Project Title: Is Extraction Of Hydrogen From Hydrocarbons Using a Metal/Alumina Membrane Kinetically
    Feasible
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Annual report for period starting 9/1/2018

Scientific activities during report period:
    The overarching goal of this research program is to apply theoretical and computational methods to estimate the kinetic barriers that govern the hypothesized separation of hydrogen from hydrocarbon materials using an oxide/metal membrane. A schematic of the imagined separation is shown in Fig. 1. The fundamental steps are: 1) abstraction of hydrogen from hydrocarbons by a catalytic oxide surface; 2) transport of hydrogen through the supporting oxide; 3) transport of the hydrogen through the metal layer; 4) recombination of 2H into H_2 at the metal surface. A key aspect of modeling these processes is the description of the atomic and electronic structure of interfaces, both molecule/surface interfaces and the oxide/metal interfaces.

Figure 1. Hydrogen separation may be achieved by combining four steps: 1, H is abstracted from an organic molecule. 2, H migrates through alumina bulk. 3, H diffuses through metal. 4, 2H associate to form a hydrogen molecule on the metal surface.

    The canonical procedure for modeling a solid surface is to apply periodic boundary conditions to a unit cell that contains vacuum space. This effectively models an infinite set of slabs separated by vacuum space. Such a slab exposes two surfaces, (the top and bottom of each slab) each having the same Miller index. The surface energy can then be estimated by taking the difference between the total energy of a unit cell of the slab and the total energy of the bulk material, (normalized by stoichiometry) and dividing by the surface area per unit cell exposed in slab model.

$$Surface\ Energy = \frac{energy\ of\ optimized\ slab - energy\ of\ optimized\ bulk}{2 * area\ of\ surface}$$

The factor of 2 accounts for the fact that two surfaces are exposed in a single unit cell. This procedure is rigorous for the case where the two surfaces are identical, but for many materials, any structurally and stoichiometrically correct slab model must necessarily expose two *different* layers of material. A schematic is shown in Fig. 2(I). Note that top surface (in the upper part of the slab labeled "A") differs form the bottom surface (in the lower part of the cell labeled "B"). In order to predict which surface is more likely to be exposed in a physical sample of material, it is necessary to estimate the surface energies for *each* of the two different surfaces. A procedure for doing so was proposed by Tian and co-workers.[1] The procedure is based on the idea that breaking a crystal first exposes two surfaces (on each of A and B) having the structure of the cleaved bulk, each of which then relaxes to minimize its surface energy.

Figure 2. Schematic unit cell models of an asymmetric slab. Note that the top and bottom surfaces of the slab differ. White area denotes vacuum. The cross-hashed region may be frozen to the bulk structure or fully relaxed.

One can then define a "cleavage energy" (E_{cleave}) as
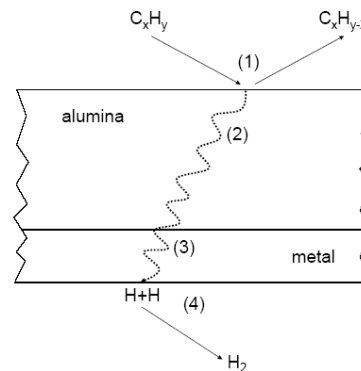
$$E_{cleave} = \frac{(E_{frozen} - E_{bulk})}{2A}$$

where E_{frozen} is the total energy of the unrelaxed slab and E_{bulk} is the energy of the optimized bulk. This cleavage energy can be thought of as shared by the two surfaces. Each surface will then release a different energy upon relaxation, leading to different surface energies (γ_A and γ_B) for the two surfaces.
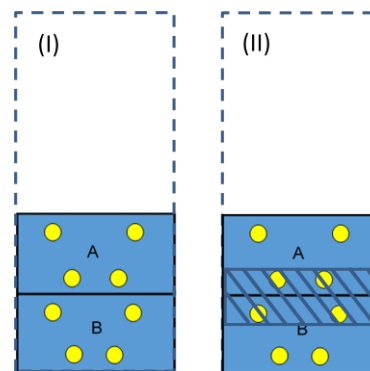
$$\gamma_A = E_{cleave} - E_{relax}^A$$
$$\gamma_B = E_{cleave} - E_{relax}^B$$

Here E_{relax}^A is the energy released by the slab when the A surface is relaxed and E_{relax}^B is the energy released by the slab when the B surface is relaxed.

    A drawback of the above procedure is that it does not reveal the differences in surface energy between the two *unrelaxed* surfaces. To address this shortcoming a new procedure was developed. Since any slab necessarily contains both an (A) and (B) surface, a set of linear equations is applied to extract the contributions from each. Using the notation (E_x^f) to denote the surface energy of the x surface frozen (i.e. cleaved bulk unrelaxed) and (E_x^r) to denote the surface energy of the x surface relaxed, it follows that:

$$E_a^f + E_b^f = \text{energy of fully frozen slab}$$
$$E_a^r + E_b^f = \text{energy of slab with A surface relaxed and B surface frozen}$$
$$E_a^f + E_b^r = \text{energy of slab with A surface frozen and B surface relaxed}$$
$$E_a^r + E_b^r = \text{energy of slab with both A and B surfaces relaxed}$$

These equations may be written in matrix form,

$$\begin{pmatrix} 1 & 1 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 0 & 0 & 1 & 1 \end{pmatrix} \begin{pmatrix} E_a^f \\ E_b^f \\ E_a^r \\ E_b^r \end{pmatrix} = \begin{pmatrix} \alpha \\ \beta \\ \gamma \\ \delta \end{pmatrix},$$

Here $(\alpha, \beta, \gamma, \delta)$ are the results of actual electronic structure calculations. The coefficient matrix is singular, therefore the method of least squares is applied to find an *approximate* vector of surface energies, using as the objective function the sum-of-squares of relative errors. To test the method, the method was applied to a model of sphalerite ZnS, a material with a simple unit cell that yields asymmetric slabs. Calculations were carried out to confirm convergence of the numerical results with respect to the thickness of the middle section of the slab for which all atom positions are frozen during optimizations. (See cross-hashed region in Fig. 2.) For both semiempirical and first-principles electronic structure calculations, the least-squares approach was found to yield surface energies within 5-15% of those produced by the method of Tian et al.[1] This difference is generally less than a few hundred meV, which is within the limits of accuracy of routine electronic structure calculations. The advantage of this linear-algebra based approach is that it reveals surface energies for both relaxed and frozen surfaces.

Studies of oxide/metal interfaces are now underway. The lowest-energy surfaces of the metal and oxide, identified as above, are interfaced to generate the best possible lattice match. An example supercell model of a Pd/Al_2O_3 interface is shown in Figure 3.
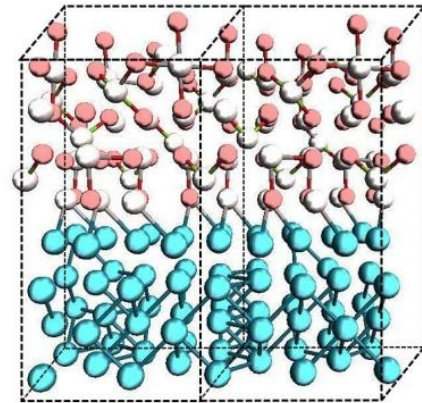
Impact of grant to-date:

A major impact of the grant has been that it facilitated knowledge transfer between generations of students in the group. Without this kind of support, much group knowledge is lost and much effort must be duplicated to rebuild the knowledge base. This first year of this project was devoted largely to student training, (although it did produce the novel theoretical/computational method for calculating surface energies for asymmetric slabs described above, for which a manuscript is being drafted). Two junior graduate students (BR - 2nd year; and NS - 1st year) are expected to carry out the majority of the planned research. Two senior graduate students (JD - 6th year; and GB - 5th year) were charged with training the junior students and were partially funded by this grant to support their training efforts. The grant thereby build science skills in the junior students and mentoring skills in the senior students.

Figure 3. Pd/alumina interface model. Pd - blue; Al - white; O - pink.

In particular, both BR and NS were trained in the use of software tools; for the construction and visualization of unit cell models, and for electronic structure calculations at the semiempirical and DFT levels on periodic solids, surface slabs and interfaces. As described above, special attention was paid to developing skill with modeling *asymmetric* slabs and interfaces as the systems of interest in this project generally possess this complicating feature. Calculations were carried out for both the christobalite and β-quartz polymorphs of SiO_2, (BR) to identify possible structures for the separation membrane catalytic oxide layer. Calculations were carried out to optimize sphalerite, (BR & NS) to identify the preferred surface exposure (BR), and to test the new method of computing surface energies (NS).

Reference:

1. Tian, X. et al. "A DFT based method for calculating the surface energies of asymmetric MoP facets". Applied Surface Science. **427**. 357-362. (2018).