Mechanistic Insights into the Hydrogenolysis of Acids over Pd-Re Catalytic Surfaces

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Abstract

First-principle density functional theory calculations were carried out to probe the mechanism for hydrogenolysis of acetic acid on different Pd-Re surfaces. Activation energies were calculated for a range of possible paths for the conversion of acetic acid to ethanol. The lowest energy routes were used to construct a probable mechanism. The results show that acetic acid reacts via an acid catalyzed dehydration at either Re Lewis acid (Re) or Brønsted acid (Re-OH) to form the acetyl surface intermediate which is subsequently hydrogenated at the Pd sites to form ethanol. We examine in detail the effects of Re/Pd ratio, formal oxidation state of Re, and presence of water on the mechanism and resulting energetics.

Keywords

Density functional theory, d-band center, deprotonation energy, hydrogenolysis, Brønsted acid sites.

Introduction

Bimetallic catalysts consisting of a late transition metal alloyed with an oxophilic metal have been studied extensively for selective deoxygenation of biomass-derived molecules to produce value added chemicals and fuels. Previous efforts have examined the hydrogenolysis of glycerol as well as other polyols over a wide range of bimetallic catalysts including Pt-Re, Pt-Ru, Au-Ru, Rh-Re and Ru-Cu (Falcone et al. (2015), Maris et al. (2007), Salazar et al. (2014)). The mechanism for polyol deoxygenation of over these alloys is thought to proceed via an acid catalyzed dehydration at the oxophilic sites followed by the subsequent hydrogenation of the resulting olefin at the reducing metal sites. Chia et al. (2011) also suggested the presence of Brønsted acid sites that carry out dehydration in hydrogenolysis of polyols and cyclic ethers. Hibbits et al. (2014) carried out theoretical calculations to determine the acidity for different Brønsted acid sites on ReOx promoted M (M = Pt, Rh, Au, Ir, Ru). The most active sites showed deprotonation energy of less than 1100 kJ/mol, similar to acid-containing zeolites. Takeda et al. (2012) recently showed that similar Re-promoted catalysts namely ReOx-M (M = Ru, Rh, Pd, Ir, Pt) are also active for the hydrogenolysis of fatty acids. Despite the progress, there are relatively few studies on the mechanism for acid hydrogenolysis. Pallasanna et al. (2002) used ab initio methods to examine the hydrogenolysis of acetic acid over model Pd(111), Re(001) and PdRe (001) and proposed that the reaction proceeds via C-O activation at the Re center to form an acetyl intermediate. The acetyl intermediate is subsequently hydrogenated to form ethanol. This study provides theoretical evidence for the synergy between Pd-Re that can be effectively tuned to increase activity and selectivity, but, it assumes that Re exists in the zero valent form. Falcone et al. (2015) showed that Re (+7, +4, +2, 0) oxidation states exist for ReOx-Pt catalyst under reducing conditions. Herein, we examine the influence of Re/Pd on the mechanism for hydrogenolysis of acetic acid on ReOx-Pd. The models used take into account the presence of different oxidation states of Re as well as the influence of water on the barriers and the reaction mechanism.

Computational Details
Dispersion corrected (D2) DFT calculations were carried out to determine adsorption energies, heats of reaction and activation barriers. PBE functional was used to estimate correlation and exchange energies. The wave functions were converged within $10^{-6}$ eV. The NEB method was used to generate an initial transition state structure which was further refined using the dimer method. Solvation by water was modeled by creating ice like hexagonal structure across the adsorbed molecule. The system was allowed to equilibrate using ab-inito molecular dynamics at 300K for 1ps and then optimized using DFT. The deprotonation energy (DPE) provides a direct measure of the Brønsted acid site strength and was calculated using the approach described by Hibbitts et al. (2014).

**Results and discussion**

Irrespective of Re/Pd ratio and presence of OH groups on the surface, the reaction proceeds via the dehydration of the acid to form an acetyl intermediate which is subsequently hydrogenated to form the alcohol product. The rate-limiting step appears to be a function of Re/Pd ratio. As Re/Pd ratio increases, the energy difference between the d-band center and the Fermi level decreases and then subsequently increases. This implies that the number of antibonding states available for bonding is a function of Re/Pd ratio. Larger energy differences between the d-band center and the Fermi level result in a greater number of antibonding states available for bonding. We would therefore expect the activation barriers for hydrogenation to be low on the Re/Pd = 8.7 and high for Re/Pd = 0.15 surfaces. The dehydration activation energies on Lewis acid sites follow the reverse trend as expected- higher Re/Pd ratios result in high activation barriers while surfaces with lower Re/Pd ratios have lower activation barriers.

The activation barrier for dehydration on Brønsted acid sites correlate with the deprotonation energies of the sites. Surfaces with Re/Pd ratios of 0.15 resulted in the lowest values of DPE (<1100 kJ/mol) whereas surfaces with Re/Pd ratios 8.7 showed the highest DPE values. The calculated dehydration barrier was found to be ~35 kJ/mol lower on Re/Pd = 0.15 than Re/Pd = 8.7.

The system with Re/Pd = 0.15 was solvated in water. The dehydration barriers were found to increase in the presence of the water since Brønsted acid sites are stabilized by hydrogen bond interactions with surrounding water molecules, thus, making it more difficult to abstract proton from the site and double protonate the acid before dehydrating it.

A new set of models were constructed to examine the higher oxidation states of Re (+4, +3 +2) with Re/Pd = 7. Current calculations indicate that the DPEs of higher oxidation states of Re are lower than that of Re (I). The dehydration barriers are expected to scale accordingly.

**Conclusions**

In this work, we have shown that the rate-limiting step is a function of electronic structure of the metal alloy, which is controlled by the Re/Pd ratio. In all cases, the minimum energy path involves acid catalyzed dehydration of acid to form the acetyl intermediate, followed by hydrogenation to form acetaldehyde species and subsequent hydrogenation to ethanol. Over the range of Re/Pd ratios examined, the dehydration barriers decrease whereas the hydrogenation barriers increase with decreasing the Re/Pd ratio.

**References:**


![Figure 1: Transition state (a) and product state (b) for Brønsted acid catalyzed dehydration on Re/Pd = 8.7](image-url)