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# Active role of buried ultrathin oxide layers in adsorption of O₂ on Au films

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## Abstract

Ultrathin oxide layers can exhibit special behavior by enabling the coupling of structural distortions and charge transfer beyond that allowed in the bulk. In this work, we show from first-principles calculations that ultrathin layers of titania, a prototypical oxide, are active in stabilizing adsorption of $O_2$ on Au overlayers. The adsorbed $O_2$ molecules induce charge redistribution in Au that penetrates to the Au–titania interface, which responds through structural distortions that lower the total energy of the system. We suggest that this effect may be of more general nature and useful in catalysis.
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## 1. Introduction

Ultrathin oxide films have attracted immense interest because of their numerous technological applications [1]. In parallel development, oxide-supported metal nanostructures have been shown to be useful as sensors [2] and catalysts [3]. In particular, the oxide support can enhance the catalytic activity of the metal nanostructure by altering its electronic properties prior to catalysis, via charge transfer [4,5] and strain [6,7]. In this work, we propose that when the support is an ultrathin reducible oxide film, atoms at the buried metal-oxide interface can rearrange in response to the presence of adsorbates on the metal film, provided the latter is sufficiently thin. This atomic relaxation at the interface lowers the total energy of the system, thereby stabilizing adsorption. We call the ability of interfacial atoms to rearrange during adsorption 'dynamic

interface fluxionality'. We demonstrate this effect on a model structure consisting of a thin Au film on an ultrathin titania layer supported on a molybdenum slab, and suggest that it will be of more general nature. Specifically, we expect that when the metal film forms strong covalent bonds with the reducible ultrathin oxide layer, while the latter does not interact strongly with its support to render it a rigid structure, dynamic interface fluxionality can take place. This effect may be exploited to design better catalysts and sensors by replacing traditional reducible oxide supports with ultrathin oxide films. Recent advances in the control of ultrathin film growth [8] indicate that this is a practical possibility.

An oxide/metal system that has attracted tremendous attention is that of oxide-supported Au nanoparticles and films, which act as excellent catalysts [9]. Theoretical studies indicate that the active sites include under-coordinated Au atoms [10,11] with rough orbitals [12], and sites at the Au-oxide interface [13,14]. Experiments also suggest that the activity of titania-supported Au films increases markedly when the Au thickness is reduced to one nearest neighbor distance in bulk Au (so-called 'bilayers') [15]. A key

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insight from theoretical studies was that the ability of Au atoms in a nanoparticle to rearrange in response to adsorbates is essential for $O_2$ adsorption [16]; this effect was called 'fluxionality' of the nanoparticle. Here, we show that the notion of fluxionality can be extended to the Au-oxide interface for ultrathin Au films on ultrathin reduced titania.

## 2. Motivation

The possibility of wetting an ultrathin titania support with Au films was recently demonstrated [15], with Mo(112) as a substrate on which the $TiO_2$ thin film was grown. CO oxidation activity in this system was >45 times greater than that reported for other Au/titania catalysts. The atomic structure of this system is unknown. However, two salient features are the strong interaction between Au and titania through Au–Ti bond formation, and the presence of ultrathin reduced titania beneath the Au film. Both of these effects have precedent in other systems [17,18]. Reducible oxides grown on a metal substrate have lower oxidation states than bulk phases due to the reducing character of the metal surface (in the present case, Mo) [17]. On bulk $TiO_2$ surfaces, Au binds almost exclusively to reduced Ti sites [18]. The availability of such sites throughout the ultrathin titania film thus allows wetting by Au. What is not clear, however, is how a strong interaction with buried ultrathin titania, or a small Au thickness, can enhance the activity of Au/titania catalysts [19].

Motivated by these questions, and knowledge [13,20] that the CO oxidation rate is limited by the availability of $O_2$ or adsorbed O on the catalyst, we study $O_2$ and O adsorption in a model ultrathin Au/titania system.

## 3. Choice of model

We first explain our choice of a structural model for this system. While this model may not be an exact representation of the experimental system (the atomic structure of which remains undetermined) it has been constructed by taking into account information from various experiments as well as from extensive simulations. More specifically, our model is motivated by the following observations.

Firstly, the substrate consists of a Mo(112) surface, which has a row-and-trough structure that makes it a useful substrate for ultrathin oxide growth. It has been proposed that the oxide grows along the troughs, forming O–Mo bonds [21]. Our simulations confirm that this is energetically preferred.

Secondly, assuming that the Ti and Mo have the same periodicity along the troughs (as suggested by LEED experiments) leads to an interface structure in which the Ti atom positions are compatible with a Au(110) lattice strained by 9.1% and −5.5% in the [001] and [1 1̄ 0] directions, respectively. Au(110) layers, with strains of 12.5% and −7.5% along these directions, have previously been grown on anatase $TiO_2$(110) up to length-scales of at least

4 nm and thicknesses of at least four layers, as shown by high resolution transmission electron microscopy [22]. Thus, with suitable growth procedures, it is plausible that the titania/Mo system can support 1 or 2 Au(110) layers over length-scales significantly greater than 4 nm. We determined the most stable such structure, shown in Fig. 1, by exploring 37 distinct initial geometries.

Thirdly, although the Ti:O stoichiometry in this favored structure is 1:2, the oxide is not fully oxidized since O is bonded to strongly-reducing Mo. The oxide atoms are arranged in a motif present on rutile $TiO_2$(110), the most stable crystal face of $TiO_2$.

Fourthly, each titania row corresponds to a row of bridging O vacancies on this surface. Such vacancies are common and can form complete rows [23]. Au can nucleate at these vacancies [18], forming Au–Ti bonds in a similar geometry as in our model [23].

We refer to the structures with 1 and 2 Au(110) layers, which consist of 3 and 5 distinct planes of Au atoms on the oxide layer, respectively, as titania/Au$_3$ (shown in Fig. 1(a)–(b)) and titania/Au$_5$ (shown in Fig. 1(c)).
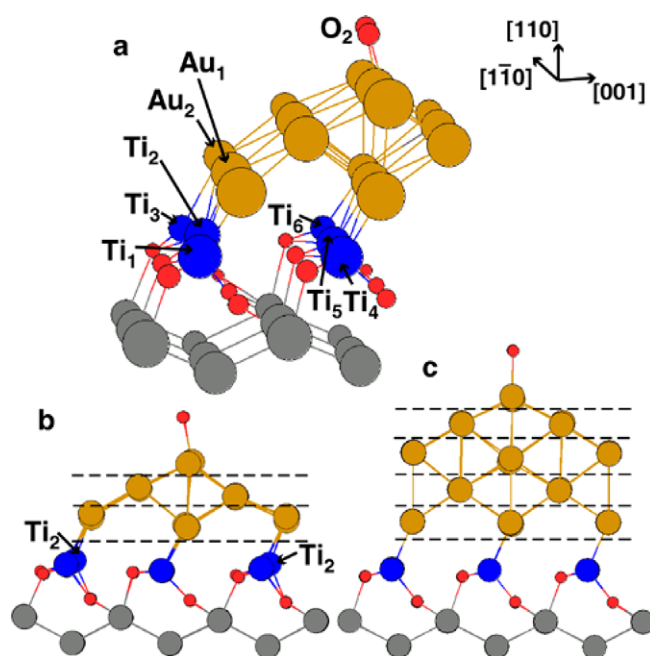


Fig. 1. (a) $O_2$ adsorbed on titania/Au$_3$. (b) View of (a) down the [1 1̄ 0]-direction. (c) $O_2$ adsorbed on titania/Au$_5$. Red, blue, gold and gray circles denote O, Ti, Au and Mo respectively. Only the top two layers of the Mo slab are shown. Crystallographic directions corresponding to those of the Au layers are indicated. Dashed lines separate the Au(110) films into 3 Au planes in titania/Au$_3$, and 5 in titania/Au$_5$. On the clean Au surface, all atoms are equivalent by periodicity in the [1 1̄ 0]-direction; Ti rows directly beneath the troughs of the Au(110) layers are also equivalent by periodicity. Thus, calculations with the clean Au surface have two Ti atoms per unit cell. For calculations with adsorbates, the period in the [1 1̄ 0]-direction of Au(110) is tripled; inequivalent atoms at the interface after $O_2$ adsorption are labeled for reference in the text. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)