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Modeling H_2 transport through a Pd or Pd/Ag membrane, and its inhibition by co-adsorbates, from first principles

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ABSTRACT

We calculate the rate of hydrogen transfer through a Pd and a Pd/Ag selective membrane using transition state theory with adsorption and activation energies calculated by DFT and nudge elastic band methods. The flux through the membrane bulk was evaluated using Fick's law with the diffusivity constant calculated from energetic barriers in the diffusing H path while accounting for adsorption and subsurface penetration. A reasonable prediction of expected permeance of a Pd membrane was achieved; the prediction of an ordered Pd_3Ag membrane was much lower than expected due to larger energetic barrier, but estimation of diffusivity in a random Pd/Ag membrane, accounting for the probability of encountering the various sites, led to permeance higher than that of Pd. Predicted energies compare well with literature data.

The inhibition due to surface adsorption of possible co-adsorbates like propylene, propane, methane, CO and water was also accounted for using DFT-calculated adsorption energies. The inhibitions of propylene and CO are expected to be significant in the corresponding membrane reactors (e.g., for propane dehydrogenation or for methane steam reforming).

1. Introduction

Pd and Pd alloy membranes have been employed in laboratory membrane reactors for the past 3 decades and are now on the verge of commercial applications. It is important, therefore, to derive a membrane transport rate expression or a microkinetic model. This entails two main tasks: an expression for hydrogen transport and an expression for the effects of co-adsorbates. The purpose of this work is to use first principles to develop a rate expression for hydrogen transport through a selective palladium or palladium silver membrane. This may be used in the future to characterize or even optimize the membrane. While these expressions are usually derived experimentally, typically the membrane permeance is measured in a system composed of hydrogen in inerts, and there were very few studies on transport inhibition due to competitive adsorption of reactants and products in a membrane reactor. First-principle calculations may be used for a fast estimate of the components that should be studied experimentally. Also, the estimate of the transport rate without inhibition should be used to ascertain that the limiting step in current commercial membranes (thicker than 5 μm) is H diffusion within the membrane. A successful application of this approach can be extended to study permeance through new membranes, i.e., to improve the efficiency and cost of hydrogen separation and recovery. Current commercial hydrogen separation membranes are limited to Pd/M (e.g., M=Ag, Cu, Ru) alloys. The popular 75Pd/25Ag membrane is studied here as well.

Possible applications of membrane in our group include processes for propane dehydrogenation (PDH) [1] and methane steam reforming [2–5] (MSR). Thus, the permeance rate expression of interest should account for the inhibition due to the surface adsorption of propane, propylene, methane, CO and water.

Several studies developed a detailed micro-kinetic model of hydrogen transport through a Pd membrane [6] using parameters that were previously estimated experimentally. The following steps were considered: (i) mass transfer to the surface or away from it, which depends on molecular diffusivity and chamber size, and diffusion through the porous support, which depends on its thickness; (ii) one-step dissociative adsorption and associative desorption; (iii) one-step subsurface penetration (i.e., surface to bulk transition or dissolution) of H and its reversal, and (iv) diffusion through the bulk Pd or Pd–Ag. Using parameters from the literature, it was concluded that with relatively thick Pd membranes ($d > 5$ μm), the important step is atomic hydrogen hopping through the Pd or Pd–Ag lattice, while with thinner membranes and lower temperatures the hydrogen dissociative

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adsorption and desorption rates are important. Mass transfer effects may become significant with thin membranes, especially in laminar flow (i.e., in permeance measurements, usually conducted in un-packed tubes). We focus therefore, on steps (ii) through (iv). The data tabulated in [6], which were calibrated using published experimental and thermodynamic data, are outlined in Section 3 when they are compared with the present predictions.

The first step of our analysis is the estimation of reaction and activation energies associated with the adsorption and diffusion of hydrogen. Several studies have used the density functional theory (DFT) to estimate the H diffusivity, and some have used the Monte Carlo simulations to estimate the effective diffusivity. Ozawa et al., [7,8] investigated the energies characterizing the process in Pd (111) and Pd/Ag(111) surface and subsurface from first principles. They have mapped the potential energy surface for the hydrogen atom motion along the Pd/Ag surface and found that the fcc1 hollow site is the preferred site on the surface and that the octahedral (O) site under the fcc2 hollow is preferred in the subsurface (see solid description below). These results are in agreement with Løvvik et al. [9] who also concluded that the most stable H adsorption position on Pd_3Ag alloy is the fcc hollow site with as many Pd neighbors as possible. Ozawa et al., [7,8] concluded that the effective diffusion path of the hydrogen atom into the Pd_3Ag subsurface starts from the fcc1 hollow site and passes through the O site under the fcc1 hollow. The energy barrier for this path was calculated to be 0.34 eV compared with diffusion energy barrier of 0.57 eV on Pd(111). They have not translated their results to permeances, as we do below.

Sholl et al., [10] have used a combination of DFT calculations and the cluster expansion method to describe interstitial H in alloys of composition Pd96M4 (i.e., a 27 atom supercell with one M atom) where M=Ag, Cu, and Rh, and a kinetic Monte Carlo scheme to find the diffusivity of H in the Pd alloys. They were able to predict the permeability of hydrogen through the membrane. A key challenge in using DFT calculations to describe interstitial H in alloys is that it has numerous structurally distinct binding sites. This was approached by performing DFT calculations for H in a collection of distinct interstitial sites, then fitting the observed results for binding energies and transition state energies to a simple lattice model in terms of parameters that describe the local environment of each site. Once a lattice model is defined, the net solubility, diffusivity, and permeability of H through the bulk alloy can be calculated using a combination of statistical mechanical calculations and kinetic Monte Carlo simulations. [10] DFT calculations showed that when one of the four atoms defining the tetrahedral (T) sites was an Ag atom, the T site was not a local minimum. Site-to-site hopping through these sites from one O site to another O site occurs with H passing through these types of T sites while passing over only one transition state [10].

Sonwane et al. [11] combined DFT and kinetic Monte Carlo simulation in order to investigate the diffusivity and permeability of hydrogen in palladium silver and palladium gold alloys. They have found that the diffusion coefficient of hydrogen decreases with the increasing Ag content, beyond an optimal composition. They have also reported that H permeability in the optimal alloy composition (~20% Ag) was three to four times higher than that of pure Pd, as may be expected from experimental results.

In the present work we use DFT and NEB to calculate the energetics of adsorption, subsurface penetration and diffusion of H atoms to estimate the permeance of a membrane. This approach differs from previous work that calculated the diffusivity of H but did not calculate the subsurface penetration or did not calculate the permeance. To the best of our knowledge, this is the first work that translates first-principle calculations to permeance. For estimating the diffusion we use 3X3X6 ordered fcc cell but use periodic boundary conditions in the diffusion direction, to imitate a large object. That approach has not yet been tested. Also, the Pd solid assumed the structure here is ordered and the diffusivity was calculated analytically accounting for the various energetic barriers in the most likely diffusion path, without resorting to Monte Carlo simulations. The estimation of preferred sites and paths in Pd/Ag layer is more intricate as it presents many such different options.

The second part of this work deals with transport inhibition due to co-adsorbates. Very few computational studies have addressed this issue. Recently, Israni and Harold [12,13] (and references therein) addressed this problem to provide data for membrane reactor (MR) design for methanol SR using a 3.7 mm OD porous α-Al_2O_3 hollow fiber coated with a 3.9 μm Pd–Ag (23% Ag) layer. That limited the temperature to $T < 300\ ^\circ C$ and the components addressed mainly CO, H_2O, CO_2, CH_3OH. They have concluded that the rate-limiting step for the H flux through the membrane was the H diffusion through the membrane. He and H_2O as co-adsorbates were experimentally found to exert negligible inhibition on hydrogen permeance (dilution effect only), CO_2 and CH_3OH presented moderate inhibition while CO inhibition was strong. Strong inhibition by CO adsorption was recorded by several studies (see references below). Adsorption by propane and propylene was also tested showing strong inhibition and membrane deactivation in the latter case [[1] and references below].

The outline of this work is as follows: after describing the numerical procedures, the energy changes due to adsorption and diffusion through the membrane are calculated using DFT. The corresponding energy barriers for the transport between layers in the subsurface are calculated using the nudge elastic band method. These energies are translated into hopping rates, diffusivities and permeance, using the transition state theory, in Section 3. The inhibition effect caused by co-adsorption is estimated in Section 4.

2. Methods

We view the membrane as composed of several layers: (i) the adsorbed one, (ii) one or several subsurface layers that are in equilibrium with the surface, and (iii) the other layers (~40,000 for 10 μm membrane) through which H diffuses by hopping. We estimate the energies and rates of transition between layers.

2.1. Structures and energies

The adsorption heats of the participating species were computed using density functional theory (DFT) with the Vienna ab initio simulation package (VASP) on a (111) surface slab with periodic boundary conditions.

The first brillouin zone is sampled with a gamma centered 3X3X1 Monkhorst–Pack k-point mesh. The cutoff energy for the plane wave basis set was set at 400 eV. Electron exchange correlation was described within the PW91 generalized gradient approximation (GGA) [14,15].

Periodic boundary conditions with 10 Å of vacuum between any two successive slabs was used except for the modeling of the inner membrane conditions where no vacuum in Z direction was introduced as explained below.

The PW91 functional employed here is widely used and is generally considered to perform very well against experiment [16,17]. Our computed adsorption energies show fairly good agreement with previous published results (see comparison of rates in Ref. [18]).

Adsorption binding energy was calculated as $\Delta E_{ads}=E_{adsorbate+slab}-E_{slab}-E_{adsorbate}$. For dissociative adsorption of the