PHYSICAL REVIEW LETTERS

Transition Metal Oxides: Extra Thermodynamic Stability as Thin Films

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(Received 25 August 2005; published 14 February 2006)

The oxides of many transition metals wet their own metal surface. The adhesion energy at this interface ($E_{\text{adh,ox/m}}$) provides extra stabilization, which lowers the O_2 pressure required for oxide stability as a thin film below that required for bulk-oxide stability by the factor $\exp[(2\gamma_{\text{g/ox}} - E_{\text{adh,ox/m}})/(tN_{\text{ox}}RT)]$, where $\gamma_{\text{g/ox}}$ is the surface energy of the oxide, t is the oxide film thickness, and N_{ox} is the oxygen concentration in the bulk oxide (moles O_2 per volume). For oxide films only ~ 1 nm thick, this correction can be many orders of magnitude. This may extend to other compounds.

Introduction.—Transition metals are used as industrial catalysts for a wide range of oxidation reactions of great importance in fuel processing, chemical production, and pollution cleanup. A key fundamental question is whether the surface under catalytic reaction conditions is metallic or is, instead, the metal's oxide. We show here that since these oxides often wet their metals, an ~ 1 nm thick film of bulklike metal oxide can be present on the metal surface at steady state when the O_2 pressure is many orders of magnitude below that required to maintain that metal's bulk oxide. We further show that this thin-film oxide can be considered as a separate thermodynamic phase whose equilibrium thickness increases to infinity as the oxygen chemical potential approaches the value required to stabilize that metal's bulk oxide. Its existence is attributable to the extra stability that arises from its adhesion energy at the underlying oxide-metal interface, just as ''surface melting'' at temperatures below the bulk melting point is driven by the adhesion of the liquid film to its underlying solid. This phenomenon may extend to nitrides, hydrides, etc.

The existence of thin oxide films on transition metal surfaces at steady state under catalytic reaction conditions where the bulk of the metal still remains unoxidized has become increasingly apparent in recent years [1–9]. The importance of the oxide's surface properties in determining the catalytic reaction's mechanism and microkinetics is undeniable, since oxides have completely different chemisorption properties than metals. It still remains controversial, however, whether these thin oxide films exist due to kinetic or thermodynamic reasons, or whether the bulk oxide would form if given infinite time. This Letter outlines thermodynamic equilibrium conditions where such thin oxide films exist but where the bulk of the metal remains unoxidized.

Bulk-oxide stability limits: The bulk dissociation pressure.—Consider the equilibrium reaction of a metal (M) with O_2 to form its bulk oxide:

$$M(s) + O_2 \rightleftharpoons MO_2(s). \tag{1}$$
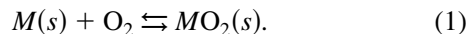
It is well known that there is only one O_2 pressure at any given temperature where both the bulk metal and the bulk

oxide are thermodynamically stable simultaneously [10–12]. This is called the ''dissociation pressure'' of the bulk oxide, $P_{\text{O2,eq}}$. Since the activity of any pure bulk solid is unity whenever it is present, the equilibrium constant for reaction (1) above, K_{eq}, is $(P_{\text{O2,eq}}/P^0)^{-1}$, where P^0 is the standard state pressure (typically 1 bar) [13]. Remember that

$$(P_{\text{O2,eq}}/P^0)^{-1} = K_{\text{eq}} = \exp(-\Delta G^0/RT)$$
$$= \exp[-(\Delta H^0 - T\Delta S^0)/RT], \tag{2}$$

where ΔG^0, ΔH^0, and ΔS^0 are the standard Gibbs free energy, enthalpy, and entropy changes, respectively, for reaction (1) per mole as written, R is the gas constant, and T is temperature [13]. Taking the logarithm and changing signs gives

$$\ln(P_{\text{O2,eq}}/P^0) = \Delta G^0/RT = (\Delta H^0/R)(1/T) - (\Delta S^0/R). \tag{3}$$

Thus, a plot of $\ln(P_{\text{O2,eq}})$ versus $1/T$ yields a straight line whose slope is $\Delta H^0/R$ [10–12], which is a special case of the van't Hoff relation [13]. An example of such a plot from experimental data for $2\text{Ag}(s) + \frac{1}{2}O_2(g) \rightleftharpoons \text{Ag}_2\text{O}(s)$ is shown in Fig. 1. Here the stoichiometry is different from Eq. (1), but Eq. (3) holds for all stoichiometries provided ΔG^0, ΔH^0, and ΔS^0 are taken per mole O_2. At O_2 pressures above such an equilibrium line, the bulk oxide is the only bulk solid phase that is stable (until a higher oxide forms), whereas below this line, the bulk metal is the only stable bulk solid. Similar lines to that in Fig. 1 have been presented for many metal oxides [10–12], or they can be calculated from commonly tabulated standard thermodynamic values for these oxides [13]. These dissociation pressure lines are very useful in expressing the stability limits of oxides. We show next that these oxides can be stable as a thin film or ''surface oxide'' phase at equilibrium for pressures far below these lines.

Surface oxide stability limits in pure O_2.—Consider now the situation where an infinite surface of some metal $M(s)$ is coated with a thin film of its oxide $MO_2(s)$ of thickness t at equilibrium in some pressure of O_2 gas, $P_{\text{O2,eq}}$. This reaction can be written
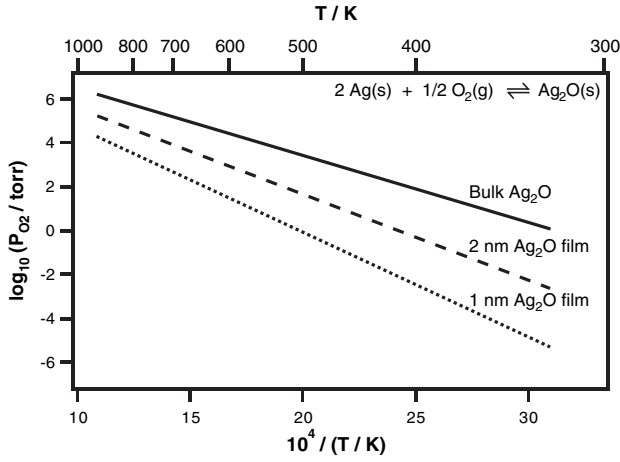
FIG. 1.   Plot of the equilibrium O_2 dissociation pressure for $Ag_2O(s)$ versus temperature in van't Hoff format. The top line is experimental data for bulk $Ag_2O(s)$ [10]. The two lower lines are predicted for thin films of $Ag_2O(s)$ of thickness 2 and 1 nm covering $Ag(s)$ using Eq. (7), assuming a reasonable value for $2\gamma_{g/ox} - E_{adh,ox/m}(-50 \ \mu J/cm^2)$. The real value of $2\gamma_{g/ox} - E_{adh,ox/m}$ could be determined from an experimental measurement of the equilibrium pressure at one thickness.

$$(n + m)M(s) + nO_2(g) \rightleftarrows nMO_2(sp) + mM(s), \quad (4)$$
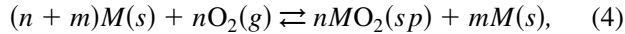
where "sp" stands for this new thermodynamic "surface phase" of the oxide, n is the number of moles of $M(s)$ that converts to MO_2(sp) per unit area, and m is the number of moles of M that remains metallic per unit area. The standard molar free energy change for this reaction, ΔG_4^0, is the same as that for reaction (1) above except that now we consider oxide films that are so thin that the contribution from surface energies can no longer be neglected. Let $\gamma_{g/m}$, $\gamma_{g/ox}$, and $\gamma_{ox/m}$ refer to the standard surface free energies per unit area of the gas-metal, gas-oxide, and oxide-metal interfaces, respectively. The change in *surface* energy for reaction (4) per unit area is

$$\gamma_{g/ox} + \gamma_{ox/m} - \gamma_{g/m} = 2\gamma_{g/ox} - E_{adh,ox/m}, \quad (5)$$

where $E_{adh,ox/m} = \gamma_{g/m} + \gamma_{g/ox} - \gamma_{ox/m}$ is the adhesion energy of the metal-oxide interface (the work to separate the oxide-metal interface). Since n moles of O_2 per unit area convert to oxide via reaction (4), the change in surface energy for reaction (4) per mole O_2 is

$$(2\gamma_{g/ox} - E_{adh,ox/m})/n = (2\gamma_{g/ox} - E_{adh,ox/m})/(tN_{ox}), \quad (6)$$

where N_{ox} is the number of moles of O_2 incorporated into the oxide per unit volume of oxide. The film's volume per unit area is just the film thickness, t. For the stoichiometry of reaction (4), N_{ox} equals the density of bulk $MO_2(s)$ divided by its molar mass, since there is 1 mol O_2 per mole MO_2.

Adding this surface energy correction to Eq. (3) gives

$$\ln(P_{O2,eq}/P^0) = \Delta G_4^0/RT = (\Delta H^0/RT) - (\Delta S^0/R)$$
$$+ [(2\gamma_{g/ox} - E_{adh,ox/m})/(tN_{ox}RT)]. \quad (7)$$

Comparing Eqs. (7) and (3) shows that Eq. (7) reduces to Eq. (3) for infinite thickness t, but that $\ln(P_{O2,eq}/P^0)$ differs by an amount $[(2\gamma_{g/ox} - E_{adh,ox/m})/(tN_{ox}RT)]$ compared to bulk oxide for an oxide film of small thickness t. Whenever the oxide film wets its metal, $E_{adh,ox/m}$ is larger than $2\gamma_{g/ox}$, and this is a *negative* correction. It is well known that the oxidation of many late transition metals often leads to thin oxidelike films (protective oxide coatings), which completely wet the metal surface from which they are grown, in some cases even epitaxially with the metal below [1–4,6–8,14–18]. This wetting is not surprising since oxide surface energies are typically much smaller than surface energies of metals [19]. Thus, it is likely that the correction term $[(2\gamma_{g/ox} - E_{adh,ox/m})/(tN_{ox}RT)]$ will be negative for many late transition metals, and thin-film surface oxides will be stable on these metals at pressures below those needed for bulk-oxide stability. For such oxides, Eq. (7) shows that a plot of $\ln(P_{O2,eq})$ versus $1/T$ for a given film thickness t will still be a straight line, but it will fall below the bulk-oxide line of Eq. (3), as in Fig. 1. This difference is inversely proportional to temperature and film thickness, and vanishes for infinite thickness.

The stoichiometric coefficients are all unity in reaction (1) discussed above. Simple correction factors must be added to Eq. (7) when dealing with reactions of more complex stoichiometry. However, if all the reaction energies and entropies are taken per mole of O_2, Eqs. (5)–(7) remain valid as written.

Let us estimate the magnitude of this thin-film correction term $[(2\gamma_{g/ox} - E_{adh,ox/m})/(tN_{ox}RT)]$ in Eq. (7), which we simplify to C/t where $C = [(2\gamma_{g/ox} - E_{adh,ox/m})/(N_{ox}RT)]$ is a constant that depends on the metal and temperature. Since values for $\gamma_{g/ox}$ and $2\gamma_{g/m}$ for transition metals are on the order of 5–80 and 100–300 $\mu J/cm^2$, respectively [19], values for $2\gamma_{g/ox} - E_{adh,ox/m}$ can be expected to be on the order of $-100 \ \mu J/cm^2$ for some of these metals. Consider $Ag_2O(s)$, whose density is 7.13 g/cm^3, giving $N_{ox} = 0.015 \ mol/cm^3$. For 500 K and assuming $2\gamma_{g/ox} - E_{adh,ox/m}$ is only $-50 \ \mu J/cm^2$, $C = [(2\gamma_{g/ox} - E_{adh,ox/m})/(N_{ox}RT)]$ is ~ -8 nm. Thus, a 2 nm thick surface oxide ($\sim$10 atomic layers) will have an offset C/t of ~ -4 at 500 K in the plot of $\ln(P_{O2,eq})$ versus $1/T$ (see Fig. 1). This corresponds to a decrease by a factor of $e^4 = 55$ in the O_2 pressure needed to maintain Ag_2O stability. For an Ag_2O film of only 1 nm thickness, this decrease in equilibrium pressure is a factor of $e^8 = \sim 3000$ (Fig. 1).

We can make a theoretical estimate of $2\gamma_{g/ox} - E_{adh,ox/m}$ for a thin Ag_2O-like film on $Ag(111)$ based on the energy of this film found by density-functional theory (DFT) in [5]. There, an oxidelike film with a

total O coverage of 1.25 monolayers (or 1.73×10^{15} O atoms/cm^2) on Ag(111) was found to have an energy that is 3.2 eV per O atom (309 kJ/mol O) lower than O gas atoms plus Ag(111). This oxygen coverage corresponds to an Ag_2O film thickness of ~ 0.93 nm (using the bulk packing density of Ag_2O of 0.031 mol O/cm^3; see above). Correcting for the enthalpy of formation of O gas (249 kJ/mol [20]), this energy of 3.2 eV gives a standard enthalpy of formation of the thin oxide film of -60 kJ/mol Ag_2O, relative to O_2 gas. This is 31 kJ/mol larger than the standard enthalpy of formation of bulk Ag_2O (-29 kJ/mol [20]). This difference is even larger if calculated using the enthalpy of bulk Ag_2O from DFT instead of this experimental value. This greater energetic stability of the thin film is due to the strong adhesion at the interface, and directly equals $2\gamma_{g/ox} - E_{adh,ox/m}$ if we ignore entropic contributions. (It was shown in those same DFT calculations that the entropic contributions are much smaller [5].) This free energy difference of -31 kJ/mol converts to -90 μJ/cm^2 by simply multiplying it by the O coverage (2.86×10^{-9} mol O/cm^2). This DFT estimate of $2\gamma_{g/ox} - E_{adh,ox/m}$ is nearly twice the estimate of -50 μJ/cm^2 assumed in Fig. 1. Thus, the factors of 55 and 3000 decrease in pressure due to surface effects (estimated above for 2 and 1 nm) would increase to $\sim 10^3$ and 10^6 via Eq. (7) using this DFT energy. The authors also showed that this oxide film would be stable at much lower O_2 pressures than bulk Ag_2O [5], but did not generalize to arbitrary thickness as does Eq. (7).

Clearly, this is a huge effect that cannot be neglected in considering which surface (oxide or metal) is exposed to the gas phase at steady state at a given temperature in a certain O_2 pressure. It arises for the same reason that surfaces can melt below the bulk melting temperature [21]: the extra energetic driving force due to the adhesion of the film in question to the solid below decreases the free energy per mole significantly when considering thin enough films, which allows a phase to exist in equilibrium at conditions well removed from its bulk stability limit.

It is not appropriate to use Eq. (7) when an oxide film has a thickness of two atomic layers (0.4 nm) or less, since no part of it would resemble a bulk oxide in structure and bonding closely enough to be considered bulklike in energy. However, it can be used when a bulklike oxide film binds to the metal surface via some interfacial structure a few layers thick, which does not resemble any bulk oxide, since the adhesion energy by definition includes the energetics resulting from this interfacial layer. In this case, the oxide's film thickness, t in Eq. (7), must be calculated from the number of O atoms per area (including this interfacial layer), assuming they are packed with the bulk oxide's density (because the definition of surface energy has interfaces of zero thickness separating phases with bulklike properties).

If $[(2\gamma_{g/ox} - E_{adh,ox/m})/(tN_{ox}RT)]$ is positive, it should *not* be included in estimating the equilibrium O_2 pressure, since the oxide will not wet the metal.

Relationship to the thermodynamics of chemisorbed oxygen atoms (O_{ad}) on the metal surface.—Let us consider the stability of oxygen adatoms as the O_2 pressure increases from zero, and the point at which the coverage of dissociatively adsorbed oxygen (θ_O) stops increasing and the growth of an oxide thin-film or a bulk-oxide particle begins. It has been proposed that, thermodynamically, the bulk oxide will start to form at the oxygen coverage, θ_O, at which the average oxygen binding energy equals the heat of oxide formation [1,17]. This is a simplification that ignores entropy. We show next that entropy is expected to make an enormous contribution here. Thus, that statement should be "Thermodynamically, the bulk oxide will start to form at the oxygen coverage, θ_O, at which the average *free energy* of oxygen adatoms exceeds the *free energy* of the oxide." More accurately, "free energy" should be "partial molar free energy" or "chemical potential" (of oxygen). As noted above, when a thin-film oxide is grown that wets the metal, the free energy of the oxide must include the correction $[(2\gamma_{g/ox} - E_{adh,ox/m})/(tN_{ox})]$.

The free energy of chemisorbed oxygen can have a huge contribution from its configurational entropy when the oxide starts to form. This arises even in the simplest model where O_{ad} is considered a lattice gas of O adatoms on lattice sites of the metal surface. As shown by Hill [22], configuration entropy's contribution to the chemical potential of an adsorbed lattice gas increases with the fractional coverage of lattice sites, θ_O, as RT ln$[\theta_O/(1 - \theta_O)]$. This free energy contribution increases from negative infinity to positive infinity as θ_O increases from 0 to 1.0. At coverages near saturation, it increases very steeply with oxygen coverage. The chemical potential of oxygen in the adsorbed lattice gas can easily become equal to that in the oxide at high coverage due to this simple contribution from configurational entropy. Of course, repulsive lateral interactions between oxygen adatoms can cause their enthalpy to increase with coverage as well [17]. However, even without a strong change in the enthalpy with coverage, configurational entropy alone will cause the oxide to become stable at high enough coverage.

Oxide stability in the presence of a reductant.— Catalytic oxidation reactions do not occur in O_2 alone, but always involve a reductant gas. Let us consider the simple case of CO oxidation:

$$CO\,(g) + \frac{1}{2}O_2(g) \leftrightharpoons CO_2(g). \qquad (8)$$
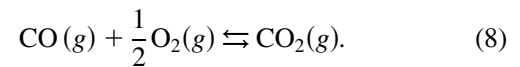
A complex kinetic and thermodynamic model with many system-dependent parameters is required for accurate prediction of oxide stability limits for a metal catalyst under such a gas mixture. However, one can easily set upper and lower limits on the minimum O_2 pressure required for stability of the bulk or surface oxides.

First, if one assumes that the surface reactions of CO are very slow compared to those of O_2, one can simply neglect the CO and use the same analyses as those outlined above. Neglecting the reductant in this way clearly sets a lower

limit on the O_2 pressure needed to make an oxide (or surface oxide) stable at equilibrium. In reality, a higher O_2 pressure will be needed, by an amount that increases as the reductant's pressure increases. However, if the O_2 pressure is not even enough to stabilize the bulk oxide or a surface oxide film of thickness t, then clearly that oxide could not be stable even if the reductant were accurately considered.

The opposite limit is to assume that the gas phase reaction comes to equilibrium rapidly on the surface, at least in terms of chemical potentials of the adsorbed reactants. This will set an upper limit on the O_2 pressure needed to make an oxide (or surface oxide) stable at equilibrium. This limit is probably closer to reality, especially for a gas like CO that has very high reaction probabilities with O_{ad} on such metals. This equilibrium requires that

$$K_{eq} = P_{CO2}/(P_{CO}P_{O2}^{1/2}), \qquad (9)$$

where K_{eq} is the equilibrium constant for reaction (8), which is already known or can be calculated easily from standard tables of thermodynamic data at any temperature [13,20]. Given the initial CO, O_2 and CO_2 partial pressures ($P_{i,in}$), it is a trivial exercise in undergraduate chemical thermodynamics to solve Eq. (9) and the appropriate mass balances (dictated by the reaction's stoichiometry) for the final (effective) pressures of CO, O_2, and CO_2 that would result if this reaction quickly came to equilibrium [13]. These mass balances are $P_{O2} = P_{O2,in} + \Delta P_{O2}$, $P_{CO} = P_{CO,in} + 2\Delta P_{O2}$, and $P_{CO2} = P_{CO2,in} - 2\Delta P_{O2}$. Substituting these into Eq. (9) leads to an equation with a single unknown, ΔP_{O2}. This can easily be solved to get ΔP_{O2} and hence the equilibrium O_2 pressure, P_{O2}. The same type of hypothetical equilibrium solution can be made for any oxidation reaction. The resulting (effective) oxygen pressure is then compared to Eqs. (3) and (7) above to determine if a bulk or surface oxide is stable. If either is predicted to be stable in this way, clearly it will be stable in reality, since the effective oxygen pressure estimated in this way sets a lower limit on the real chemical potential for oxygen on the surface.

Thus, for a given pressure of reductant like CO, one can easily calculate two limiting O_2 pressures that establish the possible range of stability of a surface oxide of any thickness t at a temperature T: One is the limit given by Eq. (7). At any O_2 pressure below this value, the oxide film will not be stable. The other is the (initial) O_2 pressure which, if it came into equilibrium with the reductant, would give a final O_2 pressure [calculated from an equation like (9)] that equals the value from Eq. (7). At any O_2 pressures above this value, the oxide film will be stable at this thickness or greater. Between these two limits, predicting the oxide film stability would require a much more complex analysis. These boundaries are somewhat related to the "constrained equilibrium thermodynamics" approach proposed by Reuter and Scheffler [6], but different in important ways.

Discussion.—There is no reason that the above discussion should be limited to oxide films. Clearly, nanometer-thin films of other compounds of metals, like nitrides, hydrides, and carbides, might be stable at conditions well removed from that bulk compound's stability limits. The temperature dependence of the dissociation pressures for the bulk nitrides and hydrides of many metals are well established [10], or can be calculated [13]. When such a compound wets the surface of its metal, its dissociation pressure will be lower as a nanometer-thin film, analogous to Eq. (7). This may be an important consideration in terms of nitride thin-film formation during ammonia synthesis over metals like Fe or Ru, for example.

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