is endothermic on the Ni-Pt-Pt surface. These changes in the thermodynamics of reactions should affect the overall selectivity toward acetaldehyde, which would be determined by calculating the activation barriers for the elementary steps.
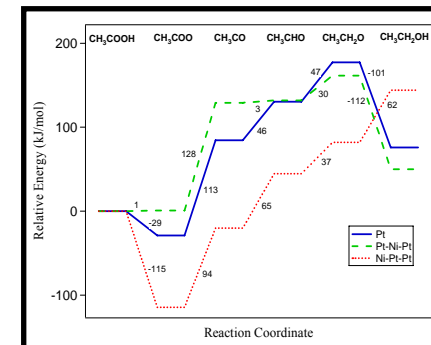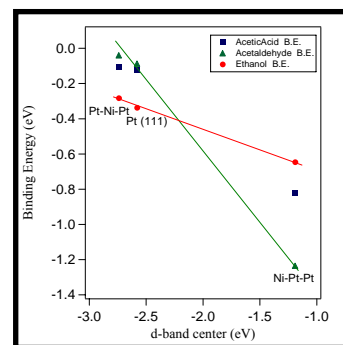

Figure 1. DFT calculated binding energies   **Figure 2.** Heats of Surface Reactions

Significance

Synthesis of aldehydes using the selective reduction of the corresponding carboxylic acid is of immense industrial importance. Aldehydes have a variety of uses, ranging from flavors and fragrances in food and chemical industries to their use as an intermediate for synthesis of agrochemicals and pharmaceutical products.[1-3] Furthermore, it has been known that the bimetallic surface can exhibit entirely different electronic and catalytic properties than the corresponding parent metal surfaces. The proposed DFT modeling on the reduction of acetic acid will also expand our correlation between the reduction selectivity with the d-band center of bimetallic surfaces, leading to possible rational design of bimetallic catalysts.

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