289aj A Density Functional Theory Study of Methane Activation on Pd/Pdo Based Catalysts

Brian R. Kromer, Kendall T. Thomson, and Fabio H. Ribeiro

Methane combustion is a very active area of current research since natural gas is expected to be used more and more as a source of energy in the future. Methane is also attractive because it emits the least amount of CO2 per unit energy of all the hydrocarbons. Many researchers have found palladium based catalysts to be the most promising for the methane combustion reaction. However, many aspects of this reaction, such as the reaction mechanism and the activation of the C-H bond, are not yet well understood. This research focuses on using DFT to help answer these questions.

We have conducted DFT calculations to study the adsorption of various species on two PdO surfaces (100 and 110) with and without oxygen defects. The most interesting results thus far have come from the adsorption of atomic oxygen and carbon on the surface. The most stable configuration for atomic oxygen was found to be on top of a surface oxygen. The stable configuration was not adsorption on the surface Pd atom, as would be intuitively expected. The adsorption energy of this configuration was determined to be -48 kcal/mole. Carbon was found to be the most strongly bound of all the species studied. Carbon has a tendency to displace a surface oxygen and then adsorb in its place. This configuration was determined to have an adsorption energy of -205 kcal/mole.

Some preliminary studies have also been carried out to determine the route by which methane is activated on the surface of the catalyst. We found two such potential activation mechanisms. The first showed a direct activation pathway in which the resulting species are CH3 bound to a surface Pd and H bound to a surface oxygen. The second pathway occurs when a molecular oxygen was adsorbed on the surface. The resulting species were then CH3 on Pd and OH bound to oxygen. Both activation pathways gave similar activation barriers of about 30 kcal/mole, which is within the range found by various experimental researchers.