Protecting the Fe Surface from Deactivation: Characterizing Pd’s Effect in the Pd/Fe Hydrodeoxygenation Catalyst

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Introduction
The replacement of liquid fossil fuels with sustainable biofuels is of significant interest to the scientific community, but currently faces numerous challenges. For bio-oils produced using pyrolysis, the most significant challenge is overcoming the high oxygen content of the bio-oils. Recent work on the hydrodeoxygenation (HDO) of phenolics has shown that noble metal promoted Fe based bimetallic catalysts have an exceptional high catalytic activity for removing the oxygen without affecting the carbon species [1,2]. The high catalytic activity of these Fe based bimetallic catalysts occurs because of a synergy between the noble metal promoter and the surface Fe [1]. However, the nature of this synergy is not well understood. In our previous work [3,4], we have established that the surface Fe is likely the active site for the adsorption and HDO of phenolics on bimetallic surfaces. The question remaining is what function does the noble metal promoter have in the bimetallic HDO catalyst? In this work, the effect of Pd doping on the reducibility of α-Fe₂O₃ and its catalytic consequences on the HDO of phenolics over the reduced Pd/Fe bimetallic catalysts was investigated via theory using density functional theory (DFT) with the results being compared to experiment.

Materials and Methods
Our theoretical calculations were performed using the Vienna Ab Initio Simulation Package (VASP) with the DFT+U method in order to better model the strong, onsite Coulombic interactions known to be present in metal oxides. The models were performed using p(1x1) supercells with symmetric surfaces with Pd promoters added to and oxygen removed from both surfaces exposed to vacuum. The energetic results were analyzed by calculating the vacancy formation energy and surface energy with respect to the formation of water while the electronic interactions during Pd adsorption and oxygen removal were characterized using the system’s density of states (DOS), differential charge density, and Bader charge analysis. A more detailed description of the methods can be found in the work by Hensley, et al.[5]

Results and Discussion
The experimental temperature programmed reduction of Fe₂O₃ nanoparticles showed that the presence of Pd on the surface significantly decreases the temperature required to reduce Fe oxide to metallic Fe (Figure 1a). We modeled this reduction by placing Pd on the α-Fe₂O₃ (0001) surface and calculated the energy required to remove an oxygen from the surface along with the surface energy of the complete and partially reduced surfaces (Figure 1b). Our results showed that the presence of Pd on the oxide surface reduced the energy required to form oxygen vacancies by 0.2-0.8 eV. From the surface energy results (Figure 1b), it is clear upon the creation of an oxygen vacancy, the Pd promoted surfaces become more stable while the clean Fe₂O₃ surface becomes less stable. These results show that the presence of Pd on the Fe₂O₃ surface energetically stabilizes the reduced Fe state. In addition to the energetic results, theory based electronic analyses, along with experimental x-ray photoelectron spectroscopy, showed that the adsorbed Pd partially donated electrons to the exposed Fe which promotes the reduction of the Fe oxide to metallic Fe. Furthermore, the addition of hydrogen to the surface with and without Pd showed that the presence of Pd on Fe₂O₃ promoted the formation of water over hydroxyl groups. Overall, our results show that the enhanced reduction of the Pd on Fe₂O₃ surfaces is caused by the electronic stabilization of the reduced metal surface and the promotion of water formation. The stabilization of the metallic Fe state, along with the increased favorability of water formation, likely protects the HDO active Fe surface from oxidation during catalysis.

Figure 1. Part (a) is the temperature programmed reduction of Fe₂O₃ nanoparticles in the absence and presence of Pd. The inserts show the surfaces used to model each experimental system. Part (b) is the theory calculated surface energy for the model Fe₂O₃ surfaces in the absence (Complete) and presence (Vacancy) of an oxygen vacancy.

Significance
The fundamental significance of this work is that we able to identify the function of the metal promoter in Fe based bimetallic HDO catalysts using a combination of theory and experiment.

References