Computational Modeling of Uranium Hydriding and Complexes

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1. Introduction

Uranium hydriding is one of the most important processes that has received considerable attention over many years\textsuperscript{1-7}. Although many experimental and modeling studies have been carried out concerning thermochemistry, diffusion kinetics and mechanisms of U-hydriding, very little is known about the electronic structure and electronic features that govern the U-hydriding process. Yet it is the electronic feature that controls the activation barrier and thus the rate of hydriding. Moreover the role of impurities and the role of the product UH\textsubscript{3} on hydriding rating are not fully understood.

An early study by Condon and Larson\textsuperscript{1} concerns with the kinetics of U-hydrogen system and a mathematical model for the U-hydriding process. They proposed that diffusion in the reactant phase by hydrogen before nucleation to form hydride phase and that the reaction is first order for hydriding and zero order for dehydriding. Condon\textsuperscript{2} has also calculated and measures the reaction rates of U-hydriding and proposed a diffusion model for the U-hydriding. This model was found to be in excellent agreement with the experimental reaction rates. From the slopes of the Arrhenius plot the activation energy was calculated as 6.35 kcal/mole. In a subsequent study Kirkpatrick\textsuperscript{3} formulated a close-form for approximate solution to Condon’s equation. Bloch and Mintz\textsuperscript{4} have proposed the kinetics and mechanism for the U-H reaction over a wide range of pressures and temperatures. They have discussed their results through two models, one, which considers hydrogen diffusion through a protective UH\textsubscript{3} product layer, and the second where hydride growth occurs at the hydride-metal interface. These authors obtained two-dimensional fits of experimental data to the pressure-temperature reactions. Kirkpatrick and Condon\textsuperscript{5} have obtained a linear solution to hydriding of uranium. These authors showed that the calculated reaction rates compared quite well with the experimental data at a hydrogen pressure of 1 atm.

Powell et al.\textsuperscript{6} have studied U-hydriding in ultrahigh vacuum and obtained the linear rate data over a wide range of temperatures and pressures. They found reversible hydrogen sorption on the UH\textsubscript{3} reaction product from kinetic effects at 21 °C. This demonstrates restarting of the hydriding process in the presence of UH\textsubscript{3} reaction product.
DeMint and Leckey\textsuperscript{7} have shown that Si impurities dramatically accelerate the U-hydriding rates.

We report our recent results of relativistic computations\textsuperscript{8} that vary from complete active space multi-configuration interaction (CAS-MCSCF) followed by multi-reference configuration interaction (MRSDCI) computations that included up to 50 million configurations for modeling of uranium-hydriding with cluster models will be presented.

\textbf{2. Results}

Figure 1 shows our computed potential energy surface for the insertion of a U site into H\textsubscript{2}. As seen from Fig.1, pure U site has to surpass a barrier of 20.9 kcal/mole for the U-hydriding. Once the barrier is surpassed a stable product is formed which is 22.4 kcal/mole more stable than the reactants. Figure 2 shows the potential energy surface of an additional H\textsubscript{2} approaching UH\textsubscript{3} as modeled by U\textsuperscript{+3} interaction with H\textsubscript{2}. The product UH\textsubscript{3} is highly ionic and thus U transfers electron density to the three hydrogens resulting in a U\textsuperscript{+3} state. As seen from Fig.2, U\textsuperscript{+3} inserts into H\textsubscript{2} spontaneously thus demonstrating the U\textsuperscript{+3} site in the product UH\textsubscript{3} binds to H\textsubscript{2} spontaneously forming a complex in which H\textsubscript{2} is separated far enough so as to cause liberation of H atoms in the presence of U.

\textbf{3. Discussion}

Our computed potential energy surfaces demonstrate a 21 kcal/mole activation energy barrier for pure U reaction with H\textsubscript{2}. However, the presence of the product UH\textsubscript{3} catalyzes the U-hydriding. We have also modeled the presence of Si impurities for the U-hydriding reaction to show that the activation barrier is lowered by the presence of Si. Our computations reveal an electron donor-acceptor model for the U-hydriding, where H\textsubscript{2} exchanges electronic density from its occupied 1\sigma\textsubscript{g} orbital to the U(6d \sigma) orbital and back donation from the U(6d \pi) orbital back to H\textsubscript{2} 1\sigma\textsubscript{u} antibonding orbital causes the dissociation of H\textsubscript{2} by U. In particular the 5f or 7s orbitals of U are not involved in the dissociation of H\textsubscript{2}. We also show that Si impurities assist the hydriding process by the spontaneous insertion of the 1\textsuperscript{D} state of Si into H\textsubscript{2}. The UH\textsubscript{3} product catalyzes the hydriding process by spontaneous formation of a complex of H\textsubscript{2} at the U\textsuperscript{+3} site, which opens up the H\textsubscript{2} bond sufficiently to cause further U-hydriding to occur spontaneously. The bond breaking process in the formation complex assists the formation of H atoms in
the presence of U. The hydrogen atoms thus formed diffuse through the cracks to cause further U-hydriding thus explaining the experimental observation of Powell et al.

REFERENCES


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We have calculated a 21 Kcal/mole activation barrier for the U-hydriding.

Figure 1 Potential Energy Surface for U-H₂ reaction

Figure 2 Potential Energy Surface for UH₃-H₂ interaction