Support of Advanced Coal Research at U.S. Colleges and Universities: IC Phase I Program: Computational Efforts in Support of Advanced Coal Research (DE-PS26-05NT42244-09)

Final Scientific/Technical Report

Pd-based metallic membranes for hydrogen separation: First principles studies of separation mechanisms aimed at knowledge-based rational formulations of improved materials.

DATE: November/2006

Suljo Linic

Assistant Professor

Department of Chemical Engineering

University of Michigan

48109, Ann Arbor, MI

Phone: 734-647-7984

Email: linic@umich.edu

Date:08/15/2005 – 08/17/2006

<u>Disclaimer</u>

Abstract

The focus in this project was to employ first principles computational methods to study the underlying molecular elementary processes that govern hydrogen diffusion through Pd membranes as well as the elementary processes that govern the CO- and S-poisoning of these membranes.

Our computational methodology integrated a multiscale hierarchical modeling approach, wherein a molecular understanding of the interactions between various species is gained from ab-initio quantum chemical Density Functional Theory (DFT) calculations, while a mesoscopic statistical mechanical model like Kinetic Monte Carlo is employed to predict the key macroscopic membrane properties such as permeability. The key developments are:

1. We have coupled systematically the ab initio calculations with Kinetic Monte Carlo (KMC) simulations to model hydrogen diffusion through the Pd based-membranes. The predicted tracer diffusivity of hydrogen atoms through the bulk of Pd lattice from KMC simulations are in excellent agreement with experiments.

2. The KMC simulations of dissociative adsorption of H_2 over Pd(111) surface indicates that for thin membranes (less than 10μ thick), the diffusion of hydrogen from surface to the first subsurface layer is rate limiting.

3. Sulfur poisons the Pd surface by altering the electronic structure of the Pd atoms in the vicinity of the S atom. The KMC simulations indicate that increasing sulfur coverage drastically reduces the hydrogen coverage on the Pd surface and hence the driving force for diffusion through the membrane.

Executive Summary

Computational chemistry and physics have a potential to impact significantly the field of hydrogen production from coal. Our long term goal is to employ quantum chemical computational concepts to develop molecular level insights into various processes that are related to hydrogen economy. The ultimate objective is to use these molecular level insights to develop a knowledge-base in support of the bottom-up rational formulations (as opposed to traditional Edisonian trial and error approaches) of new materials with superior hydrogen storage capacity, with high hydrogen separation rates, and the materials that are resistant to syngas impurities during hydrogen conversion reactions, and so on.

An important problem that is at the forefront of our efforts is hydrogen separation. In order to separate hydrogen from various impurities, such as carbon monoxide, sulfur, and various trace elements that are produced during coal gasification, different methods have been proposed. A very appealing concept is to use Pd-based metal membranes which have been shown to be selectively permeable for hydrogen molecules. These membranes are also being investigating for combined membrane/reactor systems. Even thought, the Pd-based membranes represent a promising class of materials the molecular level understanding of hydrogen interactions with these membranes is lacking. Furthermore, there are functioning problems that need to be addressed before these membranes become viable. Some of these problems are associated with damaging effects of various contaminants (sulfur and CO), membrane embrittlement, and Pd-material oxidation.

The focus in this project was to employ first principles computational methods to study the underlying molecular elementary processes that govern hydrogen diffusion through Pd membranes as well as the elementary processes that govern the CO- and S-poisoning of these membranes. We believe that the fundamental insights regarding the underlying chemical processes that govern hydrogen separation will provide a knowledge-base that will be instrumental in designing CO- and S-tolerant Pd-based alloy membranes.

Our computational methodology employs a multiscale hierarchical modeling approach, wherein a molecular understanding of the interactions between various species is gained from ab-initio quantum chemical Density Functional Theory (DFT)

calculations, while a mesoscopic statistical mechanical model like Kinetic Monte Carlo is employed to predict the key macroscopic membrane properties such as permeability. The key developments in this direction are as under:

1. We have coupled systematically the ab initio calculations with Kinetic Monte Carlo (KMC) simulations to model hydrogen diffusion through the Pd based-membranes. The predicted tracer diffusivity of hydrogen atoms through the bulk of Pd lattice from KMC simulations are in excellent agreement with experiments.

2. The KMC simulations of dissociative adsorption of H_2 over Pd(111) surface indicates that for thin membranes (less than 10μ thick), the diffusion of hydrogen from surface to the first subsurface layer is rate limiting.

3. Sulsur poisons the Pd surface by altering the electronic structure of the Pd atoms in the vicinity of the S atom. The KMC simulations indicate that increasing sulfur coverage drastically reduces the hydrogen coverage on the Pd surface and hence the driving force for diffusion through the membrane.

Experimental Approach

We have employed quantum chemical density functional theory (DFT) calculations, and state-of-the-art thermodynamic and kinetic simulations to investigate molecular level mechanisms of hydrogen separations over Pd and Pd-based alloy membranes. DFT is a methodology that is employed to efficiently solve quantum Schrodinger equation with high accuracy. DFT has become, within the last ten years, the quantum computational tool of choice in solid-state physics and surface chemistry. These tools have already had a significant impact on the discovery of novel ammonia synthesis and ethylene epoxidation catalysts. The DFT calculations are employed to obtain, from first principle and with high accuracy, the ground state geometries and energies of relevant reactants, products, and transition states involved in important elementary reactions on catalyst surfaces. In this project DFT is utilized to investigate on an atomic level the interactions of hydrogen atoms and Pd substrate.

Pd-based membranes operate by dissociative adsorption of molecular hydrogen on membrane surfaces. The dissociated atomic hydrogen diffuses through the membranes and is recombined into molecular hydrogen which desorbs on the other side of the membranes; see Figure 1(b).

Rationale for the proposed work stems from the fact that DFT can be used to accurately analyze various chemical pathways and transformations of molecules in solids, which cannot be easily accomplished by other means [3]. Also, DFT calculations when coupled with kinetic and thermodynamic simulations have significant predictive powers for formulations of novel and improved solid-state materials, see [1, 4-6].
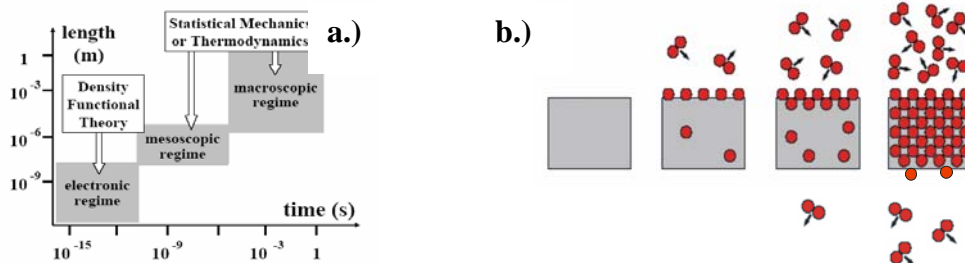

Figure 1: a.) Methodology schematic. b.) Schematics of hydrogen/Pd membrane interactions at various pressures of hydrogen.

In Figure 1(a) we show a schematic of our methodology. Elementary molecular processes that govern the behavior of a system take place in the so-called "electronic regime". These processes can be analyzed efficiently with first principles DFT calculations [1,3-6]. The complex interplay of these elementary molecular processes determines functionalities of the system [3, 4]. This interplay develops at mesoscopic and macroscopic length scales which can be analyzed by statistical mechanics and thermodynamics. In our approach we will use thermodynamic, and Kinetic Monte Carlo (KMC) simulations to connect the molecular level mechanisms, developed in the DFT calculations, to observable functionalities of investigated membrane systems [1,4-6]. For example, an important macroscopic observable is a relationship between a rate of hydrogen transport, external conditions and membrane make-up. We believe that this approach will be helpful not only for developing mechanistic insights about membrane operations but also in formulating on atomic level novel mechanisms and materials with improved performances [1].

In following sections we outline the results of our investigations

Results and Discussion

DFT and KMC studies of H2 diffusion through Pd membrane

DFT studies of elementary steps: adsorption, dissociation, and diffusion of hydrogen on Pd(111)

As mentioned in our previous reports we had performed DFT calculations of the elementary steps associated with H_2 adsorption, dissociation and diffusion on Pd(111) surface. The DFT calculations were performed using a plane wave basis set and Vanderbilt ultrasoft pseudo-potentials to describe the core-electron interactions. We utilized a 2x2x4 unit cell.
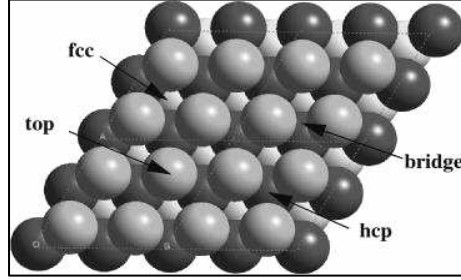

Figure 2. Surface adsorption sites on Pd(111)

Electron exchange correlation effects were described with the generalized gradient approximation (GGA) with Perdew–Wang 91 functional. A plane wave basis set with an energy cut-off of 350 eV (26 Rydberg) and Monkhorst–Pack mesh with a 3x3x1 k-point grid were utilized for all the calculations.

The dissociative adsorption of hydrogen is described by:

½ H2 + * = H*   (1)

where * indicates a Pd(111) adsorption site.

We evaluated the binding energies of H atoms on all 4 different adsorption sites: top, bridge, fcc and hcp. These adsorption sites are shown in Figure 2.

The adsorption energy of hydrogen is calculated by:

 E(H) = E(H+slab) - ½ E(H2) – E(slab)   (2)

where E(H2) is the energy of molecular hydrogen while E(H+slab) and E(slab) are the respective energies of H atom absorb on slab and the Pd(111) slab(substrate). The three terms appearing the right hand side were evaluated using DFT calculations.

The adsorption energies of various species are tabulated in Table 1.

Species	On-top	Bridge	FCC	HCP
H	-0.05	-0.52	-0.70	-0.64
S	-5.23	-5.25	-5.25	-5.25
CO*	-1.58	-2.05	-2.24	-2.23

Table 1: Adsorption energies (eV)of various species on four different sites on Pd(111) at 0.25 ML coverage.

* CO is adsorbed with C atom bound to the metal.

Table 1 shows that H atoms preferentially adsorbs on the three-fold hollow sites (hcp and fcc) of Pd(111). We also calculated the activation energy for H_2 dissociation on Pd(111) and we found that the dissociation occurs with a very small activation barrier of 0.06 eV (6 kJ/mol). This activation barrier is consistent with the experimental sticking coefficient measurements .

Figure 3: (a) octahedral and (b) tetrahedral sites for H adsorption in Pd lattice. Pd

Furthermore, we had examined the adsorption energy of H atoms adsorbed between the top and the second layer of Pd atoms. Here, H atom can adsorb in octahedral and tetrahedral sites as shown in Figure 3. We find that H atom adsorption energy is -0.35 eV (~ 35 kJ/mol) for octahedral and -0.22 eV for tetrahedral sites with respect to gas-phase H2. We have also calculated that the activation barrier for the diffusion from on surface fcc or hcp sites to the sites
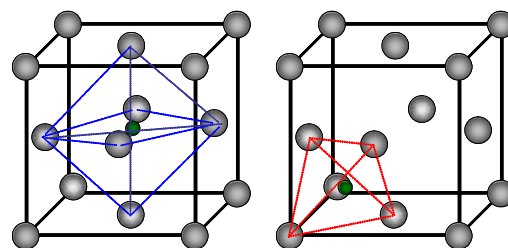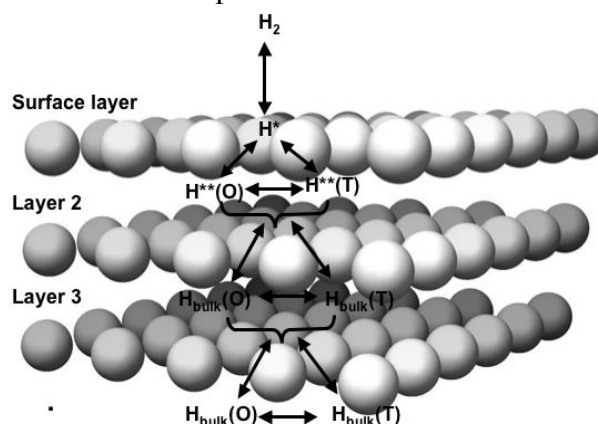

Figure 4: We depict the relevant elementary steps. The kinetic parameters for these elementary steps are tabulated in Table 2.

between the top and the second layer of Pd atoms are ~0.35 eV. We have also studied H atom adsorption in the interstitial bulk sites of Pd and calculated that H adsorption energy is -0.14 eV (~ -14 kJ/mol) for octahedral and -0.08 eV for tetrahedral bulk sites. The activation barrier for H atom diffusion from octahedral to tetrahedral bulk site is 0.11 eV and it is 0.17 eV for the diffusion from tetrahedral to octahedral sites.

DFT was further utilized to calculate the pre-exponential factors for the elementary reactions discussed above, i.e., for H_2 adsorption and dissociation and for H atom diffusion between different sites of a Pd membrane. The pre-exponential factors were calculated according to the transition state theory from the partition functions of the

relevant reactant and transition state. The partition functions were obtained in DFT calculations from the vibrational spectra of the reactants and transition states.

The thermodynamic and kinetic information for the above outlined elementary steps is summarized in Table 2. Figure 4 shows the relevant elementary steps.

Elementary step	$E_{activation}$ eV/atom	ΔH eV/atom	A /site/sec
1/2H2+∗→H∗	0.06	-0.70	10^8 (a)
H∗→1/2H2+∗	0.76	0.70	10^{11}
H∗+∗∗→H∗∗(O)+∗	0.48	0.48	10^{11}
H∗+∗∗→H∗∗(O)+∗	0.35	0.35	10^{11}
H∗∗(O)→Hbulk(O)+∗∗	0.21	0.21	10^{11}
H∗∗(O)→Hbulk(T)+∗∗	0.27	0.27	10^{11}
Hbulk(O) → Hbulk(T)	0.17	0.06	10^{11}
Hbulk(T) → Hbulk(O)	0.11	-0.06	10^{13}

Table 2: DFT calculated kinetic activation barrier, heat of reaction, and pre-exponential factors for the elementary steps associated with hydrogen diffusion through Pd membranes. (a) Units for pre-exponential factor for hydrogen adsorption from gas-phase are /site/sec/atm

Kinetic Monte Carlo (KMC) simulations

KMC utilizes the elementary step kinetic information, obtain via DFT and tabulated in Table 2, and relates it to the system macroscopic properties. A crucial macroscopic property of a membrane is the diffusivity. Below, we demonstrated that the approach combining DFT calculations and KMC yields calculated tracer diffusivities that agree very well with the experimentally measured ones. We note that this is not surprising since this system can be adequately described with these tools.

Diffusion of hydrogen through Pd membranes is an activated random-walk process that contains a series of migrations of hydrogen atoms from octahedral to near-neighbor tetrahedral interstitial sites and vice versa in a Pd fcc crystal. To initialize the KMC simulations, hydrogen atoms are randomly placed at interstitial sites in an fcc lattice of

Pd and equilibrated by performing a certain number of KMC moves described below. Each move consists of the following steps [7].

1. Identify all possible events from the current configuration.

In fcc lattice, there are 8 possible directions along which a H atom can hop from an octahedral to a neighboring tetrahedral site. Similarly, for H atom located at a tetrahedral site, there are 4 neighboring octahedral sites (See Figure 3).

2. Obtain the rates for each of these events.

The rate of hopping from any site P (tetrahedral or octahedral type) to a neighboring site Q (octahedral or tetrahedral) can be written in accordance with classical transition state theory in form of Arrheneius law expression as:

$$r_{P \to Q} = Ae^{(-E_m/kT)}$$

where E_m is the activation barrier, k is the Boltzmann constant, T is the temperature of the system and A is the pre-exponential factor which can be obtained from statistical mechanical formulation of rate expressions based on quantum mechanical modification of classical harmonic oscillator formalism [8,9]:

$$A = \left(\frac{\prod_{i=1}^{3} \omega_{P,i} \sinh(\beta h \omega_{P,i}/2)/(\beta h \omega_{P,i}/2)}{\prod_{i=1}^{2} \omega_{TS,i} \sinh(\beta h \omega_{TS,i}/2)/(\beta h \omega_{TS,i}/2)} \right)$$

where h is Planck's constant, ω is vibrational frequency of the characteristic vibrational modes (in state P or transition state "TS" as denoted by the subscript), , β is $1/kT$. Note that there is one less degree of freedom at the transition state resulting in reduction of number of vibrational modes by 1.

To evaluate the rates of hopping, the migration activation barriers (E_m) from octahedral to tetrahedral site and vise versa as well as the vibrational modes for H atom at different binding sites (needed for the computation of A) in an fcc Pd crystal were evaluated using DFT calculations (Table 2)

3. Generate a pseudorandom number gbetween 0 and 1.

Choose one of the events depending on the random number, consistent with the relative probability of all the events. An event j is chosen if

$$\gamma < \frac{\sum\limits_{i=1}^{j} r_i}{\sum\limits_{i=1}^{M_{events}} r_i}$$

where r_i is the rate of each possible hop, M_{events} is the total number of different possible hops for the hydrogen atom. Regardless of the outcome, the time is incremented by

$$\Delta t = \frac{-\ln(\gamma)}{\sum\limits_{i=1}^{M_{events}} r_i}$$

for each step.

4. Reconfigure the system according to the chosen event.

5. Update and record the new position of the hydrogen atom and time and repeat 1-4 for a sufficient number of time steps.

The tracer diffusivity of hydrogen atom is then evaluated from Einstein expression:

$$D = \lim_{t \to \infty} \left[\frac{1}{6 n_H t} \sum_{m=1}^{n_H} \left\langle \left\| \mathbf{R}(t) - \mathbf{R}(0) \right\|^2 \right\rangle_m \right]$$

Kinetic Monte Carlo (KMC) simulations: H_2 diffusion through clean Pd membrane

In Figure 5 we show the tracer diffusivity for H diffusion through Pd membrane as a function of inverse temperature, calculated in our KMC simulations. The calculated diffusion coefficients follow an Arrhenius law expression and the best fit is given as:

The calculated values are

$$D = 6.604 \times 10^{-7} e^{(-0.23 eV / kT)} m^2 / s$$

compared to the experimentally measured tracer diffusivities [10]. The agreement between experimental measurements and theoretical predictions is exceptional, corroborating the robustness of the proposed approach.

We note that when calculating the diffusivity we examine H atom diffusion through Pd bulk, i.e., the complexities due to the presence of Pd surface were not

included. To include the surface effects we have performed KMC studies of the complete process including H_2 adsorption and dissociation on Pd(111) surface, and H atom diffusion through Pd membrane (slab). In these studies we utilize the elementary step parameters obtained in DFT calculations (Table 2). The aim of these studies was to identify the slow elementary steps, i.e., the elementary steps that limit hydrogen flux.

The KMC studies demonstrated that H atom diffusion from on-surface Pd adsorption sites to the layer between the top and the second layer of Pd atoms, this is labeled layer 2 in Figure 4, is the rate-limiting step over a wide range of conditions and for the membrane thickness of up to ~ 10 μ m (this is a typical thickness of a Pd membrane).

Figure 5: KMC studies are utilized to obtain diffusivity for hydrogen diffusion through Pd membrane as a function of inverse temperature. Calculated diffusivities agree very well with the measured ones.

For thicker membranes the bulk diffusion becomes the rate-limiting step. These insights are very important since one can utilize this information to explore various ways to enhance the rate of the kinetically slow step and improve the performance. For example, if one assumes that the above described step, H atom diffusion from the top to the first inner membrane layer, is the rate-limiting, then higher fluxes can be obtained by synthesizing a membrane that will have higher rates associated with this step.
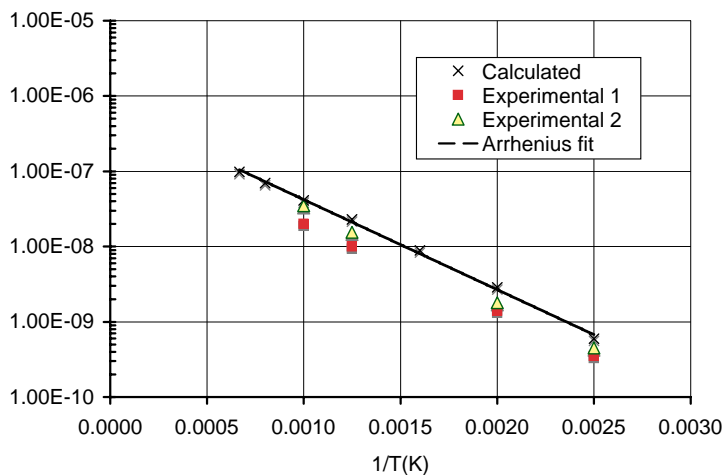
Effect of Sulfur on H₂ adsorption and diffusion

Extensive DFT calculations of H_2 dissociation over Pd(111) surface in the presence of

Sulfur were performed. A 3x3x4 layer Pd(111) slab was used for these calculations. It was seen that the dissociative adsorption of H_2 becomes highly activated in the presence of Sulfur. Dissociation activation energies varying from 0.8 eV/H atom at sites in proximity to S atom (less than 1.5 Å) on Pd (111) surface, to 0.1 eV/H atom at sites further away from S atom (~ 4.0 Å away), were seen. An analysis of the local density of states projected on the d-orbitals of the surface Pd atom in presence and absence of S atom is shown in Figure 6. It is seen
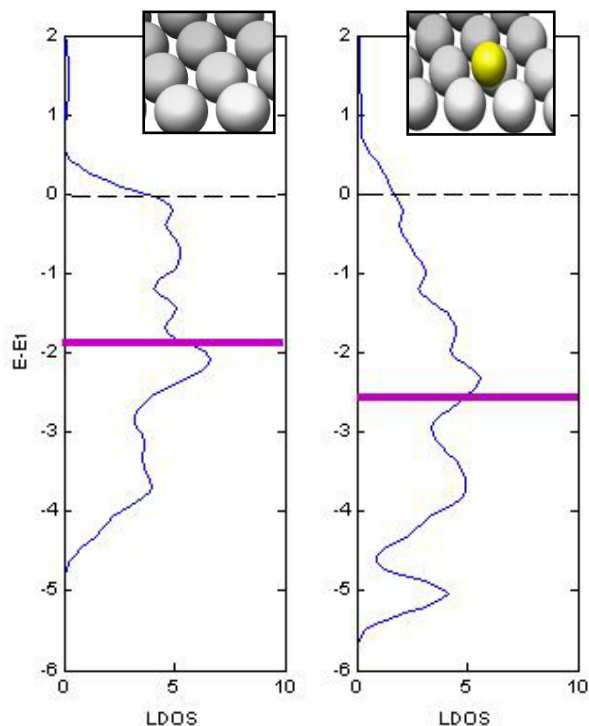

Figure 6: LDOS of d-orbitals of Pd atom on clean Pd surface and in proximity to S atom on a S poisoned surface. The solid line shows the d-band center.

that in the presence of S atom, the d-band center of the Pd atom is lowered by about 0.8 eV as compared to a Pd atom free from the effect of S. This lowering of the d-band center adversely affects the reactivity of the Pd surface by inhibiting the interactions d-band electrons with electrons in H_2 binding states. This indicates that the strong binding S atom not only has a geometric site blocking effect (corresponding to large diameter of S atom ~2 Å) but also affects the electronic structure of the surface Pd atoms and induces long range energy barriers along the dissociation pathways of H_2 over Pd(111).

In order to study the effect of S on hydrogen diffusion through Pd membranes, we performed KMC simulations of H adsorption, desorption and diffusion through the Pd surface. We assume a S-precovered Pd surface with S-atoms placed randomly over the

Pd(111) surface. Please note that such surface non-homogeneities are best modeled with KMC simulations and cannot be captured effectively with meanfield rate expressions averaged over the entire surface. As before all the rate parameters (activation energies and pre-exponential factors were obtained from DFT calculations. The

Figure 8: Effect of sulfur on the coverage of H-atom on Pd(111) surface

variation in activation energies of H_2 dissociation was modeled by a proximity to S-atom dependent activation energy. Figure 7 shows the flux of H atom through the surface (first atomic layer) at different sulfur coverages. It is seen that as the flux through the surface decreases nonlinearly with increasing sulfur coverages. At low coverages (< 0.004 ML) there is almost no change in the flux through the surface. As the coverage of S increases (> 0.04 ML) a drastic reduction (almost 2 orders of magnitude) in H_2 flux is predicted. Furthermore in Figure 8 we have plotted the coverage of H atom on the Pd(111) surface as a function of
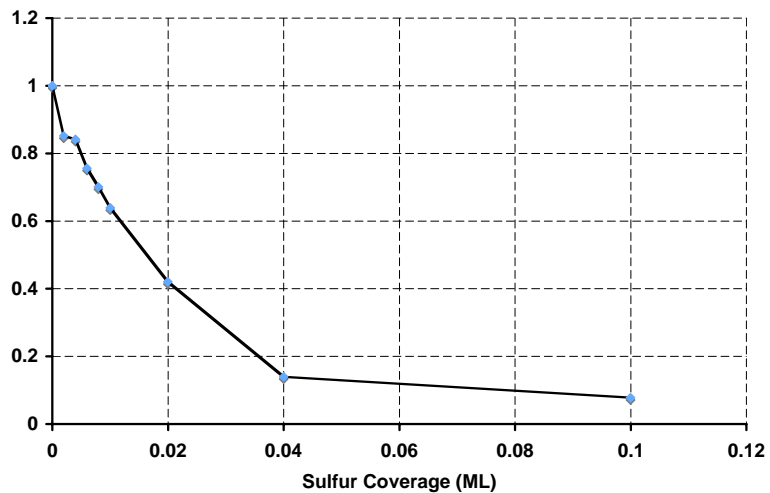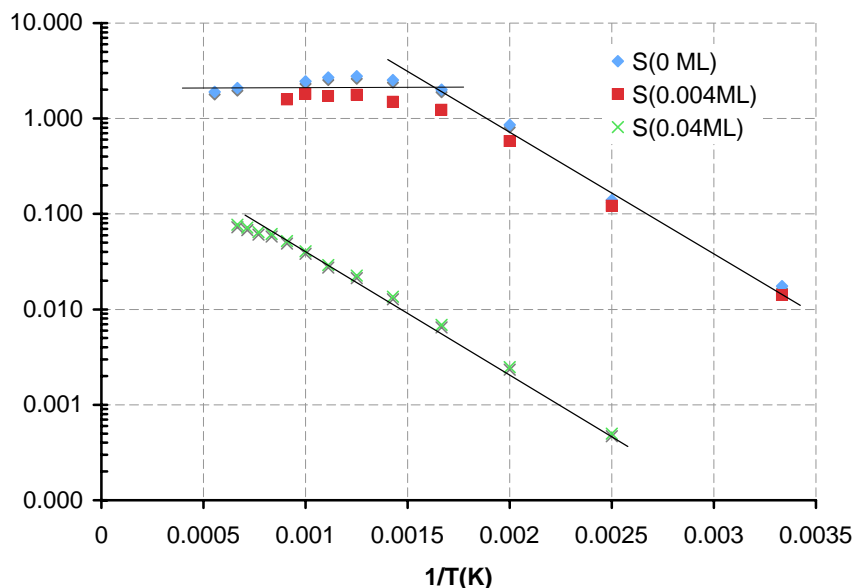

Figure 7: Effect of S coverage on H_2 flux through the surface

15

the S coverage. As seen in the figure, an increase in S coverages significantly reduces the coverage of H atom in an almost exponential fashion thus corroborating the fact that S poisoning is not only a geometric site blocking effect but also a manifestation of the long range energy barriers induced due to changes in electronic structure of the surface Pd atoms.

We believe that this work represent a critical platform for systematic and rational, as opposed to traditional trial and error approach, development of novel, more robust high-density membranes for hydrogen separation.. To illustrate how one can utilize the information obtained in first principles studies to identify novel membrane materials we present two possible strategies. For example, our studies, presented above, showed that sulfur adsorbates decrease the hydrogen flux due to the sulfur-induced increase in the activation barrier the H_2 dissociation. We have also demonstrated that the main problem with sulfur is that it negatively influences not only the Pd sites that are directly bonded to sulfur but also those Pd sites which are removed from the sulfur adsorption sites. Due to this long-range negative effect even a small sulfur surface concentration results in the dramatically reduced membrane performance, see Figure 8. One possible strategy to alleviate this problem is to selectively poison a Pd membrane with the elements which compete with sulfur for the Pd adsorption sites, but which are less damaging than sulfur, i.e., the effect of these elements on Pd should be more localized as compared to sulfur. Fist principles calculations will be useful in identifying the promising candidates. We have recently utilized similar first principles approaches in the formulations of carbon-tolerant reforming alloy catalysts. The results of the first principle studies were confirmed in multiple experiments.[11]

<u>Conclusions</u>

1. We have performed ab initio and KMC simulations to model hydrogen diffusion through the Pd based-membranes. All the rate parameters necessary for the KMC simulations have been evaluated from first principles DFT calculations.
2. The predictions pertaining to tracer diffusivity of hydrogen atoms through the bulk of Pd lattice from KMC simulations are in excellent agreement with experimental data from literature.

3. The KMC simulations of dissociative adsorption of H_2 over Pd(111) surface indicates that for thin membranes (less than 10μ thick), the diffusion of hydrogen from surface to the first subsurface layer is rate limiting. For thicker membranes the diffusion through the bulk Pd membrane is the dominant resistance. Hence, the key to enhance the hydrogen flux through Pd-based alloy/surface alloy membranes is designing thin membranes with lower energy barriers for H diffusion from surface to first layer below surface. We are currently investigating H_2 diffusion through Pd-alloys membranes.

4. The effect of sulfur on the adsorption of hydrogen was studied by performing detailed DFT calculations of co adsorption of hydrogen in presence of sulfur and coupling the insights from DFT calculations with KMC simulations of H_2 diffusion over S pre-covered Pd surface. S binds strongly on the Pd surface and poisons the Pd surface by altering the electronic structure of the Pd atoms in the vicinity of the S atom. The KMC simulations indicate that increasing sulfur coverage drastically reduces the hydrogen coverage on the Pd surface and hence the driving force for diffusion through the membrane.

We believe that this work represent a critical platform for systematic and rational, as opposed to traditional trial and error approach, development of novel, more robust high-density membranes for hydrogen separation. In these studies we have identified critical molecular steps that govern H transport through the membranes as well as a few underlying mechanisms that contribute to the poisoning of the Pd-based membranes.

Natural extension to this work would be to start designing strategies for the rational improvement of current state-of-the art membranes. The tools that allow us to analyze molecular physics and chemistry, that were utilized in this project, will almost certainly play an important role in the formulations of improved membrane materials.

Summary of Significant Accomplishments
1. We have coupled systematically ab initio calculations with Kinetic Monte Carlo simulations to model hydrogen diffusion through the Pd based-membranes. The predictions pertaining to tracer diffusivity of hydrogen atoms through the bulk of Pd lattice from KMC simulations are in excellent agreement with experimental data from literature.

2. The KMC simulations of dissociative adsorption of H_2 over Pd(111) surface indicates that for thin membranes (less than 10μ thick), the diffusion of hydrogen from surface to the first subsurface layer is rate limiting.

3. S binds strongly on the Pd surface and poisons the Pd surface by altering the electronic structure of the Pd atoms in the vicinity of the S atom. The KMC simulations indicate that increasing sulfur coverage drastically reduces the hydrogen coverage on the Pd surface and hence the driving force for diffusion through the membrane.

References

1. S. Linic, J. Jankowiak, M.A. Barteau, "Selectivity driven design of bimetallic ethylene epoxidation catalysts from first principles", Journal of Catalysis (Priority Communication), 2004, 224, 489.

2. US DOE, "Hydrogen form coal program: research, development and demonstration plan 2004-2015", June 2004.

3. Charlie Campbell, "Towards tomorrow's catalysis", Nature, 2004, 432, 282 – 283.

4. S. Linic, M. A. Barteau, "Construction of a Reaction Coordinate and a Microkinetic Model for Ethylene Epoxidation on Silver from DFT Calculations and Surface Science Experiments", Journal of Catalysis, 2003, 214, 200.

5. S. Linic, M.A. Barteau, "On the Mechanism of Cs promotion in Ethylene Epoxidation on Ag", Journal of the American Chemical Society, 2004, 126, 8086

6. Suljo Linic, Hong Piao, Kaveh Adib, Mark A. Barteau, "Ethylene Epoxidation on Ag: Identification of the Crucial Surface Intermediate by Experimental and Theoretical Investigation of its Electronic Structure", Angewandte Chemie International Edition, 2004, 43, 2918.

7. A. B. Bortz and M. H. Kalos and J. L. Lebowitz, A new algorithm for Monte Carlo simulations of Ising spin systems Journal of Computational Physics 1975, 17, 10

8. D.A. McQuarrie,"Statistical Mechanics", Chapters 9 and 11, University Science Books, Sausalito, CA, 2000.

9. L. Katz, M.Guinan, R.J.Borg, "Diffusion of H_2, D_2 and T_2, in Single Crystal Ni and Cu", Physical Review B, 1971, 4(2), 330

10. J.Volkl, G. Alefeld, "Diffusion of hydrogen in metals", Hydrogen in Metals 1, Topics in Applied Physics, 28, Springer-Verlag, 321

11. E.Nikolla, A. Holewinski, J. Schwank, S. Linic; "Controlling Carbon Surface Chemistry by Alloying: Carbon Tolerant Reforming Catalyst", Journal of the American Chemical Society, **2006**; *128*(35); 11354-11355.