Sulfur Poisoning of Pd and PdCu Alloy Hydrogen Separation Membranes

Submitted in partial fulfillment of the requirements for
the degree of
Doctor of Philosophy
in
Chemical Engineering

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May, 2011
Acknowledgements

To begin, I would like to thank the National Energy Technology Laboratory for funding my Ph.D. work and for providing me with access to their facilities. I would also like to thank the people that have helped me with my Ph.D. research, most importantly my Ph.D. advisors Professor Andy Gellman and Dr. Jim Miller, and my project manager at NETL, Dr. Bryan Morreale. I would also like to thank the rest of my Ph.D. committee: Professors John Kitchin, Myung Jhon, and Sridhar Seetharaman. I would also like to thank Dr. Bret Howard, Dr. Esteban Broitman, Dr. Vladimir Pushkarev, Dr. Petro Kondratyuk, and William Michalak for their help. Thanks again to all that have helped me complete my Ph.D. work.

Many of the results in Chapter 2 were adapted with permission from references [1, 2].
Abstract

Separation of high purity H$_2$ from coal-derived syngas is a key unit process in next generation gasification processes. Dense Pd and Pd$_{47}$Cu$_{53}$ (mol%) alloy membranes are promising candidates for separating H$_2$ from mixed gases due to their rare combination of high permeability and high selectivity to H$_2$ separation. However, ppm concentrations of H$_2$S, a coal gasification byproduct, can severely inhibit hydrogen transport across Pd and Pd$_{47}$Cu$_{53}$ membranes in the temperature range that the membrane would need to be operated in a gasification process (~500 to ~700 K). This thesis is an experimental investigation of hydrogen transport (H$_2$ dissociation and H atom permeation) across Pd and Pd$_{47}$Cu$_{53}$ alloy membranes. The objective of this thesis was to understand how H$_2$S inhibits hydrogen transport across Pd and Pd$_{47}$Cu$_{53}$ alloy membranes.

H$_2$S slows hydrogen transport across Pd membranes mainly by producing a Pd$_4$S film on the surface of the Pd membrane that is about an order-of-magnitude less permeable to hydrogen than Pd. In contrast to Pd, the Pd$_{47}$Cu$_{53}$ alloy is resistant to bulk sulfidation; H$_2$S slows hydrogen transport across Pd$_{47}$Cu$_{53}$ by decreasing the rate of H$_2$ dissociation on the Pd$_{47}$Cu$_{53}$ surface. H$_2$S also decreases the rate of H$_2$ dissociation on the Pd$_4$S surface, but not as significantly as that on the Pd$_{47}$Cu$_{53}$ surface.
At high temperatures (~900 K), the rate of hydrogen permeation through the Pd$_{47}$Cu$_{53}$ alloy is not significantly affected by 1000 ppm H$_2$S. It is likely that the sulfur tolerance exhibited by the Pd$_{47}$Cu$_{53}$ alloy at high temperatures is due to its resistance to bulk sulfidation. However, our results indicate that the Pd$_{47}$Cu$_{53}$ alloy is not thermodynamically resistant to sulfidation. Thin metal (Fe, Ni, Co, Cr, Mo, Pt) films on the surface of the Pd$_{47}$Cu$_{53}$ alloy catalyzed its corrosion to Pd$_{13}$Cu$_3$S$_7$ and Cu$_2$S during exposure to H$_2$S, which suggests that sulfidation of Pd$_{47}$Cu$_{53}$ is kinetically limited by a surface reaction. This result is important because understanding why Pd$_{47}$Cu$_{53}$ alloy membranes are resistant to sulfidation may lead to the development of membrane materials that can tolerate the harsh conditions of coal gasification processes.
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**Figure 4.1**  HD flow rates exiting a Cu foil catalyst bed (a) without an initial heat treatment and (b) with an initial heat treatment of the Cu catalyst in H₂ at 1000 K. Without the initial heat treatment, the HD flow rate exiting the Cu foil catalyst bed during the initial heating stage of the experiment (filled squares) is lower than the HD flow rate during the subsequent cooling stage (open squares). With the initial heat treatment, the HD flow rate during the initial cooling stage is nearly identical to the HD flow rate in the subsequent heating stage. The initial heat treatment to 1000 K, which may remove contaminants from the catalyst surface, was necessary to eliminate the hysteresis in the HD production rate.

**Figure 4.2**  (a) Experimental (points) and modeled (lines) HD flow rates versus temperature exiting a ~19 cm² Pd foil catalyst bed with three different feed gas conditions: 4.5 mL/min each of H₂ and D₂ (4.5H₂ / 4.5D₂), 9 mL/min each of H₂ and D₂ (9H₂ / 9D₂), and 4.5 mL/min each of H₂ and D₂ diluted with 9 mL/min of Ar (9Ar / 4.5H₂ / 4.5D₂). The discontinuity in the HD flow rate is due to a change in the Pd crystal structure from β-Pd-hydride to α-Pd-hydride with increasing temperature. Modeled HD flow rates were calculated using the H₂-D₂ exchange model, equation (4.1), and the solver-optimized values for ν_ads, E_ads, ν_des, E_des. (b) Total coverage of H and D atoms during H₂-D₂ exchange over the Pd foil catalyst bed. The coverage was calculated using equation 4.2 and the solver-optimized values for ν_ads, E_ads, ν_des, E_des.
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**Figure 4.9** Potential energy diagram of H$_2$ adsorption on BCC Pd$_{47}$Cu$_{53}$ and FCC Pd$_{47}$Cu$_{53}$.  

**Figure 4.10** Comparison of the HD flow rates exiting Pd, Cu, Pd$_{70}$Cu$_{30}$, BCC Pd$_{47}$Cu$_{53}$, and FCC Pd$_{47}$Cu$_{53}$ foil catalyst beds, each with a catalyst surface area of ~19 cm$^2$ and 9 mL/min of H$_2$ and D$_2$ in the feed gas.  

**Figure 4.11** Potential energy diagram for H$_2$ adsorption on Cu, β-Pd-hydride, α-Pd-hydride, Pd$_{70}$Cu$_{30}$, BCC Pd$_{47}$Cu$_{53}$, and FCC Pd$_{47}$Cu$_{53}$.  

**Figure 5.1** Comparison of the HD flow rates exiting a Pd foil catalyst bed without H$_2$S in the feed gas (Pd), a Pd$_4$S catalyst bed with 50 ppm H$_2$S in the feed gas (Pd$_4$S (50 ppm H$_2$S)) and a Pd$_4$S catalyst bed without H$_2$S in the feed gas (Pd$_4$S (0 ppm H$_2$S)), each with 9 mL/min of H$_2$ and D$_2$ in the feed gas. The Pd$_4$S catalyst with 50 ppm H$_2$S in the feed gas is much less active for H$_2$-D$_2$ exchange than the pure Pd catalyst bed without H$_2$S in the feed gas. The H$_2$-D$_2$ exchange activity of the Pd$_4$S catalyst without H$_2$S in the feed gas is similar to that of Pd, possibly because the Pd$_4$S surface is reduced to metallic Pd in the absence of H$_2$S.  

**Figure 5.2** HD flow rates exiting the (a) Pd foil catalyst bed and the (b) Pd$_4$S catalyst bed with 50 ppm H$_2$S in the feed gas, each with three different H$_2$/D$_2$/Ar feed gas combinations: 9 mL/min each of H$_2$ and D$_2$ (9H$_2$/9D$_2$), 4.5 mL/min each of H$_2$ and D$_2$ (4.5H$_2$/4.5D$_2$), and 4.5 mL/min each of H$_2$ and D$_2$ diluted with 9 mL/min of Ar (9Ar/4.5H$_2$/4.5D$_2$). Diluting the 4.5H$_2$/4.5D$_2$ feed gas with Ar (9Ar/4.5H$_2$/4.5D$_2$) does not significantly reduce the HD flow rate exiting the pure Pd foil catalyst bed, indicating desorption-limited
H₂-D₂ exchange. In contrast to Pd, the HD flow rate exiting the Pd₄S catalyst bed in the presence of H₂S is significantly reduced by diluting the H₂/D₂ feed gas with Ar, indicating that the rate of H₂ adsorption on Pd₄S is rate-limiting.

Figure 5.3 HD flow rates exiting a Pd₄S catalyst bed with (a) 4.5 mL/min each of H₂ and D₂ in the feed gas, (b) 9 mL/min each of H₂ and D₂ in the feed gas, and (c) 9 mL/min of Ar with 4.5 mL/min each of H₂ and D₂ in the feed gas, each with H₂S concentrations in the feed gas of 2000, 1000, 500, 200, 100, and 50 ppm. Increasing the H₂S concentration in the feed gas decreases the rate of H₂-D₂ exchange over Pd₄S with all three H₂/D₂/Ar feed gas combinations.

Figure 5.4. Ratio of the (a) HDS-to-H₂S and the (b) D₂S-to-H₂S mass spectrometer signals collected from the product gas during H₂-D₂ exchange over Pd₄S in the presence of 2000 ppm H₂S and with the three different feed gas conditions: 4.5 mL/min of H₂ and D₂ (4.5H₂ / 4.5D₂), 9 mL/min of H₂ and D₂ (9H₂ / 9D₂), and 4.5 mL/min of H₂ and D₂ diluted with 9 mL/min of Ar (9Ar / 4.5H₂ / 4.5D₂). The ratio of the HDS-to-H₂S and the D₂S-to-H₂S mass spectrometer signals is greater than the baseline values indicating that H₂S dissociated to SH and S on the Pd₄S surface. These ratios decrease towards the baseline at temperatures less than ~500 K, which is probably due to the very low rate of D₂ adsorption, and the low surface coverage of D atoms, at temperatures less than ~500 K (see Figure 5.4).

Figure 5.5 Pd-Cu phase diagram adapted from [32]. The Pd₄₇Cu₅₃ alloy has a body-centered-cubic (BCC) crystal structure at temperatures less than ~700 K and a face-centered-cubic (FCC) crystal structure at temperatures greater than ~800 K. In between ~700 K and ~800 K, the BCC and FCC phases co-exist in a two-phase structure.

Figure 5.6 Comparison of the HD flow rates exiting a BCC Pd₄₇Cu₅₃ foil catalyst bed without H₂S in the feed gas to the HD flow rates exiting a Pd₄₇Cu₅₃ foil catalyst bed with 50 ppm H₂S in the feed gas, each with 9 mL/min of H₂ and D₂ in the feed gas. Adding 50 ppm H₂S to the H₂/D₂ feed gas reduces the rate of HD production over the Pd₄₇Cu₅₃ catalyst. At ~680 K, there is a break in the HD flow rate exiting the Pd₄₇Cu₅₃ catalyst with 50 ppm H₂S in the feed gas, which we believe is due to a change in the Pd₄₇Cu₅₃ crystal structure from a mixed BCC/FCC structure at temperatures above ~680 K to a BCC structure at temperatures below ~680 K.

Figure 5.7 HD flow rates exiting (a) the BCC Pd₄₇Cu₅₃ foil catalyst bed without H₂S in the feed gas and (b) the Pd₄₇Cu₅₃ catalyst bed with 50 ppm H₂S in the feed gas, each with three different H₂/D₂/Ar feed gas
combinations: 9 mL/min of H<sub>2</sub> and D<sub>2</sub> (9H<sub>2</sub> / 9D<sub>2</sub>), 4.5 mL/min of H<sub>2</sub> and D<sub>2</sub> (4.5H<sub>2</sub> / 4.5D<sub>2</sub>), and 4.5 mL/min of H<sub>2</sub> and D<sub>2</sub> diluted with 9 mL/min of Ar (9Ar / 4.5H<sub>2</sub> / 4.5D<sub>2</sub>). Diluting the 4.5H<sub>2</sub> / 4.5D<sub>2</sub> feed gas with Ar (9Ar / 4.5H<sub>2</sub> / 4.5D<sub>2</sub>) does not significantly reduce the HD flow rate exiting the Pd<sub>47</sub>Cu<sub>53</sub> catalyst bed without H<sub>2</sub>S in the feed gas, whereas the HD flow rate exiting the Pd<sub>47</sub>Cu<sub>53</sub> catalyst bed with 50 ppm H<sub>2</sub>S in the feed gas is significantly reduced by diluting the feed gas with Ar. These observations indicate that the rate-limiting step in H<sub>2</sub>-D<sub>2</sub> exchange over Pd<sub>47</sub>Cu<sub>53</sub> is changed from HD desorption to H<sub>2</sub> adsorption by adding 50 ppm H<sub>2</sub>S to the feed gas.

**Figure 5.8** HD flow rates exiting a Pd<sub>47</sub>Cu<sub>53</sub> foil catalyst bed with H<sub>2</sub>S concentrations of 50, 100, 200, 500, 1000, and 2000 ppm in the feed gas and with H<sub>2</sub>/D<sub>2</sub>/Ar feed gas flow rates of (a) 4.5 mL/min of H<sub>2</sub> and D<sub>2</sub>, (b) 9 mL/min of H<sub>2</sub> and D<sub>2</sub>, and (c) 4.5 mL/min of H<sub>2</sub> and D<sub>2</sub> diluted with 9 mL/min of Ar. Increasing the H<sub>2</sub>S concentration in the feed gas decreases the rate of HD production over Pd<sub>47</sub>Cu<sub>53</sub>.

**Figure 5.9** HD flow rates exiting a Pd<sub>47</sub>Cu<sub>53</sub> foil catalyst bed at 623 K versus time after removing 50 ppm H<sub>2</sub>S from a feed gas with 9 mL/min each of H<sub>2</sub> and D<sub>2</sub>. The HD flow rate increases sharply immediately following removal of H<sub>2</sub>S from the feed gas, and then the flow rate increases more gradually until it reaches a steady-state ~30 minutes. The steady-state flow rate is still below the HD flow rate exiting a clean Pd<sub>47</sub>Cu<sub>53</sub> foil catalyst bed that had never been exposed to H<sub>2</sub>S. This result indicates that, in addition to blocking H<sub>2</sub> adsorption sites, H<sub>2</sub>S also reacts with the Pd<sub>47</sub>Cu<sub>53</sub> surface and irreversibly changes the H<sub>2</sub>-D<sub>2</sub> exchange activity of Pd<sub>47</sub>Cu<sub>53</sub>.

**Figure 5.10** HDS-to-H<sub>2</sub>S and D<sub>2</sub>S-to-H<sub>2</sub>S mass spectrometer signal ratios in the product gas during H<sub>2</sub>-D<sub>2</sub> exchange over a Pd<sub>47</sub>Cu<sub>53</sub> foil catalyst bed in the presence of 1000 ppm H<sub>2</sub>S. The HDS-to-H<sub>2</sub>S and D<sub>2</sub>S-to-H<sub>2</sub>S mass spectrometer signal ratios are significantly higher than the baseline, indicating that H<sub>2</sub>S dissociates to SH and S on the Pd<sub>47</sub>Cu<sub>53</sub> surface.

**Figure 5.11** Comparison of the HD flow rates exiting the Pd<sub>70</sub>Cu<sub>30</sub> catalyst bed without H<sub>2</sub>S in the feed gas to the HD flow rates exiting the Pd<sub>70</sub>Cu<sub>30</sub> catalyst bed with 50 ppm H<sub>2</sub>S in the feed gas, each with 9 mL/min of H<sub>2</sub> and D<sub>2</sub> in the feed gas. The rate of HD production over Pd<sub>70</sub>Cu<sub>30</sub> is significantly reduced by adding 50 ppm H<sub>2</sub>S to the feed gas.
Figure 5.12 HD flow rates exiting the (a) Pd<sub>47</sub>Cu<sub>53</sub> foil catalyst bed without H<sub>2</sub>S in the feed gas and the (b) Pd<sub>47</sub>Cu<sub>53</sub> foil catalyst bed with 50 ppm H<sub>2</sub>S in the feed gas, each with 9 mL/min of H<sub>2</sub> and D<sub>2</sub> (9H<sub>2</sub> / 9D<sub>2</sub>), 4.5 mL/min of H<sub>2</sub> and D<sub>2</sub> (4.5H<sub>2</sub> / 4.5D<sub>2</sub>), and 4.5 mL/min of H<sub>2</sub> and D<sub>2</sub> diluted with 9 mL/min of Ar. Diluting the feed gas with Ar does not reduce the HD flow rate exiting the Pd<sub>70</sub>Cu<sub>30</sub> catalyst bed in the absence of H<sub>2</sub>S, indicating desorption-limited H<sub>2</sub>-D<sub>2</sub> exchange. In contrast, the HD flow rate exiting the Pd<sub>70</sub>Cu<sub>30</sub> catalyst bed in the presence of 50 ppm H<sub>2</sub>S is reduced by diluting the feed gas with Ar, indicating adsorption-limited H<sub>2</sub>-D<sub>2</sub> exchange. H<sub>2</sub>S reduces the H<sub>2</sub>-D<sub>2</sub> exchange activity of Pd<sub>70</sub>Cu<sub>30</sub> by reducing the rate of H<sub>2</sub> adsorption.

Figure 5.13 HD flow rates exiting a Pd<sub>70</sub>Cu<sub>30</sub> catalyst bed with (a) 4.5 mL/min each of H<sub>2</sub> and D<sub>2</sub> in the feed gas, (b) 9 mL/min each of H<sub>2</sub> and D<sub>2</sub> in the feed gas, and (c) 9 mL/min of Ar with 4.5 mL/min each of H<sub>2</sub> and D<sub>2</sub> in the feed gas, each with H<sub>2</sub>S concentrations in the feed gas of 2000, 1000, 500, 200, 100, and 50 ppm. Increasing the H<sub>2</sub>S concentration in the feed gas decreases the rate of H<sub>2</sub>-D<sub>2</sub> exchange over Pd<sub>47</sub>Cu<sub>53</sub> with all three H<sub>2</sub>/D<sub>2</sub>/Ar feed gas combinations.

Figure 5.14 Comparison of the HD flow rates exiting Pd<sub>4</sub>S, Pd<sub>70</sub>Cu<sub>30</sub>, and Pd<sub>47</sub>Cu<sub>53</sub> foil catalyst beds with (a) 50 ppm H<sub>2</sub>S in the feed gas and (b) 2000 ppm H<sub>2</sub>S in the feed gas, each with 9 mL/min of H<sub>2</sub> and D<sub>2</sub> in the feed gas. In the 50 to 2000 ppm H<sub>2</sub>S range, the rate of HD production over Pd<sub>4</sub>S is the highest followed by Pd<sub>70</sub>Cu<sub>30</sub> and Pd<sub>47</sub>Cu<sub>53</sub>.

Figure 6.1 H<sub>2</sub> fluxes through Pd, Pd<sub>47</sub>Cu<sub>53</sub>, Pd<sub>47</sub>Cu<sub>53</sub> with a 1 µm Pd film on the surface (1µmPd / Pd<sub>47</sub>Cu<sub>53</sub>), and Pd<sub>47</sub>Cu<sub>53</sub> with a 1 monolayer Mo film on the surface (1ML Mo / Pd<sub>47</sub>Cu<sub>53</sub>) during exposure to 1000 ppm H<sub>2</sub>S at 623 K.

Figure 6.2 X-ray diffraction (XRD) patterns of a clean Pd<sub>47</sub>Cu<sub>53</sub> foil, a Pd<sub>47</sub>Cu<sub>53</sub> foil after 6 hours of exposure to 1000 ppm H<sub>2</sub>S at 623 K, and a Pd<sub>47</sub>Cu<sub>53</sub> foil with a monolayer Mo film on the surface (1ML Mo / Pd<sub>47</sub>Cu<sub>53</sub>) after 6 hours of exposure to 1000 ppm H<sub>2</sub>S at 623 K. The monolayer Mo film catalyzed the corrosion of Pd<sub>47</sub>Cu<sub>53</sub> to Pd<sub>13</sub>Cu<sub>3</sub>S<sub>7</sub> and Cu<sub>2</sub>S.

Figure 6.3 XRD patterns of a Pd<sub>47</sub>Cu<sub>53</sub> foil with a 1 µm Pd film on the surface before H<sub>2</sub>S exposure (top, blue) and after 6 hours of exposure to 1000 ppm H<sub>2</sub>S at 623 K (bottom, red). Only peaks associated with Pd and Pd<sub>47</sub>Cu<sub>53</sub> are present in the diffraction pattern of composite foil before H<sub>2</sub>S exposure. Peaks associated with Pd<sub>4</sub>S dominate the
diffraction pattern of the Pd / Pd$_{47}$Cu$_{53}$ foil after 6 hours of H$_2$S exposure.…………………………………………………………………….135

**Figure 6.4**  X-ray photoelectron spectroscopy depth profile of the Pd$_{47}$Cu$_{53}$ foil with a 1 µm Pd film on the surface after 6 hours of exposure to 1000 ppm H$_2$S in H$_2$ at 623 K showing the Pd, Cu, and S concentrations versus depth from the surface to about 200 nm into the bulk. There is a significant amount of Cu in the near surface region, indicating that the Pd film extracted Cu from the Pd$_{47}$Cu$_{53}$ foil during sulfidation………………………………………………………..137

**Figure 6.5**  Scanning electron micrograph (left) with sulfur energy dispersive spectroscopy map (right) of a cross-section of the Pd$_{47}$Cu$_{53}$ foil with a 1 µm Pd film on the surface after 6 hours of exposure to 1000 ppm H$_2$S in H$_2$ at 623 K. The white region in the sulfur EDS map highlights the sulfur-rich region in the SEM image. The thickness of this sulfur-rich region is ~4 µm, which is much thicker than the original thickness of the Pd film (1 µm). XPS depth profiling (Figure 6.4) indicates that a significant amount of Cu is present in this sulfur-rich film, indicating that the Pd film extracts Cu from the Pd$_{47}$Cu$_{53}$ foil substrate during sulfidation…………………………….138
Chapter 1

General Introduction

1.1 Summary

Dense Pd membranes are promising candidates for hydrogen separation from mixed gases because of their near-infinite selectivity for H\textsubscript{2} separation and very high permeability. However, Pd membranes are not viable for hydrogen separation from sulfur-containing gases, such as those derived from coal gasification, because H\textsubscript{2}S can severely inhibit hydrogen transport across Pd membranes in concentrations as little as ppm-levels. PdCu alloys show sulfur tolerance relative to Pd at high temperatures (~900 K), but hydrogen transport across PdCu alloys is also severely inhibited by H\textsubscript{2}S at low temperatures (~600 K). The objective of this thesis is to understand how H\textsubscript{2}S slows hydrogen transport across Pd and PdCu membranes. In this chapter, the literature relevant to the objective of this thesis is reviewed and the scope of this thesis is outlined.
1.2 Hydrogen from coal gasification

About 45% of the electricity generated in the United States in 2009 was derived from coal, mainly coal combustion power plants, and that percentage is not expected to change significantly for at least 25 years [3]. However, coal combustion power plants utilize only about one-third of the energy available in coal and were responsible for about 36% of the total CO$_2$ emissions in the United States in 2008 [4]. Next generation gasification processes are being developed that will have better efficiency, reduced CO$_2$ emissions, and more versatility than coal combustion power plants.

In contrast to coal combustion, which uses the heat generated from burning coal to drive a steam turbine, coal gasification produces mainly CO and H$_2$ (syngas) which can be used in a variety of ways. Syngas can be used to generate electricity in a gas/steam turbine combined cycle; or to produce liquid fuels via Fischer-Tropsch synthesis; or to produce H$_2$ for use in fuel cells or as a chemical commodity. H$_2$ production from syngas requires an increase in the H$_2$ yield via the water gas shift reaction, CO + H$_2$O $\leftrightarrow$ CO$_2$ + H$_2$, followed by H$_2$ separation from the H$_2$/CO$_2$ gas mixture.

Pressure swing adsorption is currently the most common industrial process for high purity (99.99%) H$_2$ separation, however, operating costs of pressure swing adsorption are high [5]. Alternatively, a membrane that is selectively permeable to H$_2$ would greatly decrease the cost of hydrogen separation if the membrane could be operated at temperatures near that of the water-gas shift reaction (~500 to ~700 K). There are several different types of H$_2$ separation
membranes, including dense polymeric, microporous ceramic, dense ceramic, porous carbon, and dense metallic membranes. Of these types of membranes, only dense metallic membranes are capable of producing very high purity H₂ at temperatures near that of the water-gas shift reaction [6]. Pd and Pd alloy membranes, in particular, have received significant attention for such applications because of their very high permeability to H₂ [7-10].

### 1.3 Pd hydrogen separation membranes

Dense Pd membranes are capable of producing very high purity H₂ from mixed gases because of the unique way in which hydrogen crosses the membrane. Molecular H₂ dissociatively adsorbs on the catalytically active Pd membrane surface, producing H atoms which are able to diffuse through the bulk of the Pd lattice and associatively desorb from the opposite surface [11]. Only H atoms permeate through dense Pd membranes at a significant rate, and a nearly infinite selectivity for hydrogen separation can be achieved by the use of dense Pd membranes [9]. The rare combination of the very high H₂ dissociation activity of the Pd surface [12-16] and the very high H atom permeability of bulk Pd [8, 9, 17] distinguishes the performance of pure Pd membranes from other pure metal membranes [17].

Pure Pd membranes are not viable options for H₂ separation from coal-derived gases because H₂S, a coal gasification byproduct, severely reduces the rate of hydrogen permeation across Pd membranes in concentrations as little as ppm-levels [9, 18, 19]. The effect of H₂S on H₂ permeation through Pd has been
studied by many groups over a wide range of temperatures (593-1173 K) and H₂S concentrations (4 to 6200 ppm H₂S) [9, 18, 20-26]. H₂S severely inhibited H₂ transport across Pd in nearly all of the experimental conditions studied [9, 18, 20, 22-26]. For example, immediately following exposure to 4 ppm H₂S, the rate of H₂ permeation through a Pd membrane was reduced to about 40% of its baseline H₂ flux and continued to decrease to less than 30% of its baseline H₂ flux over the next several days [18]. In many of the cited studies [9, 22, 25, 26], a palladium-sulfide (Pd₄S) film was observed on the surfaces of the Pd membranes following H₂S exposure. In one study [21], H₂S did not significantly reduce the rate of H₂ permeation through a Pd membrane, which was attributed to the thermodynamic instability of Pd₄S at the temperature (1173 K) of the experiment. Thus, there is circumstantial evidence that the formation of Pd₄S is at least partially responsible for retarding H₂ permeation through Pd: Pd₄S is observed when H₂ permeation through Pd is inhibited by H₂S, but H₂S has no effect on H₂ permeation through Pd at conditions where Pd₄S is unstable. The fundamental mechanisms by which H₂S and/or Pd₄S inhibit H₂ permeation through Pd, however, are not very clear.

By correlating Pd₄S growth kinetics to the decay in H₂ flux through a Pd membrane during H₂S exposure, Morreale et al. [9, 25] suggested that the very low H atom permeability of Pd₄S was responsible for the decline in H₂ flux during H₂S exposure. Others have suggested that H₂S inhibits H₂ transport through Pd by poisoning the catalytic surface for H₂ dissociation, either by blocking H atom adsorption sites [20, 22, 24, 27] or by increasing the barrier to H₂ dissociation [27, 28] or both. For example, by studying the effect of pre-adsorbed sulfur on the
temperature programmed desorption of H\textsubscript{2} on a Pd(100) surface, Burke and Madix found that each adsorbed sulfur atom blocks about 4 H atom adsorption sites. In addition to blocking H atom adsorption sites, density functional theory calculations by Wilke and Scheffler \cite{27, 28} show that pre-adsorbed sulfur atoms on the Pd(100) surface increase the barrier to H\textsubscript{2} dissociation.

In summary, Pd hydrogen separation membranes perform well in gas streams that do not contain H\textsubscript{2}S. However, Pd membranes are not viable options for hydrogen separations from gas streams that contain H\textsubscript{2}S, such as coal gasification product gases, because H\textsubscript{2}S sulfides the bulk of Pd and severely inhibits hydrogen transport across Pd membranes. PdCu alloy hydrogen separation membranes are attractive alternatives to pure Pd membranes because of their sulfur tolerance relative to Pd \cite{9, 29-31} and their high permeability to hydrogen \cite{9, 10, 18}. A brief summary of the literature regarding PdCu alloy membranes is given in the next section.

1.4 PdCu alloy hydrogen separation membranes

The Pd\textsubscript{47}Cu\textsubscript{53} (mol\%) alloy is a particularly attractive alternative to pure Pd membranes due to its high permeability, which is similar to that of Pd in the ~600 to ~700 K temperature range \cite{7, 9, 10} and its sulfur tolerance at high temperatures (~900 K) \cite{7, 9, 19}. The high permeability of the Pd\textsubscript{47}Cu\textsubscript{53} alloy is related to its crystal structure, which is body-centered-cubic (BCC) at temperatures less than ~700 K and face-centered-cubic (FCC) at temperatures
above ~800 K (see Figure 1.1) [32]. The H atom permeability of BCC Pd$_{47}$Cu$_{53}$ is about an order-of-magnitude greater than that of FCC Pd$_{47}$Cu$_{53}$ [7, 9].

![Figure 1.1](image.png)

Figure 1.1 Pd-Cu phase diagram adapted from [32]. The Pd$_{47}$Cu$_{53}$ alloy has a body-centered-cubic (BCC) crystal structure at temperatures less than ~700 K and a face-centered-cubic (FCC) crystal structure at temperatures greater than ~800 K. In between ~700 K and ~800 K, the Pd$_{47}$Cu$_{53}$ alloy has mixed BCC/FCC crystal structure. The H atom permeability of BCC Pd$_{47}$Cu$_{53}$ is about an order-of-magnitude greater than that of FCC Pd$_{47}$Cu$_{53}$.

Aside from their relatively high permeability to H$_2$, the main interest in using PdCu alloy membranes for hydrogen separation from mixed gases is due to their sulfur tolerance relative to Pd [9, 18]. There have been several studies on
the effect of H$_2$S on hydrogen permeation through PdCu alloys [7, 9, 18, 19, 21, 22, 30, 33, 34]. The results of all of these studies will not be summarized here, but the results of the Ph.D. work of Morreale [9] are the primary motivation of this thesis and his work will be summarized here briefly. Morreale characterized the effect of 1000 ppm H$_2$S on hydrogen permeation through Pd, Pd$_{70}$Cu$_{30}$, Pd$_{47}$Cu$_{53}$, and Pd$_{40}$Cu$_{60}$ membranes in the 623 to 908 K temperature range. A summary of Morreale’s results is presented in Figure 1.2, which shows the sulfur tolerance of Pd, Pd$_{70}$Cu$_{30}$, Pd$_{47}$Cu$_{53}$, and Pd$_{40}$Cu$_{60}$ membranes versus temperature. Sulfur tolerance is arbitrarily defined here as the ratio of the hydrogen flux through the Pd and PdCu membranes after 5 days of exposure to 1000 ppm H$_2$S in H$_2$ to the hydrogen flux measured during exposure to pure H$_2$:

$$\text{Sulfur Tolerance} = \frac{\text{H}_2 \text{ flux in 1000 ppm H}_2\text{S}}{\text{H}_2 \text{ flux in pure H}_2}.$$

In the 623 to 908 K temperature range, the H$_2$ flux through Pd after 5 days of exposure to 1000 ppm H$_2$S is about one-fifth the H$_2$ flux in pure H$_2$. The sulfur tolerance of the Pd$_{70}$Cu$_{30}$, Pd$_{47}$Cu$_{53}$, and Pd$_{40}$Cu$_{60}$ alloys is nearly zero at 623 K. Unlike Pd, however, the sulfur tolerance of Pd$_{70}$Cu$_{30}$, Pd$_{47}$Cu$_{53}$, and Pd$_{40}$Cu$_{60}$ increases with increasing temperature. At 908 K, all three PdCu alloys have sulfur tolerance relative to Pd and hydrogen transport through the Pd$_{47}$Cu$_{53}$ alloy is not significantly inhibited by 1000 ppm H$_2$S.
Morreale also observed that the Pd\textsubscript{47}Cu\textsubscript{53} and Pd\textsubscript{40}Cu\textsubscript{60} alloys resisted bulk sulfidation in the 623 to 908 K temperature range \cite{9}. The Pd\textsubscript{70}Cu\textsubscript{30} alloy also resisted bulk sulfidation at 908 K, but there were two different sulfur products (Pd\textsubscript{4}S and Pd\textsubscript{13}Cu\textsubscript{3}S\textsubscript{7}) observed on the surface of the Pd\textsubscript{70}Cu\textsubscript{30} alloy at 623 and 723 K. Another significant, and unexpected, result of Morreale’s Ph.D work was a link between the presence of Fe-, Cr-, and Ni-sulfide particles on the surface of

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Sulfur tolerance (ratio of the H\textsubscript{2} permeation flux after 5 days of exposure to 1000 ppm H\textsubscript{2}S to the H\textsubscript{2} permeation flux in pure H\textsubscript{2}) of Pd, Pd\textsubscript{70}Cu\textsubscript{30}, Pd\textsubscript{47}Cu\textsubscript{53}, and Pd\textsubscript{40}Cu\textsubscript{60} versus temperature (adapted from \cite{4}). The sulfur tolerance of Pd is roughly constant (~0.2) in the 623 to 908 K temperature range. The sulfur tolerance of the PdCu alloys is ~0.0 at 623 K, but the sulfur tolerance of the PdCu alloys increases with temperature. The Pd\textsubscript{47}Cu\textsubscript{53} alloy is completely sulfur tolerant at 908K.}
\end{figure}
PdCu alloys to improved sulfur tolerance. It is not clear how the Fe-, Cr-, and Ni-sulfide particles improved the sulfur tolerance of the PdCu alloys.

In summary, PdCu alloys are attractive alternatives to pure Pd membranes due to their high permeability and their sulfur tolerance relative to Pd at high temperature (~900 K). However, PdCu membranes are not viable for coal gasification processes because H$_2$S blocks hydrogen transport through PdCu membranes almost completely in the temperature range that the membrane would need to be operated (~500 to ~700 K).

1.5 Scope of the thesis

Although Pd and PdCu alloy membranes are not viable options for coal gasification processes, understanding how H$_2$S slows hydrogen transport through Pd and PdCu membranes, and why PdCu alloys are sulfur tolerant at high temperature, may lead to the development of advanced membrane materials that can tolerate the conditions of a coal gasification process. This thesis is an experimental investigation of hydrogen transport (H$_2$ dissociation and H atom permeation) across Pd and PdCu membrane. The aim of this thesis is to understand how H$_2$S slows hydrogen transport across Pd and PdCu membranes, and to understand why PdCu alloys are sulfur tolerant relative to Pd at high temperatures.

Pd and the Pd$_{47}$Cu$_{53}$ alloy have been used throughout this thesis as benchmarks for understanding hydrogen transport across dense metal membranes in the presence of H$_2$S. Two main experimental techniques were used in this
thesis. The rate of hydrogen permeation through Pd and Pd$_{47}$Cu$_{53}$ was measured in a membrane testing apparatus. A H$_2$-D$_2$ exchange experiment was developed in this thesis to investigate: (1) the effect of alloying Pd and Cu on the kinetics of H$_2$ dissociation and (2) the effect of H$_2$S on the rate of H$_2$ dissociation over Pd, Pd$_{47}$Cu$_{53}$, and Pd$_{70}$Cu$_{30}$ surfaces. The effect of H$_2$S on the bulk and surface compositions of Pd and Pd$_{47}$Cu$_{53}$ membranes was characterized by x-ray diffraction, x-ray photoelectron spectroscopy, and scanning electron microscopy.
Chapter 2
Experimental and Analytical Techniques

2.1 Summary

In this thesis, a combination of experimental and analytical techniques was used to investigate hydrogen transport across Pd and PdCu membranes. A membrane testing apparatus was used to measure the rate of H$_2$ permeation through Pd and Pd$_{47}$Cu$_{53}$ foil membranes during exposure to both pure H$_2$ and a 1000 ppm H$_2$S in H$_2$ gas mixture. A fixed bed H$_2$-D$_2$ exchange experiment was developed in this thesis to investigate the effect of H$_2$S on the rate of H$_2$ dissociation on Pd, Pd$_{70}$Cu$_{30}$, and Pd$_{47}$Cu$_{53}$ alloy surfaces. The effect of H$_2$S on the bulk and near-surface compositions of Pd and Pd$_{47}$Cu$_{53}$ was characterized by x-ray diffraction (bulk), scanning electron microscopy (bulk), and x-ray photoelectron spectroscopy (near-surface). A description of the experimental and analytical techniques, including the principles of operation of the analytical instruments, is given in this chapter.
2.2 Experimental techniques

2.2.1 Pd and Pd$_{47}$Cu$_{53}$ foil membrane testing

Hydrogen permeation through Pd and Pd$_{47}$Cu$_{53}$ foil membranes was measured using a membrane testing apparatus at the National Energy Technology Laboratory, which is shown schematically in Figure 2.1. Circular (~1.8 cm$^2$) membrane foils were cut from 25 µm thick Pd (Alfa Aesar, 99.9% metals purity) and 25 µm thick Pd$_{47}$Cu$_{53}$ (ATI Wah Chang, 99.0% metals purity) foils. The membranes were mounted into a Swagelok® VCR tube assembly and then installed in the membrane testing apparatus. The H$_2$ partial pressure in the retentate was varied from ~130 kPa to ~270 kPa while the permeated H$_2$ was collected at ambient pressure (~100 kPa). The temperature was measured using Omega type-K thermocouples positioned ~5 mm from the surface of each side of the membrane; the operating temperature was given by the average of the two temperatures. The H$_2$ flux through the membrane was measured using a bubble flowmeter (Alltech Digital Flowmeter Model 4074). Following data collection, the membranes were cooled to room temperature in He and Ar and then dismounted for characterization.
Figure 2.1 Schematic of the membrane foil testing apparatus. 25 µm thick Pd and Pd$_{47}$Cu$_{53}$ foil was mounted in a Swagelok® VCR tube assembly that was surrounded by a furnace. The foil membranes were exposed to flowing gases of pure H$_2$ or 1000 ppm H$_2$S in H$_2$ at elevated temperature and pressure while the permeated H$_2$ flux was measured with a bubble flowmeter at ambient pressure.
2.2.2 \textit{H}_2\text{-D}_2 \text{ exchange over Pd, Cu, Pd}_{70}\text{Cu}_{30}, \text{ and Pd}_{47}\text{Cu}_{53}

The effect of \textit{H}_2\text{S} on the kinetics of \textit{H}_2 \text{ dissociation over Pd, Pd}_{70}\text{Cu}_{30}, \text{ and Pd}_{47}\text{Cu}_{53} \text{ foil surfaces was investigated by a H}_2\text{-D}_2 \text{ exchange experiment that was developed in this thesis. A schematic of the H}_2\text{-D}_2 \text{ exchange reactor is shown in Figure 2.2.}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{schematic.png}
\caption{Schematic of the H}_2\text{-D}_2 \text{ exchange reactor. Pd, Cu, Pd}_{70}\text{Cu}_{30}, \text{ and Pd}_{47}\text{Cu}_{53} \text{ foil was diced into \textasciitilde1 mm}^2 \text{ pieces and packed into a quartz tube reactor surrounded by a tube furnace. H}_2\text{S}+\text{H}_2/\text{H}_2/\text{D}_2/\text{Ar} \text{ were fed to the reactor while the product gas was analyzed by a mass spectrometer. The flow rates of H}_2\text{S}+\text{H}_2, \text{ H}_2, \text{ D}_2, \text{ and Ar} \text{ to the reactor were controlled with mass flow controllers (MFC). The concentration of H}_2\text{S} \text{ in the feed gas was controlled by varying the relative flow rates of a H}_2\text{S}+\text{H}_2 \text{ gas mixture and a pure H}_2 \text{ gas cylinder.}}}
\end{figure}

H}_2\text{-D}_2 \text{ exchange experiments were performed by flowing H}_2, \text{ D}_2, \text{ Ar and a H}_2\text{S}/\text{H}_2 \text{ gas mixture through a 4 mm I.D. quartz tube reactor that was packed with}
diced Pd, Cu, Pd$_{70}$Cu$_{30}$, or Pd$_{47}$Cu$_{53}$ foil while the product gas composition was analyzed by a mass spectrometer. The total surface area of each catalyst used in the experiments was $\sim$19 cm$^2$. A metal wired fixed a thermocouple to the outside of the quartz tube reactor near the catalyst. A tube furnace (Barnstead/Thermolyne 211000) was used to heat the reactor. Mass flow controllers (Aalborg GFC 17) regulated the flow rates of H$_2$ (99.999%, Valley National Gases), D$_2$ (99.999%, Valley National Gases), Ar (99.999%, Valley National Gases), (1.09±0.02%H$_2$S)/98.9%H$_2$ (Matheson Tri-Gas), and (0.107±0.002ppmH$_2$S)/99.9%H$_2$ (Matheson Tri-Gas) to the catalyst bed. The H$_2$S concentration in the feed gas was controlled by diluting the H$_2$S/H$_2$ gas mixtures with pure H$_2$. A $\sim$1 m long, 320 µm I.D. quartz capillary (Polymicro Technologies) was sealed into the outlet of the quartz tube reactor and the product gas was sampled by a $\sim$15 cm long, 20 µm I.D quartz capillary (Polymicro Technologies) that was mounted to a vacuum chamber with a mass spectrometer (Stanford Research Systems, RGA 200).

2.3 Analytical techniques

2.3.1 X-ray diffraction

X-ray diffraction (XRD) was used to identify the bulk crystal structure and elemental composition of membrane foil samples. The basis of the XRD technique is that the atoms in a periodic crystal will scatter an incident beam of x-rays and constructive interference, or diffraction, will occur in definite directions that are related to the periodic arrangement of the atoms in the crystal lattice [35].
Figure 2.3 shows a schematic of the x-ray diffraction process. During XRD analysis of a foil sample, the incident angle of an x-ray beam with respect to the sample is varied continuously while the intensity of the diffracted x-ray beam is measured as a function of the incident angle. Peaks in the x-ray diffraction intensity occur at specific angles that are related to the spacing between crystal planes according to Bragg’s Law [35]:

\[ n\lambda = 2d_{hkl} \sin \theta \]

where \( n \) is an integer, \( \lambda \) is the wavelength of the incident x-ray beam, \( d_{hkl} \) is the distance between the (hkl) crystal planes, and \( \theta \) is the angle between the incident x-ray beam and the (hkl) crystal plane. A comparison of the x-ray diffraction pattern to a database allows the identification of crystalline compounds and crystalline structure.

X-ray diffraction (XRD) measurements of the foil surfaces were obtained using a PANalytical X’Pert Pro MPD powder diffractometer having a theta-theta configuration, a Cu x-ray source operated at 45 kV and 40 mA and an X’Celerator detector equipped with a monochromator. Patterns were recorded over a 2θ range of 30 to 90° at a step size of 0.02°. Foil samples were mounted on zero background quartz slides for analysis. Sample foils were not perfectly flat resulting in a slight peak shape distortion; however this distortion did not affect data interpretation.
Figure 2.3 Schematic of the x-ray diffraction process. An incident x-ray beam is scattered by the atoms in a crystal and constructive interference, or diffraction, occurs in specific directions that are related to the periodic arrangement of the atoms in the crystal lattice according to Bragg’s Law: $n\lambda = 2d_{hkl}\sin \theta$, where $n$ is an integer, $\lambda$ is the wavelength of the incident x-ray beam, $d_{hkl}$ is the distance between the (hkl) planes in the crystal lattice, and $\theta$ is the angle between the incident x-ray beam and the (hkl) plane. Comparison of an x-ray diffraction pattern (scattering intensity versus 2$\theta$) to a database allows for the identification of crystal structure and elemental composition.
2.3.2 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was used to characterize the chemical composition in the near-surface region (~1 to 10 nm) of foil samples. XPS depth profiling was used to characterize the chemical composition profile of foil samples as a function of depth into the sample up to ~200 nm. The basis of the XPS technique, which is shown schematically in Figure 2.4, is that an x-ray beam incident on a solid sample ejects core-level electrons (photoelectrons) from the atoms in the sample. Only photoelectrons in the near-surface region (~1 to 10 nm) have enough kinetic energy to escape the sample [36]. The kinetic energy of the photoelectrons, which is measured by an electron energy analyzer, is related to the binding energy of the core-level electrons according to:

\[ E_k = E_{hv} - E_b - \phi \]

where \( E_k \) is the kinetic energy of the photoelectron, \( E_{hv} \) is the energy of the incident x-ray beam, \( E_b \) is the binding energy of the electron, and \( \phi \) is the work function of the spectrometer. The binding energy of the core-level electrons is characteristic of the atom from which the photoelectron was generated. Therefore, XPS is a technique for characterizing the chemical composition in the near surface region of solid samples.

XPS measurements were performed on a PHI 5600ci instrument. The XPS instrument employed monochromatic aluminum K\(_\alpha\) x-rays and the pass energy of the analyzer was 58.7 eV. Elemental surface concentrations were calculated from Cu 2p\(_{3/2}\), Pd 3d\(_{5/2}\), and S 2p\(_{3/2}\) peak areas and calibrated sensitivity factors. Depth profiles of elemental composition were acquired using
Ar⁺ as the sputtering gas and XPS analysis of surface composition. The differentially-pumped ion gun was operated at 1.5 x 10⁻² Pa and 25 mA, producing a sputtering rate of approximately 10 nm/min based on the calibration of the sputter rate of a 10 nm Pt film.

**Figure 2.4** Schematic of the x-ray photoemission process. An incident x-ray beam ejects a core level electron (photoelectron) from an atom near the surface of the solid sample. The kinetic energy of the photoelectron is related to the binding energy of the electron, which is characteristic of the atom from which the photoelectron originated. The mean free path of photoelectrons is ~1 to 10 nm, making XPS a surface-sensitive technique for characterizing the chemical composition in the near surface region of solid samples.

2.3.3 *Scanning electron microscopy and energy dispersive spectroscopy*

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used to determine the thickness of sulfide films grown on the surface of Pd and Pd₄₇Cu₅₃ foils from exposure to H₂S. The basis of SEM/EDS is that a high energy (20 keV) electron beam is swept in a raster across the surface of a sample producing backscattered electrons, secondary electrons, Auger electrons
and x-rays that can be analyzed to provide topographical and elemental information about the sample. EDS analysis of the x-rays ejected from the sample provides the elemental information that was used to measure the thickness of sulfide films from cross-sections of the foil membranes that were exposed to H$_2$S.

A schematic of the x-ray emission process in EDS analysis is shown in Figure 2.5. The interaction of the incident electron beam with core-level electrons in the atoms of the sample can excite the core-level electrons to produce secondary electrons and holes in the core-level orbital from which the secondary electrons originated from. Relaxation of higher-level electrons into the core-level holes is accompanied by two possible processes: Auger electron emission or x-ray emission. The energy of the Auger electrons and of the x-rays is equal to the difference in the energy level of the higher-level and core-level electron and is characteristic of the atom from which the process occurred. By mapping the sulfur x-rays over a two-dimensional area of a cross-section of Pd and Pd$_{47}$Cu$_{53}$ foils by EDS, the thickness of the sulfide film produced during exposure to H$_2$S was determined.
2.4 Conclusions

A combination of experimental and analytical techniques was used in this thesis to investigate the effect of H\textsubscript{2}S on hydrogen transport (H\textsubscript{2} dissociation and H atom permeation) across Pd and Pd\textsubscript{47}Cu\textsubscript{53} membranes. Hydrogen permeation through Pd and Pd\textsubscript{47}Cu\textsubscript{53} foil membranes was measured both in the absence of H\textsubscript{2}S and in the presence of H\textsubscript{2}S with a membrane testing apparatus. The effect of H\textsubscript{2}S on the rate of H\textsubscript{2} dissociation on Pd, Pd\textsubscript{70}Cu\textsubscript{30}, and Pd\textsubscript{47}Cu\textsubscript{53} was investigated with a H\textsubscript{2}-D\textsubscript{2} exchange experiment that was developed in this thesis. Compositional analysis by x-ray diffraction, scanning electron microscopy, and x-
ray photoelectron spectroscopy was done to characterize the effect of H\textsubscript{2}S on the
bulk and surface compositions of Pd and Pd\textsubscript{47}Cu\textsubscript{53} foil membranes.
Chapter 3

The Effect of H$_2$S on Hydrogen Permeation through Pd and Pd$_{47}$Cu$_{53}$

3.1 Summary

In this chapter, the effect of H$_2$S on hydrogen permeation through Pd and Pd$_{47}$Cu$_{53}$ foils is contrasted. In pure H$_2$ gas, hydrogen fluxes through pure Pd and Pd$_{47}$Cu$_{53}$ foils in the 623 K to 723 K temperature range are similar. In the presence of 1000 ppm H$_2$S in H$_2$, the hydrogen fluxes through both foils are substantially reduced, but with significantly different decay patterns. Six hours after the start of H$_2$S exposure, the Pd foil remained permeable to hydrogen, with the flux decreasing slowly over time. Our results show that H$_2$S slows hydrogen permeation through Pd indirectly by producing a relatively thick (~µm) Pd$_4$S film on the Pd surface that is about an order-of-magnitude less permeable to hydrogen than pure Pd. H$_2$S also inhibits hydrogen transport through Pd directly, possibly by blocking H$_2$ dissociation sites at the Pd$_4$S surface. In contrast to Pd, the hydrogen flux through the Pd$_{47}$Cu$_{53}$ foil is undetectable within five minutes of the start of H$_2$S exposure. XPS depth profiling of the Pd$_{47}$Cu$_{53}$ foil reveals that sulfur penetrates only ~3 nm into the Pd$_{47}$Cu$_{53}$ surface. Rapid formation of a Pd-Cu-S terminal layer, which is either inactive for hydrogen dissociation or impermeable to hydrogen atoms, is responsible for the deactivation of the Pd$_{47}$Cu$_{53}$ alloy membrane in H$_2$S at 623 K. At higher temperatures, the effect of H$_2$S on hydrogen permeation through Pd$_{47}$Cu$_{53}$ diminishes and the alloy is completely sulfur tolerant at temperatures greater than ~900 K.
3.2 Introduction

Coal can be used to produce affordable supplies of H$_2$ for use as a clean fuel or as a chemical commodity. Such supplies of H$_2$ must be separated from a coal derived gas stream composed primarily of H$_2$ and CO$_2$, with several other constituents such as steam, CO, and H$_2$S, at temperatures in the ~500 to ~700 K range. Dense metal membranes, which catalyze H$_2$ dissociation and allow only atomic H to permeate their bulk, are promising candidates for H$_2$/CO$_2$ separation due in part to their potential to produce high purity hydrogen and a high pressure CO$_2$-rich stream that is amenable to sequestration. However, coal gasification also produces H$_2$S, a highly corrosive gas that can react with Pd to form Pd$_4$S [9, 25, 29, 37] via the reaction:

$$4\text{Pd} + \text{H}_2\text{S} \leftrightarrow \text{Pd}_4\text{S} + \text{H}_2.$$  

The H$_2$ flux across Pd membranes decreases rapidly during H$_2$S exposure [9, 25]. Morreale et al. [25] correlated the decay in H$_2$ flux during H$_2$S exposure to the Pd$_4$S growth kinetics measured under similar conditions. In doing so, they suggested that the decay in H$_2$ flux was due to the growth of a Pd$_4$S film on the Pd surface which has a H$_2$ permeability more than an order-of-magnitude lower than that of Pd.

To impart resistance to corrosion by H$_2$S, Pd has been alloyed with other metals [9, 21, 38-40]. Hydrogen transport through Pd-Cu alloys has received significant attention from both experimental and computational researchers [7, 9, 10, 19, 21, 22, 32-34, 38-52]. The Pd$_{47}$Cu$_{53}$ (mol%) alloy has the highest hydrogen permeability at 623 K among the Pd-Cu alloys [33, 43, 45, 46], and is
comparable in its hydrogen permeability to pure Pd at the same temperature. At higher temperatures (~900 K), hydrogen transport through Pd$_{47}$Cu$_{53}$ is not significantly inhibited by 1000 ppm H$_2$S [29]. At 623 K, however, hydrogen transport through Pd$_{47}$Cu$_{53}$ is severely inhibited by H$_2$S [7, 9, 19, 38].

In this chapter, we contrast the responses of Pd and Pd$_{47}$Cu$_{53}$ membranes to exposure to 1000 ppm H$_2$S in H$_2$ at 623 K. We analyze the compositions of the S-contaminated membranes by x-ray diffraction and x-ray photoelectron spectroscopy depth profiles to provide a framework for understanding the differences in their H$_2$S-induced performance degradation. This work shows that H$_2$S slows hydrogen transport through Pd by forming a relatively thick (~µm) Pd$_4$S layer that retains some ability to dissociate and transport hydrogen, although its H atom permeability is about an order-of-magnitude lower than that of Pd. The Pd$_{47}$Cu$_{53}$ alloy, on the other hand, forms a very thin (~nm) Pd-Cu-S layer that is completely impermeable to hydrogen at 623 K. At temperatures above ~900 K, however, H$_2$S has no effect on the rate of hydrogen permeation through Pd$_{47}$Cu$_{53}$.

3.3 Experimental

Hydrogen transport measurements were performed using foil membranes of pure Pd and Pd$_{47}$Cu$_{53}$. Circular membrane foils were cut from 25 µm thick Pd (Alfa Aesar, 99.9% metals purity) and 25 µm thick Pd$_{47}$Cu$_{53}$ (ATI Wah Chang, 99.0% metals purity) foils. The membranes were washed with acetone and mounted into a Swagelok® VCR tube assembly. The effective membrane surface
area was about 1.8 cm². Membranes were leak-tested by pressurizing the retentate (upstream) side of the membranes with 300 kPa of Ar and observing the pressure for 20 minutes. A leak-proof membrane was indicated by less than 1 kPa pressure drop on the upstream side.

Prior to making hydrogen permeation measurements, the membranes were heated to 623 K in He (retentate, upstream) and Ar (permeate, downstream). Then the retentate side of each membrane was exposed to a flowing mixture of 90% H₂/10% He (Butler Gas Products, Inc.) at 310 kPa, with the permeated H₂ collected at ambient pressure (~100 kPa). The temperature was measured using Omega type-K thermocouples positioned ~5 mm from the surface of each side of the membrane; the operating temperature was given by the average of the two temperatures. The H₂ flux through the membrane was measured using a bubble flowmeter (Alltech Digital Flowmeter Model 4074). A 1000 ppm H₂S/10% He/balance H₂ mixture (Butler Gas Products, Inc.) was introduced to the membrane surface following exposure to the 90% H₂/10% He mixture. The permeate gas composition was periodically analyzed by a gas chromatograph (Agilent Technologies Model 6890N) for its He content in order to confirm the absence of pinholes in the membrane. No He was detected in the permeate stream during the entire duration of the membrane tests, before and during H₂S exposure.

Pd₄S films were produced on the surface of Pd foils by exposure to a gas mixture with a composition of 1000 ppm H₂S / 10% He / H₂ (Butler Gas Products, Inc.) at a total pressure of 269 kPa and a temperature of 623 K. The H₂S exposure time varied from ~5 minutes for the thin (1 µm) Pd₄S films to ~24 hours for the
thicker (>15 µm) Pd₄S films. The bi-layered Pd₄S/Pd membranes were then exposed to either pure H₂ (99.99%, Butler Gas Products, Inc.) or the 1000 ppm H₂S in H₂ gas mixture while H₂ permeate flow rates were measured with a bubble flowmeter (Alltech Digital Flowmeter Model 4074) at ambient pressure. H₂ fluxes did not change over the course of the measurements (~30 minutes) and, therefore, the Pd₄S thicknesses were assumed to be constant. Following data collection, the membranes were cooled to room temperature in He and Ar and then dismounted for characterization.

X-ray diffraction (XRD) measurements of the foil surfaces were obtained using a PANalytical X’Pert Pro MPD powder diffractometer having a theta-theta configuration, a Cu x-ray source operated at 45 kV and 40 mA and an X’Celerator detector equipped with a monochromator. Patterns were recorded over a 2θ range of 30 to 90° at a step size of 0.02°. Foil samples were mounted on zero background quartz slides for analysis. Sample foils were not perfectly flat resulting in a slight peak shape distortion; however this distortion did not affect data interpretation.

Scanning electron microscope (SEM) analyses of cross-sections of the foils were performed to determine the nature of the films grown on their surface during exposure to H₂S. Cross-sectioned pieces of the Pd and Pd₄₇Cu₅₃ foils were set in epoxy and then polished with Carbimet Paper (Buehler) up to 1200 grit. The polished cross-sections were then analyzed with an Aspex Personal SEM 2000 which was operated with a 20 keV electron beam. Sulfur x-ray maps
of the cross-sections were used to quantify the thickness of the surface sulfide formed on the membrane foils.

X-ray photoelectron spectroscopy (XPS) measurements were used to determine the surface compositions of the foils and for depth profiling of the composition in the near surface region. XPS measurements were performed on a PHI 5600ci instrument. The XPS instrument employed monochromatic aluminum Kα x-rays and the pass energy of the analyzer was 58.7 eV. Elemental surface concentrations were calculated from Cu 2p_{3/2}, Pd 3d_{5/2}, and S 2p_{3/2} peak areas and calibrated sensitivity factors. Depth profiles of elemental composition were acquired using Ar⁺ as the sputtering gas and XPS analysis of surface composition. The differentially-pumped ion gun was operated at 1.5 x 10⁻² Pa and 25 mA, producing a sputtering rate of approximately 10 nm/min based on the calibration of the sputter rate of a 10 nm Pt film.

3.4 Model for extraction of permeabilities

Fick’s first law of diffusion governs H atom transport through dense Pd and PdCu membranes at steady state:

\[ J_H = \frac{D \cdot \Delta c_H}{x} \]  

(1)

where \( J_H \) is the steady-state H atom flux, \( D \) is the diffusivity of H atoms in the metal, \( \Delta c_H \) is the difference in the H atom concentration across the metal, and \( x \) is the thickness of the membrane. If the gas-phase H₂ on the high pressure side of
the membrane is in equilibrium with the H atoms dissolved near the high pressure surface of the membrane, and the gas-phase H$_2$ on the low pressure side of the membrane is in equilibrium with the H atoms dissolved near the low pressure surface of the membrane, then Sievert’s law relates the difference in the H atom concentration across the membrane, $\Delta c_H$, to the difference in the square root of the H$_2$ partial pressure across the membrane, $\Delta P_{H2}^{1/2}$:

$$\Delta c_H = S \cdot \Delta P_{H2}^{1/2}$$

(2)

where $S$ is the solubility of H atoms in the metal. Substitution of Sievert’s Law, equation (2), into Fick’s first law of diffusion, equation (1), gives:

$$J_H = \frac{DS \cdot \Delta P_{H2}^{1/2}}{x}.$$ 

(3)

Defining the H atom permeability (2 H atom basis) of the metal membrane, $k$, as:

$$k = \frac{DS}{2},$$

(4)

and substituting equation (4) into equation (3) gives the steady-state H$_2$ flux across a metal membrane, $J_{H2}$:

$$J_{H2} = \frac{k \cdot \Delta P_{H2}^{1/2}}{x}.$$ 

(5)

H$_2$ transport across composite membranes has been well described in other publications [25, 53-56], and the H$_2$ flux across a bi-layered Pd$_4$S/Pd foil can be modeled by equation (6) if H-atom diffusion is rate-limiting [25]:

$$J_{H2} = \frac{\Delta P_{H2}^{1/2}}{x_{PdS} \cdot \frac{k_{PdS}}{k_{Pd}} + x_{Pd} \cdot \frac{k_{Pd}}{k_{Pd}}}$$

(6)
where $k_{PdS}$ is the H atom permeability (2 H atom basis) of Pd$_4$S, $k_{Pd}$ is the H atom permeability (2 H atom basis) of Pd, $x_{PdS}$ is the thickness of the Pd$_4$S film, and $x_{Pd}$ is the thickness of Pd substrate. If H atom diffusion through a bi-layered Pd$_4$S/Pd foil is rate-limiting, then the H$_2$ flux should be directly proportional to $\Delta P_{H_2}^{1/2}$ with a slope that can be used to calculate the permeability of Pd$_4$S if the permeability of Pd is known and the Pd$_4$S and Pd thicknesses are known.

3.5 Results and Discussion

3.5.1 *The hydrogen permeability of Pd and Pd$_{47}$Cu$_{53}$*

H$_2$ fluxes across Pd and Pd$_{47}$Cu$_{53}$ foil were measured in pure H$_2$ to determine the H atom permeability of Pd and Pd$_{47}$Cu$_{53}$. Figure 3.1 shows the H$_2$ fluxes across (a) 25 µm thick Pd foil and (b) 25 µm thick Pd$_{47}$Cu$_{53}$ foil during exposure to pure H$_2$ in the 623 to 973 K (1023 K for Pd$_{47}$Cu$_{53}$) temperature range. As expected, H$_2$ fluxes across the Pd foil increased with increasing pressure and temperature. H$_2$ fluxes across the Pd$_{47}$Cu$_{53}$ foil also increase with increasing pressure; however, the H$_2$ flux changes non-monotonically with increasing temperature. H$_2$ fluxes across the Pd$_{47}$Cu$_{53}$ foil increase from 623 to 723 K, then decrease from 723 to 873 K, and then increase again from 873 K to 1023 K. This non-monotonic change in the H$_2$ flux with temperature is due to a change in the Pd$_{47}$Cu$_{53}$ crystal structure from body-centered-cubic (BCC) at temperatures below ~723 K to face-centered-cubic (FCC) at temperatures above ~873 K [7, 9, 10]. In the temperature range ~723 to ~873 K, the BCC and FCC crystal phases of the Pd$_{47}$Cu$_{53}$ co-exist in a mixed phase structure [7, 9, 10].
Figure 3.1. H$_2$ fluxes across 25 µm thick (a) Pd and (b) Pd$_{47}$Cu$_{53}$ foil versus Sievert’s partial pressure driving force, $\Delta P_{H_2}^{1/2}$, in the 623 to 973 K (1023 K for Pd$_{47}$Cu$_{53}$) temperature range during exposure to pure H$_2$. H$_2$ fluxes across the Pd foil increase with increasing pressure and temperature. H$_2$ fluxes across the Pd$_{47}$Cu$_{53}$ foil increase with increasing pressure, but change non-monotonically with temperature. In the 623 to 723 K temperature range, H$_2$ fluxes across the Pd$_{47}$Cu$_{53}$ foil increase with increasing temperature, then H$_2$ fluxes decrease with increasing temperature from 723 to 873 K, and then H$_2$ fluxes increase with increasing temperature from 873 to 1023 K. This non-monotonic change in H$_2$ flux is due to a change in the Pd$_{47}$Cu$_{53}$ crystal from body-centered-cubic at temperatures less than ~723 K to face-centered-cubic at temperatures greater than ~873 K [7,9,10]. The body-centered-cubic crystal structure of the Pd$_{47}$Cu$_{53}$ alloy is much more permeable to H atoms than the face-centered-cubic crystal structure of the alloy.
The H\textsubscript{2} fluxes across Pd (Figure 3.1(a)) and Pd\textsubscript{47}Cu\textsubscript{53} (Figure 3.1(b)) are directly proportional to the Sievert’s partial pressure driving force, \(\Delta P_{H_2}^{1/2}\), indicating that H atom diffusion through the bulk of the foils is rate limiting. Using equation (5) and the slopes of the fitted solid lines in Figure 3.1(a) and 3.1(b), the H atom permeability of Pd \((k_{Pd})\) and Pd\textsubscript{47}Cu\textsubscript{53} \((k_{Pd47Cu53})\) were calculated at each temperature. The H atom permeability (2 H atom basis) of Pd was fit to an Arrhenius expression:

\[
k_{Pd} = 10^{-6.33\pm0.03} \exp\left(\frac{-0.199 \pm 0.004 \text{eV}}{k_B T}\right) \text{molH}_2 \text{m} \cdot \text{s} \cdot \text{Pa}^{1/2}
\]  

(7)

where T (K) is the temperature and \(k_B\) is the Boltzmann constant. Figure 3.2(a) illustrates that our results for the H atom permeability of Pd are consistent with previous literature reports [8, 57, 58]. Figure 3.2(b) shows that our result for the H atom permeability of Pd\textsubscript{47}Cu\textsubscript{53} are also consistent with previous literature reports [9, 31].
A comparison of the H atom permeability of Pd and Pd\textsubscript{47}Cu\textsubscript{53} measured in this work, and the H atom permeability of Cu [59] and Pd\textsubscript{70}Cu\textsubscript{30} [9] from literature, is shown in Figure 3.3. The H atom permeability of Cu is about three to five orders-of-magnitude lower than that of pure Pd in the 623 to 973 K temperature range. The H atom permeability of BCC Pd\textsubscript{47}Cu\textsubscript{53} (~623 to 723 K) is similar to that of pure Pd but the permeability of FCC Pd\textsubscript{47}Cu\textsubscript{53} (~873 to 1023 K)
is about an order-of-magnitude lower than that of Pd. The H atom permeability of Pd$_{70}$Cu$_{30}$, which has only a FCC crystal structure, is about one-fifth that of pure Pd.

![Figure 3.3](image)

**Figure 3.3** Comparison of the H atom permeability of Pd and Pd$_{47}$Cu$_{53}$ measured in this work, and the H atom permeability of Cu [59] and Pd$_{70}$Cu$_{30}$ [9] from literature. The H atom permeability of Cu is about three to five orders-of-magnitude lower than that of Pd. The H atom permeability of BCC Pd$_{47}$Cu$_{53}$ (~623 to 723 K) is similar to that of Pd, but the H atom permeability of FCC Pd$_{47}$Cu$_{53}$ (~873 to 1023 K) is about an order-of-magnitude lower than that of Pd. The H atom permeability of Pd$_{70}$Cu$_{30}$, which only has a FCC crystal structure, is about one-fifth that of Pd.
3.5.2 Inhibition of H₂ transport through Pd and Pd₄₇Cu₅₃ by H₂S at 623 K

In the previous section, it was shown that the H atom permeabilities of Pd and Pd₄₇Cu₅₃ are similar in the 623 to 723 K temperature range. In this section, the effect of H₂S on hydrogen permeation through Pd and Pd₄₇Cu₅₃ foils is contrasted. We analyze the sulfur-exposed Pd and Pd₄₇Cu₅₃ foils by x-ray diffraction, scanning electron microscopy, and x-ray photoelectron spectroscopy to provide a framework for understanding the mechanisms by which H₂S slows hydrogen transport.

The transient effect of H₂S on hydrogen permeation through Pd and Pd₄₇Cu₅₃ was investigated by measuring hydrogen fluxes through Pd and Pd₄₇Cu₅₃ foil membranes, first in the absence of H₂S to establish a baseline, and then in the presence of 1000 ppm H₂S. Results of the membrane test are presented in Figure 3.4. Baseline hydrogen fluxes through the two foils were ~0.1 mol/m²/s for both Pd and Pd₄₇Cu₅₃. Assuming that Sievert’s Law is obeyed, the calculated H atom permeabilities (2 H atom basis) from the baseline H₂ fluxes were ~1.3x10⁻⁸ mol/m²/s/Pa¹/² for Pd₄₇Cu₅₃ and ~1.2x10⁻⁸ mol/m²/s/Pa¹/² for Pd; both are in good agreement with our permeabilities measured in section 3.5.1 (see Figure 3.3). Both membranes displayed significant decreases in hydrogen flux upon exposure to 1000 ppm H₂S. The hydrogen flux through the Pd₄₇Cu₅₃ foil was below the detection limit of the bubble flowmeter (< ~4x10⁻⁴ mol/m²/s) within five minutes of exposure to H₂S. In contrast, after an initially rapid decline, the hydrogen flux decay through the Pd foil slowed significantly. After
six hours of H₂S exposure, the hydrogen flux through the Pd membrane was still 10% of its baseline value.

**Figure 3.4** Hydrogen flux through 25 µm Pd (blue solid line) and Pd₄₇Cu₅₃ (red dashed line) membranes versus test duration at 623 K, total feed gas pressure of 310 kPa and total permeate pressure of ~100 kPa (ambient pressure). A 90% H₂/10% He mixture was exposed to the membrane surface during the first portion of the test and then 1000 ppm H₂S/10% He/balance H₂ was fed to the membrane surface at 6 hours. The Pd membrane was still permeable to H₂ after 6 hours of exposure to 1000 ppm H₂S whereas, the Pd₄₇Cu₅₃ membrane was impermeable to H₂ after less than 5 minutes of exposure to H₂S. Figure 3.4 is adapted from [1] with permission.

To determine whether any thick metal-sulfide compounds (corrosion layers) formed as a result of H₂S exposure, the Pd and Pd₄₇Cu₅₃ foils were analyzed by x-ray diffraction (XRD) following membrane testing. Figures 3.5(a) and 3.5(b) display the XRD patterns for the Pd and Pd₄₇Cu₅₃ foils, respectively,
including diffraction patterns of the clean Pd and Pd\textsubscript{47}Cu\textsubscript{53} foils for reference. As expected, the diffraction pattern of the clean Pd foil exhibits features that are assignable to the face-centered-cubic Pd structure. The XRD pattern of the Pd foil that was exposed to H\textsubscript{2}S is dominated by features that can be assigned to crystalline palladium sulfide (Pd\textsubscript{4}S), with only very small peaks from metallic Pd. These results illustrate that H\textsubscript{2}S exposure causes the Pd membrane to form a specific palladium sulfide reaction product, Pd\textsubscript{4}S. In contrast to the XRD results from the Pd foil, the XRD patterns of the clean Pd\textsubscript{47}Cu\textsubscript{53} foil and the Pd\textsubscript{47}Cu\textsubscript{53} foil after 6 hours of H\textsubscript{2}S exposure (Figure 3.5(b)) are nearly identical and are both assignable to the body-centered-cubic structure of Pd\textsubscript{47}Cu\textsubscript{53}. The diffraction peak intensities of the clean and H\textsubscript{2}S-exposed Pd\textsubscript{47}Cu\textsubscript{53} foils are not identical and vary from the intensities expected for an ideal body-centered-cubic Pd\textsubscript{47}Cu\textsubscript{53} powdered sample. The peak intensities observed for the clean Pd foil also vary from the intensities expected for an ideal face-centered-cubic Pd powdered sample. These variations are probably due to the fact that non-ideal solid metal foil samples were analyzed. The discrepancies in peak intensity probably reflect a preferred orientation of the metal crystallites comprising the membrane foils.
Cross-sections of the Pd and Pd$_{47}$Cu$_{53}$ foils were imaged by SEM to determine the thickness of sulfur corrosion layers on the surface of the foils. The sulfur concentration was mapped over the SEM images by EDS. SEM analysis of the Pd and Pd$_{47}$Cu$_{53}$ foils after H$_2$S exposure are presented in Figures 3.6(a) and 3.6(b), respectively; EDS mapping of sulfur concentration in the SEM images of the Pd and Pd$_{47}$Cu$_{53}$ foils are presented in Figures 3.6(c) and 3.6(d), respectively.

Figure 3.5 X-ray diffraction patterns of (a) 25 µm Pd foil before (Clean) and after exposure to 1000 ppm H$_2$S for 6 hours (Exposed to H$_2$S) and (b) 25 µm Pd$_{47}$Cu$_{53}$ foil before (Clean) and after exposure to 1000 ppm H$_2$S for 6 hours (Exposed to H$_2$S). The peaks in the diffraction pattern of the clean Pd foil are assignable to the face-centered-cubic crystal structure. The peaks in the diffraction pattern of the Pd foil exposed to H$_2$S are associated with a palladium sulfide compound, Pd$_4$S. The diffraction patterns of the clean Pd$_{47}$Cu$_{53}$ foil and the Pd$_{47}$Cu$_{53}$ foil exposed to H$_2$S are nearly identical and are associated with the body-centered cubic crystal structure of the alloy. Figure 3.5 is adapted from [1] with permission.
A noticeable difference in the roughness of the Pd and Pd\textsubscript{47}Cu\textsubscript{53} foil surfaces exposed to H\textsubscript{2}S is evident from the SEM images in Figure 3.6; the surface of the Pd foil (Figure 3.6(a)) is significantly rougher than that of the Pd\textsubscript{47}Cu\textsubscript{53} foil (Figure 3.6(b)). Sulfidation of the Pd foil surface to Pd\textsubscript{4}S is probably responsible for the fact that the Pd foil surface is rougher than that of the Pd\textsubscript{47}Cu\textsubscript{53} foil, which did not form any sulfur compounds that could be detected by XRD. EDS reveals a sulfur-rich layer on the surface of the Pd foil (Figure 3.6(c)), which XRD identified as a Pd\textsubscript{4}S film, that is \(6.6 \pm 0.9 \text{ µm}\) thick (average of 75 different thickness measurements across the entire length of the Pd foil cross-section). In contrast to the sulfur film observed on the Pd foil, EDS (Figure 3.6(d)) did not detect a significant amount of sulfur on the Pd\textsubscript{47}Cu\textsubscript{53} foil after H\textsubscript{2}S exposure. EDS analyzes x-rays from a relatively large volume within the sample, however, and thus, it is not able to detect sulfur contamination in a very thin layer near the surface of the Pd\textsubscript{47}Cu\textsubscript{53} membrane.
XPS depth profiles of the Pd and Pd\textsubscript{47}Cu\textsubscript{53} foils were collected to detect sulfur contamination near the membrane surfaces that may be undetectable by XRD and EDS analysis. XPS composition depth profiles of the Pd and Pd\textsubscript{47}Cu\textsubscript{53} foils after six hours of H\textsubscript{2}S exposure are presented in Figures 3.7(a) and 3.7(b), respectively. The Pd foil (Figure 3.7(a)) has a stoichiometry in the near-surface region.

**Figure 3.6** Scanning electron micrographs of cross-sections of the (a) Pd and (b) Pd\textsubscript{47}Cu\textsubscript{53} foils that were exposed to H\textsubscript{2}S for 6 hours. Sulfur x-ray mapping in the SEM images of the (c) Pd and (d) Pd\textsubscript{47}Cu\textsubscript{53} cross-sections highlight the S-rich regions in white. After 6 hours of H\textsubscript{2}S exposure, the thickness of the Pd\textsubscript{4}S film produced on the surface of the Pd foil ((a) and (c)) was ~6.6 µm thick. In contrast to Pd, there was no sulfur detected in the cross-section of the Pd\textsubscript{47}Cu\textsubscript{53} foil by SEM/EDS. Figure 3.6 is adapted with permission from [1].
region (~200 nm) that is approximately constant at Pd:S ≈ 4:1, which is consistent with the presence of Pd₄S as indicated by the XRD results. In contrast, S appears only very near the top-surface of the Pd₄₇Cu₅₃ alloy membrane (Figure 3.7(b)); its signal decayed to zero after Ar⁺ sputtering only ~3 nm into the bulk of the Pd₄₇Cu₅₃ membrane.

**Figure 3.7** X-ray photoelectron spectroscopy depth profiles of the (a) 25 µm Pd and (b) 25 µm Pd₄₇Cu₅₃ membranes exposed to 1000 ppm H₂S for 6 hours. Elemental concentrations are shown for Pd, S, and Cu. The sputtering rate is ~10 nm/min as measured using a pure Pt film. The Pd:S ratio in the near-surface region (~200 nm) of the Pd foil is roughly constant at 4:1, which is consistent with Pd₄S stoichiometry. Sulfur was detected only a few nm into the bulk of the Pd₄₇Cu₅₃ foil exposed to H₂S. Figure 3.7 is adapted with permission from [1].

Pd and Pd₄₇Cu₅₃ membranes clearly respond differently to H₂S exposure at 623 K. We believe that the different responses of the hydrogen flux to H₂S exposure exhibited by the two membranes are related to the evolution of their
surface compositions during H$_2$S exposure. Furthermore, two different mechanisms may be responsible for the inhibition of hydrogen transport through the two membranes: poisoning of the catalytic dissociation of H$_2$ at the surface and reduced permeability of hydrogen through the bulk of the membrane.

The observation of non-zero flux through the Pd foil during H$_2$S exposure indicates that the membrane surface retained H$_2$ dissociation activity. The continuous slow decline of the hydrogen flux through the Pd membrane is indicative of an increasing resistance to hydrogen transport, which is consistent with hydrogen atom diffusion being retarded by a slowly thickening, dense, low-permeability Pd$_4$S corrosion layer on the surface. This mechanism has been suggested by Morreale, et al. who estimated the hydrogen permeability of Pd$_4$S at 623 K to be $\sim 1/20^{th}$ that of Pd by correlating Pd$_4$S growth kinetics to the decline in hydrogen flux through a Pd membrane during H$_2$S exposure [9, 25]. The steep initial decline in hydrogen flux through the Pd membrane immediately following H$_2$S exposure may be due to a rapid initial corrosion rate that slows as diffusion of Pd and/or S ions through the Pd$_4$S scale becomes slower. Another possible explanation for the rapid initial decline in hydrogen flux through the Pd membrane following H$_2$S exposure is that the catalytic activity of the Pd$_4$S surface may be significantly lower than that of Pd. As the thickness of the low-permeability Pd$_4$S film grows beyond a critical value, hydrogen atom diffusion through the bulk becomes rate limiting. A third explanation for the evolution of the hydrogen flux is that there may be a significant barrier to hydrogen atom
transport across the Pd$_4$S/Pd interface that dominates transport initially but becomes insignificant as the Pd$_4$S thickness grows beyond a critical value.

The immediate decline in hydrogen flux through the Pd$_{47}$Cu$_{53}$ membrane at the start of H$_2$S exposure must be related to the properties of its thin Pd-Cu-S terminal layer. Neither XRD nor XPS depth profiling could identify this thin Pd-Cu-S terminal layer as a specific compound and, therefore, the mechanism of its formation is not clear. Presumably this layer is either inactive for hydrogen dissociation or it displays near-zero hydrogen atom permeability.
3.5.3 The hydrogen permeability of Pd₄S

In the previous section, it was shown that exposure of Pd to H₂S resulted in the formation of a relatively thick (~µm) Pd₄S film on the surface of the Pd foil. In this section, the influence of Pd₄S film formation on slowing hydrogen transport through Pd is investigated in more detail. The effect of Pd₄S film thickness on the H₂ flux across Pd₄S/Pd foils was investigated by measuring H₂ fluxes across Pd₄S/Pd foils with various Pd₄S film thicknesses. Pd₄S films were produced by exposing the upstream surface of pure Pd foils to a 1000 ppm H₂S / 10% He / H₂ gas mixture at a total pressure of 269 kPa and a temperature of 623 K in the membrane testing apparatus. H₂ fluxes were measured using pure H₂ to prevent Pd₄S growth during measurements and to eliminate the effects of H₂S on H₂ transport; H₂ fluxes did not vary over the course of the measurements (~30 minutes) and, therefore, the Pd₄S thicknesses can be assumed to be constant throughout the experiment. Following membrane testing, the Pd₄S film thicknesses were measured by cross-sectional optical microscopy of the Pd₄S/Pd foils. Figure 3.8 shows the H₂ fluxes across Pd₄S/Pd foils with Pd₄S thicknesses of 0 (pure Pd), 1, 2, 6, and 14 µm at 623 K. Due to the low permeability of Pd₄S relative to Pd, the H₂ fluxes decrease as the Pd₄S thickness increases.
Figure 3.8  \( \text{H}_2 \) fluxes across bi-layered Pd\(_4\)S/Pd foils with Pd\(_4\)S thicknesses of 0 (pure Pd), 1, 2, 6, and 14 µm during exposure to pure \( \text{H}_2 \) at 623 K. Pd\(_4\)S films were produced on the surface of Pd by exposure to 1000 ppm H\(_2\)S / 10\% He/ \( \text{H}_2 \) at 623 K and a total pressure of 269 kPa. H\(_2\)S exposure times varied from ~5 minutes for the 1 µm Pd\(_4\)S film to ~24 hours for the 14 µm Pd\(_4\)S film. The \( \text{H}_2 \) partial pressure in the feed gas was varied from 128 to 266 kPa while the permeated \( \text{H}_2 \) was collected at ambient (101 kPa) pressure. \( \text{H}_2 \) fluxes decrease as the Pd\(_4\)S thickness increases due to the low permeability of Pd\(_4\)S relative to Pd. Figure 3.8 is taken with permission from [2].
To determine whether \( \text{H}_2\text{S} \) inhibits \( \text{H}_2 \) transport across \( \text{Pd}_4\text{S/Pd} \) by factors in addition to the presence of the \( \text{Pd}_4\text{S} \) film, \( \text{H}_2 \) fluxes across \( \text{Pd}_4\text{S/Pd} \) foils were measured during exposure to a 1000 ppm \( \text{H}_2\text{S} / 10\% \text{ He} / \text{H}_2 \) gas mixture. Figure 5 shows the \( \text{H}_2 \) fluxes across a 14 \( \mu \text{m} \) \( \text{Pd}_4\text{S/Pd} \) foil during exposure to both pure \( \text{H}_2 \) and a 1000 ppm \( \text{H}_2\text{S} / 10\% \text{ He} / \text{H}_2 \) feed gas mixture at 623 K. In both pure \( \text{H}_2 \) and in the \( \text{H}_2\text{S}/\text{H}_2 \) gas mixture, \( \text{H}_2 \) fluxes did not change significantly over the course of the measurements (~30 minutes); therefore, the \( \text{Pd}_4\text{S} \) thickness can be assumed to be constant throughout the experiment. At all \( \text{H}_2 \) pressures, the \( \text{H}_2 \) fluxes across the 14 \( \mu \text{m} \) \( \text{Pd}_4\text{S/Pd} \) foil were significantly lower in the 1000 ppm \( \text{H}_2\text{S} \) in \( \text{H}_2 \) gas mixture than in pure \( \text{H}_2 \). \( \text{H}_2 \) fluxes across bi-layered \( \text{Pd}_4\text{S/Pd} \) foils were also measured at 673 K with a ~14 \( \mu \text{m} \) \( \text{Pd}_4\text{S} \) film, 723 K with a ~19 \( \mu \text{m} \) \( \text{Pd}_4\text{S} \) film, and 773 K with a ~22 \( \mu \text{m} \) \( \text{Pd}_4\text{S} \) film, both in pure \( \text{H}_2 \) and in the 1000 ppm \( \text{H}_2\text{S} / 10\% \text{ He} / \text{H}_2 \) feed gas mixture. At all temperatures and \( \text{Pd}_4\text{S} \) film thicknesses, the \( \text{H}_2 \) fluxes across the bi-layered \( \text{Pd}_4\text{S/Pd} \) foils were lower in the \( \text{H}_2\text{S}/\text{H}_2 \) gas mixture than in pure \( \text{H}_2 \). Given the relatively low \( \text{H}_2 \) fluxes, the low \( \text{He} \) concentration, and the low \( \text{H}_2\text{S} \) concentration, gas-phase hydrogen transport near the surface of the membranes (i.e. concentration polarization) is probably not the cause of the reduced \( \text{H}_2 \) flux in the 1000 ppm \( \text{H}_2\text{S} / 10\% \text{ He} / \text{H}_2 \) feed gas relative to that in the pure \( \text{H}_2 \) feed gas. Therefore, \( \text{H}_2\text{S} \) probably inhibits one or more molecular processes at the \( \text{Pd}_4\text{S} \) surface. \( \text{H}_2\text{S} \) may inhibit the \( \text{H}_2 \) dissociation reaction by blocking \( \text{H}_2 \) adsorption sites or by increasing the barrier to \( \text{H}_2 \) dissociation. The effect of \( \text{H}_2\text{S} \) on \( \text{H}_2 \) dissociative adsorption on \( \text{Pd}_4\text{S} \) will
be discussed in more detail in Chapter 5. Alternatively, H₂S may inhibit H-atom transport from the surface to the sub-surface of Pd₄S.

**Figure 3.9** H₂ fluxes across a 14 µmPd₄S / Pd foil at 623 K during exposure to pure H₂ and a 1000 ppm H₂S / 10% He / H₂ gas mixture (H₂ + H₂S). The H₂ partial pressure in the feed gas was varied from 128 to 266 kPa while the permeated H₂ was collected at ambient (101 kPa) pressure. H₂ fluxes across the 14 µmPd₄S / Pd foil are significantly lower in the H₂ + H₂S gas mixture than in the pure H₂ feed gas which could be due to H₂S blocking of H₂ dissociation sites. Figure 3.9 is taken with permission from [2].

During exposure to pure H₂ at varying pressure in the 623 to 773 K temperature range, the H₂ fluxes are directly proportional to $\Delta P_{H_2}^{1/2}$ and intersect the origin, which indicates that H atom diffusion through the bulk of the foil is rate-limiting and that the Pd₄S layer is essentially dense. Therefore, the H atom
permeability of Pd$_4$S can be calculated using equation (6). The temperature
dependence of the H atom permeability (2 H atom basis) of Pd$_4$S ($k_{\text{Pd}_4\text{S}}$) is given by an Arrhenius expression:

$$k_{\text{Pd}_4\text{S}} = 10^{-7.5 \pm 0.2} \exp\left(\frac{(-0.22 \pm 0.03) \text{eV}}{k_B T} \right) \frac{\text{molH}_2}{\text{m} \cdot \text{s} \cdot \text{Pa}^{1/2}}$$

(8)

where T (K) is the temperature and $k_B$ is the Boltzmann constant. Figure 3.10 is
an Arrhenius plot that compares the H atom permeability (2 H atom basis) of Pd
and Pd$_4$S measured in this work and the H atom permeability of Pd$_4$S determined
by Morreale by correlation of Pd$_4$S growth kinetics to H$_2$ permeability decay in
the presence of H$_2$S [25]. Except for the measurement made at 623 K, our results
for the H atom permeability of Pd$_4$S are in very good agreement with the
experimental results reported by Morreale; the H atom permeability of Pd$_4$S is
about an order-of-magnitude lower than that of Pd. The small difference between
our results and those of Morreale at 623 K may be due to the fact that the latter
were determined from measurements made in the presence of H$_2$S. As described
earlier, in addition to reacting with Pd to form Pd$_4$S, H$_2$S may also block H$_2$
dissociation sites on the Pd$_4$S surface. In this work, the H atom permeability of
Pd$_4$S was determined from measurements of H$_2$ transport across bi-layered
Pd$_4$S/Pd foils during exposure to pure H$_2$. For all of the bi-layered Pd$_4$S/Pd foils
from which the H atom permeability of Pd$_4$S was measured, more than 90% of the
total resistance to hydrogen transport was attributable to the Pd$_4$S film and,
therefore, our method for calculating the H atom permeability of Pd$_4$S should be
reasonably accurate. The good agreement between our results and the results from Morreale [25] illustrates that the decay in H$_2$ flux through a Pd foil during H$_2$S exposure is mainly due to the growth of a low permeability Pd$_4$S film on the Pd surface.

**Figure 3.10** Comparison of the H atom permeability of Pd (closed squares) and the H atom permeability of Pd$_4$S measured in this work (closed circles) and in the work of Morreale (open triangles) [25]. The H atom permeability of Pd$_4$S was measured using bi-layered Pd$_4$S foils with Pd$_4$S thicknesses of ~14 µm at 623 K, ~14 µm at 673 K, ~19 µm at 723 K, and ~22 µm at 773 K. The solid fitted lines for the H atom permeability of Pd and Pd$_4$S are described by equations (7) and (8), respectively.
3.5.4 High temperature sulfur tolerance by $Pd_{47}Cu_{53}$

At 623 K, the $Pd_{47}Cu_{53}$ alloy is impermeable to $H_2$ in the presence of 1000 ppm $H_2S$ (see Figure 3.4). A thin (~nm) Pd-Cu-S layer forms on the surface of the $Pd_{47}Cu_{53}$ alloy that blocks all hydrogen transport through the alloy. At higher temperatures, however, the influence of $H_2S$ on hydrogen permeation through $Pd_{47}Cu_{53}$ becomes weaker. Figure 3.11 shows the $H_2$ fluxes through $Pd_{47}Cu_{53}$ versus Sievert’s partial pressure driving force during exposure to pure $H_2$ and 1000 ppm $H_2S$ at (a) 673 K, (b) 773 K, (c) 873 K, and (d) 973 K. $H_2S$ completely blocks hydrogen transport through $Pd_{47}Cu_{53}$ at 673 K. At 773 K, the $H_2$ flux through $Pd_{47}Cu_{53}$ in the presence of $H_2S$ is non-zero but is still much lower than the $H_2$ flux in pure $H_2$. At 873 K, the difference between the $H_2$ flux measured in pure $H_2$ and the $H_2$ flux measured in 1000 ppm $H_2S$ becomes smaller. At 973 K, there is not a significant difference in the $H_2$ flux measured in pure $H_2$ and that measured in 1000 ppm $H_2S$. At 973 K, the $H_2$ fluxes vary linearly with the Sievert’s partial pressure driving force and intersect the origin, indicating that $H$ atom diffusion is rate-limiting. At 773 and 873 K, however, the $H_2$ fluxes do not intersect the origin. This indicates that Sievert’s law is violated and $H$ atom diffusion through the bulk of $Pd_{47}Cu_{53}$ is not rate-limiting at 773 and 873 K. It is possible that, in the presence of 1000 ppm $H_2S$ at temperatures less than ~900 K, the surface $H_2$ dissociation reaction is not faster than the rate of $H$ atom diffusion through the bulk of $Pd_{47}Cu_{53}$.
Figure 3.11  H₂ fluxes through Pd₄₇Cu₅₃ versus Sievert’s partial pressure driving force during exposure to pure H₂ (clean H₂) and in the presence of 1000 ppm H₂S (H₂ + H₂S) at (a) 673 K, (b) 773 K, (c) 873 K, and (d) 973 K. The effect of H₂S on the H₂ flux through Pd₄₇Cu₅₃ diminishes with increasing temperature. At 973 K, hydrogen transport through Pd₄₇Cu₅₃ is not significantly affected by 1000 ppm H₂S.
If we arbitrarily define sulfur tolerance as the ratio of the H\textsubscript{2} flux in the presence of 1000 ppm H\textsubscript{2}S to the H\textsubscript{2} flux in pure H\textsubscript{2},

\[
\text{Sulfur Tolerance} = \frac{\text{H}_2 \text{ flux in 1000 ppm H}_2\text{S}}{\text{H}_2 \text{ flux in pure H}_2},
\]

then the sulfur tolerance of Pd\textsubscript{47}Cu\textsubscript{53} at 623 K is zero. Figure 3.12 shows the sulfur tolerance of Pd\textsubscript{47}Cu\textsubscript{53} in the 623 to 1023 K temperature range. The sulfur tolerance of Pd\textsubscript{47}Cu\textsubscript{53} increases smoothly from zero at 623 K to one at ~900 K, at which point exposure to 1000 ppm H\textsubscript{2}S has no effect on the rate of H\textsubscript{2} permeation through Pd\textsubscript{47}Cu\textsubscript{53}. There are several possible explanations for both the low sulfur tolerance at low temperatures and the high sulfur tolerance at high temperatures. At low temperature, the Pd-Cu-S surface is either inactive for H\textsubscript{2} dissociation or is impermeable to H atoms. The sulfur tolerance observed at high temperatures could be due to a lower stability of the thin Pd-Cu-S terminal layer at high temperature or simply due to higher H\textsubscript{2} dissociation rates or higher rates of H atom transport from the surface to the bulk at high temperature. The effect of H\textsubscript{2}S on H\textsubscript{2} dissociation over Pd\textsubscript{47}Cu\textsubscript{53} will be discussed further in Chapter 5.
Figure 3.12  Sulfur tolerance, which is defined as the ratio of the H$_2$ flux measured in the presence of 1000 ppm H$_2$S to the H$_2$ flux measured in pure H$_2$, of the Pd$_{47}$Cu$_{53}$ alloy versus temperature. The sulfur tolerance of the Pd$_{47}$Cu$_{53}$ alloy increases smoothly from zero at 623 K to one at ~900 K, at which point exposure to 1000 ppm H$_2$S has no effect on hydrogen permeation through the alloy.
3.6 Conclusions

In the 623 to 723 K temperature range, the intrinsic H atom permeabilities of Pd and Pd$_{47}$Cu$_{53}$ are similar; however, their responses to 1000 ppm H$_2$S at 623 K are significantly different. The Pd membrane is still permeable to H$_2$ after 6 hours of H$_2$S exposure with a H$_2$ flux that decreases slowly over time. In contrast, the Pd$_{47}$Cu$_{53}$ alloy is impermeable to H$_2$ after less than 5 minutes of H$_2$S exposure. Analysis of the Pd and Pd$_{47}$Cu$_{53}$ foils by x-ray diffraction, scanning electron microscopy, and x-ray photoelectron spectroscopy shows that H$_2$S reacts with Pd to form a relatively thick (~µm) palladium sulfide (Pd$_4$S) film, whereas sulfur penetrates only a few nm into the bulk of Pd$_{47}$Cu$_{53}$. The very low H atom permeability of Pd$_4$S, which is about an order-of-magnitude lower than that of Pd, is partially responsible for retarding hydrogen permeation through Pd; however, H$_2$S also inhibits hydrogen transport across Pd directly, possibly by blocking H$_2$ dissociation sites. The thin Pd-Cu-S layer that forms on the surface of the Pd$_{47}$Cu$_{53}$ alloy during H$_2$S exposure is either inactive for H$_2$ dissociation or is impermeable to H atoms at 623 K. At higher temperatures, the influence of H$_2$S on hydrogen permeation through Pd$_{47}$Cu$_{53}$ decreases until exposure at ~900 K to 1000 ppm H$_2$S has no effect on the rate of H$_2$ permeation.
Chapter 4

The Kinetics of H₂-D₂ Exchange over Pd, Cu, and PdCu Surfaces

4.1 Summary

PdCu alloy membranes are promising candidates for hydrogen separation from sulfur-containing gas mixtures. H₂ adsorption and desorption are important steps in hydrogen transport across PdCu membranes, but the kinetics of H₂ adsorption and desorption on PdCu surfaces is not well understood. In this chapter, the energetics of H₂ adsorption and desorption on Pd, Cu, and PdCu surfaces is investigated by microkinetic analysis of the H₂-D₂ exchange reaction (H₂ + D₂ → 2HD) over fixed beds of Pd, Cu, Pd₇₀Cu₃₀, and Pd₄₇Cu₅₃ foil at near-ambient pressure. The rate of H₂-D₂ exchange over Cu, which is the least active H₂-D₂ exchange catalyst in this study, is limited by the rate of H₂ and D₂ adsorption due to the large activation barrier to H₂ adsorption on Cu (0.54 ± 0.06 eV). The crystal structures of Pd (β-Pd-hydride and α-Pd-hydride) and of Pd₄₇Cu₅₃ (body-centered-cubic (BCC) and face-centered-cubic (FCC)) have a significant impact on the kinetics of H₂-D₂ exchange. The activation barriers to H₂ adsorption on β-Pd-hydride (0.3 ± 0.1 eV), α-Pd-hydride (0.12 ± 0.04 eV), Pd₇₀Cu₃₀ (0.09 ± 0.02 eV), BCC Pd₄₇Cu₅₃ (0.15 ± 0.02 eV), and FCC Pd₄₇Cu₅₃ (0.00 ± 0.02 eV) are relatively small compared to that on Cu. The rate of H₂-D₂ exchange over these catalysts (other than Cu) is determined mostly by the rate of H₂ desorption (desorption-limited). As expected, the order of decreasing H₂-D₂ exchange activity in the desorption-limited catalysts (FCC Pd₄₇Cu₅₃ > Pd₇₀Cu₃₀ > BCC
Pd$_{47}$Cu$_{53}$ > β-Pd-hydride > α-Pd-hydride) follows closely the order of increasing barrier to H$_2$ desorption: FCC Pd$_{47}$Cu$_{53}$ (0.46 ± 0.03 eV) < Pd$_{70}$Cu$_{30}$ (0.52 ± 0.02 eV) < β-Pd-hydride (0.63 ± 0.03 eV) < BCC Pd$_{47}$Cu$_{53}$ (0.67 ± 0.03 eV) < α-Pd-hydride (0.68 ± 0.06 eV). These results are significant because they show that, although the rate of H$_2$ adsorption on Cu is very low, Pd can be alloyed with as much as ~50 mol% Cu without significantly reducing H$_2$ adsorption rates.
4.2 Introduction

Pd membranes are attractive options for hydrogen separation and purification applications because of their near-infinite selectivity to H₂ separation and their high permeability to H₂ [10, 17]. However, pure Pd is susceptible to hydrogen embrittlement from the expansion of the Pd lattice during β-Pd-hydride formation [60, 61]. Furthermore, H₂S, a coal gasification byproduct, severely inhibits hydrogen permeation through pure Pd [1, 7, 9, 22, 24, 25]. PdCu alloys have exhibited resistance to hydrogen embrittlement [62] and improved sulfur tolerance relative to Pd [9, 19, 22, 29, 33, 34]. Pd₇₀Cu₃₀ and Pd₄₇Cu₅₃ (mol%) are two particularly attractive PdCu alloy compositions because of their sulfur tolerance and because of their relatively high permeability to H₂ [7, 9, 10, 19, 21]. Unlike the Pd₇₀Cu₃₀ alloy, which has only a FCC crystal structure in the temperature range of ~500 K to ~1200 K [9, 10], the Pd₄₇Cu₅₃ crystal structure is body-centered-cubic (BCC) at temperatures below ~700 K, and face-centered-cubic (FCC) at temperatures above ~800 K [10, 22, 43]. The H₂ permeability of the BCC crystal structure of Pd₄₇Cu₅₃ is about an order-of-magnitude greater than that of the FCC crystal structure of Pd₄₇Cu₅₃ [7, 9, 10].

In order to separate H₂ from mixed gas streams, Pd-based membranes must dissociatively adsorb H₂ on the upstream surface of the membrane and recombinatively desorb H₂ from the downstream surface. The energetics of H₂ dissociation over pure Pd and pure Cu have been well characterized; H₂ dissociates on Pd without significant activation barriers [12-16], whereas H₂ dissociation over Cu is hindered by a very large activation barrier (~0.5-0.7 eV)
However, the effect of alloying Pd with Cu on the energetics of the H₂ dissociation reaction is not well understood.

In this chapter, the energetics of H₂ dissociative adsorption and recombinative desorption on Pd, Cu, Pd₇₀Cu₃₀, and Pd₄₇Cu₅₃ foil surfaces is investigated by microkinetic analysis of the H₂-D₂ exchange reaction (H₂ + D₂ → 2HD) over these metals at near ambient pressure. We will show that there is a large activation barrier (~0.54 eV) to dissociative adsorption of H₂ on the Cu surface. In contrast, barriers to H₂ dissociation over Pd, Pd₇₀Cu₃₀, and Pd₄₇Cu₅₃ are relatively small. We will also show that the crystal structures of Pd (β-Pd-hydride and α-Pd-hydride) and of Pd₄₇Cu₅₃ (BCC and FCC) have a significant impact on the kinetics of H₂-D₂ exchange. Our results indicate that, although Cu has a very low H₂ dissociation activity, Pd can be alloyed with as much as ~50 mol% Cu without significantly reducing H₂ dissociation rates.

4.3 Experimental

H₂-D₂ exchange experiments were performed by flowing H₂, D₂, and Ar through a 4 mm I.D. quartz tube reactor that was packed with diced Pd, Cu, Pd₇₀Cu₃₀, or Pd₄₇Cu₅₃ foil while the product gas composition was analyzed by a mass spectrometer. A schematic of the H₂-D₂ exchange reactor is shown in Chapter 2 (Figure 2.2). The Pd (Alfa Aesar, 25 µm thick, 99.9% metals purity), Cu (Alfa Aesar, 100 µm thick, 99.95% metals purity), Pd₇₀Cu₃₀ (ACI Alloys, Inc., 100 µm thick, 99.0% metals purity), and Pd₄₇Cu₅₃ (ATI Wah Chang, 25 µm thick, 99.0% metals purity) foil was diced into ~1 mm² pieces. The total surface
area of each catalyst used was ~19 cm$^2$. A thermocouple was fixed with a metal wire to the outside of the quartz tube reactor near the catalyst. A tube furnace (Barnstead/Thermolyne 211000) was used to heat the reactor. Mass flow controllers (Aalborg GFC 17) regulated the flow rates of H$_2$ (99.999%, Valley National Gases), D$_2$ (99.999 %, Valley National Gases), and Ar (99.999%, Valley National Gases) to the catalyst bed. A ~1 m long, 320 µm I.D. quartz capillary (Polymicro Technologies) was sealed into the outlet of the quartz tube reactor and the product gas was sampled by a ~15 cm long, 20 µm I.D quartz capillary (Polymicro Technologies) that was mounted to a vacuum chamber with a mass spectrometer (Stanford Research Systems, RGA 200).

The Pd$_{47}$Cu$_{53}$ alloy has a BCC crystal structure at temperatures below ~700 K and a FCC crystal structure at temperatures above ~800 K [10, 22, 43]. H$_2$-D$_2$ exchange experiments were performed over both the BCC and FCC phases of the Pd$_{47}$Cu$_{53}$ alloy. Over the temperature range that the experiments with the Pd$_{47}$Cu$_{53}$ alloy were conducted (200-500 K), only the BCC crystal structure was stable. To produce the FCC crystal structure, the alloy was first annealed at ~1000 K for ~24 and then cooled quickly (~15 minutes) to ~400 K to quench the FCC crystal structure. To produce the BCC structure, the Pd$_{47}$Cu$_{53}$ alloy was annealed in H$_2$ at ~700 K for ~48 hours. The crystal structures of the BCC and FCC alloy were verified by x-ray diffraction (XRD) following H$_2$-D$_2$ exchange experiments. The crystal structures of BCC Pd$_{47}$Cu$_{53}$ and of FCC Pd$_{47}$Cu$_{53}$ did not change during the H$_2$-D$_2$ exchange experiments.
Each catalyst was initially heated in $\text{H}_2$ to $\sim 700 \text{ K}$ ($\sim 1000 \text{ K}$ for Cu and FCC Pd$_{37}$Cu$_{53}$) and held at that temperature for $\sim 24$ hours. We found that this heat treatment was necessary because a hysteresis in the HD production rate was observed when the experiments began at low temperature without an initial heat treatment. Figure 4.1 shows the HD flow rate exiting a Cu foil catalyst bed (a) without the initial heat treatment and (b) with the initial heat treatment. Without the initial heat treatment, $\text{H}_2$-$\text{D}_2$ exchange rates were measured over the Cu foil catalyst bed during heating of the Cu foil catalyst and then during the cooling of the catalyst. The HD flow rate exiting the Cu foil catalyst bed was lower during the initial heating of the catalyst than it was during the subsequent cooling of the catalyst. With the initial heat treatment to 1000 K, the experiment was done during cooling from high temperature and then during heating. The HD flow rate exiting the Cu foil catalyst bed was nearly identical during the cooling and heating branches after the initial heat treatment to 1000 K. It is possible that this initial heat treatment in $\text{H}_2$ is necessary to remove contaminants from the catalyst surface.
After the initial heat treatment, the H$_2$/D$_2$/Ar feed gas mixture was introduced to the reactor. Three different feed gas conditions were used, which are summarized in Table 4.1, to exercise the kinetic model over a range of flow rates and partial pressures of H$_2$ and D$_2$. The total pressure in the reactor was measured with a Baratron pressure gauge. Starting from the temperature of the heat treatment, the catalyst was cooled in a step-wise fashion. Steady-state H$_2$, D$_2$, and HD mass spectrometer signals were collected at constant temperature to minimize

![Figure 4.1 HD flow rates exiting a Cu foil catalyst bed (a) without an initial heat treatment and (b) with an initial heat treatment of the Cu catalyst in H$_2$ at 1000 K. Without the initial heat treatment, the HD flow rate exiting the Cu foil catalyst bed during the initial heating stage of the experiment (filled squares) is lower than the HD flow rate during the subsequent cooling stage (open squares). With the initial heat treatment, the HD flow rate during the initial cooling stage is nearly identical to the HD flow rate in the subsequent heating stage. The initial heat treatment to 1000 K, which may remove contaminants from the catalyst surface, was necessary to eliminate the hysteresis in the HD production rate.](image-url)
the effect of H (or D) evolution from, or absorption into, the bulk of the catalyst on the kinetics of the reaction.

Table 4.1  Flow rates of H\textsubscript{2} (\(F_{\text{H2,feed}}\)), D\textsubscript{2} (\(F_{\text{D2,feed}}\)), and Ar (\(F_{\text{Ar,feed}}\)) in the three different feed gas conditions used during H\textsubscript{2}-D\textsubscript{2} exchange experiments. Also listed is the total pressure (\(P_{\text{total}}\)) in the reactor with the three feed gas conditions.

<table>
<thead>
<tr>
<th>Feed Gas Condition</th>
<th>(F_{\text{H2,feed}}) (mL/min)</th>
<th>(F_{\text{D2,feed}}) (mL/min)</th>
<th>(F_{\text{Ar,feed}}) (mL/min)</th>
<th>(P_{\text{total}}) (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9H\textsubscript{2}/9D\textsubscript{2}</td>
<td>9</td>
<td>9</td>
<td>0</td>
<td>121</td>
</tr>
<tr>
<td>4.5H\textsubscript{2}/4.5D\textsubscript{2}</td>
<td>4.5</td>
<td>4.5</td>
<td>0</td>
<td>113</td>
</tr>
<tr>
<td>9Ar/4.5H\textsubscript{2}/4.5D\textsubscript{2}</td>
<td>4.5</td>
<td>4.5</td>
<td>9</td>
<td>135</td>
</tr>
</tbody>
</table>

Mass spectrometer signals were calibrated assuming that the H\textsubscript{2}, D\textsubscript{2}, and HD mass spectrometer signals sampled from the product gas were proportional to the H\textsubscript{2}, D\textsubscript{2}, and HD partial pressures exiting the catalyst bed in between the baseline (0% conversion) and equilibrium conversion. Baseline H\textsubscript{2}, D\textsubscript{2}, and HD mass spectrometer signals were collected by sampling the feed gas directly without passing them through the catalyst bed. At equilibrium the H\textsubscript{2}/D\textsubscript{2}/HD composition in the product gas is given by:

\[
\frac{P^2_{\text{HD}}}{P_{\text{H2}} P_{\text{D2}}} = 4.16 \exp \left( -\frac{77.7}{T} \right).
\]
where $P_{H2}$, $P_{D2}$, and $P_{HD}$ are the partial pressures of H$_2$, D$_2$, and HD at equilibrium [74]. H$_2$, D$_2$, and HD partial pressures were then converted into H$_2$, D$_2$, and HD flow rates:

$$F_i = \frac{F_{\text{total}} \cdot P_i}{P_{\text{total}}}.$$ 

where $F_i$ is the flow rate of each species, $F_{\text{total}}$ is the total flow rate, $P_i$ is the partial pressure of each species, and $P_{\text{total}}$ is the total pressure. The HD flow rates exiting the catalyst bed during H$_2$-D$_2$ exchange experiments were used for microkinetic analysis of the H$_2$-D$_2$ exchange reaction.

### 4.4 Kinetic model

We made three basic assumptions in deriving the microkinetic model of the H$_2$-D$_2$ exchange reaction:

1) The H$_2$-D$_2$ exchange reaction can be modeled by considering only dissociative adsorption and recombinative desorption of H$_2$, D$_2$, and HD.

2) Isotopic effects can be ignored (i.e. the adsorption rate constants are the same for H$_2$, D$_2$, and HD; and the desorption rate constants are the same for H$_2$, D$_2$, and HD).

3) The activation barriers and pre-exponents in the rate constants for adsorption and desorption are independent of coverage and temperature.

With these three simplifying assumptions, derivation of the H$_2$-D$_2$ exchange kinetic model requires substitution of the microkinetic expression for the rate of
HD production into the integral mole balance on HD. A detailed derivation of the microkinetic model is given in the Appendix. The flow rate of HD exiting the foil catalyst bed \( F_{\text{HD, out}} \) is given by:

\[
F_{\text{HD, out}} = F_{\text{H2, feed}} \left[ 1 - \exp \left( -\frac{k_{\text{ads}} P_{\text{total}} A}{F_{\text{total}}} \left( 1 + \sqrt{\frac{2 k_{\text{ads}}}{k_{\text{des}}} P_{\text{H2, feed}}} \right) \right) \right]
\] (4.1)

where \( F_{\text{H2, feed}} \) is the flow rate of H\(_2\) in the feed gas, \( k_{\text{ads}} \) is the adsorption rate constant, \( P_{\text{total}} \) is the total pressure in the reactor, \( A \) is the catalyst surface area, \( F_{\text{total}} \) is the total gas flow rate through the reactor, \( k_{\text{des}} \) is the desorption rate constant, and \( P_{\text{H2, feed}} \) is the partial pressure of H\(_2\) in the feed gas. The adsorption rate constant, \( k_{\text{ads}} \), and the desorption rate constant, \( k_{\text{des}} \), have Arrhenius forms:

\[
k_{\text{ads}} = \nu_{\text{ads}} \exp \left( -\frac{E_{\text{ads}}}{k_B T} \right)
\]

\[
k_{\text{des}} = \nu_{\text{des}} \exp \left( -\frac{E_{\text{des}}}{k_B T} \right)
\]

where \( \nu_{\text{ads}} \) is the adsorption pre-exponent, \( E_{\text{ads}}^{\ddagger} \) is the adsorption activation barrier, \( \nu_{\text{des}} \) is the desorption pre-exponent, \( E_{\text{des}}^{\ddagger} \) is the desorption activation barrier, \( k_B \) is the Boltzmann constant, and \( T \) is the temperature. The total coverage of H and D atoms during H\(_2\)-D\(_2\) exchange is given by:

\[
\theta = \sqrt{\frac{2 k_{\text{ads}}}{k_{\text{des}}} P_{\text{H2, feed}}} .
\] (4.2)
The partial pressures of H\(_2\) and D\(_2\) were the same in all experiments so that the coverages of H and D could be assumed to be the same. Equation (4.2) implies that the coverage of H and D atoms is constant along the length of the catalyst bed. To determine the values of \(\nu_{\text{ads}}\), \(E_{\text{ads}}^\parallel\), \(\nu_{\text{des}}\), and \(E_{\text{des}}^\parallel\) that describe H\(_2\) adsorption and desorption on each catalyst, the experimental and modeled HD flow rates exiting the reactor (\(F_{\text{HD, out}}\)) were first normalized by the flow rate of HD exiting the reactor at equilibrium conversion (\(F_{\text{HD}}^{eq}\)):

\[
X_{\text{HD}} = \frac{F_{\text{HD, out}}}{F_{\text{HD}}^{eq}},
\]

where \(X_{\text{HD}}\) is the conversion of HD. A numerical solver was then used to minimize the error between the model-predicted and experimental HD conversion by adjusting \(ln(\nu_{\text{ads}}), E_{\text{ads}}^\parallel, ln(\nu_{\text{des}}), \) and \(E_{\text{des}}^\parallel\). The uncertainty in these solver-optimized parameters was estimated with a “SolverAid” program [75].

### 4.5 Results and discussion

#### 4.5.1 \(H_2-D_2\) exchange over Pd

\(H_2-D_2\) exchange over Pd was carried out by feeding \(H_2\), D\(_2\), and Ar to a Pd foil catalyst bed while the product gas composition was analyzed by a mass spectrometer. Mass spectrometer signals were then converted into flow rates and HD conversion. Figure 4.2(a) shows the HD flow rates exiting the Pd catalyst bed with the three different feed gas conditions: 9 mL/min each of \(H_2\) and D\(_2\), 4.5 mL/min each of \(H_2\) and D\(_2\), and 4.5 mL/min each of \(H_2\) and D\(_2\) diluted with 9 mL/min of Ar.
There is a discontinuity in the HD flow rate exiting the Pd foil catalyst bed at ~410 K for both of the pure H$_2$/D$_2$ feed gases and at ~400 K for the Ar/H$_2$/D$_2$ feed gas. The discontinuity in the HD flow occurs at a temperature that is close to the temperature of the β-Pd-hydride to α-Pd-hydride phase transition at a H$_2$ partial pressure of ~1 atm (see Figure 4.3) [76-78].
The β-Pd-hydride to α-Pd-hydride phase transition decreases with decreasing H₂ partial pressure, which is consistent with the observation that the discontinuity in the HD flow rate in Figure 4.2 (a) occurs at a lower temperature for the Ar/H₂/D₂ feed gas than that for the H₂/D₂ feed gases. Therefore, the discontinuity in the HD flow rate exiting the Pd foil catalyst bed is likely due to the β-Pd-hydride to α-Pd-hydride phase transition with increasing temperature; the α-Pd-hydride phase exhibits a lower H₂-D₂ exchange activity than the β-Pd-hydride phase.

**Figure 4.3** Pressure-temperature diagram of the palladium-hydrogen system adapted from [78]. At a hydrogen pressure of ~1 atm, the temperature of the β-Pd-hydride to α-Pd-hydride phase transition is ~400 K, which is similar to the temperature of the discontinuity in the HD flow rate exiting the Pd foil catalyst bed (Figure 4.2(a)). The temperature of the β-Pd-hydride to α-Pd-hydride phase transition decreases with decreasing hydrogen pressure, which could explain why the temperature of the discontinuity in the HD flow rate exiting the Pd foil catalyst bed (Figure 4.2(a)) occurs at a lower temperature when the H₂ pressure in the feed gas is reduced by diluting the H₂/D₂ feed gas with Ar.
It is worth noting that each data point used to generate Figure 4.2(a) was collected at constant temperature; a much different result is obtained by performing the H\textsubscript{2}-D\textsubscript{2} exchange experiment over Pd while increasing the temperature of the catalyst at a constant rate. Figure 4.4 shows the partial pressures of H\textsubscript{2}, D\textsubscript{2}, HD, and Ar in the product gas during H\textsubscript{2}-D\textsubscript{2} exchange over the Pd foil catalyst bed while the catalyst temperature was increased at a constant rate of 10 K/min and with feed gas flow rates of 9 mL/min of Ar and 4.5 mL/min each of H\textsubscript{2} and D\textsubscript{2}. Because Ar is an inert gas, one would expect that the Ar partial pressure in the product gas would remain constant over the course of the reaction. Instead, there is a dip in the Ar partial pressure in the temperature range ~420 and ~460 K. In that same temperature range, there is a spike in the H\textsubscript{2} and HD partial pressures, and a dip in the D\textsubscript{2} partial pressure. We believe that H\textsubscript{2} evolution from the Pd bulk during the β-Pd-hydride to α-Pd-hydride phase transition is responsible for the spike in the H\textsubscript{2} partial pressure and the dip in the Ar partial pressure. The β-Pd-hydride phase has a much higher concentration of H atoms in its bulk (H:Pd ≈ 0.6) than the α-Pd-hydride phase (H:Pd ≈ 0.03) [79] and, therefore, a large amount of hydrogen must evolve from the Pd bulk during the β-Pd-hydride to α-Pd-hydride phase transition. The solubility of H in Pd is much higher than the solubility of D in Pd [80], which could explain why no spike was observed in the D\textsubscript{2} partial pressure. The temperature of the discontinuity in the steady-state HD flow rate exiting the Pd foil catalyst bed (~400 K) is not exactly the same as the temperature of the spike in the H\textsubscript{2} partial pressure while
the Pd catalyst temperature was increased at a constant rate (~420 to ~460 K). This is probably because the $\beta$-Pd-hydride to $\alpha$-Pd-hydride phase transition does not occur instantaneously.

**Figure 4.4** Partial pressures of $H_2$, $D_2$, HD, and Ar in the product gas during $H_2$-$D_2$ exchange over a Pd foil catalyst bed during heating of the catalyst at 10 K/min and with feed gas flow rates of 9 mL/min of Ar and 4.5 mL/min each of $H_2$ and $D_2$. The spike in the $H_2$ partial pressure in the temperature range ~420 and ~460 K, and the dip in the Ar partial pressure in the same temperature range, is likely due to hydrogen evolution from the bulk of Pd during the $\beta$-Pd-hydride to $\alpha$-Pd-hydride phase transition. The higher solubility of H in Pd than that of D in Pd could explain why no spike was observed in the $D_2$ partial pressure.
To determine the parameters that describe H\textsubscript{2} adsorption ($v_{\text{ads}}$ and $E_{\text{ads}}^\ddagger$) and H\textsubscript{2} desorption ($v_{\text{des}}$ and $E_{\text{des}}^\ddagger$) on β-Pd-hydride and α-Pd-hydride, a numerical solver was used to minimize the error between the modeled and the experimental HD conversion (HD flow rate divided by the HD flow rate at equilibrium) by adjusting $\ln(v_{\text{ads}})$, $E_{\text{ads}}^\ddagger$, $ln(v_{\text{des}})$, and $E_{\text{des}}^\ddagger$. We modeled H\textsubscript{2}-D\textsubscript{2} exchange over β-Pd-hydride and α-Pd-hydride separately. The solver-optimized values for the parameters associated with the β-Pd-hydride phase are summarized in Table 4.2.

Table 4.2 Summary of the adsorption pre-exponents ($v_{\text{ads}}$), adsorption barriers ($E_{\text{ads}}^\ddagger$), desorption pre-exponents ($v_{\text{des}}$), desorption barriers ($E_{\text{des}}^\ddagger$), and heats of adsorption of H\textsubscript{2} ($\Delta E_{\text{ads}}$) on β-Pd-hydride and α-Pd-hydride.

<table>
<thead>
<tr>
<th></th>
<th>$v_{\text{ads}}$ (mol/m\textsuperscript{2}/s/Pa)</th>
<th>$E_{\text{ads}}^\ddagger$ (eV)</th>
<th>$v_{\text{des}}$ (mol/m\textsuperscript{2}/s)</th>
<th>$E_{\text{des}}^\ddagger$ (eV)</th>
<th>$\Delta E_{\text{ads}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-Pd-hydride</td>
<td>$10^{-3.7} \pm 0.7$</td>
<td>0.3 ± 0.1</td>
<td>$10^{5.8} \pm 0.4$</td>
<td>0.63 ± 0.03</td>
<td>-0.3 ± 0.1</td>
</tr>
<tr>
<td>α-Pd-hydride</td>
<td>$10^{-5.4} \pm 0.4$</td>
<td>0.12 ± 0.04</td>
<td>$10^{6.3} \pm 0.8$</td>
<td>0.68 ± 0.06</td>
<td>-0.56 ± 0.07</td>
</tr>
</tbody>
</table>

Using the solver-optimized values for $v_{\text{ads}}$, $E_{\text{ads}}^\ddagger$, $v_{\text{des}}$, and $E_{\text{des}}^\ddagger$ associated with the β-Pd-hydride phase, HD flow rates were calculated with the H\textsubscript{2}-D\textsubscript{2} exchange model, equation (4.1), at temperatures less than 410 K (400 K for the 9Ar / 4.5H\textsubscript{2} / 4.5D\textsubscript{2} feed gas). At temperatures greater than 410 K (400 K for the 9Ar / 4.5H\textsubscript{2} / 4.5D\textsubscript{2} feed gas), the solver-optimized parameters associated with the α-Pd-hydride phase were used to calculate HD flow rates. Figure 4.2(a) shows that the modeled HD flow rates fit the experimental HD flow rates reasonably well for both the β-Pd-hydride and α-Pd-hydride phases.
The total coverage of H and D atoms during H\textsubscript{2}-D\textsubscript{2} exchange over Pd was calculated with equation (4.2) and the solver-optimized values for \(v_{\text{ads}}\), \(E_{\text{ads}}^\dagger\), \(v_{\text{des}}\), and \(E_{\text{des}}^\dagger\). The values of \(v_{\text{ads}}\), \(E_{\text{ads}}^\dagger\), \(v_{\text{des}}\), and \(E_{\text{des}}^\dagger\) associated with the \(\beta\)-Pd-hydride phase were used to calculate the total coverage at temperatures less than 410 K (400 K for the 9Ar / 4.5H\textsubscript{2} / 4.5D\textsubscript{2} feed gas); and the values of \(v_{\text{ads}}\), \(E_{\text{ads}}^\dagger\), \(v_{\text{des}}\), and \(E_{\text{des}}^\dagger\) associated with the \(\alpha\)-Pd-hydride were used to calculate the coverage at temperatures greater than 410 K (400 K for the 9Ar / 4.5H\textsubscript{2} / 4.5D\textsubscript{2}). Figure 4.2(b) shows the total coverage of H and D atoms during H\textsubscript{2}-D\textsubscript{2} exchange over Pd with the three different feed gas conditions. At low temperature (~300 K), the \(\beta\)-Pd-hydride surface is nearly saturated with H and D atoms. As the temperature increases, the total coverage decreases for all three feed gas conditions. Diluting the H\textsubscript{2}/D\textsubscript{2} feed gas with Ar (9Ar / 4.5H\textsubscript{2} / 4.5D\textsubscript{2}), which reduces the rate of H\textsubscript{2} and D\textsubscript{2} adsorption by lowering the H\textsubscript{2} and D\textsubscript{2} partial pressures, reduces the total coverage of H and D atoms. At ~410 K (400 K for the 9Ar / 4.5H\textsubscript{2} / 4.5D\textsubscript{2}), there is a discontinuity in the total coverage due to the \(\beta\)-Pd-hydride to \(\alpha\)-Pd-hydride phase transition. As the temperature increases further in the \(\alpha\)-Pd-hydride region, the total coverage continues to decrease.

The discontinuity in the HD flow rate exiting the Pd foil catalyst bed (Figure 4.2(a)) clearly indicates that there is a difference in the energetics of H\textsubscript{2} adsorption/desorption on the \(\beta\)-Pd-hydride and \(\alpha\)-Pd-hydride surfaces. A comparison of the potential energy of H\textsubscript{2} adsorption on \(\beta\)-Pd-hydride and \(\alpha\)-Pd-hydride is shown in Figure 4.5. There is a significantly larger barrier to H\textsubscript{2} adsorption on the \(\beta\)-Pd-hydride (0.3 ± 0.1 eV) surface than on the \(\alpha\)-Pd-hydride
(0.12 ± 0.04 eV) surface. The heat of adsorption ($\Delta E_{ads} = E_{ads}^+ - E_{des}^+$) of H$_2$ on the β-Pd-hydride surface (-0.3 ± 0.1 eV) is significantly less negative than that on the α-Pd-hydride surface (-0.56 ± 0.07 eV), indicating that H atoms are less stable on the β-Pd-hydride surface than on the α-Pd-hydride surface. The activation barrier to H$_2$ desorption from β-Pd-hydride (0.63 ± 0.03 eV) is not significantly different than that from α-Pd-hydride (0.68 ± 0.06).

There are two main differences in the β-Pd-hydride and α-Pd-hydride phases that might explain the apparent differences in the H$_2$ adsorption activation barrier and the heat of adsorption of H$_2$ on the two phases. First, the lattice constant of β-Pd-hydride (~4.02 Å) is significantly larger than the lattice constant

\[ \text{Energy} \ (\text{eV}) \]

\[ \begin{align*}
0.6 & \quad 0.4 \\
0.2 & \quad 0.0 \\
-0.2 & \quad 0.6 \\
-0.4 & \quad 0.2 \\
-0.6 & \quad 0.0 \\
\end{align*} \]

\[ \text{H}_2 \ (g) \]

\[ \text{H} - \cdot \text{H} \]

\[ \begin{align*}
\text{2H} \ (ad) & \quad \beta\text{-Pd-hydride} \\
\alpha\text{-Pd-hydride} & \end{align*} \]

\[ \text{Figure 4.5} \] Potential energy diagram for H$_2$ adsorption on β-Pd-hydride and α-Pd-hydride.
of $\alpha$-Pd-hydride (~3.89 Å) [81]. Expansion of the Pd lattice has been shown to increase the stability of hydrogen adsorption [82], however, which is not consistent with our observation that H atoms are more stable on the surface that has a smaller lattice constant ($\alpha$-Pd-hydride). Increasing the lattice constant of other metals (e.g. Ru [83]) has also been shown to decrease barriers to adsorption, which is also not consistent with our observations that the barrier to H$_2$ adsorption is larger on the surface with a larger lattice constant ($\beta$-Pd-hydride). Second, there is a much higher concentration of H atoms in the bulk of $\beta$-Pd-hydride (H:Pd $\approx$ 0.6) than in the bulk of $\alpha$-Pd-hydride (H:Pd $\approx$ 0.03) [78]. There may also be a higher concentration of H atoms in the sub-surface (the layer just below the surface) of $\beta$-Pd-hydride than in the sub-surface of $\alpha$-Pd-hydride. Sykes et al. [84] have shown that H atoms in the Pd(111) sub-surface destabilized H atoms at sites directly above the sub-surface H atoms. Therefore, it is possible that there is a large concentration of H atoms in the sub-surface of $\beta$-Pd-hydride that could destabilize H atom adsorption relative to $\alpha$-Pd-hydride, which may have a much lower concentration of sub-surface H atoms.

There have been many experimental [12, 13, 77, 85-87] and theoretical [27, 28, 77, 88] studies of H$_2$ adsorption and desorption on Pd surfaces. Most of the experimental studies of H$_2$ adsorption and desorption on Pd were done with Pd single crystals in ultra-high vacuum. A comparison of our results to many of those in literature is not straightforward because, in this work, polycrystalline Pd foil was used and there was evidence of bulk Pd-hydride formation from exposure to near-ambient pressures of hydrogen. There have been few studies of H$_2$
adsorption and desorption on polycrystalline Pd-hydride surfaces at near-ambient pressure [77, 85, 87]. In one study [77], the activation barriers to H₂ desorption from β-Pd-hydride and α-Pd-hydride were determined from kinetic analysis of H₂-D₂ exchange over a thin Pd film at near-ambient pressures. The authors reported activation barriers for H₂ desorption from β-Pd-hydride (~0.33 eV) and α-Pd-hydride (~0.27 eV) that were much lower than the values obtained in this work (0.63 ± 0.03 eV on β-Pd-hydride and 0.68 ± 0.06 on α-Pd-hydride). In their calculation of the desorption barrier, they assumed that the surface was saturated with H atoms and it is possible that an erroneous assumption about the coverage may have influenced their calculation of the H₂ desorption barrier. For example, if we assume that the β-Pd-hydride and α-Pd-hydride surfaces are saturated with H and D atoms in our calculation of the H₂ desorption activation barrier, we obtain activation barriers to H₂ desorption (0.54 eV for β-Pd-hydride and 0.38 eV for α-Pd-hydride) that are significantly lower than if we account for the changing coverage over the temperature range of the H₂-D₂ exchange reaction.

In the same study [77], the energetics of H₂ adsorption on a model Pd-hydride (H:Pd = 0.75) was investigated by density functional theory (DFT) calculations. The authors’ results for the adsorption barrier, the desorption barrier, and the heat of adsorption of H₂ on the model Pd-hydride were all in good agreement with those values obtained on β-Pd-hydride in this work. The authors calculated a H₂ adsorption barrier on the model Pd-hydride of ~0.28 eV at high coverage of H [77]: our results indicate that the barrier to H₂ adsorption on β-Pd-hydride is 0.3 ± 0.1 eV at coverages in the range 0.5 to 1. The DFT calculated
heat of adsorption of H\textsubscript{2} on the model Pd-hydride at high coverage [77] was -0.40 eV, which is close to the heat of adsorption of H\textsubscript{2} on \(\beta\)-Pd-hydride obtained in this work (-0.3 \pm 0.1 eV). The calculated activation barrier to H\textsubscript{2} desorption on the model Pd-hydride was about 0.68 eV at high coverage [77], which is also close to the activation barrier to H\textsubscript{2} desorption on \(\beta\)-Pd-hydride obtained in this work (0.63 \pm 0.03 eV). Although there is a shortage of experimental data on the energetics of H\textsubscript{2} dissociation on Pd-hydride surfaces, our results are in good agreement with DFT calculations.

In summary, there is a discontinuity in the rate of H\textsubscript{2}-D\textsubscript{2} exchange over the Pd foil catalyst bed at \(\sim\)400 K that is related to the \(\beta\)-Pd-hydride to \(\alpha\)-Pd-hydride phase transition. Microkinetic analysis of the H\textsubscript{2}-D\textsubscript{2} exchange reaction indicates that the energetics of H\textsubscript{2} adsorption on \(\beta\)-Pd-hydride are significantly different than those on \(\alpha\)-Pd-hydride. The activation barrier to H\textsubscript{2} adsorption on the \(\beta\)-Pd-hydride surface (0.3 \pm 0.1 eV) is significantly higher than that on the \(\alpha\)-Pd-hydride surface (0.12 \pm 0.04 eV); and the heat of adsorption of H\textsubscript{2} on the \(\beta\)-Pd-hydride surface (-0.3 \pm 0.1 eV) is significantly less negative than that on the \(\alpha\)-Pd-hydride surface (-0.56 \pm 0.07 eV). These differences may be related to differences in sub-surface H atom concentrations in the two phases or due to the differences in the lattice constants of \(\beta\)-Pd-hydride (4.02 Å) and \(\alpha\)-Pd-hydride (3.89 Å).
4.5.2 $H_2$-$D_2$ exchange over Cu

$H_2$-$D_2$ exchange over Cu was carried out using a methodology similar to that used for Pd. Figure 4.6(a) shows the HD flow rates exiting the Cu foil catalyst bed with the three different feed gas conditions: 9 mL/min each of $H_2$ and $D_2$, 4.5 mL/min each of $H_2$ and $D_2$, and 4.5 mL/min each of $H_2$ and $D_2$ diluted with 9 mL/min of Ar. In contrast to Pd, there are no discontinuities in the HD flow rate exiting the Cu foil catalyst bed and there was no evidence of Cu-hydride formation.
Figure 4.6 (a) Experimental (points) and modeled (lines) HD flow rates versus temperature exiting a Cu foil catalyst bed with three different feed gas conditions: 4.5 mL/min each of H\(_2\) and D\(_2\) (4.5H\(_2\) / 4.5D\(_2\)), 9 mL/min each of H\(_2\) and D\(_2\) (9H\(_2\) / 9D\(_2\)), and 4.5 mL/min each of H\(_2\) and D\(_2\) diluted with 9 mL/min of Ar (9Ar / 4.5H\(_2\) / 4.5D\(_2\)). Modeled HD flow rates were calculated with equation (4.1) and the solver-optimized values for \(v_{ads}\), \(E_{ads}^\ddagger\), \(v_{des}\), \(E_{des}^\ddagger\). (b) Total coverage of H and D atoms during H\(_2\)-D\(_2\) exchange over the Cu foil catalyst bed. The total coverage was calculated using equation (4.2) and the solver-optimized values for \(v_{ads}\), \(E_{ads}^\ddagger\), \(v_{des}\), \(E_{des}^\ddagger\).
The values of $v_{ads}$, $E_{ads}^\dagger$, $v_{des}$, $E_{des}^\dagger$ that describe H$_2$ adsorption and desorption on Cu were determined by using a numerical solver to minimize the error between the modeled and the experimental HD conversion by adjusting $ln(v_{ads})$, $E_{ads}^\dagger$, $ln(v_{des})$, and $E_{des}^\dagger$. The solver-optimized parameters for H$_2$-D$_2$ exchange over Cu were as follows: $v_{ads} = 10^{-3.4 \pm 0.5}$ mol/m$^2$/s/Pa, $E_{ads}^\dagger = 0.54 \pm 0.06$ eV, $v_{des} = 10^4 \pm 5$ mol/m$^2$/s, and $E_{des}^\dagger = 0.6 \pm 0.7$ eV. The large uncertainty in the desorption pre-exponent ($10^4 \pm 5$ mol/m$^2$/s) and desorption barrier (0.6 \pm 0.7 eV) indicates that the rate of H$_2$-D$_2$ exchange is insensitive to the parameters associated with H$_2$ desorption and, therefore, that the rate of H$_2$-D$_2$ exchange over Cu is limited by the rate of H$_2$ adsorption. HD flow rates exiting the Cu foil catalyst were calculated with the H$_2$-D$_2$ exchange model, equation (4.1), and the solver-optimized values for $v_{ads}$, $E_{ads}^\dagger$, $v_{des}$, and $E_{des}^\dagger$; Figure 4.6(a) shows that the model fits the experimental data very well. Because the rate of H$_2$-D$_2$ exchange over Cu is limited by the rate of H$_2$ and D$_2$ adsorption, which depends on the H$_2$ and D$_2$ partial pressures, diluting the 4.5H$_2$ / 4.5D$_2$ feed gas with Ar (9Ar / 4.5H$_2$ / 4.5D$_2$) significantly reduces the HD flow rate exiting the Cu foil catalyst bed. This was observed experimentally and was accurately predicted by the model.

Using the solver-optimized values for $v_{ads}$, $E_{ads}^\dagger$, $v_{des}$, and $E_{des}^\dagger$, the total coverage of H and D atoms during H$_2$-D$_2$ exchange over Cu was calculated with equation (4.2) and is plotted in Figure 4.6(b). In contrast to the total coverage of H and D atoms on Pd during H$_2$-D$_2$ exchange (Figure 4.2(b)), the total coverage of H and D atoms on the Cu surface is nearly constant throughout the temperature
range of the H2-D2 exchange reaction, and is about one-tenth the saturation coverage. The coverage of H and D atoms is low because the activation barrier to H2 adsorption on Cu is high (0.54 ± 0.06 eV) and, as a result, the rate of adsorption is low.

The energetics of H2 adsorption and desorption on Cu has been well characterized experimentally [65, 66, 68-70] and theoretically [63, 64, 67, 71, 73] in the literature. Most of the reported values for the H2 adsorption barrier on Cu single crystals are within the 0.5 to 0.7 eV range [64-73]. Our analysis indicates that the activation barrier to H2 adsorption on polycrystalline Cu foil is 0.54 ± 0.06 eV, which is in good agreement with the literature. Although the value for the H2 desorption barrier on Cu (0.6 ± 0.7 eV) obtained from this work has a large uncertainty, Campbell and Campbell [68] reported a barrier to H2 desorption on Cu(110) of ~0.57 eV, which is similar to our mean value.

4.5.3 H2-D2 exchange over Pd70Cu30

In this section, the energetics of H2 dissociation over Pd70Cu30 is investigated by microkinetic analysis of the H2-D2 exchange reaction over a Pd70Cu30 foil catalyst bed. Figure 4.7(a) shows the HD flow rates exiting a Pd70Cu30 foil catalyst bed with the three different feed gas conditions.
Microkinetic analysis of H$_2$-D$_2$ exchange over Pd$_{70}$Cu$_{30}$ was done by minimizing the error between the modeled and the experimental HD conversion. The solver-optimized values of these parameters are as follows: $v_{\text{ads}} = 10^{5.6 \pm 0.2}$ mol/m$^2$/s/Pa, $E_{\text{ads}}^\dagger = 0.09 \pm 0.02$ eV, $v_{\text{des}} = 10^{5.7 \pm 0.3}$ mol/m$^2$/s, $E_{\text{des}}^\dagger = 0.52 \pm 0.02$ eV. These are the first reported experimental measurements of the activation
barriers to H\textsubscript{2} adsorption or desorption on the Pd\textsubscript{70}Cu\textsubscript{30} surface, to the best of our knowledge. Using the mean values of these solver-optimized parameters, the predicted HD flow rates were calculated with the H\textsubscript{2}-D\textsubscript{2} exchange model, equation (4.1). A comparison of the modeled and experimental HD flow rates is shown in Figure 4.7(a); the model fits the experimental data very well.

The total coverage of H and D atoms during H\textsubscript{2}-D\textsubscript{2} exchange over Pd\textsubscript{70}Cu\textsubscript{30} was calculated using equation (4.2) and the solver-optimized values for \(v_{\text{ads}}, E_{\text{des}}^{\dagger}, v_{\text{des}}^{\dagger}, \) and \(E_{\text{ads}}^{\dagger}.\) Figure 4.7(b) shows the total coverage of H and D atoms during H\textsubscript{2}-D\textsubscript{2} exchange over Pd\textsubscript{70}Cu\textsubscript{30} with the three different feed gas conditions. The evolution of the total coverage on the Pd\textsubscript{70}Cu\textsubscript{30} surface with increasing temperature is similar to that on Pd and dissimilar to that on Cu. At low temperature (~250 K), the Pd\textsubscript{70}Cu\textsubscript{30} surface is nearly saturated with H and D atoms. As the temperature increases, the total coverage decreases. Diluting the feed gas with Ar reduces the rate of adsorption and reduces the total coverage of H and D atoms.

Diluting the H\textsubscript{2}/D\textsubscript{2} feed gas with Ar did not significantly reduce the rate of HD production over the Pd\textsubscript{70}Cu\textsubscript{30} foil catalyst bed (Figure 4.7(a)). This indicates that the rate of H\textsubscript{2}-D\textsubscript{2} exchange over the Pd\textsubscript{70}Cu\textsubscript{30} foil catalyst was controlled by the rate of H\textsubscript{2} desorption, which is independent of the H\textsubscript{2} and D\textsubscript{2} partial pressures, rather than by the rate of H\textsubscript{2} adsorption. As a result, there was a relatively high coverage of H and D atoms during H\textsubscript{2}-D\textsubscript{2} exchange over Pd\textsubscript{70}Cu\textsubscript{30} (Figure 4.7(b)). Microkinetic analysis of H\textsubscript{2}-D\textsubscript{2} exchange over Pd\textsubscript{70}Cu\textsubscript{30} also indicates that the
barrier to $\text{H}_2$ adsorption on Pd$_{70}$Cu$_{30}$ (0.09 ± 0.02 eV) is small relative to the barrier to $\text{H}_2$ desorption on Pd$_{70}$Cu$_{30}$ (0.52 ± 0.02 eV).

4.5.4 $\text{H}_2$-$\text{D}_2$ exchange over Pd$_{47}$Cu$_{53}$

The Pd$_{47}$Cu$_{53}$ alloy has a body-centered-cubic crystal (BCC) crystal structure at temperatures less than ~700 K and a face-centered-cubic (FCC) crystal structure at temperatures above ~850 K [9, 32, 43, 62, 89]. $\text{H}_2$-$\text{D}_2$ exchange was performed over both the BCC and FCC phases of the Pd$_{47}$Cu$_{53}$ alloy. We will show that the crystal structure of Pd$_{47}$Cu$_{53}$ has a significant impact on the kinetics of $\text{H}_2$-$\text{D}_2$ exchange.

$\text{H}_2$-$\text{D}_2$ exchange over BCC Pd$_{47}$Cu$_{53}$ and FCC Pd$_{47}$Cu$_{53}$ was performed by flowing $\text{H}_2$, $\text{D}_2$, and Ar through BCC and FCC Pd$_{47}$Cu$_{53}$ foil catalyst beds while the product gas was analyzed by a mass spectrometer. The procedure for preparing the BCC and FCC phases is given in Section 4.2. Figure 4.8(a) shows the HD flow rates exiting the BCC and FCC Pd$_{47}$Cu$_{53}$ foil catalyst beds with three different feed gas conditions. The FCC crystal structure of the Pd$_{47}$Cu$_{53}$ alloy is significantly more active for $\text{H}_2$-$\text{D}_2$ exchange than the BCC crystal structure.
Microkinetic analysis of the H$_2$-D$_2$ exchange reaction over the BCC and FCC phases of Pd$_{47}$Cu$_{53}$ was done by minimizing the error between the modeled and experimental HD conversions by adjusting $ln(\nu_{ads})$, $E^\dagger_{ads}$, $ln(\nu_{des})$, and $E^\dagger_{des}$. The solver-optimized values of these parameters associated with the BCC and FCC phases of Pd$_{47}$Cu$_{53}$ are summarized in table 4.2. To our knowledge, these are the first reported measurements of the barriers to H$_2$ adsorption and desorption.

Figure 4.8 (a) Experimental (points) and modeled (lines) HD flow rates versus temperature exiting a Pd$_{47}$Cu$_{53}$ foil catalyst bed with a body-centered-cubic (BCC) crystal structure and with a face-centered-cubic (FCC) crystal structure. Modeled HD flow rates were calculated using the H$_2$-D$_2$ exchange model, equation (4.1), and the solver-optimized values for $\nu_{ads}$, $E^\dagger_{ads}$, $\nu_{des}$, $E^\dagger_{des}$. (b) Total coverage of H and D atoms during H$_2$-D$_2$ exchange over the BCC and FCC Pd$_{47}$Cu$_{53}$ foil catalyst beds. The coverage was calculated using equation (4.2) and the solver-optimized values for $\nu_{ads}$, $E^\dagger_{ads}$, $\nu_{des}$, $E^\dagger_{des}$.
on BCC or FCC Pd$_{47}$Cu$_{53}$ surfaces. Using the solver-optimized parameters, HD flow rates were calculated for the BCC and FCC phases of Pd$_{47}$Cu$_{53}$ with the three different feed gas conditions. Figure 4.8(a) shows that the model fits the experimental data reasonably well.

**Table 4.3** Summary of the adsorption pre-exponents ($\nu_{\text{ads}}$), adsorption barriers ($E_{\text{ads}}^\dagger$), desorption pre-exponents ($\nu_{\text{des}}$), desorption barriers ($E_{\text{des}}^\dagger$), and heats of adsorption of H$_2$ ($\Delta E_{\text{ads}}$) on BCC Pd$_{47}$Cu$_{53}$ and FCC Pd$_{47}$Cu$_{53}$.

<table>
<thead>
<tr>
<th></th>
<th>$\nu_{\text{ads}}$ (mol/m$^2$/s/Pa)</th>
<th>$E_{\text{ads}}^\dagger$ (eV)</th>
<th>$\nu_{\text{des}}$ (mol/m$^2$/s)</th>
<th>$E_{\text{des}}^\dagger$ (eV)</th>
<th>$\Delta E_{\text{ads}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCC Pd$<em>{47}$Cu$</em>{53}$</td>
<td>$10^{-5.2} \pm 0.2$</td>
<td>$0.15 \pm 0.02$</td>
<td>$10^{7.4} \pm 0.5$</td>
<td>$0.67 \pm 0.03$</td>
<td>$-0.52 \pm 0.04$</td>
</tr>
<tr>
<td>FCC Pd$<em>{47}$Cu$</em>{53}$</td>
<td>$10^{-6.6} \pm 0.2$</td>
<td>$0.00 \pm 0.02$</td>
<td>$10^{6.5} \pm 0.5$</td>
<td>$0.46 \pm 0.03$</td>
<td>$-0.46 \pm 0.03$</td>
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</table>

The total coverages of H and D atoms during H$_2$-D$_2$ exchange over BCC and FCC Pd$_{47}$Cu$_{53}$, which are plotted in Figure 4.8(b), were calculated with equation (4.2) and the solver-optimized values of $\nu_{\text{ads}}$, $E_{\text{ads}}^\dagger$, $\nu_{\text{des}}$, and $E_{\text{des}}^\dagger$. At low temperatures (~200 K), both the BCC and FCC Pd$_{47}$Cu$_{53}$ surfaces are nearly saturated with H and D atoms. As the temperature increases, and desorption rate increases, the total coverage decreases on both surfaces. The coverage decreases more rapidly on the FCC phase of Pd$_{47}$Cu$_{53}$ due to the smaller activation barrier to H$_2$ desorption on the FCC surface ($0.46 \pm 0.03$ eV) than on the BCC surface ($0.67 \pm 0.03$ eV).
Clearly, the crystal structure of Pd$_{47}$Cu$_{53}$ has a significant impact on the kinetics of H$_2$-D$_2$ exchange due to the differences in the energetics of H$_2$ adsorption and desorption on the two phases of Pd$_{47}$Cu$_{53}$. A potential energy diagram that compares the energetics of H$_2$ adsorption on BCC and FCC Pd$_{47}$Cu$_{53}$ is shown in Figure 4.9. The activation barriers to H$_2$ adsorption on BCC Pd$_{47}$Cu$_{53}$ (0.15 ± 0.02 eV) and on FCC Pd$_{47}$Cu$_{53}$ (0.00 ± 0.02 eV) are not large and H$_2$ adsorption rates on both surfaces were high. As a result, the rate of H$_2$-D$_2$ exchange over both the BCC and FCC Pd$_{47}$Cu$_{53}$ surfaces was influenced more by the rate of H$_2$ desorption than by the rate of adsorption. The higher H$_2$-D$_2$ exchange activity exhibited by the FCC phase of Pd$_{47}$Cu$_{53}$ is due to a lower activation barrier to H$_2$ desorption on FCC Pd$_{47}$Cu$_{53}$ (0.46 ± 0.03 eV) than that on BCC Pd$_{47}$Cu$_{53}$ (0.67 ± 0.03 eV).
4.5.5 *Comparison of H₂-D₂ exchange over Pd, Cu, Pd₇₀Cu₃₀, and Pd₄₇Cu₅₃*

A comparison of the HD flow rates exiting the Pd, Cu, Pd₇₀Cu₃₀, BCC Pd₄₇Cu₅₃, and FCC Pd₄₇Cu₅₃ catalyst beds, with 9 mL/min each of H₂ and D₂ in the feed gas, is shown in Figure 4.10. The H₂-D₂ exchange activity of Cu is much lower than that of Pd, Pd₇₀Cu₃₀, and Pd₄₇Cu₅₃ (BCC and FCC); and the PdCu alloys are more active for H₂-D₂ exchange than Pd.

![Figure 4.9 Potential energy diagram for H₂ adsorption on BCC Pd₄₇Cu₅₃ and FCC Pd₄₇Cu₅₃](image-url)
The differences in the H\textsubscript{2}-D\textsubscript{2} exchange activity of the catalysts are due to the differences in the energetics of H\textsubscript{2} adsorption and desorption on these catalysts. A comparison of the potential energy of H\textsubscript{2} adsorption on β-Pd-hydride, α-Pd-hydride, Cu, Pd\textsubscript{70}Cu\textsubscript{30}, BCC Pd\textsubscript{47}Cu\textsubscript{53}, and FCC Pd\textsubscript{47}Cu\textsubscript{53} is shown in Figure 4.11. Table 4.4 lists the parameters that describe H\textsubscript{2} adsorption and desorption (ν\textsubscript{ads}, $E^\dagger_{\text{ads}}$, ν\textsubscript{des}, $E^\dagger_{\text{des}}$, and Δ$E_{\text{ads}}$) on β-Pd-hydride, α-Pd-hydride, Cu, Pd\textsubscript{70}Cu\textsubscript{30}, BCC Pd\textsubscript{47}Cu\textsubscript{53}, and FCC Pd\textsubscript{47}Cu\textsubscript{53}.

Figure 4.10 Comparison of the HD flow rates exiting Pd, Cu, Pd\textsubscript{70}Cu\textsubscript{30}, BCC Pd\textsubscript{47}Cu\textsubscript{53}, and FCC Pd\textsubscript{47}Cu\textsubscript{53} foil catalyst beds, each with a catalyst surface area of ~19 cm\textsuperscript{2} and 9 mL/min of H\textsubscript{2} and D\textsubscript{2} in the feed gas.
Table 4.4 Summary of the adsorption pre-exponents ($\nu_{\text{ads}}$), adsorption barriers ($E_{\text{ads}}^\ddagger$), desorption pre-exponents ($\nu_{\text{des}}$), desorption barriers ($E_{\text{des}}^\ddagger$), and heats of adsorption of H$_2$ ($\Delta E_{\text{ads}}$) on β-Pd-hydride, α-Pd-hydride, Cu, Pd$_{70}$Cu$_{30}$, BCC Pd$_{47}$Cu$_{53}$, and FCC Pd$_{47}$Cu$_{53}$ from this work.

<table>
<thead>
<tr>
<th></th>
<th>$\nu_{\text{ads}}$ (mol/m$^2$/s/Pa)</th>
<th>$E_{\text{ads}}^\ddagger$ (eV)</th>
<th>$\nu_{\text{des}}$ (mol/m$^2$/s)</th>
<th>$E_{\text{des}}^\ddagger$ (eV)</th>
<th>$\Delta E_{\text{ads}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-Pd-hydride</td>
<td>$10^{3.7 \pm 0.7}$</td>
<td>$0.3 \pm 0.1$</td>
<td>$10^{5.8 \pm 0.4}$</td>
<td>$0.63 \pm 0.03$</td>
<td>$-0.3 \pm 0.1$</td>
</tr>
<tr>
<td>α-Pd-hydride</td>
<td>$10^{5.4 \pm 0.4}$</td>
<td>$0.12 \pm 0.04$</td>
<td>$10^{6.3 \pm 0.8}$</td>
<td>$0.68 \pm 0.06$</td>
<td>$-0.56 \pm 0.07$</td>
</tr>
<tr>
<td>Cu</td>
<td>$10^{3.4 \pm 0.5}$</td>
<td>$0.54 \pm 0.06$</td>
<td>$10^{1 \pm 5}$</td>
<td>$0.6 \pm 0.7$</td>
<td>$0.0 \pm 0.7$</td>
</tr>
<tr>
<td>Pd$<em>{70}$Cu$</em>{30}$</td>
<td>$10^{5.6 \pm 0.2}$</td>
<td>$0.09 \pm 0.02$</td>
<td>$10^{5.7 \pm 0.3}$</td>
<td>$0.52 \pm 0.02$</td>
<td>$-0.43 \pm 0.03$</td>
</tr>
<tr>
<td>BCC Pd$<em>{47}$Cu$</em>{53}$</td>
<td>$10^{5.2 \pm 0.2}$</td>
<td>$0.15 \pm 0.02$</td>
<td>$10^{7.4 \pm 0.5}$</td>
<td>$0.67 \pm 0.03$</td>
<td>$-0.52 \pm 0.04$</td>
</tr>
<tr>
<td>FCC Pd$<em>{47}$Cu$</em>{53}$</td>
<td>$10^{6.6 \pm 0.2}$</td>
<td>$0.00 \pm 0.02$</td>
<td>$10^{6.5 \pm 0.5}$</td>
<td>$0.46 \pm 0.03$</td>
<td>$-0.46 \pm 0.03$</td>
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</table>
Cu is the least active H$_2$-D$_2$ exchange catalyst in this study due to the large activation barrier to H$_2$ adsorption on Cu (0.54 ± 0.06 eV). In contrast, barriers to H$_2$ adsorption on β-Pd-hydride (0.3 ± 0.1 eV), α-Pd-hydride (0.12 ± 0.04 eV), Pd$_{70}$Cu$_{30}$ (0.09 ± 0.02 eV), BCC Pd$_{47}$Cu$_{53}$ (0.15 ± 0.02 eV), and FCC Pd$_{47}$Cu$_{53}$ (0.00 ± 0.02 eV) are relatively small and the rate of H$_2$-D$_2$ exchange over these catalysts is determined largely by the rate of H$_2$ desorption (desorption-limited). FCC Pd$_{47}$Cu$_{53}$ has the highest H$_2$-D$_2$ exchange activity of the desorption-limited catalysts because the activation barrier to H$_2$ desorption on FCC Pd$_{47}$Cu$_{53}$ (0.46 ± 0.03 eV) is the smallest. As expected, the order of decreasing H$_2$-D$_2$ exchange activity of the desorption-limited catalysts (FCC Pd$_{47}$Cu$_{53}$ < Pd$_{70}$Cu$_{30}$ < BCC Pd$_{47}$Cu$_{53}$ < β-Pd-hydride < α-Pd-hydride) follows closely the order of increasing activation barrier to H$_2$ desorption: FCC Pd$_{47}$Cu$_{53}$ (0.46 ± 0.03 eV) < Pd$_{70}$Cu$_{30}$ (0.52 ± 0.02 eV) < β-Pd-hydride (0.63 ± 0.03 eV) < BCC Pd$_{47}$Cu$_{53}$ (0.67 ± 0.03 eV) < α-Pd-hydride (0.68 ± 0.06 eV).

The heat of adsorption of H$_2$ ($\Delta E_{\text{ads}}$) on α-Pd-hydride is the lowest (most negative) of the catalysts and, therefore, H atoms are the most stable on α-Pd-hydride. The order of increasing heat of adsorption of H$_2$ (decreasing stability of H atoms) on the catalysts is as follows: α-Pd-hydride ($\Delta E_{\text{ads}} = -0.56 ± 0.07$ eV) < BCC Pd$_{47}$Cu$_{53}$ ($\Delta E_{\text{ads}} = -0.52 ± 0.04$ eV) < FCC Pd$_{47}$Cu$_{53}$ ($\Delta E_{\text{ads}} = -0.46 ± 0.03$ eV) < Pd$_{70}$Cu$_{30}$ ($\Delta E_{\text{ads}} = -0.43 ± 0.03$ eV) < β-Pd-hydride ($\Delta E_{\text{ads}} = -0.3 ± 0.1$ eV) < Cu ($\Delta E_{\text{ads}} = 0.0 ± 0.7$ eV). The heat of adsorption of H$_2$ on the PdCu alloys is not much greater (less negative) than that on α-Pd-hydride, indicating that alloying Pd with Cu does not drastically reduce the stability of H atom adsorption.
The pre-exponent for H₂ desorption ($v_{\text{des}}$) is $\sim 10^6 \text{ mol/m}^2/\text{s}$ for all of the catalysts used in this study, which is close to the value that would be expected from statistical mechanics ($\sim 10^7 \text{ mol/m}^2/\text{s}$) if the partition functions of the initial state (adsorbed 2H) and the transition state cancel each other [74]:

$$v_{\text{des}} \approx \frac{k_B T}{h} N_{\text{avo}} \sigma_{\text{site}} \approx \left(10^{13} \frac{1}{\text{s}}\right)\left(10^{-24} \text{ mol}\right)\left(10^{18} \frac{1}{\text{m}^2}\right) = 10^7 \frac{\text{mol}}{\text{m}^2\text{s}},$$

where $k_B$ is Boltzmann’s constant, $T$ is temperature, $h$ is Planck’s constant, $N_{\text{avo}}$ is Avogadro’s number, and $\sigma_{\text{site}}$ is the adsorption site density of a close-packed surface. The pre-exponent for H₂ adsorption ($v_{\text{ads}}$) is $\sim 10^{-6} \text{ mol/m}^2/\text{s}/\text{Pa}$ for all of the catalysts used in this study. Predicting a pre-exponent for H₂ adsorption from statistical mechanics is more complicated than that for H₂ desorption because the partition functions in the initial state (gas) and the transition state do not cancel each other.

The results of this study are significant because it has been shown that (1) the crystal structures of Pd ($\beta$-Pd-hydride and $\alpha$-Pd-hydride) and of Pd₄₇Cu₅₃ (BCC and FCC) have a significant impact on the energetics of H₂ adsorption and desorption; and (2) although the H₂ dissociation activity of Cu is very low, Pd can be alloyed with as much as $\sim 50 \text{ mol\%}$ Cu without significantly reducing H₂ adsorption rates.
4.6 Conclusions

The energetics of H\textsubscript{2} adsorption on Pd, Cu, Pd\textsubscript{70}Cu\textsubscript{30}, and Pd\textsubscript{47}Cu\textsubscript{53} were investigated in this study by microkinetic analysis of the H\textsubscript{2}-D\textsubscript{2} exchange reaction over fixed foil catalyst beds of these catalysts. We found that the crystal structure of Pd (β-Pd-hydride and α-Pd-hydride) and of Pd\textsubscript{47}Cu\textsubscript{53} (BCC and FCC) have a significant impact on the kinetics of H\textsubscript{2}-D\textsubscript{2} exchange. The H\textsubscript{2}-D\textsubscript{2} exchange activity of FCC Pd\textsubscript{47}Cu\textsubscript{53} was the highest of all the catalysts in this study and the H\textsubscript{2}-D\textsubscript{2} exchange activity of the catalysts decreases in the following order: FCC Pd\textsubscript{47}Cu\textsubscript{53} > Pd\textsubscript{70}Cu\textsubscript{30} > BCC Pd\textsubscript{47}Cu\textsubscript{53} > β-Pd-hydride > α-Pd-hydride >> Cu. The very low H\textsubscript{2}-D\textsubscript{2} exchange activity of the Cu catalyst is due to the large activation barrier to H\textsubscript{2} adsorption on Cu (0.54 ± 0.06 eV). Activation barriers to H\textsubscript{2} adsorption on β-Pd-hydride (0.3 ± 0.1 eV), α-Pd-hydride (0.12 ± 0.04 eV), Pd\textsubscript{70}Cu\textsubscript{30} (0.09 ± 0.02 eV), BCC Pd\textsubscript{47}Cu\textsubscript{53} (0.15 ± 0.02 eV) and FCC Pd\textsubscript{47}Cu\textsubscript{53} (0.00 ± 0.02 eV) are small relative to that for Cu and the rate of H\textsubscript{2}-D\textsubscript{2} exchange over these catalysts was determined largely by the rate of H\textsubscript{2}, D\textsubscript{2}, and HD desorption (desorption-limited). These results are significant for H\textsubscript{2} separation membrane applications because it shows that Pd can be alloyed with as much as ~50 mol% Cu without significantly reducing H\textsubscript{2} dissociation rates. The order of decreasing H\textsubscript{2}-D\textsubscript{2} exchange activity in the desorption-limited catalysts is nearly the same as the order of increasing activation barrier for H\textsubscript{2} desorption: FCC Pd\textsubscript{47}Cu\textsubscript{53} (0.46 ± 0.03 eV) < Pd\textsubscript{70}Cu\textsubscript{30} (0.52 ± 0.02 eV) < β-Pd-hydride (0.63 ± 0.03 eV) < BCC Pd\textsubscript{47}Cu\textsubscript{53} (0.67 ± 0.03 eV) < α-Pd-hydride (0.68 ± 0.06 eV).
Chapter 5

H₂-D₂ Exchange over Pd₄S, Pd₄₇Cu₅₃, and Pd₇₀Cu₃₀ in the Presence of H₂S

5.1 Summary

In this chapter, the effect of H₂S on the rate of H₂ dissociative adsorption on Pd₄S, Pd₄₇Cu₅₃, and Pd₇₀Cu₃₀ foil catalyst beds is investigated by performing H₂-D₂ exchange (H₂ + D₂ ↔ 2HD) over these catalysts in the presence of 50 to 2000 ppm H₂S. Qualitatively, H₂S has the same effect on the rate of H₂-D₂ exchange over Pd₄S, Pd₄₇Cu₅₃, and Pd₇₀Cu₃₀: increasing the concentration of H₂S in the H₂/D₂/Ar feed gas reduces the rate of HD production by reducing the rate of H₂ adsorption on these catalysts. It is likely that H₂S, or other sulfur species such as SH or S, blocks H₂ adsorption sites on the surfaces of these catalysts and the number of sites blocked for H₂ adsorption increases with increasing H₂S concentration in the feed gas. However, H₂S also causes an irreversible change in the intrinsic H₂-D₂ exchange activity of Pd₄₇Cu₅₃, possibly by forming surface sulfides that are difficult to reduce by removing H₂S from the feed gas. In the presence of 50 to 2000 ppm H₂S, the rate of H₂ dissociative adsorption is highest on the Pd₄S catalyst followed by Pd₇₀Cu₃₀ and Pd₄₇Cu₅₃. Although we have not investigated a wide range of PdCu alloy compositions, our results show that, in the presence of 50 to 2000 ppm H₂S, increasing the Cu content in PdCu alloys reduces the rate of H₂ dissociation on the alloy.
5.2 Introduction

$\text{H}_2\text{S}$ slows hydrogen transport through Pd membranes indirectly, by producing a Pd$_4$S film on the Pd surface that is about an order-of-magnitude less permeable to H atoms than Pd, and also slows transport directly, possibly by blocking $\text{H}_2$ dissociation sites on the Pd$_4$S surface Pd [2, 25]. Pd$_{70}$Cu$_{30}$ and Pd$_{47}$Cu$_{53}$ alloys are much more resistant to bulk sulfidation than Pd [1, 9, 29] and hydrogen transport through these alloys is not significantly affected by $\text{H}_2\text{S}$ at temperatures near 900 K [7, 9, 19]. At lower temperatures (~600 K), however, $\text{H}_2\text{S}$ blocks hydrogen transport through Pd$_{70}$Cu$_{30}$ and Pd$_{47}$Cu$_{53}$ alloys almost completely [9]. Because these alloys do not form thick sulfides, it has been suggested that $\text{H}_2\text{S}$ poisons the catalytic activity of their surfaces for $\text{H}_2$ dissociation [9]. However, there is very little direct evidence to support this hypothesis. The effect of $\text{H}_2\text{S}$ on $\text{H}_2$ dissociative adsorption on Pd$_4$S, Pd$_{47}$Cu$_{53}$, and Pd$_{70}$Cu$_{30}$ surfaces has not been investigated to the best of our knowledge.

In this chapter, $\text{H}_2$-$\text{D}_2$ exchange over Pd$_4$S, Pd$_{47}$Cu$_{53}$, and Pd$_{70}$Cu$_{30}$ foil catalyst beds was performed with varying concentrations of $\text{H}_2\text{S}$ (50 to 2000 ppm) in the feed gas to investigate the effect of $\text{H}_2\text{S}$ on $\text{H}_2$ dissociative adsorption on these surfaces. We will show that increasing the $\text{H}_2\text{S}$ concentration in the feed gas reduces the rate of $\text{H}_2$ dissociative adsorption on these catalysts and, as a result, decreases the rate of HD production over these catalysts. We will also show that, in the presence of $\text{H}_2\text{S}$, the $\text{H}_2$ dissociation activity of these catalysts decreases with increasing Cu content in the alloy.
5.3 Experimental

H₂-D₂ exchange experiments over Pd alloy foils in the presence of H₂S were performed in a manner similar to the exchange experiments performed in pure H₂ (Chapter 4), except that H₂S was added to the H₂/D₂/Ar feed gas mixture. We used six different H₂S concentrations in the H₂/D₂/Ar feed gas: 50, 100, 200, 500, 1000, and 2000 ppm. The concentration of H₂S in the feed gas mixture was controlled by diluting either a (1.09±0.02%H₂S)/H₂ gas mixture (Matheson Tri-Gas) or a (0.107±0.002%H₂S)/H₂ gas mixture (Matheson Tri-Gas) with pure H₂ (99.999% purity, Valley National Gases). The 0.107%H₂S/H₂ gas mixture was used for H₂S concentrations of 50, 100, and 200 ppm; the 1.09%H₂S/H₂ gas mixture was used for H₂S concentrations of 500, 1000, and 2000 ppm. Three different H₂/D₂/Ar feed gas combinations were used for each H₂S concentration: 9 mL/min of H₂ and D₂ (9H₂ / 9D₂), 4.5 mL/min of H₂ and D₂ (4.5H₂ / 4.5D₂), and 4.5 mL/min of H₂ and D₂ diluted with 9 mL/min of Ar (9Ar / 4.5H₂ / 4.5D₂). The total pressure in the reactor was measured with a Baratron pressure gauge and was as follows: 104 kPa for the 4.5H₂ / 4.5D₂ feed gases; 107 kPa for the 9H₂ / 9D₂ feed gases; and 111 kPa for the 9Ar / 4.5H₂ / 4.5D₂ feed gases. Table 5.1 lists the H₂S concentrations and flow rates of the feed gases used in the eighteen different feed gas conditions used for H₂-D₂ exchange experiments in the presence of H₂S.

The total surface area of the foil catalysts used in all experiments was ~19 cm². The Pd₄S catalyst was initially prepared in the H₂-D₂ exchange reactor by flowing a 1.09%H₂S/H₂ gas mixture over a pure Pd (Alfa Aesar, 25 µm thick, 99.9% metals purity) foil catalyst bed for ~40 hours at 773 K. Based on the
kinetics of Pd sulfidation [25], this exposure should have been more than sufficient to completely sulfide the Pd foil catalyst bed to Pd$_4$S.

Prior to the H$_2$-D$_2$ exchange experiments, the Pd$_4$S, Pd$_{70}$Cu$_{30}$ and Pd$_{47}$Cu$_{53}$ foil catalyst beds were heated to ~1000 K in a 1000 ppm H$_2$S in H$_2$ gas mixture and held at that temperature for ~16 hours. After the initial heat treatment, the H$_2$S/H$_2$/D$_2$/Ar feed gas mixture was introduced to the reactor and the product gas composition was analyzed by a mass spectrometer. Steady-state mass spectrometer signals were collected at constant temperature and the temperature was decreased in a step-wise fashion.
Table 5.1 Feed gas flow rates for the 18 different feed gas conditions used in H₂-D₂ exchange experiments in the presence of H₂S.

<table>
<thead>
<tr>
<th>Feed Gas Condition</th>
<th>H₂S concentration (ppm)</th>
<th>1%H₂S/H₂</th>
<th>0.1%H₂S/H₂</th>
<th>H₂</th>
<th>D₂</th>
<th>Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5H₂ / 4.5D₂</td>
<td>2000 ± 200</td>
<td>1.65</td>
<td>0</td>
<td>2.86</td>
<td>4.5</td>
<td>0</td>
</tr>
<tr>
<td>4.5H₂ / 4.5D₂</td>
<td>1000 ± 200</td>
<td>0.83</td>
<td>0</td>
<td>3.68</td>
<td>4.5</td>
<td>0</td>
</tr>
<tr>
<td>4.5H₂ / 4.5D₂</td>
<td>500 ± 200</td>
<td>0.41</td>
<td>0</td>
<td>4.09</td>
<td>4.5</td>
<td>0</td>
</tr>
<tr>
<td>4.5H₂ / 4.5D₂</td>
<td>200 ± 20</td>
<td>0</td>
<td>1.68</td>
<td>2.82</td>
<td>4.5</td>
<td>0</td>
</tr>
<tr>
<td>4.5H₂ / 4.5D₂</td>
<td>100 ± 20</td>
<td>0</td>
<td>0.84</td>
<td>3.66</td>
<td>4.5</td>
<td>0</td>
</tr>
<tr>
<td>4.5H₂ / 4.5D₂</td>
<td>50 ± 20</td>
<td>0</td>
<td>0.42</td>
<td>4.08</td>
<td>4.5</td>
<td>0</td>
</tr>
<tr>
<td>9H₂ / 9D₂</td>
<td>2000 ± 100</td>
<td>3.31</td>
<td>0</td>
<td>5.73</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>9H₂ / 9D₂</td>
<td>1000 ± 100</td>
<td>1.65</td>
<td>0</td>
<td>7.36</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>9H₂ / 9D₂</td>
<td>500 ± 100</td>
<td>0.83</td>
<td>0</td>
<td>8.18</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>9H₂ / 9D₂</td>
<td>200 ± 10</td>
<td>0</td>
<td>3.37</td>
<td>5.63</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>9H₂ / 9D₂</td>
<td>100 ± 10</td>
<td>0</td>
<td>1.69</td>
<td>7.31</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>9H₂ / 9D₂</td>
<td>50 ± 10</td>
<td>0</td>
<td>0.84</td>
<td>8.16</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>9Ar / 4.5H₂ / 4.5D₂</td>
<td>2000 ± 100</td>
<td>3.31</td>
<td>0</td>
<td>1.23</td>
<td>4.5</td>
<td>9</td>
</tr>
<tr>
<td>9Ar / 4.5H₂ / 4.5D₂</td>
<td>1000 ± 100</td>
<td>1.65</td>
<td>0</td>
<td>2.86</td>
<td>4.5</td>
<td>9</td>
</tr>
<tr>
<td>9Ar / 4.5H₂ / 4.5D₂</td>
<td>500 ± 100</td>
<td>0.83</td>
<td>0</td>
<td>3.68</td>
<td>4.5</td>
<td>9</td>
</tr>
<tr>
<td>9Ar / 4.5H₂ / 4.5D₂</td>
<td>200 ± 10</td>
<td>0</td>
<td>3.37</td>
<td>1.13</td>
<td>4.5</td>
<td>9</td>
</tr>
<tr>
<td>9Ar / 4.5H₂ / 4.5D₂</td>
<td>100 ± 10</td>
<td>0</td>
<td>1.68</td>
<td>2.82</td>
<td>4.5</td>
<td>9</td>
</tr>
<tr>
<td>9Ar / 4.5H₂ / 4.5D₂</td>
<td>50 ± 10</td>
<td>0</td>
<td>0.84</td>
<td>3.66</td>
<td>4.5</td>
<td>9</td>
</tr>
</tbody>
</table>
5.4 Results and discussion

5.4.1 H$_2$-D$_2$ exchange over Pd$_4$S in the presence of H$_2$S

H$_2$-D$_2$ exchange over Pd$_4$S was carried out by feeding a H$_2$S/H$_2$/D$_2$/Ar gas mixture to a Pd$_4$S foil catalyst bed while the product gas composition was analyzed with a mass spectrometer. Six different concentrations of H$_2$S (50, 100, 200, 500, 1000, and 2000 ppm) were used in the feed gas, each with three different H$_2$, D$_2$, and Ar feed gas flow rates for a total of 18 different feed gas conditions. Figure 5.1 shows the HD flow rates exiting a Pd foil catalyst bed without H$_2$S in the feed gas compared to the HD flow rates exiting a Pd$_4$S catalyst bed with 50 ppm H$_2$S in the feed gas, each with 9 mL/min of H$_2$ and D$_2$ in the feed gas. The HD flow rates exiting the Pd$_4$S catalyst bed without H$_2$S in the feed gas are also shown in Figure 5.1. The rate of HD production over the Pd$_4$S catalyst bed without H$_2$S in the feed gas is similar to the rate of HD production over the pure Pd foil catalyst bed. It is likely that the H$_2$-D$_2$ exchange activity of Pd$_4$S in the absence of H$_2$S is similar to that of Pd because, in the absence of H$_2$S, the Pd$_4$S surface is reduced to metallic Pd. In the presence of 50 ppm H$_2$S, however, the rate of HD production over the Pd$_4$S catalyst is much lower than that over the Pd catalyst in the absence of H$_2$S.
Figure 5.1 Comparison of the HD flow rates exiting a Pd foil catalyst bed without H$_2$S in the feed gas (Pd), a Pd$_4$S catalyst bed with 50 ppm H$_2$S in the feed gas (Pd$_4$S (50 ppm H$_2$S)) and a Pd$_4$S catalyst bed without H$_2$S in the feed gas (Pd$_4$S (0 ppm H$_2$S)), each with 9 mL/min of H$_2$ and D$_2$ in the feed gas. The Pd$_4$S catalyst with 50 ppm H$_2$S in the feed gas is much less active for H$_2$-D$_2$ exchange than the pure Pd catalyst bed without H$_2$S in the feed gas. The H$_2$-D$_2$ exchange activity of the Pd$_4$S catalyst without H$_2$S in the feed gas is similar to that of Pd, possibly because the Pd$_4$S surface is reduced to metallic Pd in the absence of H$_2$S.
The low rate of HD production over Pd₄S in the presence of 50 ppm H₂S, relative to the HD production rate over the Pd without H₂S in the feed gas, is either due to a low rate of H₂ adsorption or due to a low rate of H₂ desorption. To determine which of these steps (adsorption or desorption) is rate-limiting, we observed the effect of diluting the feed gas with Ar on the HD production rate. Figure 5.2 shows the HD flow rates exiting the (a) Pd foil catalyst bed without H₂S in the feed gas and the (b) Pd₄S catalyst bed with 50 ppm H₂S in the feed gas, each with three different H₂/D₂/Ar feed gas combinations: 9 mL/min of H₂ and D₂, 4.5 mL/min of H₂ and D₂, and 4.5 mL/min of H₂ and D₂ diluted with 9 mL/min of Ar. Diluting the 4.5H₂ / 4.5D₂ feed gas with Ar (9Ar / 4.5H₂ / 4.5D₂) does not significantly reduce the HD flow rate exiting the Pd foil catalyst bed (Figure 5.1(a)). This observation indicates that the rate of HD desorption, which is independent of the H₂ and D₂ partial pressure, is rate-limiting and the rate of H₂ adsorption is relatively high. In contrast to Pd, diluting the 4.5H₂ / 4.5D₂ feed gas with Ar (9Ar / 4.5H₂ / 4.5D₂) significantly reduces the HD flow rate exiting the Pd₄S catalyst bed in the presence of 50 ppm H₂S (Figure 5.2(b)), which indicates that H₂ adsorption is rate-limiting. Therefore, the low rate of H₂ adsorption on the Pd₄S surface in the presence of 50 ppm H₂S is responsible for its much lower H₂-D₂ exchange activity than that of Pd without H₂S in the feed gas.
Figure 5.2 HD flow rates exiting the (a) Pd foil catalyst bed and the (b) Pd₄S catalyst bed with 50 ppm H₂S in the feed gas, each with three different H₂/D₂/Ar feed gas combinations: 9 mL/min each of H₂ and D₂ (9H₂ / 9D₂), 4.5 mL/min each of H₂ and D₂ (4.5H₂ / 4.5D₂), and 4.5 mL/min each of H₂ and D₂ diluted with 9 mL/min of Ar (9Ar / 4.5H₂ / 4.5D₂). Diluting the 4.5H₂ / 4.5D₂ feed gas with Ar (9Ar / 4.5H₂ / 4.5D₂) does not significantly reduce the HD flow rate exiting the pure Pd foil catalyst bed, indicating desorption-limited H₂-D₂ exchange. In contrast to Pd, the HD flow rate exiting the Pd₄S catalyst bed in the presence of H₂S is significantly reduced by diluting the H₂/D₂ feed gas with Ar, indicating that the rate of H₂ adsorption on Pd₄S is rate-limiting.
Figure 5.2 suggests that the low H$_2$-D$_2$ exchange activity of Pd$_4$S in the presence of H$_2$S (relative to Pd in the absence of H$_2$S) is due to a much lower rate of H$_2$ adsorption on Pd$_4$S than on Pd. It is not clear from Figure 5.2(b) whether the Pd$_4$S surface has an intrinsically low H$_2$ dissociation activity, or if H$_2$S reduces the rate of H$_2$ adsorption directly, or both. To determine whether H$_2$S reduces the rate of H$_2$ adsorption on Pd$_4$S directly, H$_2$-D$_2$ exchange over the Pd$_4$S catalyst was performed with H$_2$S concentration varying from 50 to 2000 ppm. Figure 5.3 shows the HD flow rates exiting the Pd$_4$S catalyst bed with 50, 100, 200, 500, 1000, and 2000 ppm H$_2$S in the feed gas and with three different H$_2$/D$_2$/Ar feed gas combinations: (a) 4.5 mL/min each of H$_2$ and D$_2$ (4.5H$_2$ / 4.5D$_2$), (b) 9 mL/min each of H$_2$ and D$_2$ (9H$_2$ / 9D$_2$), and (c) 4.5 mL/min of H$_2$ and D$_2$ diluted with 9 mL/min of Ar (9Ar / 4.5H$_2$ / 4.5D$_2$). For all three H$_2$/D$_2$/Ar feed gas combinations, increasing the H$_2$S concentration in the feed gas decreases the rate of H$_2$-D$_2$ exchange over the Pd$_4$S catalyst monotonically. These results indicate that H$_2$S is directly involved in reducing the rate of H$_2$ adsorption on Pd$_4$S, possibly by blocking H$_2$ dissociation sites.
Figure 5.3 HD flow rates exiting a Pd₄S catalyst bed with (a) 4.5 mL/min each of H₂ and D₂ in the feed gas, (b) 9 mL/min each of H₂ and D₂ in the feed gas, and (c) 9 mL/min of Ar with 4.5 mL/min each of H₂ and D₂ in the feed gas, each with H₂S concentrations in the feed gas of 2000, 1000, 500, 200, 100, and 50 ppm. Increasing the H₂S concentration in the feed gas decreases the rate of H₂-D₂ exchange over Pd₄S with all three H₂/D₂/Ar feed gas combinations.
It is not clear from Figure 5.3 whether H$_2$S blocks H$_2$ dissociation sites, or if H$_2$S dissociates on the Pd$_4$S surface to SH and/or S which could also block H$_2$ dissociation sites. However, there was evidence that H$_2$S dissociated on the surface to SH and S. Figure 5.4(a) shows the ratio of the HDS-to-H$_2$S mass spectrometer signals sampled from the product gas during H$_2$-D$_2$ exchange over Pd$_4$S in the presence of 2000 ppm H$_2$S and with the three different H$_2$/D$_2$/Ar feed gas combinations. Figure 5.4(b) shows the ratio of the D$_2$S-to-H$_2$S mass spectrometer signals. The baseline HDS-to-H$_2$S and D$_2$S-to-H$_2$S ratios were determined by sampling the feed gas directly without passing through the Pd$_4$S catalyst bed.
The ratio of the HDS-to-H₂S mass spectrometer signals (Figure 5.4(a)) is significantly greater than the baseline value in the 400 K to 900 K temperature range, which indicates that H₂S dissociated to SH on the Pd₄S surface, and D atoms reacted with SH on the Pd₄S surface to produce HDS. The D₂S-to-H₂S mass spectrometer ratios (Figure 5.4(b)) are also significantly greater than the...
baseline values. In the 500 K and 800 K temperature range, the HDS-to-H2S and the D2S-to-H2S ratios are roughly constant and it appears that the H2S/HDS/D2S gas mixture is equilibrated in this temperature range. At temperatures less than \(~500\) K, the HDS-to-H2S and the D2S-to-H2S ratios decrease sharply and approach the baseline ratios. This is probably due to the very low rate of D2 dissociative adsorption on the Pd4S surface at temperatures less than \(~500\) K and in the presence of 2000 ppm H2S (see Figure 5.3). At temperatures less than \(~500\) K, the HDS-to-H2S ratio (Figure 5.4(a)) decreases slightly faster for the feed gas diluted with Ar (9Ar / 4.5H2 / 4.5D2), than with the other two feed gases. This could be due to the lower rate of D2 adsorption, and the lower coverage of D atoms, when the H2/D2 feed gas is diluted with Ar. Diluting the feed gas with Ar does not result in a sharper decline in the D2S-to-H2S ratio (Figure 5.4(b)) at temperatures less than \(~500\) K. This may be an artifact of the Ar isotope at mass 36 that interferes with the D2S signal at the same mass.

In conclusion, the H2-D2 exchange activity of Pd4S in the presence of H2S is much lower than that of Pd in the absence of H2S due to the much lower rate of H2 adsorption on Pd4S relative to Pd. Increasing the H2S concentration in the feed gas decreases the rate of H2-D2 exchange over Pd4S, which indicates that H2S is actively involved in reducing the rate of H2 adsorption on Pd4S. It is likely that H2S, SH, or S blocks H2 dissociative adsorption sites on the Pd4S surface, although it is not clear which of these species (H2S, SH, or S) is primarily responsible for reducing the rate of H2 adsorption on Pd4S.
5.4.2 $H_2$-$D_2$ exchange over $Pd_{47}Cu_{53}$ in the presence of $H_2S$

In Chapter 4, it was shown that the rate of $H_2$-$D_2$ exchange over a $Pd_{47}Cu_{53}$ alloy was dependent on the crystal structure of the alloy, which is body-centered-cubic (BCC) at temperatures less than $\sim 700$ K and face-centered-cubic (FCC) at temperatures greater than $\sim 800$ K (see Figure 5.5) [32]. $H_2$ adsorption on both BCC and FCC $Pd_{47}Cu_{53}$ was not hindered by large activation barriers and the rate of $H_2$-$D_2$ exchange over both phases was limited by the rate of HD desorption. In this section, the effect of $H_2S$ on the rate of $H_2$-$D_2$ exchange over $Pd_{47}Cu_{53}$ is investigated.
**Figure 5.5** Pd-Cu phase diagram adapted from [32]. The Pd$_{47}$Cu$_{53}$ alloy has a body-centered-cubic (BCC) crystal structure at temperatures less than ~700 K and a face-centered-cubic (FCC) crystal structure at temperatures greater than ~800 K. In between ~700 K and ~800 K, the BCC and FCC phases co-exist in a two-phase structure.

H$_2$-D$_2$ exchange over Pd$_{47}$Cu$_{53}$ was carried out by feeding a H$_2$S/H$_2$/D$_2$/Ar gas mixture to a Pd$_{47}$Cu$_{53}$ foil catalyst bed while the product gas composition was analyzed by a mass spectrometer. Figure 5.6 shows the HD flow rates exiting a BCC Pd$_{47}$Cu$_{53}$ foil catalyst bed without H$_2$S in the feed gas compared to the HD flow rates exiting a Pd$_{47}$Cu$_{53}$ foil catalyst bed with 50 ppm H$_2$S in the feed gas, each with 9 mL/min of H$_2$ and D$_2$ in the feed gas. Adding 50 ppm H$_2$S to the feed
gas significantly reduces the rate of HD production over the Pd\textsubscript{47}Cu\textsubscript{53} alloy; the onset of H\textsubscript{2}-D\textsubscript{2} exchange over Pd\textsubscript{47}Cu\textsubscript{53} without H\textsubscript{2}S in the feed gas begins at a temperature that is ~200 K lower than that over Pd\textsubscript{47}Cu\textsubscript{53} in the presence of 50 ppm H\textsubscript{2}S.

![Graph showing HD flow rates](image)

**Figure 5.6** Comparison of the HD flow rates exiting a BCC Pd\textsubscript{47}Cu\textsubscript{53} foil catalyst bed without H\textsubscript{2}S in the feed gas to the HD flow rates exiting a Pd\textsubscript{47}Cu\textsubscript{53} foil catalyst bed with 50 ppm H\textsubscript{2}S in the feed gas, each with 9 mL/min of H\textsubscript{2} and D\textsubscript{2} in the feed gas. Adding 50 ppm H\textsubscript{2}S to the H\textsubscript{2}/D\textsubscript{2} feed gas reduces the rate of HD production over the Pd\textsubscript{47}Cu\textsubscript{53} catalyst. At ~680 K, there is a break in the HD flow rate exiting the Pd\textsubscript{47}Cu\textsubscript{53} catalyst with 50 ppm H\textsubscript{2}S in the feed gas, which we believe is due to a change in the Pd\textsubscript{47}Cu\textsubscript{53} crystal structure from a mixed BCC/FCC structure at temperatures above ~680 K to a BCC structure at temperatures below ~680 K.
At ~680 K, there is a break in the HD flow rate exiting the Pd_{47}Cu_{53} catalyst bed in the presence of 50 ppm H\textsubscript{2}S (see Figure 5.6). The temperature of this break is similar to the temperature of the phase boundary between the BCC phase and the mixed BCC/FCC two-phase region of Pd_{47}Cu_{53} (see Figure 5.5). Therefore, we believe that the break in the HD flow rate exiting the Pd_{47}Cu_{53} foil catalyst bed at ~680 K is due to a change in the crystal structure of Pd_{47}Cu_{53} from a mixed BCC/FCC two-phase structure at temperatures above ~680 K to a BCC structure at temperatures below ~680 K; and the H\textsubscript{2}-D\textsubscript{2} exchange activity of Pd_{47}Cu_{53} is different in these two different regions.

The HD production rate over Pd_{47}Cu_{53} is limited by either the rate of H\textsubscript{2} adsorption or by the rate of HD desorption. It is relatively straightforward to identify the rate-limiting step by observing the effect of diluting the feed gas with Ar on the rate of HD production. Figure 5.7 shows the HD flow rates exiting the (a) BCC Pd_{47}Cu_{53} foil catalyst bed without H\textsubscript{2}S in the feed gas and (b) the Pd_{47}Cu_{53} foil catalyst bed with 50 ppm H\textsubscript{2}S in the feed gas, each with three different H\textsubscript{2}/D\textsubscript{2}/Ar feed gas combinations. In the absence of H\textsubscript{2}S (Figure 5.7(a)), diluting the feed gas with Ar does not significantly reduce the rate of HD production over Pd_{47}Cu_{53} catalyst. This indicates that the rate of HD desorption, which is independent of the H\textsubscript{2} and D\textsubscript{2} partial pressure, limits the rate of HD production over Pd_{47}Cu_{53} in the absence of H\textsubscript{2}S. In the presence of 50 ppm H\textsubscript{2}S (Figure 5.7(b)), the HD flow rate exiting the Pd_{47}Cu_{53} catalyst bed is significantly reduced by diluting the feed gas with Ar, indicating that, in the presence of 50 ppm H\textsubscript{2}S, the HD production rate over Pd_{47}Cu_{53} is limited by the rate of H\textsubscript{2}.
adsorption. Therefore, the rate-limiting step in H₂-D₂ exchange over Pd₄₇Cu₅₃ is changed from HD desorption to H₂ adsorption by adding 50 ppm H₂S to the feed gas; and the rate of H₂-D₂ exchange over Pd₄₇Cu₅₃ is much lower with 50 ppm H₂S in the feed gas than without (see Figure 5.6) due to the much lower rate of H₂ adsorption on Pd₄₇Cu₅₃ in the presence of 50 ppm H₂S.

Figure 5.7 HD flow rates exiting (a) the BCC Pd₄₇Cu₅₃ foil catalyst bed without H₂S in the feed gas and (b) the Pd₄₇Cu₅₃ catalyst bed with 50 ppm H₂S in the feed gas, each with three different H₂/D₂/Ar feed gas combinations: 9 mL/min of H₂ and D₂ (9H₂ / 9D₂), 4.5 mL/min of H₂ and D₂ (4.5H₂ / 4.5D₂), and 4.5 mL/min of H₂ and D₂ diluted with 9 mL/min of Ar (9Ar / 4.5H₂ / 4.5D₂). Diluting the 4.5H₂ / 4.5D₂ feed gas with Ar (9Ar / 4.5H₂ / 4.5D₂) does not significantly reduce the HD flow rate exiting the Pd₄₇Cu₅₃ catalyst bed without H₂S in the feed gas, whereas the HD flow rate exiting the Pd₄₇Cu₅₃ catalyst bed with 50 ppm H₂S in the feed gas is significantly reduced by diluting the feed gas with Ar. These observations indicate that the rate-limiting step in H₂-D₂ exchange over Pd₄₇Cu₅₃ is changed from HD desorption to H₂ adsorption by adding 50 ppm H₂S to the feed gas.
The concentration of H$_2$S in the feed gas was varied from 50 to 2000 ppm to determine the effect of H$_2$S concentration on the rate of HD production over Pd$_{47}$Cu$_{53}$. Figure 5.8 shows the HD flow rates exiting the Pd$_{47}$Cu$_{53}$ foil catalyst bed with H$_2$S concentrations of 50, 100, 200, 500, 1000, and 2000 ppm and (a) 4.5 mL/min of H$_2$ and D$_2$, (b) 9 mL/min of H$_2$ and D$_2$, and (c) 4.5 mL/min of H$_2$ and D$_2$ diluted with 9 mL/min of Ar. Increasing the H$_2$S concentration in the feed gas decreases the HD production rate over Pd$_{47}$Cu$_{53}$ for all three different H$_2$/D$_2$/Ar feed gas combinations. Because the rate of HD production over Pd$_{47}$Cu$_{53}$ is limited by the rate of H$_2$ adsorption, it is likely that H$_2$S decreases the HD production rate over Pd$_{47}$Cu$_{53}$ by blocking H$_2$ adsorption sites; and increasing the H$_2$S concentration in the feed gas increases the number of H$_2$ adsorption sites that are blocked by sulfur species (H$_2$S, SH, or S).
Increasing the H$_2$S concentration in the feed gas decreases the rate of HD production over Pd$_{47}$Cu$_{53}$.
In Figure 5.8, there are visible breaks in the HD flow rates at ~680 K and at ~810 K. The temperature of these breaks is similar to the temperature of the phase boundaries in the Pd$_{47}$Cu$_{53}$ crystal structure (see Figure 5.5). At temperatures above ~810 K, the Pd$_{47}$Cu$_{53}$ alloy has a FCC crystal structure and at temperatures less than ~680 K the alloy has a BCC crystal structure. In between ~680 K and ~810 K, the BCC and FCC phases co-exist in a mixed structure. The breaks in the HD flow rate exiting the Pd$_{47}$Cu$_{53}$ foil catalyst bed could be due to changes in the Pd$_{47}$Cu$_{53}$ crystal structure, and these different phases of Pd$_{47}$Cu$_{53}$ have different H$_2$-D$_2$ exchange activities. This is not an unexpected result, as the H$_2$-D$_2$ exchange activities of BCC Pd$_{47}$Cu$_{53}$ and FCC Pd$_{47}$Cu$_{53}$ were shown to be significantly different in Chapter 4.

In addition to blocking H$_2$ adsorption sites, it is also possible that H$_2$S reacts with the Pd$_{47}$Cu$_{53}$ surface and alters its intrinsic H$_2$ dissociation activity. To determine whether H$_2$S reduces the rate of H$_2$ adsorption on Pd$_{47}$Cu$_{53}$ more than by simply blocking H$_2$ adsorption sites, H$_2$S was removed from the feed gas during H$_2$-D$_2$ exchange over Pd$_{47}$Cu$_{53}$. Figure 5.9 shows the HD flow rates exiting the Pd$_{47}$Cu$_{53}$ foil catalyst bed versus time after removing 50 ppm H$_2$S from the feed gas at 623 K. The HD flow rate exiting a clean Pd$_{47}$Cu$_{53}$ foil catalyst that had never been exposed to H$_2$S is marked with a dashed line for comparison. Immediately after removing H$_2$S from the feed gas, the HD flow rate exiting the Pd$_{47}$Cu$_{53}$ catalyst bed increases sharply and then gradually approaches a steady-state after ~30 minutes. The steady-state flow rate exiting the sulfur-exposed Pd$_{47}$Cu$_{53}$ catalyst is still well below that of the clean Pd$_{47}$Cu$_{53}$ catalyst.
This suggests that H$_2$S reacts with the Pd$_{47}$Cu$_{53}$ surface and irreversibly alters its H$_2$-D$_2$ exchange activity. The sharp increase in the HD flow rate immediately following removal of H$_2$S from the feed gas is probably due to an increase in the number of available H$_2$ adsorption sites as the rate of H$_2$S adsorption decays to zero. The gradual increase in the HD flow rate over time could be due to the removal of weakly adsorbed sulfur species on the Pd$_{47}$Cu$_{53}$ surface. Strongly bound surface sulfides may be present on the Pd$_{47}$Cu$_{53}$ surface after 50 minutes of exposure to pure H$_2$, and these sulfides may be significantly less active for H$_2$-D$_2$ than the clean Pd$_{47}$Cu$_{53}$ surface.
The irreversible decrease in the H$_2$-D$_2$ exchange activity of Pd$_{47}$Cu$_{53}$ from H$_2$S exposure (Figure 5.9) could be due to the formation of surface sulfides that have an intrinsically lower H$_2$-D$_2$ exchange activity than the clean Pd$_{47}$Cu$_{53}$ surface. Although we do not have proof that surface sulfides are the cause of the irreversible change the H$_2$-D$_2$ exchange activity of Pd$_{47}$Cu$_{53}$, there is evidence that H$_2$S dissociated on the Pd$_{47}$Cu$_{53}$ surface to SH and S. Figure 5.10 shows the ratio
of the HDS-to-H\textsubscript{2}S and the D\textsubscript{2}S-to-H\textsubscript{2}S mass spectrometer signals collected from the product gas during H\textsubscript{2}-D\textsubscript{2} exchange over Pd\textsubscript{47}Cu\textsubscript{53} in the presence of 1000 ppm H\textsubscript{2}S. These ratios are significantly greater than the baseline ratios, which were determined by sampling the feed gas directly without passing through the Pd\textsubscript{47}Cu\textsubscript{53} catalyst bed. This indicates that H\textsubscript{2}S dissociated to SH and S on the surface and these species reacted with D atoms on the Pd\textsubscript{47}Cu\textsubscript{53} surface to produce HDS and D\textsubscript{2}S. At temperatures below ~600 K, the HDS-to-H\textsubscript{2}S and the D\textsubscript{2}S-to-H\textsubscript{2}S ratios decrease, which is probably due to the low rate of D\textsubscript{2} adsorption on Pd\textsubscript{47}Cu\textsubscript{53} at these temperatures (see Figure 5.8) and, as a result, the low coverage of D atoms on the Pd\textsubscript{47}Cu\textsubscript{53} surface. These dissociated sulfur species (SH and S) could react with the Pd\textsubscript{47}Cu\textsubscript{53} surface to form surface sulfides and irreversibly change the H\textsubscript{2}-D\textsubscript{2} exchange activity of Pd\textsubscript{47}Cu\textsubscript{53}. 
In summary, the rate of HD production over Pd\textsubscript{47}Cu\textsubscript{53} is significantly reduced by adding H\textsubscript{2}S to the feed gas due to the much lower rate of H\textsubscript{2} adsorption on Pd\textsubscript{47}Cu\textsubscript{53} in the presence of H\textsubscript{2}S than without H\textsubscript{2}S in the feed gas. Increasing the H\textsubscript{2}S concentration in the feed gas decreases the rate of H\textsubscript{2} adsorption on the Pd\textsubscript{47}Cu\textsubscript{53} further. This suggests that H\textsubscript{2}S blocks H\textsubscript{2} adsorption sites and the number of H\textsubscript{2} adsorption sites blocked by H\textsubscript{2}S increases with

**Figure 5.10** HDS-to-H\textsubscript{2}S and D\textsubscript{2}S-to-H\textsubscript{2}S mass spectrometer signal ratios in the product gas during H\textsubscript{2}-D\textsubscript{2} exchange over a Pd\textsubscript{47}Cu\textsubscript{53} foil catalyst bed in the presence of 1000 ppm H\textsubscript{2}S. The HDS-to-H\textsubscript{2}S and D\textsubscript{2}S-to-H\textsubscript{2}S mass spectrometer signal ratios are significantly higher than the baseline, indicating that H\textsubscript{2}S dissociates to SH and S on the Pd\textsubscript{47}Cu\textsubscript{53} surface.
increasing H$_2$S concentration. In addition to blocking H$_2$ adsorption sites, H$_2$S also causes in irreversible change in the H$_2$-D$_2$ exchange activity of Pd$_{47}$Cu$_{53}$. It is possible that H$_2$S causes the formation of surface sulfides that have an intrinsically lower H$_2$-D$_2$ exchange activity than the clean Pd$_{47}$Cu$_{53}$ surface.

5.4.3. H$_2$-D$_2$ exchange over Pd$_{70}$Cu$_{30}$ in the presence of H$_2$S

H$_2$-D$_2$ exchange over Pd$_{70}$Cu$_{30}$ was carried out similar to that over Pd$_4$S and Pd$_{47}$Cu$_{53}$, with H$_2$S concentrations in the feed gas varying from 50 to 2000 ppm. Unlike the Pd$_{47}$Cu$_{53}$ alloy, the crystal structure of the Pd$_{70}$Cu$_{30}$ alloy (see Figure 5.5) is FCC in the entire temperature range of the H$_2$-D$_2$ exchange reaction (400 to 1000 K). A comparison of the HD flow rates exiting a Pd$_{70}$Cu$_{30}$ foil catalyst without H$_2$S in the feed gas to the HD flow rates exiting a Pd$_{70}$Cu$_{30}$ foil catalyst bed with 50 ppm H$_2$S in feed gas, each with 9 mL/min of H$_2$ and D$_2$ in the feed gas, is shown in Figure 5.11. Adding 50 ppm H$_2$S to the feed gas significantly reduces the H$_2$-D$_2$ exchange activity of Pd$_{70}$Cu$_{30}$. 
To determine whether H$_2$S decreases the rate of HD production over Pd$_{70}$Cu$_{30}$ by decreasing the rate of H$_2$ adsorption, we first had to determine whether the rate of H$_2$-D$_2$ exchange over Pd$_{70}$Cu$_{30}$ is limited by the rate of H$_2$ adsorption. Figure 5.12 shows the HD flow rates exiting the (a) Pd$_{70}$Cu$_{30}$ foil catalyst bed without H$_2$S in the feed gas and (b) the Pd$_{70}$Cu$_{30}$ foil catalyst bed with 50 ppm H$_2$S in the feed gas, each with three different H$_2$/D$_2$/Ar feed gas combinations. The HD flow rate exiting the Pd$_{70}$Cu$_{30}$ catalyst bed without H$_2$S in the feed gas is not reduced by diluting the feed gas with Ar and, therefore, HD

**Figure 5.11** Comparison of the HD flow rates exiting the Pd$_{70}$Cu$_{30}$ catalyst bed without H$_2$S in the feed gas to the HD flow rates exiting the Pd$_{70}$Cu$_{30}$ catalyst bed with 50 ppm H$_2$S in the feed gas, each with 9 mL/min of H$_2$ and D$_2$ in the feed gas. The rate of HD production over Pd$_{70}$Cu$_{30}$ is significantly reduced by adding 50 ppm H$_2$S to the feed gas.
desorption is rate-limiting in the absence of H$_2$S. In the presence of 50 ppm H$_2$S, the rate of HD production over Pd$_{70}$Cu$_{30}$ is reduced by diluting the feed gas with Ar, indicating adsorption-limited H$_2$-D$_2$ exchange. Therefore, H$_2$S reduces the H$_2$-D$_2$ exchange activity of Pd$_{70}$Cu$_{30}$ by lowering the rate of H$_2$ adsorption.

**Figure 5.12** HD flow rates exiting the (a) Pd$_{47}$Cu$_{53}$ foil catalyst bed without H$_2$S in the feed gas and the (b) Pd$_{47}$Cu$_{53}$ foil catalyst bed with 50 ppm H$_2$S in the feed gas, each with 9 mL/min of H$_2$ and D$_2$ (9H$_2$ / 9D$_2$), 4.5 mL/min of H$_2$ and D$_2$ (4.5H$_2$ / 4.5D$_2$), and 4.5 mL/min of H$_2$ and D$_2$ diluted with 9 mL/min of Ar. Diluting the feed gas with Ar does not reduce the HD flow rate exiting the Pd$_{70}$cu$_{30}$ catalyst bed in the absence of H$_2$S, indicating desorption-limited H$_2$-D$_2$ exchange. In contrast, the HD flow rate exiting the Pd$_{70}$Cu$_{30}$ catalyst bed in the presence of 50 ppm H$_2$S is reduced by diluting the feed gas with Ar, indicating adsorption-limited H$_2$-D$_2$ exchange. H$_2$S reduces the H$_2$-D$_2$ exchange activity of Pd$_{70}$Cu$_{30}$ by reducing the rate of H$_2$ adsorption.
H$_2$-D$_2$ exchange over Pd$_{70}$Cu$_{30}$ was performed with H$_2$S concentrations in the feed gas varying from 50 to 2000 ppm to determine whether increasing the H$_2$S concentration would decrease the rate of H$_2$ adsorption on Pd$_{70}$Cu$_{30}$. Figure 5.13 shows the HD flow rates exiting the Pd$_{70}$Cu$_{30}$ foil catalyst bed with H$_2$S concentrations of 50, 100, 200, 500, 1000, and 2000 ppm and with (a) 4.5 mL/min of H$_2$ and D$_2$, (b) 9 mL/min of H$_2$ and D$_2$, and (c) 4.5 mL/min of H$_2$ and D$_2$ diluted with 9 mL/min of Ar. Increasing the H$_2$S concentration in the feed gas decreases the rate of HD production over Pd$_{70}$Cu$_{30}$. It is likely that H$_2$S decreases the rate of H$_2$ adsorption on Pd$_{70}$Cu$_{30}$ by blocking H$_2$ adsorption sites and the number of sites blocked increases with H$_2$S concentration in the feed gas.
Figure 5.13 HD flow rates exiting a Pd\textsubscript{70}Cu\textsubscript{30} catalyst bed with (a) 4.5 mL/min each of H\textsubscript{2} and D\textsubscript{2} in the feed gas, (b) 9 mL/min each of H\textsubscript{2} and D\textsubscript{2} in the feed gas, and (c) 9 mL/min of Ar with 4.5 mL/min each of H\textsubscript{2} and D\textsubscript{2} in the feed gas, each with H\textsubscript{2}S concentrations in the feed gas of 2000, 1000, 500, 200, 100, and 50 ppm. Increasing the H\textsubscript{2}S concentration in the feed gas decreases the rate of H\textsubscript{2}-D\textsubscript{2} exchange over Pd\textsubscript{70}Cu\textsubscript{30} with all three H\textsubscript{2}/D\textsubscript{2}/Ar feed gas combinations.
5.4.4 Comparison of \( H_2-D_2 \) exchange over \( \text{Pd}_4\text{S} \), \( \text{Pd}_{47}\text{Cu}_{53} \), and \( \text{Pd}_{70}\text{Cu}_{30} \) in the presence of \( H_2\text{S} \)

A comparison of the HD flow rates exiting the \( \text{Pd}_4\text{S} \), \( \text{Pd}_{47}\text{Cu}_{53} \), and \( \text{Pd}_{70}\text{Cu}_{30} \) foil catalyst beds with (a) 50 ppm \( H_2\text{S} \) in the feed gas and with (b) 2000 ppm \( H_2\text{S} \) in the feed gas is shown in Figure 5.14. With both 50 ppm and 2000 ppm \( H_2\text{S} \) in the feed gas, the rate of HD production over \( \text{Pd}_4\text{S} \) is the highest followed by \( \text{Pd}_{70}\text{Cu}_{30} \) and \( \text{Pd}_{47}\text{Cu}_{53} \). This result also implies that, in the 50 to 2000 ppm \( H_2\text{S} \) range, the rate of \( H_2 \) dissociative adsorption is the highest on \( \text{Pd}_4\text{S} \) followed by \( \text{Pd}_{70}\text{Cu}_{30} \) and \( \text{Pd}_{47}\text{Cu}_{53} \). We have not investigated a wide enough range of PdCu alloy compositions to make a general comment about the effect of alloying Pd and Cu on the rate of \( H_2 \) adsorption; however, in the presence of \( H_2\text{S} \), the rate of \( H_2 \) adsorption on the catalysts in this study decreases with increasing Cu content in the alloy.
Figure 5.14 Comparison of the HD flow rates exiting Pd$_4$S, Pd$_{70}$Cu$_{30}$, and Pd$_{47}$Cu$_{53}$ foil catalyst beds with (a) 50 ppm H$_2$S in the feed gas and (b) 2000 ppm H$_2$S in the feed gas, each with 9 mL/min of H$_2$ and D$_2$ in the feed gas. In the 50 to 2000 ppm H$_2$S range, the rate of HD production over Pd$_4$S is the highest followed by Pd$_{70}$Cu$_{30}$ and Pd$_{47}$Cu$_{53}$. 
5.5 Conclusions

In this chapter, the effect of H$_2$S on H$_2$-D$_2$ exchange over Pd$_4$S, Pd$_{70}$Cu$_{30}$, and Pd$_{47}$Cu$_{53}$ was investigated. The results of this investigation were qualitatively the same for all three catalysts. Adding 50 ppm H$_2$S to the H$_2$/D$_2$/Ar feed gas reduced the rate of HD production, relative to the HD production rate in the absence of H$_2$S, by reducing the rate of H$_2$ adsorption. Increasing the H$_2$S concentration in the feed gas up to 2000 ppm decreased the rate of HD production further by decreasing the rate of H$_2$ dissociative adsorption. It is not clear how H$_2$S decreases the rate of H$_2$ adsorption, but it is possible that H$_2$S, or other sulfur species such as SH or S, blocks H$_2$ dissociation sites. The rate of H$_2$-D$_2$ exchange over Pd$_4$S was the highest of the catalysts in this study followed by Pd$_{70}$Cu$_{30}$ and Pd$_{47}$Cu$_{53}$. Our results show that there may be a link between increasing Cu content in PdCu alloys and reduced H$_2$ dissociation activity in the presence of H$_2$S.
Chapter 6

Surface Modification and Sulfidation of Pd\textsubscript{47}Cu\textsubscript{53}

6.1. Summary and introduction

Previous work at the National Energy Technology Laboratory (B.D. Morreale, Ph.D. thesis, University of Pittsburgh, 2006) linked the presence of small particles of Ni-, Cr-, and Fe-sulfides (contaminants from stainless steel fixtures) on the surface of PdCu alloys to improved sulfur tolerance. We hypothesized that these Ni-, Cr-, and Fe-sulfide particles improve the sulfur tolerance of PdCu alloys by acting as sulfur tolerant H\textsubscript{2} dissociation catalysts. This hypothesis was tested in this thesis by modifying the surfaces of Pd\textsubscript{47}Cu\textsubscript{53} alloys with thin (~1 monolayer to 1 µm) films of Ni, Cr, Fe, Co, Mo, Pt, and Pd and measuring the rate of H\textsubscript{2} permeation through the modified Pd\textsubscript{47}Cu\textsubscript{53} alloys in the presence of 1000 ppm H\textsubscript{2}S. These thin films did not improve the sulfur tolerance of the Pd\textsubscript{47}Cu\textsubscript{53} alloy; however, monolayer films of Ni, Cr, Fe, Co, Mo, and Pt unexpectedly catalyzed the corrosion of the Pd\textsubscript{47}Cu\textsubscript{53} alloy to Pd\textsubscript{13}Cu\textsubscript{5}S\textsubscript{7} and Cu\textsubscript{2}S. Our results show that the Pd\textsubscript{47}Cu\textsubscript{53} alloy is not thermodynamically corrosion resistant, and its corrosion is kinetically limited by a surface reaction that is catalyzed by small amounts of other metals including Mo, Ni, Co, Fe, Pt, and Cr.
6.2 Experimental

Pd\(_{47}\)Cu\(_{53}\) surfaces were modified by depositing Mo, Fe, Ni, Co, Cr, Pd, and Pt thin films onto their surfaces. Membrane samples were cut from 25 µm thick Pd\(_{47}\)Cu\(_{53}\) foils (ATI Wah Chang, 99.0% metals purity). Thin film deposition was performed in an ultra-high vacuum system equipped with a magnetron sputter source (1.3” MAK sputter gun, MeiVac, Inc.). Mo, Fe, Ni, Co, Cr, Pd, and Pt sputtering targets were purchased from ACI Alloys Inc. and were all 99.9% metals purity. Prior to deposition, the substrate surfaces were cleaned by Ar\(^+\) etching. Deposition was performed at constant power (25 W) with a background Ar pressure of 3 mTorr. Film thicknesses were monitored during deposition with a quartz crystal microbalance (Maxtek BSH-150) positioned next to the Pd\(_{47}\)Cu\(_{53}\) foil and the composition of the film was verified following deposition by analysis with Auger electron spectroscopy (LK Technologies EG3000 electron gun and MINICMA\(^{TM}\) electron energy analyzer). Following preparation of the modified Pd\(_{47}\)Cu\(_{53}\) foil, the vacuum chamber was vented to atmospheric pressure and the membrane foil was mounted in the membrane testing apparatus.

The procedure for making hydrogen permeation measurements, and for characterizing the membrane samples by x-ray diffraction, scanning electron microscopy, and x-ray photoelectron spectroscopy, is given in Chapter 3.
6.3 Results and discussion

Pd$_{47}$Cu$_{53}$ membrane surfaces were modified by thin films of Fe, Ni, Cr, Co, Mo, Pt, and Pd with thicknesses ranging from ~1 monolayer to 1 µm. Their performance in the membrane testing apparatus was then evaluated by measuring the rate of H$_2$ permeation through the membranes in the presence of 1000 ppm H$_2$S. Except for at the very beginning of H$_2$S exposure, the sulfur tolerance of all of the surface-modified Pd$_{47}$Cu$_{53}$ membranes was not significantly better than the unmodified Pd$_{47}$Cu$_{53}$ membrane. Figure 6.1 shows the H$_2$ fluxes through Pd, unmodified Pd$_{47}$Cu$_{53}$, Pd$_{47}$Cu$_{53}$ with a 1 ML Mo film on the surface (1ML Mo / Pd$_{47}$Cu$_{53}$), and Pd$_{47}$Cu$_{53}$ with a 1 µm Pd film (1µmPd / Pd$_{47}$Cu$_{53}$) during exposure to 1000 ppm H$_2$S at 623 K. The H$_2$ flux through the unmodified Pd$_{47}$Cu$_{53}$ membrane decays to zero in less than 5 minutes of H$_2$S exposure, whereas the Pd membrane is still permeable to H$_2$ after 6 hours of H$_2$S exposure. The H$_2$ flux through the Pd$_{47}$Cu$_{53}$ membrane with a 1 monolayer Mo film on the surface decays to zero about 20 minutes after H$_2$S exposure, which is not a significant improvement over the unmodified Pd$_{47}$Cu$_{53}$ membrane. The sulfur tolerance of the Pd$_{47}$Cu$_{53}$ membrane with a 1 µm Pd film is significantly better than the unmodified Pd$_{47}$Cu$_{53}$ at the beginning of H$_2$S exposure, but the H$_2$ flux through the 1µmPd / Pd$_{47}$Cu$_{53}$ membrane decays to zero after about 6 hours of H$_2$S exposure. Therefore, the sulfur tolerance of the modified Pd$_{47}$Cu$_{53}$ membranes was not significantly better than the unmodified Pd$_{47}$Cu$_{53}$ membranes after 6 hours of H$_2$S exposure and the modified Pd$_{47}$Cu$_{53}$ membranes did not have better sulfur tolerance than pure Pd.
Although modifying the surface of Pd$_{47}$Cu$_{53}$ with thin metal films did not significantly improve the sulfur tolerance of the alloy, there was a significant and unexpected difference in the interaction of H$_2$S with the unmodified and the modified Pd$_{47}$Cu$_{53}$ alloy. Figure 6.2 shows the x-ray diffraction patterns of a clean Pd$_{47}$Cu$_{53}$ foil, a Pd$_{47}$Cu$_{53}$ foil after 6 hours of exposure to 1000 ppm H$_2$S at 623 K, and a Pd$_{47}$Cu$_{53}$ foil with a monolayer Mo film on the surface (1 ML Mo / Pd$_{47}$Cu$_{53}$) after 6 hours of exposure to 1000 ppm H$_2$S at 623 K. The peak

**Figure 6.1** H$_2$ fluxes through Pd, Pd$_{47}$Cu$_{53}$, Pd$_{47}$Cu$_{53}$ with a 1 µm Pd film on the surface (1µmPd / Pd$_{47}$Cu$_{53}$), and Pd$_{47}$Cu$_{53}$ with a 1 monolayer Mo film on the surface (1ML Mo / Pd$_{47}$Cu$_{53}$) during exposure to 1000 ppm H$_2$S at 623 K.
positions in the diffraction patterns of the clean Pd$_{47}$Cu$_{53}$ foil and the Pd$_{47}$Cu$_{53}$ foil after 6 hours of exposure to 1000 ppm H$_2$S are nearly identical, indicating that the Pd$_{47}$Cu$_{53}$ alloy resisted bulk sulfidation by H$_2$S. There are additional peaks in the diffraction pattern of the 1 ML Mo / Pd$_{47}$Cu$_{53}$ foil exposed to H$_2$S that are not present in the diffraction pattern of the unmodified Pd$_{47}$Cu$_{53}$ exposed to H$_2$S; these peaks are associated with two different sulfide compounds: Pd$_{13}$Cu$_3$S$_7$ and Cu$_2$S. These results suggest that the monolayer film of Mo catalyzed the corrosion of Pd$_{47}$Cu$_{53}$ to Pd$_{13}$Cu$_3$S$_7$ and Cu$_2$S.
Monolayer films of Fe, Cr, Ni, Co, and Pt also catalyzed the corrosion of Pd\textsubscript{47}Cu\textsubscript{53} to Pd\textsubscript{13}Cu\textsubscript{3}S. The observation that monolayer-thick metal films catalyze the corrosion of Pd\textsubscript{47}Cu\textsubscript{53} indicates that the Pd\textsubscript{47}Cu\textsubscript{53} alloy is not thermodynamically corrosion resistant. Corrosion of Pd\textsubscript{47}Cu\textsubscript{53} must be kinetically limited by a surface reaction that is catalyzed by the thin metal films. There are several possible surface reactions that must take place for Pd\textsubscript{47}Cu\textsubscript{53} to corrode to Pd\textsubscript{13}Cu\textsubscript{3}S\textsubscript{7} and Cu\textsubscript{2}S. First, H\textsubscript{2}S must dissociate on the Pd\textsubscript{47}Cu\textsubscript{53} surface to S.

Figure 6.2 X-ray diffraction (XRD) patterns of a clean Pd\textsubscript{47}Cu\textsubscript{53} foil, a Pd\textsubscript{47}Cu\textsubscript{53} foil after 6 hours of exposure to 1000 ppm H\textsubscript{2}S at 623 K, and a Pd\textsubscript{47}Cu\textsubscript{53} foil with a monolayer Mo film on the surface (1ML Mo / Pd\textsubscript{47}Cu\textsubscript{53}) after 6 hours of exposure to 1000 ppm H\textsubscript{2}S at 623 K. The monolayer Mo film catalyzed the corrosion of Pd\textsubscript{47}Cu\textsubscript{53} to Pd\textsubscript{13}Cu\textsubscript{3}S\textsubscript{7} and Cu\textsubscript{2}S.
Then diffusion of S from the surface to the subsurface must take place to form bulk Pd$_{13}$Cu$_3$S$_7$ and Cu$_2$S. Either of these surface reactions may be catalyzed by the thin metal films. However, we have evidence that H$_2$S dissociates readily on the unmodified Pd$_{47}$Cu$_{53}$ surface. During H$_2$-D$_2$ exchange over Pd$_{47}$Cu$_{53}$ in the presence of 1000 ppm H$_2$S (Chapter 5), there was a significant amount of HDS and D$_2$S in the product gas, indicating that H$_2$S dissociates on the Pd$_{47}$Cu$_{53}$ surface and reacts with D atoms. Therefore, it is likely that corrosion of Pd$_{47}$Cu$_{53}$ is not kinetically limited by the H$_2$S dissociation reaction and the thin metal films may instead catalyze the penetration of S into the Pd$_{47}$Cu$_{53}$ subsurface. It is possible that these thin metal films strain the surface and reduce the activation barrier to sulfur penetration into the Pd$_{47}$Cu$_{53}$ subsurface.

Monolayer-thick films of Mo, Fe, Cr, Ni, Co, and Pt catalyzed the corrosion of Pd$_{47}$Cu$_{53}$ to Pd$_{13}$Cu$_3$S$_7$ and Cu$_2$S. Thicker films of some these metals produced different corrosion products. In some cases, no detectable corrosion products were formed with thicker films. Table 6.1 lists the corrosion products that were detected by XRD after 1000 ppm H$_2$S exposure to Pd$_{47}$Cu$_{53}$ foils modified by Co, Cr, Fe, Mo, Ni, Pd, and Pt films with thicknesses varying from 1 monolayer to 1 µm. Co, Mo, and Pd films of 1 nm catalyzed the corrosion of Pd$_{47}$Cu$_{53}$ to Pd$_{13}$Cu$_3$S$_7$ and Cu$_2$S similarly to the monolayer-thick films of these metals. 10 nm and 100 nm Cr films on the Pd$_{47}$Cu$_{53}$ surface, however, did not catalyze the corrosion of Pd$_{47}$Cu$_{53}$ and no bulk sulfides were detected by XRD. 100 nm Co, Fe, and Ni films on the Pd$_{47}$Cu$_{53}$ surface did not catalyze the corrosion of Pd$_{47}$Cu$_{53}$, but Co-, Fe-, and Ni-sulfides were detected. Therefore,
monolayer films of Co, Cr, Fe, Mo, Ni, and Pt catalyzed the corrosion of Pd$_{47}$Cu$_{53}$ to Pd$_{13}$Cu$_3$S$_7$ and Cu$_2$S but thicker films of these metals did not always catalyze the corrosion of Pd$_{47}$Cu$_{53}$. It is not clear why the monolayer films are more effective at catalyzing the corrosion of Pd$_{47}$Cu$_{53}$. It is possible that the monolayer films create sufficient strain in the Pd$_{47}$Cu$_{53}$ surface to allow penetration of S into the subsurface, but thicker films of these metals increase the resistance to diffusion of S into the Pd$_{47}$Cu$_{53}$ subsurface.

Table 6.1 Corrosion products that were detected by x-ray diffraction following exposure of modified Pd$_{47}$Cu$_{53}$ foils to 1000 ppm H$_2$S in H$_2$ at 623 K. Pd$_{47}$Cu$_{53}$ surfaces were modified by thin films of Co, Cr, Fe, Mo, Ni, Pd, and Pt with thicknesses ranging from 1 monolayer to 1 µm. Exposure of the 1 µm Pd film film (highlighted) to H$_2$S produced a corrosion product that has a crystal structure similar to Pd$_4$S, but with a significant amount of Cu incorporated into its lattice.

<table>
<thead>
<tr>
<th></th>
<th>1 ML</th>
<th>1 nm</th>
<th>10 nm</th>
<th>100 nm</th>
<th>1 µm</th>
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</thead>
<tbody>
<tr>
<td>Co</td>
<td>Pd$_{13}$Cu$_3$S$_7$ + Cu$_2$S</td>
<td>Pd$_{13}$Cu$_3$S$_7$ + Cu$_2$S</td>
<td>Co$_9$S$_8$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>Pd$_{13}$Cu$_3$S$_7$ + Cu$_2$S</td>
<td>no &quot;thick&quot; sulfides</td>
<td>no &quot;thick&quot; sulfides</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>Pd$_{13}$Cu$_3$S$_7$ + Cu$_2$S</td>
<td>Fe-sulfide (spalled)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>Pd$_{13}$Cu$_3$S$_7$ + Cu$_2$S</td>
<td>Pd$_{13}$Cu$_3$S$_7$ + Cu$_2$S</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>Pd$_{13}$Cu$_3$S$_7$ + Cu$_2$S</td>
<td>Ni-sulfide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>Pd$_{13}$Cu$_3$S$_7$ + Cu$_2$S</td>
<td>Pd$_{13}$Cu$_3$S$_7$ + Cu$_2$S</td>
<td>Pd$_{13}$Cu$_3$S$_7$ + Cu$_2$S</td>
<td>Pd$_4$S</td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>Pd$_{13}$Cu$_3$S$_7$ + Cu$_2$S</td>
<td></td>
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</tr>
</tbody>
</table>
Pd films up to 100 nm catalyzed the corrosion of Pd₄₇Cu₅₃ to Pd₁₃Cu₃S₇ and Cu₂S; however, exposure of a Pd₄₇Cu₅₃ foil with a 1 µm Pd film to 1000 ppm H₂S at 623 K produced a corrosion product with a crystal structure that is similar to Pd₄S. Figure 6.3 shows the XRD patterns of a Pd₄₇Cu₅₃ foil with a 1 µm Pd film on the surface (1µmPd / Pd₄₇Cu₅₃) before H₂S exposure and after 6 hours of exposure to 1000 ppm H₂S in H₂ at 623 K. As expected, the diffraction pattern of the 1µmPd / Pd₄₇Cu₅₃ foil before H₂S exposure shows only peaks that are associated with Pd and Pd₄₇Cu₅₃. The diffraction pattern of the composite 1µmPd / Pd₄₇Cu₅₃ foil after 6 hours of H₂S exposure is dominated by features that are associated with the Pd₄S crystal structure and not the Pd₁₃Cu₃S₇ or Cu₂S crystal structures. Therefore, increasing the Pd film thickness from 100 nm to 1 µm increased the selectivity towards Pd₄S production relative to Pd₁₃Cu₃S₇ and Cu₂S.
Although the crystal structure of the corrosion product that resulted from exposing the 1 μm Pd / Pd_{47}Cu_{53} foil to H_{2}S is similar to Pd_{4}S, x-ray photoelectron spectroscopic depth profiling in the near surface region of the 1 μm Pd / Pd_{47}Cu_{53} foil indicates that there was a significant amount of Cu incorporated into the Pd_{4}S lattice. Figure 6.4 shows an x-ray photoelectron spectroscopy depth profile of the 1 μm Pd / Pd_{47}Cu_{53} foil after 6 hours of exposure to 1000 ppm H_{2}S

![XRD patterns of a Pd_{47}Cu_{53} foil with a 1 μm Pd film on the surface before H_{2}S exposure (top, blue) and after 6 hours of exposure to 1000 ppm H_{2}S at 623 K (bottom, red). Only peaks associated with Pd and Pd_{47}Cu_{53} are present in the diffraction pattern of composite foil before H_{2}S exposure. Peaks associated with Pd_{4}S dominate the diffraction pattern of the Pd / Pd_{47}Cu_{53} foil after 6 hours of H_{2}S exposure.](image)
at 623 K. In the near-surface region (~200 nm) of the 1 µm Pd / Pd\textsubscript{47}Cu\textsubscript{53}, there is a significant amount of Cu, indicating that the thin Pd film extracted Cu from the Pd\textsubscript{47}Cu\textsubscript{53} foil substrate during sulfidation. The metal (Pd + Cu)-to-S ratio in the near-surface region is still ~4:1, which is the Pd:S ratio in Pd\textsubscript{4}S. Figure 6.5 shows a scanning electron micrograph (SEM) of a cross-section of the 1 µm Pd / Pd\textsubscript{47}Cu\textsubscript{53} foil after 6 hours of exposure to 1000 ppm H\textsubscript{2}S at 623 K with a sulfur EDS map to highlight the sulfur rich region in the SEM image. After 6 hours of H\textsubscript{2}S exposure, the thickness of the sulfur corrosion product was ~4 µm, which is much thicker than the original thickness of the Pd film (1 µm) that was deposited onto the Pd\textsubscript{47}Cu\textsubscript{53} foil. XRD, XPS depth profiling and SEM/EDS analysis of the sulfur-exposed 1 µm Pd / Pd\textsubscript{47}Cu\textsubscript{53} foil indicate that the thin 1 µm Pd film extracted Cu from the Pd\textsubscript{47}Cu\textsubscript{53} foil substrate during sulfidation to produce a corrosion product that has a crystal structure similar to that of Pd\textsubscript{4}S but with a significant amount of Cu incorporated into the crystal lattice.
Figure 6.4 X-ray photoelectron spectroscopy depth profile of the Pd$_{47}$Cu$_{53}$ foil with a 1 μm Pd film on the surface after 6 hours of exposure to 1000 ppm H$_2$S in H$_2$ at 623 K showing the Pd, Cu, and S concentrations versus depth from the surface to about 200 nm into the bulk. There is a significant amount of Cu in the near surface region, indicating that the Pd film extracted Cu from the Pd$_{47}$Cu$_{53}$ foil during sulfidation.
Figure 6.5 Scanning electron micrograph (left) with sulfur energy dispersive spectroscopy map (right) of a cross-section of the Pd$_{47}$Cu$_{53}$ foil with a 1 µm Pd film on the surface after 6 hours of exposure to 1000 ppm H$_2$S in H$_2$ at 623 K. The white region in the sulfur EDS map highlights the sulfur-rich region in the SEM image. The thickness of this sulfur-rich region is ~4 µm, which is much thicker than the original thickness of the Pd film (1 µm). XPS depth profiling (Figure 6.4) indicates that a significant amount of Cu is present in this sulfur-rich film, indicating that the Pd film extracts Cu from the Pd$_{47}$Cu$_{53}$ foil substrate during sulfdation.
6.4 Conclusions

In an attempt to impart sulfur tolerance in the Pd$_{47}$Cu$_{53}$ alloy at low temperatures, Pd$_{47}$Cu$_{53}$ surfaces were modified by thin films of Mo, Fe, Ni, Co, Cr, Pd and Pt with thicknesses ranging from 1 monolayer to 1 µm. Although the sulfur tolerance of the modified Pd$_{47}$Cu$_{53}$ alloys was not significantly better than the unmodified alloy, valuable insight into PdCu corrosion mechanisms was gained from these experiments. Monolayer-thick films of Mo, Fe, Ni, Co, Cr, and Pt catalyzed the corrosion of Pd$_{47}$Cu$_{53}$ to Pd$_{13}$Cu$_3$S$_7$ and Cu$_2$S, which suggests that the Pd$_{47}$Cu$_{53}$ alloy is not thermodynamically corrosion resistant. Corrosion of the Pd$_{47}$Cu$_{53}$ alloy is kinetically limited by a surface reaction that is catalyzed by these thin films. It is likely that these thin metal films aid sulfur penetration into the Pd$_{47}$Cu$_{53}$ bulk, perhaps by straining the Pd$_{47}$Cu$_{53}$ surface. Different corrosion products were formed by depositing thicker films on Pd$_{47}$Cu$_{53}$ foil surfaces. A 1 µm Pd film on the surface of a Pd$_{47}$Cu$_{53}$ foil extracted Cu from the Pd$_{47}$Cu$_{53}$ foil substrate during sulfidation to produce a ~4 µm-thick Pd-Cu-S corrosion product that had a crystal structure similar to that of Pd$_4$S but with a significant amount of Cu incorporated into the lattice.
Chapter 7

General Conclusions

The aim of this thesis was to understand how H$_2$S slows hydrogen transport through Pd and PdCu alloy hydrogen separation membranes. Although there are still many gaps in our understanding of sulfur poisoning, we have found that H$_2$S can inhibit hydrogen transport through Pd and PdCu membranes by two different mechanisms: (1) by producing a low permeability sulfide film on the membrane surface, and (2) by decreasing the rate of H$_2$ dissociation on the membrane surface.

Throughout this thesis we have used pure Pd and Pd$_{47}$Cu$_{53}$ as benchmarks for understanding hydrogen transport and sulfur poisoning mechanisms. The Pd$_{47}$Cu$_{53}$ alloy has been identified as a promising alternative to pure Pd hydrogen separation membranes due in part to its high permeability, which is related to its BCC crystal structure at temperatures less than ~700 K. At temperatures greater than ~800 K, the Pd$_{47}$Cu$_{53}$ alloy has a FCC crystal structure and a H$_2$ permeability that is about an order-of-magnitude less than that of BCC Pd$_{47}$Cu$_{53}$. We have shown for the first time that the surface H$_2$ dissociation reaction is also significantly different on BCC Pd$_{47}$Cu$_{53}$ than that on FCC Pd$_{47}$Cu$_{53}$; the activation barrier to H$_2$ dissociation on FCC Pd$_{47}$Cu$_{53}$ is significantly lower than that on BCC Pd$_{47}$Cu$_{53}$. In addition, the activation barriers to H$_2$ dissociation on both BCC and FCC Pd$_{47}$Cu$_{53}$ surfaces are not significantly higher than the
activation barrier to H₂ dissociation on pure Pd. This thesis has shown that, in the absence of H₂S, Pd can be alloyed with ~50 mol% Cu without significantly reducing H₂ dissociation rates on the surface or the rate of H atom permeation through its bulk.

There is a significant difference in the effect of H₂S on hydrogen transport through Pd and Pd₄₇Cu₅₃ membranes, which we believe is due to a difference in how H₂S interacts with the two membranes. At 623 K, the rate of hydrogen permeation through Pd and Pd₄₇Cu₅₃ membranes is significantly reduced by exposure to 1000 ppm H₂S, but with significantly different decay patterns. The Pd₄₇Cu₅₃ membrane is impermeable to H₂ in less than 5 minutes of H₂S exposure, whereas the Pd membrane is still permeable to hydrogen after 6 hours of H₂S exposure. Compositional analysis of the Pd and Pd₄₇Cu₅₃ membranes indicates that H₂S exposure produced a thick (~µm) Pd₄S film on the surface of the Pd membrane. In contrast, sulfur penetrated only a few nanometers into the bulk of the Pd₄₇Cu₅₃ membrane. These results have led us to believe that H₂S slows hydrogen transport through Pd and Pd₄₇Cu₅₃ membranes by different mechanisms.

H₂S slows hydrogen transport across Pd membranes mainly by producing a Pd₄S film on the Pd surface that is about an order-of-magnitude less permeable to hydrogen than Pd. In contrast to Pd, our results strongly suggest that H₂S blocks hydrogen transport across Pd₄₇Cu₅₃ membranes by decreasing the rate of H₂ dissociation on the Pd₄₇Cu₅₃ surface. The kinetics of H₂-D₂ exchange over Pd₄₇Cu₅₃ in the presence of H₂S (Chapter 5) need to be analyzed with a microkinetic model to understand how H₂S decreases the rate of H₂ dissociation
on the Pd\textsubscript{47}Cu\textsubscript{53} surface; but it appears that H\textsubscript{2}S (or other sulfur species) blocks a significant fraction of the Pd\textsubscript{47}Cu\textsubscript{53} surface for H\textsubscript{2} dissociation. H\textsubscript{2}S also decreases the rate of H\textsubscript{2} dissociation on Pd\textsubscript{4}S surfaces, but H\textsubscript{2}S has a more significant effect on the rate of H\textsubscript{2} dissociation on Pd\textsubscript{47}Cu\textsubscript{53} than on Pd\textsubscript{4}S.

The effect of H\textsubscript{2}S on hydrogen transport across Pd\textsubscript{47}Cu\textsubscript{53} diminishes with increasing temperature until H\textsubscript{2}S has no effect on hydrogen permeation through Pd\textsubscript{47}Cu\textsubscript{53} at temperatures greater than \(~900\) K. It is likely that the sulfur tolerance exhibited by the Pd\textsubscript{47}Cu\textsubscript{53} alloy is related to its resistance to bulk sulfidation. However, it is not well understood why the Pd\textsubscript{47}Cu\textsubscript{53} alloy resist bulk sulfidation. Our results indicate that the Pd\textsubscript{47}Cu\textsubscript{53} alloy is not thermodynamically sulfidation resistant; its sulfidation is kinetically limited by a surface reaction that is catalyzed by thin metal (Fe, Ni, Co, Cr, Mo, Pt) films on the surface of Pd\textsubscript{47}Cu\textsubscript{53}. This finding warrants further investigation because understanding why the Pd\textsubscript{47}Cu\textsubscript{53} alloy resists bulk sulfidation may lead to the development of advanced membrane materials that could be implemented into a coal gasification process.
Appendix: derivation of the H$_2$-D$_2$ exchange kinetic model

The integral mass balance on HD is

\[ \int_{F_{HD,0}}^{F_{HD,\text{out}}} \frac{dF_{HD}}{r_{HD}} = A, \tag{A1} \]

where \( dF_{HD} \) is the differential HD flow rate, \( F_{HD,\text{out}} \) is the HD flow rate exiting the catalyst bed, \( A \) is the catalyst surface area, and \( r_{HD} \) is the HD production rate [90]. The HD production rate, \( r_{HD} \), is given by the microkinetic expression:

\[ r_{HD} = 2k_{\text{des}} \theta_H \theta_D - k_{\text{ads}} P_{HD} (1 - \theta_H - \theta_D)^2 \tag{A2} \]

where \( k_{\text{des}} \) is the HD desorption rate constant, \( \theta_H \) is the coverage of H atoms, \( \theta_D \) is the coverage of D atoms, \( k_{\text{ads}} \) is the HD adsorption rate constant, and \( P_{HD} \) is the HD partial pressure. Because we are assuming that isotopic effects are negligible, and the partial pressures of H$_2$ and D$_2$ are equal for all experiments, the coverages of H (\( \theta_H \)) and D (\( \theta_D \)) atoms are each assumed to be equal to one-half of the total coverage (\( \theta \)):

\[ \theta_H = \theta_D = \frac{\theta}{2}. \]

Therefore, the microkinetic expression for the rate of HD production is:

\[ r_{HD} = 2k_{\text{des}} \left( \frac{\theta}{2} \right)^2 - k_{\text{ads}} P_{HD} (1 - \theta)^2. \tag{A3} \]

To substitute the microkinetic expression for the rate of HD production, equation (A3), into the mass balance on HD, equation (A1), the HD partial pressure in equation (A3) must be converted into HD flow rate, \( F_{HD} \):

\[ r_{HD} = 2k_{\text{des}} \left( \frac{\theta}{2} \right)^2 - k_{\text{ads}} F_{HD} P_{total} (1 - \theta)^2 \tag{A4} \]
where

\[ F_{\text{HD}} = \frac{F_{\text{total}} P_{\text{HD}}}{P_{\text{total}}} \]

and \( P_{\text{total}} \) is the total pressure and \( F_{\text{total}} \) is the total flow rate. Substituting the HD production rate, equation (A4), into the integral mass balance on HD, equation (A1), gives:

\[
\int_0^{F_{\text{HD, out}}} \frac{dF_{\text{HD}}}{2k_{\text{des}} \left( \frac{\theta}{2} \right)^2} - \frac{k_{\text{ads}} F_{\text{HD}} P_{\text{total}} (1 - \theta)^2}{F_{\text{total}}} = A
\]  

(A5)

Integrating equation (A5) and solving for the flow rate of HD exiting the catalyst bed gives:

\[
F_{\text{HD, out}} = \frac{k_{\text{des}} F_{\text{total}} \theta^2}{2k_{\text{ads}} P (1 - \theta)^2} \left[ 1 - \exp \left( - \frac{k_{\text{adv}} P A (1 - \theta)^2}{F_{\text{total}}} \right) \right]
\]  

(A6)

At steady-state, the change in the coverage of H (and D) atoms is zero:

\[
\frac{d\theta_H}{dt} = 0 = 2k_{\text{ads}} P_{\text{H}_2} (1 - \theta_H - \theta_D)^2 + k_{\text{ads}} P_{\text{HD}} (1 - \theta_H - \theta_D)^2 - 2k_{\text{des}} \theta_H^2 - 2k_{\text{des}} \theta_H \theta_D
\]

where \( P_{\text{H}_2} \) is the \( \text{H}_2 \) partial pressure and all of the other variables are defined above. Again, we assume that the coverages of H and D atoms are each equal to one-half of the total coverage:

\[
\theta_H = \theta_D = \frac{\theta}{2}
\]

Therefore, the change in the coverage of H atoms is given by:

\[
\frac{d\theta_H}{dt} = 0 = 2k_{\text{ads}} P_{\text{H}_2} (1 - \theta)^2 + k_{\text{ads}} P_{\text{HD}} (1 - \theta)^2 - k_{\text{des}} \theta^2.
\]
Solving for $\theta$ gives:

$$\theta = \sqrt{\frac{2 k_{ads} P_{H_2, feed}}{k_{des}}} \left(1 + \sqrt{2 k_{ads} P_{H_2, feed}}ight)$$

(A7)

where $P_{H_2, feed}$ is the partial pressure of $H_2$ in the feed gas, which is related to $P_{H_2}$ and $P_{HD}$ by the stoichiometry of the reaction:

$$P_{H_2} = P_{H_2, feed} - \frac{1}{2} P_{HD}$$

Substitution of the expression for the total coverage of H and D atoms, equation (A7), into the expression for the flow rate of HD exiting the reactor, equation (A6), gives the H$_2$-D$_2$ exchange kinetic model:

$$F_{HD, out} = F_{H_2, feed} \left[1 - \exp\left(-\frac{k_{ads} P_{total}}{F_{total} \left(1 + \sqrt{2 k_{ads} P_{H_2, feed}}\right)^2}\right)\right]$$

where

$$F_{H_2, feed} = \frac{F_{total} P_{H_2, feed}}{P_{total}}.$$
References


