Density Functional Theory (DFT) simulations have been used to successfully describe heterogeneously catalyzed reaction mechanisms in the gas phase, but describing liquid phase heterogeneously catalyzed reactions is still hindered due to a lack of understanding of the relationship between the solvent and the surface-bound species. This relationship has at least three components: 1) liquid-phase molecules interact with the surface species through dispersion interactions and/or chemical binding, 2) liquid molecules can adsorb to the catalyst, altering its chemical composition, and 3) the liquid environment can alter the adsorbate surface interaction[1,2,3,4]. These effects can also influence the reactant surface coverage on the catalyst by stabilizing adsorbates through hydrogen bonding or dispersion forces[5,6], thus increasing adsorbate chemical potentials and coverages. Both solvent molecules and coadsorbed molecules can influence catalytic activity through interactions with the reactants, which can alter binding energies and activation energies[7]. Therefore, solvation and surface coverage are intimately linked, and this link must be defined in order to understand catalysis in the liquid phase and, more importantly, to effectively design catalysts for liquid-phase reactions. Given that many catalysts for liquid-phase reactions are carried out over expensive transition metal catalysts, catalyst design focused on incorporation of cheaper catalyst materials would enable more widespread utilization of systems such as fuel cells.

In this work, we study the link between solvation and surface coverage in terms of Pt-catalyzed CO oxidation with OH, which is thought to be the rate-limiting step at direct methanol fuel cell (DMFC) anodes[8], and which is also important in the aqueous phase reforming of glycerol[9,10]. Simulations are conducted using the Vienna Ab-Initio Simulation Package[11] (VASP) with Projector-Augmented Wave[12] (PAW) pseudopotentials and the Perdue, Burke, and Erzenhof[13] (PBE) exchange/correlation functional. The DFT-D2[14] method is used to compute dispersion forces. Kinetic calculations are performed using the climbing image-nudged elastic band (ci-NEB) method[15]. We compare interaction energies between several explicit solvation models at various adsorbate coverages of CO and OH to determine the optimal solvation model. We consider a 2-D ice-like monolayer, a 3-D Ih ice lattice, a liquid-like 3-D water environment formed by "melting" the ice lattice at various temperatures using molecular dynamics (MD), and a 3-D water environment formed by randomly placing water molecules in the simulation box to form a vapor-like model. We also consider adsorbate coverages up to 1/3rd of a monolayer (ML).

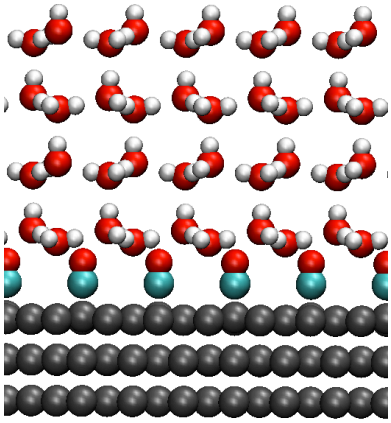


Figure 1: CO adsorbed on the Pt(111) surface under the 3D Ih ice lattice at a coverage of 1/9th ML.
Color code: Pt=grey, C=teal, O=red, and H=white.

Results show that adsorption site, solvation model, water configuration, adsorbate coverage, and dispersion forces all heavily influence the water-adsorbate interaction energies, which we calculate using

$$\text{Pt (aq)} + \text{Pt-CO (vacuum)} \rightarrow \text{Pt (vacuum)} + \text{Pt-CO (aq)}$$

Other important findings are that

1. Interaction energies cannot be correlated solely to the adsorbate dipole. For example, the interaction energies for FCC- and HCP-bound CO are 2.0 eV stronger than for atop-bound CO, despite that the dipole for atop-bound CO is more than three times larger (7.7 Debye versus 2.2 Debye).
2. Coverage has a remarkable effect on the interaction energies. For example, the interaction energies for CO adsorbates decrease by up to 1.0 eV as the coverage increases from 1/9th to 1/3rd ML.

3. Including dispersion corrections has a significant effect on the calculated interaction energies. For example, the interaction energy of atop CO at $1/9^{th}$ ML increases by 0.8 eV when the D2 method is turned on.

We summarize our findings by providing suggestions about how to explicitly include solvation in computational catalysis at moderate computational expense.

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