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” hydroxide or hydroxyl 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 briefly as well.

1.0 Introduction

Aqueous phase heterogeneous catalysis, i.e., where the catalyst is a transition metal and the reaction is carried out in liquid H₂O, has been of interest recently for at least three reasons: 1) widespread interest into the aqueous phase reforming (APR) of biomass derivatives,[1-11] which is encompassed under the umbrella of aqueous phase heterogeneous catalysis, 2) tightening of environmental hazard regulations, which are motivating a move toward “greener” solvents and low temperature processing,[12-14] and 3) increasing reports of the roles of water on catalytic

activity,[15, 16] which seem to be significant. 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 H₂O 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 rearrangement of the H₂O 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 H₂O on heterogeneous catalysis.

2.0 Spectroscopic Methods for use in Aqueous Phase

Many of the roles of H₂O on molecular-level phenomena occurring at interfaces seem to be reversible upon removal of the water environment, necessitating the use of *in situ* experimental 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, sum frequency generation spectroscopy (SFG) is a nonlinear laser spectroscopy. In this method, two beams of light are directed to the interface between two phases, and the resulting beam, which is the sum of the frequencies of the two incident beams, is directed to a detector, where its 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. Attenuated total reflection infrared spectroscopy (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 Figure 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, since the light does not transmit through the liquid.[32, 35]

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 (dotted line). 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.

3.0 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_2O 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_2O 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 H₂O molecules were 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 CH₂OH* and C₃H₇O₃* 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 H₂O molecules (e.g., see Figure 2a) to a full liquid structure. Some examples are shown in Figure 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 Figure 2b), as well as more “disordered” liquid-like structures (e.g., see Figure 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 (see Figure 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]

Fig. 2. Examples of some commonly used explicit solvation models. (a) Two H_2O 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_3OH^* 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 Ref. [51], [52] and [53], respectively, with permission from Elsevier.

Modeling liquid water, where there is not just one configuration, requires sampling over multiple configurations of H_2O 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 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_2O molecules involved in hydrogen bonds with catalytic surface

intermediates in order to estimate the decay times for hydrogen bonds between liquid H₂O molecules and CO* and CH₂OH* surface intermediates. By our estimates, the decay times for these hydrogen bonds are ~5 ps and ~30 ps, respectively (Figure 3). These results indicate the need for careful MD sampling. In general, AIMD is too expensive to generate more than a couple of uncorrelated configurations per adsorbate, and thus we have used classical MD in our work.[43] That said, another important consideration is how to calculate the energy of interaction between the H₂O molecules and the catalyst and adsorbates. AIMD uses quantum methods and is thus highly accurate. Classical MD uses non-bonding potentials such as the Lennard-Jones + Coulomb (LJ+C) model. While there are several excellent sets of LJ+C parameters for liquid H₂O,[66-70] and even for metal catalyst surfaces,[71] parameter sets for surface adsorbates are not well-established. In our classical MD simulations, we have used LJ+C potentials with parameters that were derived for liquid phase molecules.[43] An upcoming publication from our group will show that while these exhibit good accuracy for calculating some properties, they can give energies that are significantly different than quantum mechanics in others.[72]

Fig. 3. Rotational time correlation function (top) and mean square displacement (bottom) for hydrogen bonds formed between liquid H_2O molecules and CO^* and CH_2OH^* adsorbates on $\text{Pt}(111)$, calculated for this paper. Computational methods and other relevant details are provided in the Supporting Information and in Refs. [43] and [73]. The decay time for the hydrogen bonds can be estimated as the times where the error bars become appreciable.

4.0 Water Interactions at Metal Surfaces and Their Influences on Catalytic Phenomena

The roles of H_2O molecules on heterogeneous catalysis that we discuss in this short review depend on the water structure and thus require explicit solvation. They are hydrogen bonding with catalyst surface intermediates and acting as co-catalysts.

4.1 Hydrogen Bonding with Catalyst Surface Intermediates

Hydrogen bonding influences the adsorption of certain species. For example, water influences both the binding geometry and energy of acetone on Ru(0001). Whereas in gas phase, acetone binds iso-energetically in two different configurations (with adsorption energies of -0.47 eV), in the presence of a H_2O molecule, one structure is energetically preferable (by 0.18 eV) due to the formation of a hydrogen bond with water (Figure 4).[74] Similar stabilization has been found for $\text{C}_3\text{H}_7\text{O}^*$,[43] CH_3OH^* ,[59, 75, 76] CH_2OH^* ,[43] CH_3O^* ,[76] H_2COOH^* ,[76] HCOOH^* ,[76] HCOO^* ,[76] CH_2O_2^* ,[77] NH_2^* ,[55] and OH^* [78] on various metal (111) and (211) surfaces. Okamoto et al. found that the energies of most of the steps along the methanol dehydrogenation pathway (i.e., $\text{CH}_3\text{OH}^* + 4^* \rightarrow \text{CO}^* + 4\text{H}^*$) are affected by interactions with water, with the energy of the $\text{CO}^* + 4\text{H}^*$ product being 0.7 eV less exothermic in water than in gas phase.[53] Those authors attributed the 0.7 eV energy difference to a loss of hydrogen bonds along the dehydrogenation pathway. Interestingly, interactions with water were found to have a destabilizing effect on H^* , OH^* , and O^* on an electrified Pt(332) surface.[79] In contrast, no stabilization or destabilization effect was observed for O^* on non-electrified Pt(111).[78] Preliminary (unpublished) results from our group agree that H_2O does not form a hydrogen bond with or enhance the energy of O^* on neutral Pt(111); however, we do find that H_2O hydrogen bonds with O^* on $\text{Ag}_3\text{Pd}(111)$ and increases the O^* bond strength by 0.25 eV.[80] We have also found that H_2O forms hydrogen bonds with CO^* but that it has a negligible effect on its adsorption energy.[43] Interestingly, ATR-IR studies indicate that H_2O enhances the polarization of CO^* on a Pt catalyst, causing a shift in the CO stretch (from 2065 cm^{-1} in gas phase to 2015 cm^{-1} in aqueous phase) along with a fourfold increase in the IR intensity.[34] DFT calculations suggest that this red shift is due to increased π back-donation from the Pt surface to CO^* . [81]

The increase in polarization could explain why CO^* forms hydrogen bonds with H_2O , but it is unclear why interactions with H_2O have no influence on the CO^* adsorption energy. In contrast, the binding energies of CO^* [82] and O_2^* [60, 82] have been found to be enhanced by water on Au and AuCu nanoparticles. Multiple papers from the Neurock group indicate that the adsorption energies of charged species (specifically, acetate, OH, H, $\text{CH}_2\text{OH}^\delta$, and $\text{CH}_x\text{O}^\delta$) are enhanced by hydrogen bonding,[57, 58, 83] and Santana et al. suggested that the adsorption strengths of HSO_4^- anions are enhanced because H_2O molecules reduce the Coulombic repulsion between them.[84]

Fig. 4. Acetone and water co-adsorbed to Ru(0001). This adsorption configuration of acetone is stabilized by 0.18 eV through formation of a hydrogen bond (depicted with annotated line). Dark brown spheres = C, pink = H, red = O, light brown = Ru. Adapted from Ref. [74] with permission from The Royal Society of Chemistry.

4.2 Acting as a Co-Catalyst

One of the main roles of H_2O in catalysis is co-catalyzing certain reaction steps, e.g., proton transfers and dissociation of O_2^* . Water molecules facilitate proton transfers through the process of hydrogen shuttling, where H^+ are transferred through a hydrogen bonding network, forming

$H_{(2n+1)}O_n^+$ complexes. For example, Nie et al. [51] found that in the electrochemical reduction of CO_2 over Cu(111), the $CO_2^* + H^* \rightarrow COOH^* + *$ reaction proceeds through a transition state that comprises $H_5O_2^+$. Specifically, H^* forms a bond with a H_2O molecule, which in turn transfers one of its hydrogens to another H_2O molecule, which donates a different hydrogen to CO_2^* (Figure 5). The same authors also found that the $CO^* + H^* \rightarrow COH^* + *$ reaction initiates from a $CO^* + H_5O_2^+$ reactant state and proceeds to a $COH^* + 2H_2O$ product. Similarly, using AIMD simulations, Hartnig and Spohr found that on Pt(111), the reaction $CH_2OH^* + * \rightarrow CH_2O^* + H^*$, which is part of the mechanism for catalytic methanol oxidation, proceeds through a $H_5O_2^+$ intermediate,[59] and Neurock reported that the $CH_3OH^* + * \rightarrow CH_2OH^* + H^*$ step in the same mechanism proceeds through H_3O^+ . [83] Neurock and Iglesia found hydrogen shuttling to play a significant role in Fischer-Tropsch synthesis,[85] and Huang et al. reported that several steps in the methanol steam reforming process, e.g., $CH_3OH^* + * \rightarrow CH_3O^* + H^*$, involve hydrogen shuttling.[76] Santana et al. studied electrochemical hydrogen oxidation using AIMD and found a number of $H_{(2n+1)}O_n^+$ products with stoichiometry up to $H_9O_4^+$. [62, 63]

In a similar mechanism (albeit without forming $H_{(2n+1)}O_n^+$ complexes), H_2O donates a hydrogen to O_2^* in catalytic O_2 dissociation, forming OOH^* and OH^* . [60, 86-88] The OH^* eventually combines with the residual hydrogen atom, recovering the H_2O molecule. This process is illustrated in the context of aqueous phase CO oxidation in Figure 6.

Fig. 5. Optimized structures and transition state for CO_2^* reduction to COOH^* on a Cu surface. The proton transfer is facilitated by a H_5O_2^+ complex at the transition state. Color key: red = O, white = H, gray = C, pink = Cu. Labeled atoms in the top row are to clarify the proton transfer process. Atoms labeled “1” are initially part of water molecule #1, and atoms labeled “2” are initially part of water molecule #2. Adapted from Ref. [51], with permission from Elsevier.

Fig. 6. H_2O -assisted CO oxidation pathway on supported Au/ TiO_2 . (1) $\text{H}_2\text{O} + \text{O}_2 \rightarrow \text{OOH} + \text{OH}$. (2) $\text{OOH} + \text{CO} \rightarrow \text{COOH} + \text{O}$. (3) $\text{COOH} + \text{O} \rightarrow \text{CO}_2 + \text{OH}$. (4) $\text{CO} + \text{OH} \rightarrow \text{COOH}$. (5) $\text{COOH} + \text{OH} \rightarrow \text{CO}_2 + \text{H}_2\text{O}$. From Ref. [86]. Adapted with permission from AAAS.

5.0 Changes in Water Structure at Hydrophobic Surfaces

These types of phenomena, which involve interactions with hydroxide (OH^-) or hydroxyl ($\text{OH}^\cdot$) groups at the water interface, are believed to significantly influence the rate of organic synthesis.[89-100] Briefly, water/oil interfaces increase conversion in organic cycloaddition reactions.[96, 98] For example, in the reaction between pentadiene and dimethylfumarate, the conversion after 30 minutes was 75% when a water/oil interface was present and 56% when a D_2O /oil interface was present, compared to 40% when the reactants were well mixed in water and 16% when well-mixed with an alternate solvent, tetrahydrofuran.[98] The authors postulated two theories about why this rate enhancement occurs: 1) the transition state hydrogen bonds with “dangling” hydroxyl (i.e., $\text{OH}^\cdot$) groups at the water/oil interface, or 2) excess hydroxide (i.e., OH^-) groups at the water/oil interface promote effective acid-base catalysis.[98]

In general, the structure of bulk liquid water attempts to maximize hydrogen bonding. When any hydrophobic interface (e.g., oil, Pt) is present, the water cannot form a complete set of hydrogen bonds,[101-104] and thus the H_2O molecules at the interface exhibit behaviors that deviate from bulk phenomena. Simulations suggest that water molecules near a water/oil interface dissociate, creating a network of OH^- and H_3O^+ (Figure 7),[104] supporting hypothesis 2 above, and experiments performed with SFG spectroscopy,[20, 103-110] SC Raman spectroscopy,[21] and other methods [111] support the dangling $\text{OH}^\cdot$ hypothesis (hypothesis 1) and further suggest that the $\text{OH}^\cdot$ groups point toward the hydrophobic species (Figure 7). Further studies are needed to fully understand the behaviors of H_2O molecules at hydrophobic interfaces, and whether these phenomena are general or if they only occur at water/oil interfaces. However, given that transition metal surfaces are hydrophobic, water/transition metal interfaces may promote similar behaviors as water/oil interfaces, which would influence catalysis. This

suggests that catalytic chemistry at water/transition metal interfaces depends on the structure of water at the interface. Therefore, explicit solvation methods that produce realistic water structures, including allowing for HO-H dissociation, are needed to fully understand the role of water on aqueous phase heterogeneous catalysis.

Fig. 7. Schematic illustration of the simulated water structure at a water/hydrocarbon (oil) interface. The structure modulates between having dangling -OH (left) and OH^- (right) groups oriented toward the oil. Color key: dark gray spheres = C, light gray = H, red = O. Dotted lines are hydrogen bonds. The transparent rectangle depicts the interface between water and the hydrocarbon (oil). Reprinted from Ref. [104], with the permission of AIP Publishing.

Simulations of water on hydrophobic surfaces have predicted that interfacial water structure affects the aggregation of hydrophobic molecules at these surfaces.[101, 102, 112-119] The studies demonstrate that the presence of an extended hydrophobic interface with water promotes the aggregation of hydrophobic molecules. Recent studies with spherically-shaped hydrophobic molecules have attributed the increased aggregation of these molecules near a water/extended hydrophobic surface interface to the enhanced fluctuations in water density near these surfaces relative to bulk water. The fluctuations can be modulated based on the strength of interactions between water and the surface.[101, 113, 120] This is relevant to reactions when

considering multiple adsorbates at the catalyst surface. With multiple hydrophobic reactants, the close proximity could enable interactions that allow for locally enhanced concentrations and thus reaction rates. Therefore, in aqueous phase, the structure of liquid water in the presence of an extended hydrophobic surface could play a role in the reaction mechanism. A better understanding of the interfacial properties of water and their effects on aggregation of molecules near these interfaces can provide an added dimension to the reaction kinetics. Furthermore, a better understanding of how the interfacial water interacts with the reactants at the extended hydrophobic surface can provide insights into reaction mechanisms at water/hydrophobic surface interfaces.

6.0 Conclusions and Outlook

In this manuscript, we have reviewed two well-established ways in which H_2O molecules explicitly influence surface chemistry in heterogeneous catalysis: hydrogen bonding with surface intermediates and acting as co-catalysts. Additionally, we have discussed similar phenomena that occur at the water/oil interface in organic synthesis. Given that transition metals, particularly flat, monometallic surfaces that have uniform charge distributions, are hydrophobic, these phenomena may provide insights into the roles of H_2O on aqueous phase heterogeneous catalysis as well.

The literature on the structure of liquid H_2O at water/oil interfaces in organic synthesis indicates that hydroxyl and/or hydroxide groups point into the hydrophobic environment, making themselves available for promoting catalytic phenomena, such as interacting with a transition state or promoting acid-base catalysis. On a catalyst surface, H_2O molecules, dangling $-\text{OH}$ groups, and/or $\text{OH}^-/\text{H}_3\text{O}^+$ pairs may promote analogous behavior. The presence of adsorbates may also affect the structure of H_2O at the catalyst interface, which could also influence the ways in which H_2O molecules influence catalytic chemistry.

Indeed, simulations that include H₂O molecules at the catalyst interface show that the H₂O molecules play a significant role in catalysis. To clarify the precise roles of water on heterogeneous catalysis, simulations that provide realistic structures of liquid water at catalyst interfaces are needed. To date, the structure of water at catalyst interfaces has been modeled using quantum mechanics, *ab initio* molecular dynamics, and classical molecular dynamics. Structures obtained purely with quantum mechanics are unrealistic since quantum mechanics is carried out at 0 K and thus does not account for configurational disorder. Molecular dynamics (and Monte Carlo) simulations incorporate temperature effects and thus provide more realistic structures of liquid water. That said, balancing computational expense with chemical accuracy using MD (or MC) is not straightforward. In this work, we presented data that suggest that the relaxation times for hydrogen bonds formed between H₂O molecules and hydrophilic surface intermediates can exceed 30 ps. Even to obtain 10 configurations of H₂O around such adsorbates would then require a 300 ps MD production run. While AIMD could be used to obtain such a simulation for a single adsorbate, it is computationally intractable if an entire reaction network's worth of adsorbates is to be evaluated. Alternatively, classical potentials (and combinations of classical potentials and quantum methods) can be used; however, their reliabilities for modeling catalytic intermediates and transition states has not been validated.

Reactive force fields such as ReaxFF [121] may play a very helpful role in understanding the specific roles of H₂O on transition metal-catalyzed reactions. These force fields are parameterized using data from quantum mechanics and then used in "classical" molecular dynamics (or Monte Carlo). Once the force fields are parameterized, they are then significantly less expensive than AIMD. MD simulations involving reactive force fields over transition metal surfaces and transition metal surfaces that comprise a variety of hydrophobic and hydrophilic

surface adsorbates will likely provide useful information about the structure of liquid H₂O at the catalyst interface, which will advance our understanding about the specific ways in which H₂O molecules influence catalytic phenomena.

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liquid H_2O

bound
intermediate

transition metal
catalyst