Hydrogen Dissociation on Pd₄S Surfaces

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Exposure of Pd-based hydrogen purification membranes to H₂S, a common contaminant in coal gasification streams, can cause membrane performance to deteriorate, either by deactivating surface sites required for dissociative H₂ adsorption or by forming a low-permeability sulfide scale. In this work, the composition, structure, and catalytic activity of Pd₄S, a surface scale commonly observed in Pd–membrane separation of hydrogen from sulfur-containing gas streams, were examined using a combination of experimental characterization and density functional theory (DFT) calculations. A Pd₄S sample was prepared by exposing a 100 μ m Pd foil to H₂S at 908 K. Both X-ray photoemission depth profiling and low energy ion scattering spectroscopic (LEISS) analysis reveal slight sulfur-enrichment of the top surface of the sample. This view is consistent with the predictions of DFT atomistic thermodynamic calculations, which identified S-terminated Pd₄S surfaces as energetically favored over corresponding Pd-terminated surfaces. Activation barriers for H₂ dissociation on the Pd₄S surfaces were calculated. Although barriers are higher than on Pd(111), transition state theory analysis identified reaction pathways on the S-terminated surfaces for which hydrogen dissociation rates are high enough to sustain the separation process at conditions relevant to gasification applications.

I. Introduction

Hydrogen, produced by gasification of carbon-based materials such as coal, is an important component of strategies to address issues of fuel supply stability and CO₂-related climate change.¹ Generating hydrogen from coal presents significant technical challenges, including the need for large-scale separation of H₂ from mixed gas streams that contain CO₂ and several minor impurities, most notably H₂S. Dense, Pd-based membranes have received significant attention for the gas separation application.² Molecular hydrogen dissociatively adsorbs on the surface of a palladium membrane and hydrogen atoms diffuse rapidly through its bulk.³ Recombination of the hydrogen atoms on the opposite surface of the membrane and desorption of molecular hydrogen complete a sequence of atomic processes that effectively separates hydrogen from all other components of the mixed gas stream.³ For separation of hydrogen from gas mixtures that are free of inhibitors, atomic diffusion limits overall transport when the Pd membrane is thicker than about 3 μ m; for thinner membranes, the dissociation process can be the limiting factor.³ Hydrogen transport through Pd-based membrane has been widely studied, both theoretically and experimentally, with several published reports appearing in recent years.^{4–9}

The performance of Pd-based membranes can be compromised in a number of ways. It is well-known that sulfur contaminants commonly found in fossil fuels can cause deterioration of membrane performance and reduction of membrane lifetime.^{1,10} Sulfur compounds decompose and deposit sulfur atoms on the surface of the membrane to form S–Pd bonds which modify the structure of the metal valence band, typically

Figure 1. Permeation test of the 100 μ m Pd membrane at 723 K. Upon addition of 1000 ppm of H₂S, H₂ flux drops significantly as Pd₄S scale forms.

by decreasing the density of states near the Fermi level. These electronic perturbations suppress the catalytic activity of the membrane surface.¹¹

Exposure of a Pd membrane to H₂S has also been linked to formation of thick Pd₄S surface scales.^{9,12,13} Figure 1 shows a typical hydrogen flux response of a pure palladium membrane in the presence of H₂S.¹² In this experiment, a baseline flux of clean hydrogen through a 100 μ m thick Pd membrane was first established at 723 K. Then, 1000 ppm of H₂S was added to the mixture and the flux was measured throughout 100 h of exposure to H₂S. The measured hydrogen flux (points, left-side axis) falls exponentially during H₂S exposure. The curve (right-side axis) shows the thickness of the Pd₄S scale layer estimated by analysis of the flux data using a combined scale growth and hydrogen atom diffusion kinetic model.^{9,12} The decrease in the hydrogen flux as the sulfide scale grows is attributed to the low diffusivity of hydrogen atoms in the scale.¹³

The observation of nonzero hydrogen transport through a membrane that is terminated by a Pd₄S scale suggests that the

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Pd₄S surface is itself active for dissociation of molecular hydrogen. However, no fundamental information about the behavior of H₂ on Pd₄S surfaces is currently available from either experiment or theory. Thus, the present work was undertaken to enhance our understanding of hydrogen dissociation on Pd₄S surfaces, employing an approach that combines experimental characterization of surface composition with first-principles computational study of surface structure and H₂ dissociation energetics. We demonstrate that the highly stable S-terminated Pd₄S faces, while less active for H₂ dissociation than pure Pd, likely possess sufficient activity to sustain transport rates needed for the separation application.

II. Experimental and Theoretical Methods

A. Experimental. A Pd foil (Alfa Aesar, 99.99%, 100 μm thick) was sulfided in an apparatus we described previously.¹² The foil was placed inside a quartz reaction chamber and exposed to a 1000 ppm of H₂S, 10% He, balance H₂ mixture at 908 K for 2.75 h, conditions which have been shown to produce a Pd₄S scale of approximately 8 μm .¹²

Images of the surface morphologies of the of the Pd foil before and after sulfiding were acquired with an ADE phase-shift MicroXAM 3D noncontact optical surface profiler. The images shown were zoomed from the original 131 $\mu\text{m} \times 99.0 \mu\text{m}$ image (752 $\times$ 482 pixels). Additionally, the before and after samples were examined with a scanning electron microscope equipped with energy dispersive X-ray analysis (SEM/EDS, Aspex LLC PSEM 2000).

X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI 5600ci instrument with monochromatic Al K α X-rays and analyzer pass energy of 58.7 eV. Elemental concentrations were calculated from Pd 3d_{5/2} and S 2p_{3/2} peak areas and calibrated sensitivity factors. Elemental depth profiles were acquired by using argon ion sputtering. The differentially pumped ion gun was operated at 1.5×10^{-2} Pa and 25 mA, delivering a sputtering rate of approximately 10 nm/min.

X-ray diffraction measurements were obtained with a PANalytical X'Pert Pro MPD powder diffractometer having a θ – θ 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° 2θ . Foil samples were mounted on zero background quartz slides for analysis.

The top-surface composition of the Pd₄S sample was characterized by low energy ion scattering spectroscopy (LEISS). Experiments were performed in an ultrahigh vacuum chamber (base pressure = 1.3×10^{-8} Pa) equipped with a He⁺ ion gun (Specs IQE 12/38) and energy analyzer (Specs PHOIBOS 150MCD). The 750 eV He⁺ ions were specularly reflected from the sample at an angle of $\sim 50^\circ$ from the surface normal. Low incident ion currents of ~ 50 nA ($\sim 1.5 \times 10^{13}$ He⁺/cm² over the course of a single 60 s experiment) were used to minimize potential damage by incident He⁺. Before the LEISS experiment, the sample was heated to 500 K to desorb loosely bound surface contaminants; the surface analysis was performed at 400 K. For two reasons, precise quantification of Pd₄S top-layer composition with LEISS data is difficult. First, the sulfur feature is small, reflecting a preference for He⁺ to neutralize, rather than scatter, during its interaction with surface S atoms.¹⁴ Second, it is likely that surface C and O, from adsorption of background gases in the chamber, preferentially bind to Pd atoms, and thus attenuate the Pd signal. We estimate that the uncertainty in our estimate of the top-layer S/Pd ratio of the Pd₄S sample, using Pd(111)-S($\sqrt{3} \times \sqrt{3}$)R30° ($\theta = 0.33$ ML) for calibration, is as high as $\pm 50\%$.

B. Theoretical. All calculations are performed with use of first-principles density functional theory (DFT) and the generalized gradient approximation (GGA) for the exchange correlation functional as implemented in the Vienna Ab Initio Simulation Package (VASP) code.^{15,16} The VASP code employs an efficient, robust, and fast iterative matrix diagonalization scheme for evaluating the self-consistent solution of the Kohn–Sham functional. The GGA functional due to Perdew–Burke–Erzerhoff (PBE)¹⁷ was employed to calculate the exchange–correlation energy. Other than those in its local density component, all parameters of this functional are fundamental constants. The nonempirical PBE functional fulfills many of the physical and mathematical requirements of DFT. The electron–ion interaction was described by the projector-augmented wave (PAW) method.¹⁸ PAW potentials reconstruct the exact valence wave function with all nodes in the core region. The Kohn–Sham one-electron valence eigenstates were expanded in terms of plane-wave basis sets with a cutoff energy of 280 eV. For the primitive tetragonal bulk cell of Pd₄S (containing two formula units of Pd₄S), Brillouin-zone sampling was performed on a dense Monkhorst–Pack k -point mesh of $15 \times 5 \times 11$ points.¹⁹ To simulate the various terminations of low-index Pd₄S surfaces, we used slabs with periodic boundary conditions in three directions. To ensure the decoupling of the adjacent slabs, a 15 Å thick vacuum region was employed. The lattice constants were fixed at bulk optimized conditions. We used a k -point mesh of $7 \times 7 \times 1$ to sample the two-dimensional electronic Brillouin zone of the periodic slabs. A Methfessel–Paxton smearing of $\sigma = 0.1$ eV was used to improve convergence and the corrected energy for $\sigma \rightarrow 0$ was employed. Throughout this study, symmetric slabs were employed with a thickness up to 41 layers containing at most 42 atoms per slab. All the atoms were relaxed with the three innermost center layers fixed to their bulk values.

We linked our DFT results with concepts from thermodynamics in order to investigate the relative stability of the various considered surfaces.²⁰ We compared their surface free energies, defined as

$$\gamma(P, T) = \frac{1}{2A} [G - \sum_i N_i \mu_i(P, T)] \quad (1)$$

Here, G denotes the Gibbs free energy of the solid, which exposes a surface with area A . For the determination of A , the bottom and the top side of the slab are taken into account resulting in a factor of 2. N_i and μ_i are the number and the chemical potential of species i present in the system ($i = \text{Pd}$ and S). Because the surface is in equilibrium with the underlying bulk sulfide, the two chemical potentials, μ_{Pd} and μ_{S} , are related via the Gibbs free energy of the bulk. That is, $4 \mu_{\text{Pd}} + \mu_{\text{S}} = g_{\text{Pd}_4\text{S}}^{\text{bulk}}(T, p)$, where $g_{\text{Pd}_4\text{S}}^{\text{bulk}}$ denotes the Gibbs free energy per formula unit. Inserting this constraint in eq 1 leads to a surface free energy as a function of the chemical potential of S,

$$\gamma(P, T) = \frac{1}{2A} \left(G - \frac{N_{\text{Pd}}}{4} g_{\text{Pd}_4\text{S}}^{\text{bulk}} + \left(\frac{N_{\text{Pd}}}{4} - N_{\text{S}} \right) \mu_{\text{S}} \right) \quad (2)$$

The difference in the Gibbs free energy of the slab and the bulk phase entering into the evaluation of $\gamma(P, T)$ consists of contributions from the difference in the corresponding total energies, from changes in vibrational and configurational free energy, and from the PV term. The PV term for solids is negligibly small and can be omitted.²⁰ For the configurational free energies, a full evaluation of this term requires the use of statistical mechanics approaches, like Monte Carlo simulation, to completely sample the configu-

Figure 2. Images of clean Pd foil acquired by phase shift microscope (a) and SEM (b) and Pd foil after exposure to H_2S at 908 K acquired by phase shift microscope (c) and SEM (d).

rational space. However, the use of this approach in conjunction with DFT is computationally prohibitive. It should be noted that the first-principles thermodynamics approach adopted here was for a rather coarse comparison of the stability of structures with a defined periodicity. Thus, the configurational contribution was not considered since for every included structure there is only one specific configuration. The vibrational contribution, $\Delta\gamma^{\text{vib}}$, can be evaluated in a quasiharmonic approximation.²⁰ However, in practice, this is computationally demanding. As is apparent in eq 2, only the *difference* of the Gibbs free energy between the surface and the bulk enters the expression for $\gamma(P,T)$; it has been shown that this contribution usually cancels to a large extent.²⁰ The Gibbs free energy of the surface and slab then reduce to the internal energies which can be directly obtained from DFT calculations.

The term μ_{S} can only be varied within certain boundaries. For μ_{S} , the lower boundary is defined by the decomposition of sulfide into Pd metal and sulfur. The upper boundary is determined by gas phase conditions that are so sulfur rich that formation of bulk sulfur is preferred. Appropriate and well-defined estimates for the limits of μ_{S} indicated above are thus given by $\Delta H_{\text{f,Pd}_4\text{S}}^{\text{bulk}}(T=0\text{K},p=0) < \mu_{\text{S}} - E_{\text{S}}^{\text{bulk}} < 0$. The term $\Delta H_{\text{f,Pd}_4\text{S}}^{\text{bulk}}(T=0\text{K},p=0)$ is the low-temperature limit for the heat of formation of Pd_4S . $E_{\text{S}}^{\text{bulk}}$ is the total energy of the S atom in the α phase of bulk sulfur. μ_{S} was referenced to the reaction $\text{H}_2\text{S}_{(\text{g})} + (*) = \text{S}(*) + \text{H}_{2(\text{g})}$, where $(*)$ denotes a binding site on the surface. In this case, μ_{S} can be written as²¹

$$\mu_{\text{S}} = [\Delta h_{\text{H}_2\text{S}}(T,p^0) - \Delta h_{\text{H}_2}(T,p^0)] + [E_{\text{H}_2\text{S}}^{\text{vib}} - E_{\text{H}_2}^{\text{vib}}] + [E_{\text{H}_2\text{S}} - E_{\text{H}_2}] - T[s_{\text{H}_2\text{S}}(T,p^0) - s_{\text{H}_2}(T,p^0)] + k_{\text{B}}T \ln(p_{\text{H}_2\text{S}}/p_{\text{H}_2}) \quad (3)$$

For standard pressure $p^0 = 1$ bar, the differences in enthalpy (Δh_{gas}) and entropy (s_{gas}) of a H_2S or H_2 molecule can be found

in standard thermodynamics tables. $E_{\text{gas}}^{\text{vib}}$ represents the zero-point vibration energies for the molecule, which is estimated from the experimental values for the molecular vibration frequencies. The μ_{S} in eq 3 depends on the partial pressure ratio $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$ and not on the individual partial pressures.

To explore the most likely pathways for H_2 dissociation on the surfaces, the nudged elastic band (NEB) technique was employed.²² NEB is a method for finding saddle points and minimum energy paths between known reactants and products. A discrete representation of the reaction path was employed, with the points (movable images) along the path being relaxed by using first derivative information only. In this work, seven movable images were used in the search for the saddle point of each elementary reaction step mentioned above. An initial chain of images is constructed between the initial reactants and final reaction products by using linear interpolation between the two end points. The transition state of the optimized reaction coordinate was approximated by the image of highest energy. The overall reaction energy ΔE_{rxn} was calculated by using the expression

$$\Delta E_{\text{rxn}} = \sum E_{\text{prod}} - \sum E_{\text{react}} \quad (4)$$

where the first and second terms represent the sum of energies of products and reactants, respectively. On the basis of this convention, a positive ΔE_{rxn} corresponds to an endothermic reaction.

III. Results and Discussion

A. Surface Analysis of the Sulfided Pd Foil. Panels a and b of Figure 2 show images of the clean Pd foil acquired by using a phase shift microscope and SEM. Panels c and d of Figure 2 show corresponding images of the sulfided foil. Sulfidation clearly roughens the surface, creating topographical

Figure 3. X-ray photoelectron spectroscopy depth profile of the sulfided Pd foil. The sputtering rate is ~ 10 nm/min based on a pure Pt film. Top surface (sputtering time = 0) stoichiometry is Pd:S $\approx$ 2; farther into the sample stoichiometry is Pd:S $\approx$ 4.

features on the order of $2\ \mu\text{m}$ in both width and height. Results of a 60 s (~ 10 nm) XPS depth profile of the sulfided foil appear in Figure 3. Analysis before sputtering (time = 0 in the figure) suggests a slight excess of S at the top surface, Pd:S $\approx$ 2:1. After just 6 s of sputtering (~ 1 nm), the stoichiometry of the sample reaches a steady state value near that expected for Pd₄S. Results of X-ray diffraction analysis of the clean and sulfided foils appear in Figure 4. XRD clearly identifies Pd₄S as the bulk sulfide formed under the conditions of H₂S exposure used to grow the surface layer. The orientation of Pd₄S crystal faces is approximately random.

The LEIS spectrum of the sulfided palladium foil, shown in Figure 5, is dominated by a feature at ~ 705 eV, which is assigned to Pd. The inset shows smaller features at lower energies that are assigned to C and O, most likely due to adsorption of small amounts of CO from the background, and surface S. The S signal is weak and noisy, reflecting both a small scattering cross section in the LEIS experiment and roughness of the sample surface. Significantly, its presence clearly confirms a top layer that contains both Pd and S atoms. As noted earlier, precise quantification of top-surface composition is difficult. Our best estimate of top-surface stoichiometry, using a Pd(111)-S($\sqrt{3} \times \sqrt{3}$)R30 ($\theta = 0.33$ ML) spectrum for calibration, is Pd_{2.5}±1S. This result is consistent with the XPS analysis, supporting the presence a slight excess of S at the top-surface of the sample.

B. Pd₄S Surfaces and Their Interaction with H₂: DFT Calculations. Having experimentally confirmed the composition of the surface region of Pd₄S, we investigated the surfaces using DFT calculations. We took a basic approach, focusing on all possible (1 $\times$ 1) terminations of the low index faces of Pd₄S. For reference, we began by studying the structural properties of bulk Pd₄S. Pd₄S crystallizes in a tetragonal structure within the space group D_{4d}^{23} (see Figure 6).²³ The unit cell contains two formula units of Pd₄S with S atoms at all corners and in the center (0, 0, 0; 0.5, 0.5, 0.5), and the Pd atoms at (0.5 $\pm$ x, 0.5 $\mp$ y, -z), (0.5 $\pm$ y, 0.5 $\pm$ x, z), ($\pm$ x, $\pm$ y, z), and ($\mp$ y, $\pm$ x, -z). The experimental internal coordinates are $x_{\text{exp}} = 0.358$, $y_{\text{exp}} = 0.230$, and $z_{\text{exp}} = 0.155$, while the experimental lattice constants are $a_{\text{exp}} = 5.115\ \text{\AA}$ and $c_{\text{exp}} = 5.590\ \text{\AA}$.²³ Within our DFT approach, the calculated structural data are compiled in Table 1. These results were obtained by relaxation of the unit cell with respect to the lattice and internal parameters.

The experimental bulk structure is used as the starting point in the energy minimization procedures. The calculated lattice constants, $a = 5.199\ \text{\AA}$ and $c = 5.663\ \text{\AA}$, are within 2% of the experimental values. The slight overestimation of the lattice

Figure 4. X-ray diffraction patterns of the clean Pd foil (bottom) and the bulk Pd₄S surface layer formed after exposure to H₂S at 908 K. All diffraction peaks observed from the sulfided foil are attributable to Pd₄S. For clarity, the full diffraction patterns are not shown.

constants is in line with analogous DFT-GGA studies for other transition metals, metal oxides, and metal sulfides.^{24–27} The internal coordinates $x = 0.352$, $y_{\text{exp}} = 0.233$, and $z_{\text{exp}} = 0.157$ compare favorably with the experimental data. Each S atom is surrounded by eight Pd atoms. Each Pd atom is surrounded by two S atoms at distances of 2.37 and 2.51 $\text{\AA}$, and seven Pd atoms ranging from 2.81 to 2.87 $\text{\AA}$. These results are within $\sim 1\%$ of experimental values. The energy of formation of Pd₄S was also calculated within DFT; the computed value is -1.05 eV. Our result compares well with the experimentally measured enthalpy of formation, -1.03 ± 0.12 eV.²⁸

There are four low index surfaces for Pd₄S: the (001), (100), (110), and (111) surfaces. For the (001) face, there are three different surface terminations. In one termination, top-layer S atoms are more populous than in the bulk and they reside at an elevation slightly above nearest-neighbor Pd atoms. We refer to this arrangement as “S-terminated”, or Pd₄S(001)-S. The other two (001) faces are correspondingly “Pd-terminated”. For the Pd₄S(100) (equivalent to (010)) and Pd₄S(111) faces, there exist five different terminations, one S-terminated and four Pd-terminated. The Pd₄S(110) surface also has five different terminations: two are S-terminated, two are Pd-terminated and in one top-layer Pd and S atoms are approximately coplanar.

Plots of surface free energy as a function of sulfur chemical potential, μ_{S} , for the 18 considered terminations are shown in Figure 7. The $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$ partial pressure ratios corresponding to μ_{S} at temperatures in the range relevant to the separation application appear below the μ_{S} axis. At any given μ_{S} , the structure with the lowest surface free energy (i.e., the lowest lying line) is the most stable. Lines with a negative slope correspond to the surfaces with an excess of S atoms compared to the stoichiometric concentration. Thus, they will become more favorable under S-rich conditions. Comparing the plots for each face, the high relative stability of the S-termination is easily recognized. The (110) face with roughly coplanar termination exhibits comparatively low surface energy. All other considered terminations are higher in energy, especially those with Pd-terminations (shown as pale gray lines in Figure 7). The energetic preference for S-terminated variants of the low index faces is consistent with the LEIS and XPS characterization of the sulfided Pd foil, which identified a slight excess of sulfur at the sample's top-surface.

To verify our assumption that the vibrational component of surface free energy can be neglected, we estimated $\Delta\gamma^{\text{vib}}$ for selected Pd- and S-terminated surfaces at 908 K. Following ref 20, $\Delta\gamma^{\text{vib}}$ can be obtained from the difference between the bulk

Figure 5. LEIS spectrum of the sulfided palladium (Pd_4S) sample, acquired at 400 K after heating to 500 K. The spectrum is dominated by the Pd feature at 705 eV. Small features assigned to C, O, and S appear at lower energies (inset).

Figure 6. The bulk unit cell of Pd_4S . Dark spheres represent Pd atoms and white spheres represent S atoms.

TABLE 1: Calculated Lattice Constants, Internal Coordinates, and S–Pd and Pd–Pd Bond Lengths for the Tetragonal Structure of Pd_4S Compared to Experimental Values²³

	DFT	experiment
a_o (Å)	5.199	5.115
c_o (Å)	5.663	5.590
x	0.352	0.358
y	0.233	0.230
z	0.157	0.155
$r(\text{S–Pd})$ (Å)	2.37–2.51	2.34–2.48
$r(\text{Pd–Pd})$ (Å)	2.81–2.87	2.78–2.87

and surface vibrational modes plus vibrational contribution due to excess or deficient atoms. We observed that contributions of $\Delta\gamma^{\text{vib}}$ to total surface free energy were on the order of -10 eV/Å² for both Pd- and S-terminated surfaces. Thus, formal incorporation of the vibrational term would have neither changed the stability rank-order of surfaces shown in Figure 7 nor led us to modify our conclusions.

Significant relaxation effects are seen for the various Pd_4S surfaces investigated here. In particular, displacements of surface and subsurface layers were observed. This relaxation pattern leads to surface bond lengths that are generally different compared to those in the bulk (the theoretical value). We illustrate this point further in Figure 8 using the lowest energy $\text{Pd}_4\text{S}(110)\text{-S}$ structure as a typical example. The elevation difference between S and Pd atoms in the top surface (Δ_{12}) is

Figure 7. Calculated surface free energies of various Pd_4S surfaces as functions of the change in S chemical potential. Unfavorable Pd-terminated surface phases are indicated by pale gray lines. Corresponding $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$ axes at $T = 620, 720,$ and 905 K are included.

Figure 8. Schematic top and side views of the optimized geometry of the $\text{Pd}_4\text{S}(110)\text{-S}$ surface. White spheres represent the S atoms while the dark gray ones represent the Pd atoms. The surface S–Pd bond lengths, first (Δ_{12}) and second interlayer spacing (Δ_{23}), are labeled accordingly. Values in parentheses correspond to the bulk values.

smaller than that for the corresponding atoms in the bulk: 0.42 Å vs. 0.46 Å. Likewise, the displacement between top-layer and next-layer Pd atoms (Δ_{23}) is smaller at the surface than in the bulk: 0.46 Å vs. 1.08 Å. This relaxation pattern is also reflected in the S–Pd bond lengths at the surface. The long S–Pd bond present in the bulk is absent; the bond lengths between top-layer S nearest-neighbor Pd atoms do not show significant variation (2.30 – 2.37 Å). The corresponding bulk values range from 2.34 to 2.53 Å.

The energetics of H_2 dissociation on the Pd_4S faces were examined by using the NEB method. The mechanistic aspect of the dissociation process was characterized, with particular attention given to the thermochemistry and reaction barriers. This type of study is a valuable complement to our experimental efforts since it allows direct interrogation of atomic scale phenomena which cannot be observed with current experimental techniques. Given the high relative stability (low energy) of the S-terminated faces, supported by the results of LEIS and XPS characterization of surface composition, we focused on the $\text{Pd}_4\text{S}(001)\text{-S}$, $\text{Pd}_4\text{S}(100)\text{-S}$, and $\text{Pd}_4\text{S}(110)\text{-S}$ faces of Pd_4S .

Figure 9. Schematic top view of the initial (IS), transition (TS), and final (FS) states for the H₂ dissociation reaction on the Pd₄S(110)-S surface. The final state consists of H atoms chemisorbed on the S sites (pathway A). Small and large white spheres represent the H and S atoms, respectively, while the dark gray ones represent the Pd atoms.

We considered two reaction trajectories. The first (pathway A) starts with the gas-phase H₂ far from the surface and whose bond axis is parallel to the surface. It ends at a stable state of H atoms coadsorbed on a single surface S atom within the (3 × 3) surface supercell. We illustrate this trajectory for the lowest energy structure, Pd₄S(110)-S, in Figure 9, which shows the computed initial, transition, and final states for the dissociation process. The trajectory can be divided into three main steps: (i) The H–H bond is initially stretched as it approached the surface. (ii) The H–H bond is further stretched accompanied by enhanced interaction between the H and the surface atoms; the transition state is reached when the distance between the H fragments is 1.24 Å. (iii) After the transition state, the H fragments continue to separate to form two separate H atoms at the S site. The transition state is more product-like than reactant-like (i.e., late transition state). The H–H distance is elongated by 0.50 Å compared to the molecularly adsorbed H₂, which suggests that the molecule is practically broken.

We probed a second trajectory (pathway B) in which metal sites are involved in the dissociation process. This trajectory also starts with a gas-phase H₂ oriented parallel to the surface, but it ends with one or both of the dissociated H fragments adsorbed on top-surface Pd sites. This scenario is illustrated in Figure 10 for the same Pd₄S(110)-S structure. This pathway can also be divided into three steps: (i) The H₂ species first moves toward the surface with each H heading toward neighboring S and Pd surface atoms; as the molecule approaches the surface, the H–H bond is stretched. (ii) The H atoms then move further away from each other and the interaction between the H atoms and the surface becomes more significant. The transition state is also structurally more product-like and is characterized by H...H separation of 1.82 Å. (iii) After the transition state, the H fragments continue to come apart, eventually ending up in their preferred configuration.

To determine if the initial orientation of the hydrogen molecule influences the dissociation mechanism, the calculations were repeated for H₂ that is initially positioned normal to the surface. The general characteristics of the resulting trajectory are similar to those of the case where H₂ is initially oriented parallel to the surface. The transition state remains product-like and the calculated dissociation barrier is essentially the same. The only significant difference is that, at the outset, the

Figure 10. Schematic top view of the initial (IS), transition (TS), and final (FS) states for the H₂ dissociation reaction on the Pd₄S(110)-S surface, with a final state in which one of the H fragments is chemisorbed on a metal site (pathway B).

Figure 11. Relative energy diagram for H₂ dissociation on the S-terminated Pd₄S surfaces considered in this study. The states labeled (a), (b), and (c) correspond to gas phase, adsorbed, and dissociated H₂, respectively. Pathway B labeled 1 corresponds to a final state with one of the H fragments on the metal sites. Pathway B labeled 2 corresponds to a final state where both H fragments are on the metal sites. The dotted line shows the maximum activation barrier for a 100 cm³/cm²/min dissociation rate at 723 K.

molecule rotates to orient itself parallel to the surface as it approaches the substrate.

Computed energy profiles for H₂ dissociation on Pd₄S(001)-S, Pd₄S(100)-S, and Pd₄S(110)-S surfaces are shown in Figure 11. For reference, the energy profile for H₂ dissociation on the Pd(111) surface was also calculated. Dissociation is thermally activated on all Pd₄S surfaces, with the magnitude of reaction energies and activation barriers depending on plane and very strongly on reaction trajectory. Overall, the reaction energies and activation barriers are significantly lower for pathway B, suggesting that dissociation is more facile when surface Pd atoms participate. On the Pd(111) surface, the dissociation barrier is lower and the reaction energy is exothermic relative to both trajectories on the sulfur-terminated Pd₄S surfaces.

For the gasification application, the key issue is whether or not the Pd₄S surfaces have sufficient activity for hydrogen dissociation to sustain the separation process. Using DFT-predicted barriers as inputs, we applied basic transition state theory to estimate E_a at which the dissociation rate could fall below 100 cm³/cm²/min, the 2010 flux target for membrane-based hydrogen separation technologies established by DOE for its hydrogen from coal research program.²⁹ We used the dissociation rate equation

$$\text{rate} = (kT/h)\theta_{\text{H}_2} \exp(-E_a/kT) \quad (5)$$

Assuming hydrogen surface coverage, $\theta_{\text{H}_2} = 7.6 \times 10^{14} \text{ H}_2/\text{cm}^2$ ($\text{H}/\text{Pd} = 1$), the E_a that corresponds to $100 \text{ cm}^3/\text{cm}^2/\text{min}$ at 723 K (a typical temperature for the separation process) is approximately 1.2 eV. Higher E_a results in dissociation rates that fall below the $100 \text{ cm}^3/\text{cm}^2/\text{min}$ requirement. As shown in Figure 11, reaction trajectories in which surface Pd atoms participate in the dissociation process (pathway B) have E_a below 1.2 eV and would thus dissociate H_2 at rates in excess of the DOE target.

IV. Conclusions

Using a combination of experimental characterization and detailed DFT calculations, the composition, structure, and chemical activity of the Pd_4S layer that forms on Pd membranes upon exposure to H_2S were investigated. Experimental characterization of a Pd_4S sample reveals a top-surface which is slightly enriched in sulfur relative to the bulk. This view is supported by the results of DFT calculations, which predict that S-terminated low-index surfaces are more stable than their Pd-terminated counterparts. Theoretical investigations of H_2 dissociation on the S-terminated faces of Pd_4S were also carried out. Although the predicted dissociation barriers are higher on the S-terminated Pd_4S surfaces than on clean Pd surfaces, transition state theory dissociation rate analysis suggests that dissociation rates on Pd_4S are sufficiently fast to sustain the separation process at conditions relevant to gasification applications.

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