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Effects of surface thermodynamics on hydrogen isotope exchange kinetics in palladium: Particle and flow models



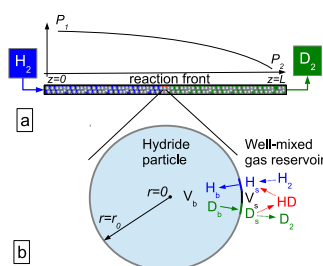
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HIGHLIGHTS

- A detailed surface reaction is incorporated into models of hydrogen isotope exchange in palladium.
- Surface hydride stability causes a large activation barrier and strong temperature dependence.
- The transition between solid-phase diffusion- and surface-limited reactions is delineated.
- The model identifies conditions for optimal performance of isotope exchange columns.

GRAPHICAL ABSTRACT



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ABSTRACT

Palladium is an important material for separation of hydrogen from other gases, separation of hydrogen isotopes, and for hydrogen storage. Its main advantages are its high selectivity and rapid, highly reversible uptake and release of hydrogen at near-ambient temperatures and pressures. Toward a more comprehensive understanding of its behavior, we present particle and continuum multiphysics mathematical models of the coupled reactive transport of hydrogen isotopes in the context of a single palladium sphere, and of flow in a packed palladium hydride bed. The models consider rates of chemical reactions and mass transport within a hydride bed, and incorporate a multistep reaction mechanism involving the metal bulk, metal surface, and gas phases. A unique feature in this formulation is that the chemical reaction model accounts for all absorption, adsorption, and diffusion activation energies. In particular, the adsorption energy is believed to depend strongly on the composition and atom-scale structure of the surface. We perform a parametric study to evaluate the effects of temperature, surface adsorption energy, and hydride particle radius on the isotope exchange kinetics. The models are useful in designing optimal hydride beds operating at various temperatures, with varied hydride particle size, and surface conditions.

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1. Introduction

Palladium and its alloys can absorb and release hydrogen under mild conditions with relatively little structural change. While too expensive for large-scale hydrogen storage, the metal has proven useful for separation. No other gases can easily enter and leave pal-

ladium, so it can serve as a membrane for highly selective separation of hydrogen from other gases in industrial processes (Ward and Dao, 1999). In a mixture of hydrogen isotopes, lighter isotopes have a significantly stronger preference for absorption, so this metal has proven valuable for isotope separation (Heung et al., 2011).

The performance of palladium in these applications is strongly sensitive to conditions at the surface. Dissociative adsorption of hydrogen is an intermediate step to its absorption, and the surface is also an intermediate during the reverse process. In gas separation applications, trace amounts of other reactive gases such as carbon

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monoxide or hydrogen sulfide can block hydrogen adsorption sites (Outka and Foltz, 1991), and significantly reduce rates of hydrogen transport through a membrane. This can be alleviated by alloying, and operating at elevated temperatures, among other strategies to facilitate desorption of blocking species (Paglieri and Way, 2002; Yun and Oyama, 2011). Transport rates are slow at low temperatures, in part because the surface hydride is quite stable, and must overcome a high activation barrier to absorb into the bulk metal or desorb as a diatomic gas molecule. Surface modifications have been proposed with the goal of destabilizing the surface hydride (Greeley and Mavrikakis, 2005).

As new strategies emerge to address these performance issues, it is helpful to have a theoretical model for a separation process that can evaluate the mechanisms behind each strategy, and account for the various phenomena that occur simultaneously, in order to determine which of them have the most important effects. Such a model should straightforwardly map to the results of experiments that can rapidly and clearly test the same hypotheses.

Isotope exchange is a valuable experimental technique that can be connected to an established modeling approach (Foltz and Melius, 1987). In this technique, one isotope, e.g. deuterium (D), is stored in the solid powdered-metal phase. Another isotope, e.g., protium (H) flows through the Pd powder such that deuterium is extracted from the powder and replaced with protium. The key advantage of this experiment is that it facilitates study of hydrogen-isotope reaction kinetics and transport rates independently of the rates of Pd lattice expansion and contraction that occur when the total amount of hydrogen isotopes stored in the Pd varies significantly. The focus of this paper will be limited to the isotope exchange reaction involving Pd hydride in the concentrated (β) phase; we emphasize that it does not directly apply to cases involving the dilute (α) hydride phase or mixed-phase systems.

Isotope exchange has been the subject of several experimental and theoretical studies (Foltz and Melius, 1987; Outka and Foltz, 1991; Fukada et al., 1995; Charton et al., 1999; Bakaev, 2009; Larson et al., 2011; James et al., 2012). Among the earliest reported studies is that of Foltz and Melius (1987) who developed a simple mathematical model of the two-way isotope exchange of protium and deuterium in Pd. They also performed experiments by injecting one isotope as a gas through a cylindrical powder bed, and measured the gas composition at the bed outlet. Using appropriate reaction rates, good agreement was found between the measured and simulated gas composition at the bed outlet. Outka and Foltz (1991) later extended this to account for blocking of adsorption sites by reactive gases. A similar model was fit to experimental data to derive an isotope separation factor that varied with temperature (Fukada et al., 1995). A more recent model improved the model of Foltz and Melius by considering the effects of temperature and pressure on the stoichiometry and gas compositions (Charton et al., 1999). These models do not explicitly connect the thermodynamics and kinetics of the metal surface. They are based on the assumption that the isotope exchange is limited by either the kinetics of the surface reaction or the diffusion of hydride in the solid. The former case is dominant for small powder particles and/or high temperatures, while the latter case is dominant for large particles and low temperatures. It is of industrial significance to have control over these factors. For example, decreasing the surface adsorption energy may result in a faster isotope exchange, hence a faster process. Previous studies of separation membranes (Ward and Dao, 1999) and catalysis of reactions involving hydrogen (Greeley and Mavrikakis, 2005) have examined the importance of surface thermodynamics on these applications. The studies of Larson et al. (2011) advanced the thermodynamic treatment of the Foltz and Melius approach. James et al. (2012) also developed a detailed model of solid-phase diffusion of hydride and deuteride.

We seek a more detailed understanding of how surface kinetics affect exchange rates, and how surface thermodynamics affect surface

kinetics. In particular, the surface hydride of palladium is more thermodynamically stable than the bulk hydride. This leads to a high occupancy of surface sites, and an activation barrier to surface-to-bulk transport. Chemical modification of the surface, such as creation of a near-surface alloy, is expected to destabilize the surface hydride, making it easier for surface hydrides to overcome the activation barrier to the bulk state, and increase the population of surface vacancies (Greeley and Mavrikakis, 2005). Varying the surface energy in a model aids understanding of its impact on predicted exchange rates.

The focus of this paper is to develop a detailed surface chemical kinetics model and to couple it to the most recent models of gas flow (Larson et al., 2011) and hydride diffusion in the solid phase (James et al., 2012), to create a more complete mathematical model of an isotope exchange reactor, thereby allowing comparison of flow rates, rates of transport through the surface, and bulk diffusion rates all within a single, unified model. However, the transport phenomena involved in such a detailed model spread over different time and length scales. Accounting for these phenomena simultaneously requires the discretization of both the gas-flow domain and the solid-particle domain, making the computational cost unreasonably high. Instead, two sub-models are developed. In the first sub-model, the particle-diffusion model of James et al. (2012) is coupled with the detailed surface-kinetics model. The results of this sub-model enable us to assess whether the surface kinetics or the bulk particle diffusion is rate limiting depending on the particle size, the temperature, and the surface adsorption energy. When this sub-model informs us that the particle diffusion is not rate limiting and can be neglected, the second sub-model can be used. In this model, the one-dimensional reactive gas flow model of Larson et al. (2011) is coupled with the detailed surface kinetics model. It is a model of an isotope exchange experiment in a cylindrical palladium hydride bed that accounts for the dependence of overall reaction kinetics on the thermodynamics of surface states. These two sub-models are sketched in Fig. 1.

2. Chemical reactions

The exchange of hydrogen and deuterium between the gas phase and the solid phase takes place in four successive steps. First, the gas is transported to the near-surface by mass convection through the boundary layer adjacent to the surface of the particles.

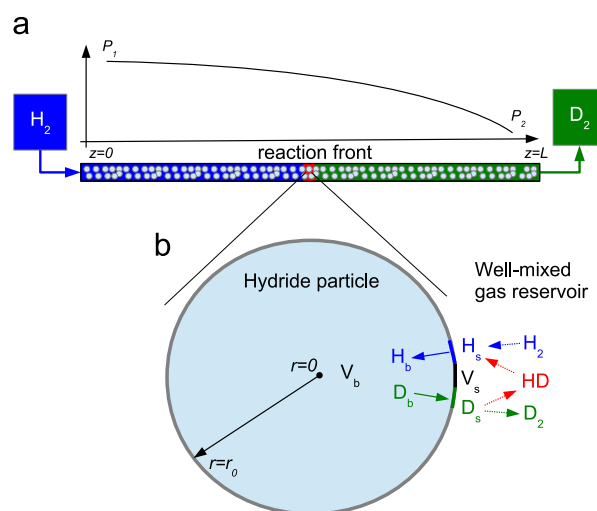


Fig. 1. Schematics of the two sub-models of hydrogen isotope exchange developed in this paper. (a) The one-dimensional reactive gas flow model coupled with the detailed surface kinetics model. The reactor tube is filled with palladium powder and connected to two tanks at pressures P_1 and P_2 . (b) A magnified view around one palladium spherical particle of radius r_0 showing the particle-diffusion model coupled with the detailed surface-kinetics model. The species V is a vacancy. The subscripts 'b' and 's' denote bulk and surface species, respectively.

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