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Surface Science Prospectives

Surface science of complex environmental interfaces: Oxide and carbonate surfaces in dynamic equilibrium with water vapor

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ABSTRACT

Surface scientists are dealing more and more with complex systems that are challenging to investigate from both experimental and theoretical perspectives. The surface science of complex interfaces, such as environmental interfaces under ambient conditions of temperature and relative humidity, requires both advances in experimental and theoretical methods in order for conceptual insights to emerge. In this prospective, several aspects of environmental interfaces and the field of environmental surface science are discussed. These include: (i) adsorbed water on oxide and carbonate interfaces; (ii) surface chemistry of oxide and carbonate interfaces in the presence of co-adsorbed water; (iii) solvation of ions by co-adsorbed water on environmental interfaces; and (iv) research needs and challenges in environmental surface science.

1. Introduction

Much of the groundbreaking work on surfaces began with Irving Langmuir who received the Nobel Prize in Chemistry in 1932 “for his discoveries and investigations in surface chemistry”. As the field continued, there was a push toward more controlled experiments in “pristine” environments done under ultra-high vacuum conditions on ideal, model systems such as single crystal surfaces. These *surface science studies* from 1965 until now continue and have provided a wealth of information on the nature of surfaces in ultra-high vacuum; and detailed information on surface sites, including defect sites that are present on nearly all surfaces, even ideal surfaces, and surface structure, surface atom rearrangement from surface relaxation and surface reconstruction. The use of scanning tunneling microscopy to investigate the adsorption and chemistry of molecules on specific sites has led to a great deal of insight into the behavior of molecules on well-defined surfaces. Thus the field continued on and The Nobel Prize in Chemistry was awarded in surface chemistry an unprecedented second time in 2007 when Gerhard Ertl was awarded the 2007 Nobel Prize in Chemistry “for his studies of chemical processes on solid surfaces”. On December 8, 2007, Gerhard Ertl gave his Nobel lecture “Reactions at solid surfaces: From atoms to complexity” at Stockholm University.

The surface science of increasing complex interfaces is a challenging area that is expected to continue for years to come. Complex interfaces include: nanoparticles surfaces with edge and corner sites contributing to more than 25% of the atoms present on the surface; catalyst surfaces under *operando conditions*; environmental interfaces under conditions of ambient temperature and relative humidity; liquid interfaces and biological interfaces including biofilms.

As a co-organizer of a recent symposium on the physical chemistry of environmental interfaces and co-editor of a journal issue on the symposium topic, I was struck by the number of high quality surface science studies of these complex interfaces. One prominent theme that emerged in the symposium is the importance of water interactions with metal oxides surfaces. Metal oxide surfaces are important environmental interfaces for a number of reasons [1–3]. Metal oxides are widely used as catalysts and catalyst supports in environmental remediation. Metal oxide minerals found in nature can adsorb contaminants and control the transport of pollutants in ground water systems. Metal oxides are a component of mineral dust aerosol in the Earth’s atmosphere [4]. Furthermore, semiconductor metal oxides are important photocatalysts in both engineered and natural systems and water plays an important role in these photocatalytic reactions.

Thus, there is increasing interest in understanding metal oxide surfaces under ambient conditions of temperature and relative humidity and the role of co-adsorbed water on the chemistry of interfaces under ambient conditions. These studies can provide insight into heterogeneous catalysis, environmental processes and corrosion. Specific topics of discussion at this recent symposium on environmental interfaces included both experimental and theoretical analyses of: (i) oxides (e.g. TiO_2) [5] in photocatalysis and the role of co-adsorbed water; (ii) oxide minerals in aqueous and humid environments (e.g. α-Fe_2O_3 and α-Al_2O_3); (iii) oxide miner-

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als with adsorbed organic layers and the influence of these layers on water adsorption; and (iv) the influence of co-adsorbed water on the reactivity of oxide surfaces.

Although there is a rich literature on the surface science and surface chemistry of oxides, many of these studies are done in ultra-high vacuum. Complementing these UHV surface science studies is a large body of literature on oxide surfaces in aqueous environments. The surface science of oxides at gas–solid interface under ambient conditions as a function of temperature and relative humidity is not as well understood.

Fig. 1 shows these different regimes of water activity, $a(\mathrm{H_2O})$, defined as

$$a(\mathrm{H_2O}) = P(\mathrm{H_2O})/P_0(\mathrm{H_2O}) = \mathrm{RH}, \tag{1}$$

where RH is the relative humidity, and $P(\mathrm{H_2O})$ and $P_0(\mathrm{H_2O})$ are the water vapor pressure and the water saturated vapor pressure, respectively. These different regimes of water activity span many orders of magnitude. The nature of the oxide surface being explored and the conceptual framework in which to understand the properties of oxide surfaces change within these different regimes of water activity. It is the middle regime, i.e. the humid conditions with adsorbed water, which is of interest here. In particular, this surface science prospective focuses *on the structure and reactivity of oxide surfaces, and other environmental interfaces, in the presence of a dynamic adsorbed water layer, i.e. in equilibrium with water vapor, as a function of relative humidity* (RH). Because of the very nature of surface science prospectives, this article will discuss and present only a *few* examples of some recent studies that strive to gain fundamental information about the molecular nature of oxide surfaces under ambient conditions of temperature and relative humidity, how this dynamic adsorbed water layer influences the reaction chemistry of environmental interfaces and solvates adsorbed ions. Finally, a brief discussion of future research needs and directions is presented.

2. Adsorbed water on environmental interfaces

Recent experimental and theoretical studies of water adsorption on surfaces have provided new insights into our understanding of environmental interfaces under ambient conditions of temperature and relative humidity. Some of these advances have come about through of the development of new experimental tools including synchrotron-based X-ray methods [6].

One such advance is the ambient pressure photoelectron spectroscopy (APPES). The details of the instrument, its mode of operation and a number of environmental applications using APPES have been recently reviewed by Salmeron and Schlög [7]. Quantifying water adsorption on oxide surfaces under ambient conditions of temperature and relative humidity is one area that APPES has been successfully applied [7,8]. Water adsorption on $\mathrm{TiO_2}(1\,1\,0)$ is shown here as an example of the use of APPES. The spectra shown in Fig. 2 are of the O1s region at low and high relative humidity. Multiple peaks observed in the spectra represent photoelectrons of different binding energies for lattice oxygen atoms, surface O–H groups and two forms of water: molecular adsorbed and gas-phase. From these data, it can be seen that the binding energy for the adsorbed water peak decreases at higher coverage. The change in binding energy is a result of water molecules initially preferentially binding to surface hydroxyl groups at low coverages and once these sites are filled water molecules bind to other sites on the surface. The low %RH XPS data, where %RH = RH × 100, are curve fit as shown in Fig. 2a. Furthermore once the spectra are deconvoluted into different spectral components, the intensities can be analyzed and surface coverages of the individual adsorbed components, O–H and $\mathrm{H_2O}$, can be obtained, as shown in Fig. 2b and c.

It can be seen that the coverage of molecular water increases as a function of increasing RH where as the hydroxyl groups do not. In addition, it is seen that the formation of hydroxyl groups occur immediately upon exposing $\mathrm{TiO_2}(1\,1\,0)$ to water at a very low RH of $\sim 5 \times 10^{-4}$. As shown by the data plotted in Fig. 2c, the onset of molecular water adsorption occurs after the formation of surface hydroxyl groups. Based on these results as well as additionally measured isotherms and isobars, a model was proposed by Ketteler et al. whereby at very low RH water first dissociates on the surface in oxygen vacancies [8]. The dissociation results in O–H occupying bridge sites. Water molecules then hydrogen bond to these O–H groups, thus surface hydroxyls are proposed to be nucleation sites for water adsorption. The initial O–H:$\mathrm{H_2O}$ complexes that form are characterized by high enthalpies of adsorption (-72 kJ/mol). After these sites are saturated, only then does water adsorption occupy other sites and configurations on the surface. For additional water adsorption above 0.5 ml, the enthalpy of adsorption approaches the bulk enthalpy of condensation of -45 kJ/mol. These data and quantitative insights on the behavior of water adsorbed on $\mathrm{TiO_2}$ would have been difficult without the type of quantitative data provided by APPES.

Other techniques to study water adsorption on surfaces include infrared spectroscopy. Fig. 2 shows water adsorption on $\mathrm{MgO}(1\,0\,0)$ as a function of increasing RH [9]. Foster and co-workers have previously measured water uptake on $\mathrm{MgO}(1\,0\,0)$ at ambient temperatures [10]. Based on their analysis of the vibrational bands due to molecular adsorbed water at 3388 and 1641 $\mathrm{cm^{-1}}$, they suggested that the adsorbed water layer grows in via three-dimensional island formation. The presence of a new higher wavenumber band at 3696 $\mathrm{cm^{-1}}$, whose intensity increases with repeated water

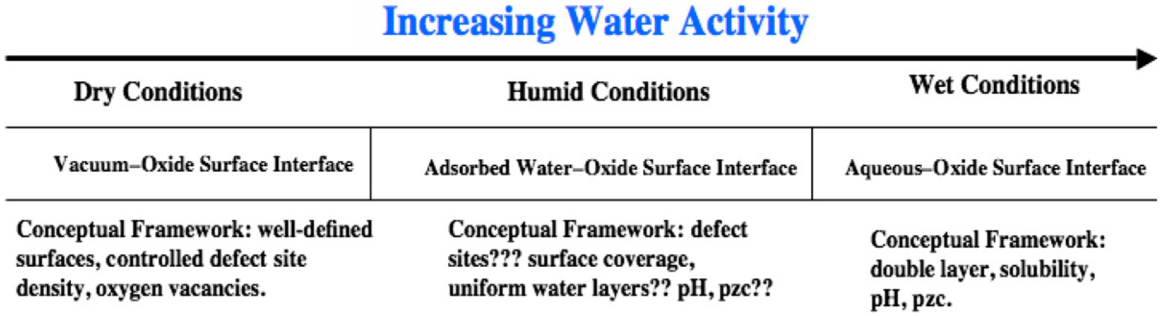

Fig. 1. The diagram shows that as the environment goes from dry to humid to wet, i.e. as the water activity increases over several orders of magnitude, the nature of oxide surfaces under these different environmental conditions changes. The conceptual theoretical framework in which to understand the atomic and molecular nature of oxide surfaces in the presence of increasing water activity changes and for the intermediate regime of humid environments there is clearly a lack of understanding of oxide surfaces and other environmental interfaces.