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## On the water structure at hydrophobic interfaces and the roles of water on transition-metal catalyzed reactions: A short review

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### ABSTRACT

Interest into the roles of water on aqueous phase heterogeneous catalysis is burgeoning. This short review summarizes the influences of hydrogen bonding on adsorption and how water molecules act as co-catalysts in aqueous phase heterogeneous catalysis. These phenomena, which involve interactions and/or reactions with “dangling” hydroxyl or hydroxide groups from nearby water molecules, are related to interfacial phenomena that have been observed at water/oil interfaces in organic synthesis. The hypothesized water structures at water/oil interfaces in organic synthesis is presented, and predictions about how analogous structural effects could influence catalytic chemistry at water/transition metal interfaces are discussed. The focus of this review is on computational methods and observations, but some experimental methods and findings are discussed as well.

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### 1. Introduction

Aqueous phase heterogeneous catalysis, e.g., where the catalyst is a transition metal surface and the reaction is carried out in liquid H<sub>2</sub>O, is of interest for at least three reasons: 1) widespread interest into the aqueous phase reforming (APR) of biomass derivatives [1–11], which utilizes aqueous phase heterogeneous catalysis, 2) tightening of environmental hazard regulations, which are moving toward “greener” solvents and low temperature processing [12–14], and 3) increasing reports of the significance of the roles of water on catalytic activity [15,16]. We are interested in aqueous phase heterogeneous catalysis because we would like to understand the ways in which the water environment influences catalytic phenomena.

The drive to understand the roles of water is motivated, at least in part, by catalyst design. Theoretically, a unique catalyst that optimizes activity and selectivity (and minimizes cost) exists for every possible chemical reaction. To design such a catalyst requires understanding, in molecular-level detail, the chemistry that occurs as reactants are catalytically converted to products. Since we started working on this review, two other reviews, which discuss various roles of water on heterogeneous catalysis, were published.

Davies reviewed the roles of water on catalytic oxidations and Fischer-Tropsch synthesis [17], and Li and co-workers reviewed the experimentally observed roles of water on several specific reactions as well as mechanistic insights (solvation, H-transfer, providing H and OH, removal of C) that have been elucidated from modeling [18].

In this short review, we discuss the roles of water that are influenced by the structure of water at the catalyst interface. First, we discuss methods for learning about the structure and roles of water at catalyst surfaces and hydrophobic interfaces, generally. The focus of this review is on computational results and challenges; however, we do present some results from experiments, and thus we briefly describe the experimental methods that were used. We then discuss how hydrogen bonding influences adsorption and how H<sub>2</sub>O molecules co-catalyze surface reactions. Generalizing metal catalysts as hydrophobic surfaces, we briefly review research about the water structure at hydrophobic interfaces. Specifically, we discuss the re-arrangement of the H<sub>2</sub>O structure at water/oil interfaces that has been observed both experimentally and computationally in organic synthesis. We conclude by providing an outlook on research needs for better understanding the molecular-level roles of H<sub>2</sub>O molecules on heterogeneous catalysis.

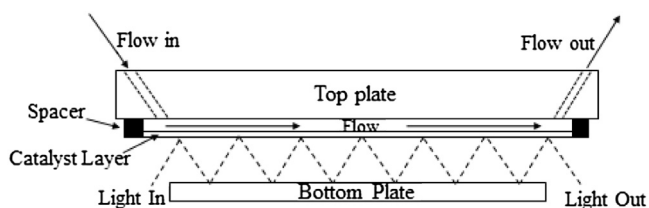
### 2. Spectroscopic methods for use in aqueous phase catalysis

Many of the roles of H<sub>2</sub>O molecules on molecular-level phenomena occurring at interfaces seem to be reversible upon removal of the water environment, necessitating the use of *in situ* experimen-

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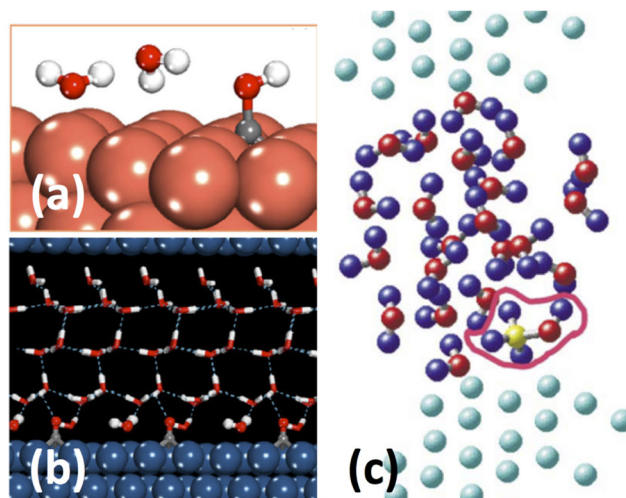


**Fig. 1.** A homemade ATR-IR flow cell. A catalyst layer is deposited in a thin film on the ATR crystal, and the reactant is passed over it in the top plate (arrows). An infrared light beam (dashed line) is directed to the bottom of the ATR crystal at or above the critical angle for internal reflection. Adapted with permission from [24,33] Copyright (2003, 2006), respectively, with permission from American Chemical Society.

tal methods. The experiments discussed in this review use three *in situ* spectroscopic techniques: sum frequency generation (SFG) [19,20], solute-corrected (SC) Raman [21], and attenuated total reflection infrared spectroscopy (ATR-IR) [22–29]. These methods and their applications for studying chemical phenomena at aqueous interfaces have been reviewed previously [20,21,30–32]. Briefly, SFG is a nonlinear laser spectroscopy. In this method, two beams of light are directed to the interface between the two phases, and the resulting beam, which is the sum of the frequencies of the two incident beams, is directed to a detector, where the resultant intensity is calculated. Unlike Raman spectroscopy, SFG can be used in systems with inversion symmetry, but the frequency range where it is useful is limited [20]. SC Raman spectroscopy employs a laser light beam that emits both Rayleigh scattering, i.e., light at the same intensity as the incident beam, and a Raman spectrum, i.e., light that has shifted in energy due to interacting with the molecular vibrations. The Raman spectrum is then broken down into solute and solvent components. An important and unique aspect of SC Raman is that it can provide molecular-level details about the solvent structure [21]. We review such results below. ATR-IR probes molecular vibrations at the catalyst interface. In ATR-IR, an infrared beam is directed through a crystal such that total internal reflectance occurs (i.e., the light is reflected back and forth along the length of the ATR crystal, as shown in Fig. 1), concentrating the analysis to the region near the catalyst surface [33,34]. An evanescent wave is generated at the ATR crystal interface (from the infrared light interacting with the surface) that probes the catalyst surface and the interstitial solution along the length of the reactor. Contributions from liquid molecules are minimized, because the light does not transmit through the liquid [32,35].

### 3. Methods for modeling the structure of liquid water in aqueous phase heterogeneous catalysis

There are two main methods for modeling solvation, with explicit and implicit water. In explicit models, water is treated as individual H<sub>2</sub>O molecules, while in implicit models, it is represented by a structureless, continuous medium. Implicit models are computationally efficient, since they average over the degrees of freedom (DOF) of the water environment rather than taking the configurations of many H<sub>2</sub>O molecules explicitly into account [36–40]. Faheem and Heyden have compared explicit and implicit methods for calculating the energetics of C–C bond cleavage in ethylene glycol on Pt(111) and found that the two methods give similar results [41]. A recent paper by Montemore and Medlin [42] compared implicit and explicit solvation models for alkyl chain growth on Cu(111) and found that both perform equally well for small chain molecules, but longer chain molecules require explicit models in order to properly capture the extent of solvation. Interestingly, their results suggested that continuum models over-solvate long chain molecules, by allowing solvent into regions that would be sterically-inaccessible if explicit H<sub>2</sub>O molecules were



**Fig. 2.** Examples of some commonly used explicit solvation models. (a) Two H<sub>2</sub>O molecules near a COH\* intermediate on a Cu surface, (b) two bilayers of hexagonal ice surrounding a CO\* intermediate on a Pt surface, and (c) liquid-like water solvating a CH<sub>3</sub>OH\* intermediate (circled) on a Pt surface. The water structures in (a) and (b) were obtained with density functional theory (DFT), and the structure in (c) was obtained using *ab initio* molecular dynamics (AIMD). Parts (a), (b) and (c) were adapted from Refs. [51], [52] and [53], respectively, with permission from Elsevier.

used. Our group has found that the adsorption energy of CO\* is the same under both implicit and explicit water, while the adsorption energies of CH<sub>2</sub>OH\* and C<sub>3</sub>H<sub>7</sub>O<sub>3</sub>\* are different [43]. Wang and Liu also found that explicit models were needed to properly model formic acid adsorption on Pt [44]. Thus, the choice of model seems to depend on the system under consideration as well as the properties that need to be calculated.

Many varieties of explicit methods have been employed, and the number of water molecules that have been included ranges from one or two H<sub>2</sub>O molecules (e.g., see Fig. 2a) to a full liquid structure. Some examples are shown in Fig. 2. Models employing full water structures have used ice-like structures, e.g., comprising one or more bilayers of crystalline ice above the catalyst surface (e.g., see Fig. 2b), as well as more “disordered” liquid-like structures (e.g., see Fig. 2c). When ice structures are used, decisions about the configuration of the ice relative to the surface must be made. For example, bilayers of hexagonal ice comprise two types of O–H bonds: parallel to the surface and perpendicular to the surface (e.g., see Fig. 2b) [45]. The perpendicular O–H bond can either orient the H atom toward or away from the surface, and the energetic preference depends on various factors [46–50]. We find that this choice has a noticeable effect on the binding energy of CO\* [43].

Modeling liquid water, where there is not just one configuration, requires sampling over multiple configurations of H<sub>2</sub>O molecules. Sampling has been performed using *ab initio* molecular dynamics (AIMD) [49,53–63], quantum mechanics/molecular mechanics (QM/MM) [41], and classical molecular dynamics [43]. In general, it is important to include enough simulation time in between configurations to ensure that the different configurations are uncorrelated. The decay times for hydrogen bonds in bulk liquid water have been measured to be ~1.2 ps [64,65], and thus the time between two configurations in a molecular dynamics (MD) trajectory of bulk liquid water should be greater than 1.2 ps to avoid configurational bias. We have calculated the rotational time correlation function (rotational motion) and the mean square displacement (translational motion) of the H<sub>2</sub>O molecules involved in hydrogen bonds with catalytic surface intermediates in order to estimate the decay times for hydrogen bonds between liquid H<sub>2</sub>O molecules and CO\* and CH<sub>2</sub>OH\* surface intermediates. By our estimates, the decay times for these hydrogen bonds are ~5 ps and

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