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Surface termination effects on metal atom adsorption on α-alumina

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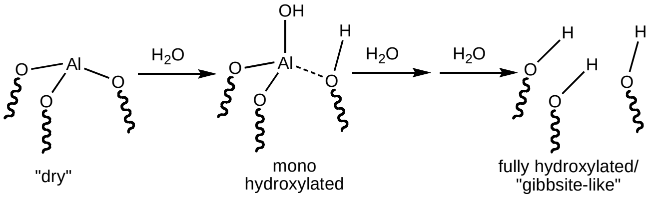
ABSTRACT

To examine the effect of chemical environment on metal-support bonding, the low coverage adsorption and reaction of late transition metal (Pt, Pd, Au, and Ag) atoms on a hydrogen-free and fully hydroxylated α-alumina (0001) surface are compared using supercell models and density function theory. These two surface terminations represent the limits of a completely dehydrated ("dry") and fully hydroxylated ("gibbsite-like") surface. Metal atoms exhibit similar site preferences and the same relative binding energies on the two, in the order Pt > Pd > Ag > Au. Pt, Pd, and Au bind covalently atop single O atoms, and this binding is facilitated on the dry surface by the availability of charge-accepting Lewis acidic Al sites. Ag has the lowest ionization potential of the group, binds electrostatically to both surfaces and preferentially at three-fold O sites, and as a consequence of charge delocalization exhibits greater coverage dependence in its binding. A distinguishing characteristic of the fully hydroxylated surface is the ability to exchange hydrogen between support and metal: transfer from support to metal is highly endothermic for Pd, Ag, and Au but slightly exothermic for Pt, suggesting that such transfer may be important both in Pt-alumina binding and reactivity.

1. Introduction

Oxide-supported transition metal particles are the archetypal structures of heterogeneous catalysis [1,2]. The catalytic reactivity of supported particles can be a function of numerous factors, including particle composition, size, morphology, electronic state, and surface environment. The last of these becomes particularly important in the limit of the smallest metal clusters, where most, if not all, metal atoms are in direct contact with a support surface. Understanding the chemical interactions between metal and support is one key to the design of highly active, selective, and robust catalysts, and thus has been an area of intense experimental and computational research [1,2]. This research is complicated by the difficulties in fully characterizing the metal-support interaction under relevant environmental conditions of pressure, temperature, and humidity [3].

Alumina (Al_2O_3) is one of the most common technological metal oxide supports for catalysis [1,4]. It exists in a variety of polymorphs, many of which incorporate some degree of bulk or surface hydroxylation. Even in the case of the most stable α-alumina, or corundum, form, experiments and simulations indicate the existence of a variety of surface terminations depending on the presence of water. Experiments [5–8] and theoretical studies [9–14] agree that under ultra-high vacuum (UHV) conditions, the non-polar Al-terminated (0001) surface is the lowest in energy. This surface exposes three-coordinate Al ions and four-coordinate oxygen ions, with the Al atoms relaxed nearly into the surface plane [15]



Water readily adsorbs to and dissociates on this "dry" alumina surface [11,13,16–19]. The initial dissociation of water occurs across surface Al_s–O_s bonds to form Al_s–OH and O_s–H surface hydroxyl groups. At high exposures of water, this dissociation process is found in simulation [11,17–19] and experiments [16,20] to terminate in the formation of a fully hydroxylated surface that resembles gibbsite, or $Al(OH)_3$, in which all surface Al^{3+} cations are replaced with 3 H^+ cations. From analysis of the relative stabilities of these various surface terminations, this transition from dry to monohydroxylated to fully hydroxylated surfaces is expected to occur over the range of temperature and humidity conditions typical of heterogeneous catalysis. Similarly, careful analysis of γ-alumina stability

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indicates that it too can expose both unhydroxylated and hydroxylated surfaces under practically relevant conditions [21].

The structures and mechanisms of metal atom adsorption on the dry alumina surface have been explored using density functional theory (DFT) simulations, although general consensus has not always been achieved [22–30]. For instance, Hinnemann and Carter have described the adsorption of Pt atoms on the dry alumina surface in terms of Pt–O covalent bonding [22], while a more ionic bond with charge transfer from Pt to O was proposed by Verdozzi et al. [23] Pd has been found to bind more weakly to the dry surface than does Pt [22,25], although again the mechanism of Pd binding has been debated [23–27]. The binding of Ag and Au is reported to be much weaker than that of Pd and Pt [23,28–30]. Polarization is said to dominate the binding of Au to the surface [28], while charge transfer is thought to have a large contribution to Ag–surface interaction [28,30]. Comparatively little work has been done to explore the effects of environmental surface modifications on the interaction of metal particles with supports [31–33]. The adsorption and diffusion of single Ag atoms has been compared on various terminations of dry and hydroxylated α-alumina with density functional theory (DFT) simulation [29]. Complete hydroxylation is found to reduce the binding between Ag and the support, while partial hydroxylation enhances such interaction. Valero and coworkers have similarly used simulation to demonstrate the weakening effect of hydroxylation on the binding and diffusion of Pd atoms on γ-alumina [34]. The unusually large Pt–Pt distances observed for alumina-supported Pt_3 clusters have been attributed to strong interactions with surface hydroxyls [33]. Hydroxylated surfaces offer the potential for spillover of hydrogen from support to catalyst particle, a phenomenon well known in heterogeneous catalysis [35,36]. Spillover of hydrogen from hydroxyl groups to adsorbed metal atoms has been reported to contribute to the bonding of early transition metals (Cr, Fe, Ni, Cu, Mo, Ru) to alumina [37,38].

To date there have been no systematic comparisons of the binding of different metals on unhydroxylated and hydroxylated oxide surfaces at the low coverages relevant to catalysis. In this work, we use DFT simulations to interrogate the effects of surface hydroxylation on metal atom binding at an otherwise undefected α-alumina surface. We choose as surface models the two limits of the fully dry, Al-terminated surface and the fully hydroxylated surface. We compare the binding of three noble metals (Pd, Pt, and Ag) well known to exhibit useful catalytic properties when supported on alumina, as well as Au, widely of interest for its catalytic activity in highly dispersed forms. We find that metal adsorption is stronger on the dry surface than on the fully hydroxylated surface and follows the order of Pt > Pd > Ag > Au on both surfaces. The interactions can be understood in terms of a charge transfer and dative bonding model in most cases, but Ag exhibits unique site preferences and bonding modes that can be traced to its low ionization potential. On the fully hydroxylated surface, an additional covalent bonding is possible driven by hydrogen spillover from the surface to the metal atom, but such spillover is found to be favorable only for Pt.

2. Computational details

Plane-wave, supercell DFT calculations were carried with the *VASP* code [39–41]. The interaction of valence electrons with frozen cores were described using the projector augmented wave (PAW) method [42], and plane waves were included up to an energy cutoff of 400 eV. The exchange and correlation energies were computed using the spin-polarized Perdew–Wang 91 form (PW91) of the generalized gradient approximation (GGA) [43]. A Gaussian smearing function with a width of 0.05 eV was applied to states near the Fermi level to facilitate convergence; the final state are found to have integer occupancies as expected for these insulating systems. Electronic energies were converged to 10^{-4} eV, and ionic relaxations were considered converged when the forces on the ions were less than 0.03 eV/Å.

Bulk α-alumina has a distorted hexagonal structure with six formula units (Al_2O_3) per unit cell. The PAW-GGA lattice constants, $a = b = 4.81$ Å and $c = 13.12$ Å [44], slightly exceed the experimental values of 4.76 and 12.99 Å [45]. The former are used for all reported calculations. An Al-terminated 12-layer slab was used to simulate the dry α-alumina (0001) surface with the bottom five layers fixed in their bulk locations and seven top-most layers allowed to relax. To minimize lateral interactions between adsorbates and vertical interactions between slab images, a 2×2 surface supercell with a vacuum region of 18 Å was used. Overall supercell dimensions were $9.61 \times 9.61 \times 26.34$ Å and contained 80 atoms. A $3 \times 3 \times 1$ Γ-centered **k**-point mesh was found to be sufficient to converge electronic energies. Calculated surface relaxations are consistent with previous reports [13,15,23,46,47]. The hydroxylated α-alumina surface is generated from the dry surface by replacing each of the Al ions in the top-most layer with three surface H [11,13,16,19]. In this case, overall supercell dimensions are the same as that for the dry surface and contained 88 atoms. Car–Parrinello molecular dynamics simulations show that the surface hydroxyls dynamically reorient between in-plane and out-of-plane orientations at ambient temperatures, with two-thirds pointing out-of-plane and one-third in plane on average [17].

The energies of isolated transition metal (M) atoms (Pt, Pd, Au, and Ag) were calculated in a 10 Å cubic supercell including only the Γ point. Because the proper description of atomic multiplets is not possible within DFT, we choose as reference states spin-polarized, spherically symmetric atoms with the correct ground state orbital occupancies. To explore the potential energy surface for metal adsorption, single metal atoms were located at various high and low-symmetry sites on the 2×2 surface at a coverage of one per 12 surface oxygen atoms and metal–adsorbate binding energy calculated by difference

$$E_B = E_{M/Al_2O_3} - (E_{Al_2O_3} + E_M)$$

The absolute adatom binding energies can be affected by the choice of bulk or relaxed termination of the slab underside, in particular for electropositive atoms like Al [22]. By comparison of our results with previous studies [22,29], we find no evidence of a strong effect for the late d block metals studied here. Nonetheless, this choice should be kept in mind when comparing absolute energies between different studies.

To provide insight into the origins of and differences in surface binding, charge density differences are calculated for the adsorbate–substrate system according to

$$\Delta\rho = \rho_{M/Al_2O_3} - (\rho^{fix}_{Al_2O_3} + \rho_M)$$

where ρ_{M/Al_2O_3} is the charge density of the total system, $\rho^{fix}_{Al_2O_3}$ is the charge density of the alumina surface fixed at the adsorbed geometry, and ρ_M is the electron density of a metal atom isolated in the same periodic box. Local densities of states (LDOS) in spherical regions around atoms are calculated using the PAW-based fast projection method implemented in *VASP*. The vacuum potential is evaluated in each case and used to align the LDOS to a common energy reference.

3. Results

We contrast here the binding of Pd, Pt, Ag, and Au atoms at the Al-terminated α-alumina (0001) surface with that at the fully hydroxylated surface. Fig. 1 illustrates top and side views of both