Surface Science 650 (2016) 210–220

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Promotional effects of chemisorbed oxygen and hydroxide in the activation of C–H and O–H bonds over transition metal surfaces

David Hibbitts [a,c], Matthew Neurock [a,b,d,*]

[a] Department of Chemical Engineering, University of Virginia, Charlottesville, VA 22904, United States
[b] Department of Chemistry, University of Virginia, Charlottesville, VA 22904, United States
[c] Department of Chemical Engineering, University of Florida, Gainesville, FL, United States
[d] Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States

ARTICLE INFO

Available online 29 January 2016

Keywords:
Density functional theory
Transition metal surfaces
Oxygen
Hydroxide
Charge analysis
C–H and O–H activation

ABSTRACT

Electronegative coadsorbates such as atomic oxygen (O*) and hydroxide (OH*) can act as Brønsted bases when bound to Group 11 as well as particular Group 8–10 metal surfaces and aid in the activation of X–H bonds. First-principle density functional theory calculations were carried out to systematically explore the reactivity of the C–H bonds of methane and surface methyl intermediates as well as the O–H bond of methanol directly and with the assistance of coadsorbed O* and OH* intermediates over Group 11 (Cu, Ag, and Au) and Group 8–10 transition metal (Ru, Rh, Pd, Os, Ir, and Pt) surfaces. C–H as well as O–H bond activation over the metal proceeds via a classic oxidative addition type mechanism involving the insertion of the metal center into the C–H or O–H bond. O* and OH* assist C–H and O–H activation over particular Group 11 and Group 8–10 metal surfaces via a σ-bond metathesis type mechanism involving the oxidative addition of the C–H or O–H bond to the metal along with a reductive deprotonation of the acidic C–H and O–H bond over the M–O* or M–OH* site pair. The O*- and OH*-assisted C–H activation paths are energetically preferred over the direct metal catalyzed C–H scission for all Group 11 metals (Cu, Ag, and Au) with barriers that are 0.4–1.5 eV lower than those for the unassisted routes. The barriers for O*- and OH*-assisted C–H activation of CH_4 on the Group 8–10 transition metals, however, are higher than those over the bare transition metal surfaces by as much as 1.4 eV. The C–H activation of adsorbed methyl species show very similar trends to those for CH_4 despite the differences in structure between the weakly bound methane and the covalently adsorbed methyl intermediates. The activation of the O–H bond of methanol is significantly promoted by O* as well as OH* intermediates over both the Group 11 metals (Cu, Ag, and Au) as well as on all Group 8–10 metals studied (Ru, Rh, Pd, Os, Ir, and Pt). The O*- and OH*-assisted CH_3O–H barriers are 0.6 to 2.0 eV lower than unassisted barriers, with the largest differences occurring on Group 11 metals. The higher degree of O*- and OH*-promotion in activating methanol over that in methane and methyl is due to the stronger interaction between the basic O* and OH* sites and the acidic proton in the O–H bond of methanol versus the non-acidic H in the C–H bond of methane. A detailed analysis of the binding energies and the charges for O* and OH* on different metal surfaces indicates that the marked differences in the properties and reactivity of O* and OH* between the Group 11 and Group 8–10 metals is due to the increased negative charge on the O-atoms (in O* as well as OH*) bound to Group 11 metals. The promotional effects of O* and OH* are consistent with a proton-coupled electron transfer and the cooperative role of the metal-O* or metal-OH* pair in carrying out the oxidative addition and reductive deprotonation of the acidic C–H and O–H bonds. Ultimately, the ability of O* or OH* to act as a Brønsted base depends upon its charge, its binding energy on the metal surface (due to shifts in its position during X–H activation), and the acidity of the H-atom being abstracted.

1. Introduction

Atomic oxygen (O*) is an important intermediate that is formed in many catalytic systems [1] carried out over transition metal catalysts in the presence of oxygen or water including CO oxidation [2–4], methane partial oxidation and reforming [5–10], alcohol oxidation [11–16] or oxygen reduction [16–21]. These reactions are often carried out on supported transition metal nanoparticles which are predominantly comprised of low-index terraces. Madix et al. were the first to show that oxygen bound to Group 11 transition metal (Cu and Ag) surfaces behaves as a Brønsted base and promotes the activation of strong but acidic O–H bonds in water [22,23], methanol [24–26], ethanol [27],

---

[*] Corresponding author at: Department of Chemical Engineering and Materials Science, 421 Washington Ave. SE, Minneapolis, MN 55455-0132 United States.
E-mail address: mneurock@umn.edu (M. Neurock).

http://dx.doi.org/10.1016/j.susc.2016.01.012

formic acid [28–30] and acetic [31] acid, as well as acidic C–H bonds of acetylene [32,33] and propylene [34]. Later work expanded these ideas from the promotional effects of O* on Cu and Ag to Au surfaces involved in the oxidation and coupling of alcohols [15,35–41], oxidation of alkenes [42], and oxidative dehydrogenation of acids [43–47]. Similar results show that O* can also act as a Brønsted base and promote the oxidation of alcohols and the decomposition of organic acids over specific non-noble metal Pd [48–52] and Pt [53] surfaces.

More recent studies, inspired by the work of Madix on Group 11 metals, showed that O* also facilitates activation of O–H bonds of alcohols through a proton-coupled electron transfer like mechanism on Pd and Pt surfaces, and confirmed earlier work on Au close-packed surfaces [15,16]. A key step in forming the active oxygen in the transition state in these reactions involves a shift of O* from its stable three-fold site to a bridge during the activation of C–H bonds of CH_4 over metal-O* site pairs at higher O* coverages on Pt, Rh, and Pd catalysts during the partial oxidation CH_4.

More generally, the reactivity of O* on group 11 and other transition metal surfaces can be extended to other electrophilic adsorbates such adsorbed hydroxide (OH*) and alkoxide (OR*) intermediates that can withdraw electron density from the metal to form negatively charged surface intermediates. Adsorbed hydroxide (OH*) on Group 11 and certain Group 8–10 transition metal surfaces is thought to act as a Brønsted base and promote CO oxidation [54–56], aqueous-phase alcohol oxidation [14–16], electrocatalytic oxidation of alcohols (at elevated potentials or pH) [57–58] as well as electrocatalytic reduction of oxygen [20, 59,60]. The surface O* and OH* intermediates in these systems can be formed via the activation of oxygen or water [57,59,60] or introduced by the addition of base (such as NaOH). Similar to O*, the adsorbed OH* withdraws electron density from the surface to form a negatively charged surface intermediate that behaves as a Brønsted base [15,16, 57] where it can activate acidic C–H and O–H bonds or carry out nucleophilic attack on CO and CC bonds that form during oxidation or oxidative dehydrogenation reactions [15,61,62]. Similarly, adsorbed alkoxides (OR*) produced in the catalytic conversion of alcohols over Cu supported on silica, have been shown to take on basic character and aid in catalyzing aldol condensation and esterification reactions [63,64].

While previous studies have demonstrated the ability of O*, OH* and, more generally, OR* adsorbates to act as Brønsted bases, these studies have been limited to a relatively few transition metal surfaces. Herein we attempt to understand the influence of the transition metal on the basicity and reactivity of O* and OH* over close-packed Group 8–10 transition metals (Ru, Rh, Pd, Os, Ir, Pt) as well as Group 11 (Cu, Ag, Au) metal surfaces. We carry out first-principle density functional theory (DFT) calculations to systematically compare the barriers to activate the C–H bonds of CH_4 and CH_3* as well as O–H bonds of CH_3OH via metal catalyzed unimolecular decomposition, O*-assisted, and OH*-assisted routes (Eqs. (1)–(3)).

$$R{-}H + {*} \rightarrow R^* + H^* \quad (1)$$

$$R{-}H + O^* \rightarrow R^* + OH^* \quad (2)$$

$$R{-}H + OH^* \rightarrow R^* + H_2O^* \quad (3)$$

where $R{-}H = [CH_3{-}H, {*}CH_2{-}H, CH_3O{-}H]$

2. Methods

Density functional theory calculations were carried out using periodic, planewave-based methods implemented in VASP [65–68]. The planewaves were constructed with an energy cutoff of 396 eV using projector augmented-wave (PAW) potentials [69,70]. The RPBE form of the generalized gradient approximation (GGA) [71–73] was used to calculate gradient corrections to the exchange and correlation energies as it has been shown to be more accurate than PBE [71] or PW-91 [74] functionals [75]. While RPBE does very well in calculating strongly bound adsorbates, it tends to underpredict the adsorption energy for systems with significant van der Waal interactions. These systems would require the use of hybrid functionals or GGA functionals which specifically account for van der Waals interactions through explicit terms or the introduction of empirical DFT-D corrections. Previous work, however, on O*- and OH*-assisted activations of alcohol molecules on Pd, Pt, and Au reached identical conclusions to the work herein using the PW-91 form of the GGA, [15–16] which 'overbinds' adsorbates [75]. The agreement of this study with those performed previously indicates that the choice of functional does not alter the conclusions of these studies. The closed-packed transition metal surfaces were modeled using a 4 × 4 unit cell with four atomic metal layers along with a vacuum layer with a size of *3 times* the lattice parameter (at least 10 Å) in between slabs in the z-direction. The bottom two metal layers of the slab were fixed in their bulk positions in order to mimic the bulk surfaces used experimentally. The forces on all of the adsorbate atoms as well as the metal atoms within the top two metal layers were converged to less than 0.05 eV/Å. The wave functions were converged to within 10^{-6} eV and the forces were computed using an FFT grid with a cutoff of twice the planewave cutoff. The first Brillouin zone was sampled using a Monkhorst-pack [74] scheme with a 3 × 3 × 1 k-point mesh. The optimized geometries were subsequently used to carry out single-point calculations with a 6 × 6 × 1 k-point mesh to determine the final electronic energies (E_0). Converged wavefunctions were transformed into a set of localized quasiatomic orbitals (QUAMBOs) [76–79] and used to carry out Löwdin population analyses [80,81] to determine the charges on the individual atoms.

The methyl (CH_3*) binding energies (BE) were calculated with respect to the gas phase CH_3 radical species (BE^{rad}) and also with respect to the more stable gas phase CH_4 and H_2 molecules (BE^{mol}) as shown in Eqs. (1) and (2), respectively.

$$BE^{rad} = E[CH_3{*}] - E[Surf] - E[CH_3] \quad (1)$$

$$BE^{mol} = E[CH_3{*}] - E[Surf] - (E[CH_4] - {}^{1}/_{2}E[H_2]) \quad (2)$$

The binding energies for oxygen were calculated solely with reference to the gas phase free radical O species (BE^{rad}).

A two-stage approach was adopted to locate transition states along the minimum energy reaction paths. The minimum energy reaction path and initial estimates of the transition state were calculated using a nudged elastic band (NEB) [82] calculations with 16 intermediates converged until the force normal to the reaction path was less than 0.3 eV/Å. The NEB transition states were subsequently used as input to the Dimer calculations [83] to isolate and refine the transition state. Dimer calculations were converged until the normal force was less than 0.05 eV/Å with a 3 × 3 × 1 k-point mesh followed by a single-point energy calculation using an 6 × 6 × 1 k-point mesh (similar to the optimizations described above). The mode of the dimer method was examined to ensure that it belonged to the appropriate C–H or O–H bond breaking reactions.

3. Results and discussion

3.1. Electronic nature of O* on Group 8–11 metals

In order to understand the effects of O* and OH* in promoting the surface chemistry, we first examine in detail the changes in the electronic properties and the changes in the binding of these species as we change the metal. More specifically we explore a range of Group 8–10 (Ru, Rh, Pd, Os, Ir, Pt) as well as Group 11 transition metals (Cu, Ag, Au). The results from calculations carried out herein at low coverages indicate that O* preferentially binds to three-fold fcc and hcp sites on the closed-packed (111) fcc or (0001) hcp surfaces (Fig. 1),