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Model catalyst studies with single crystals and epitaxial thin oxide films

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Abstract

The paper describes recent results from our relatively new program to perform detailed studies of the catalytic properties of metal-oxide materials; in particular, to effect a determination of the active catalytic site(s) and the mechanism for reactions over this especially important class of heterogeneous catalysts. Issues of structure-sensitivity, poisoning and promotion, and competing reaction mechanisms are critical questions that need to be addressed in a detailed manner for catalysis by oxides. As just one important example, both surface (Langmui–Hinshelwood) and direct (Eley–Rideal) reaction mechanisms have been proposed for the selective catalytic reduction (SCR) reaction of nitrogen oxides (NO_x) over vanadia/titania catalysts. For this program, we are using a number of unique, state-of-the-art capabilities available in the Environmental Molecular Sciences Laboratory (EMSL) at Pacific Northwest National Laboratory; for example, the first molecular beam epitaxy (MBE) system dedicated to the growth of model metal-oxide films, and a unique moderate-pressure catalytic reactor/surface science apparatus. We describe the growth, characterization, and water adsorption properties of a thin Fe_3O_4(0 0 1) film grown on a lattice-matched MgO(0 0 1) substrate. Because our moderate pressure catalysis studies are preliminary at this point, we instead describe our previous results on the CO oxidation reaction over a Ru(0 0 0 1) model catalyst to demonstrate the utility of the experimental approach. We specifically discuss the possibility that this reaction occurs by an Eley–Rideal mechanism.
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1. Introduction

A number of recent discussions [1–4] concerning the state of catalysis science and engineering have emphasized the important role that ultrahigh vacuum (UHV) surface science has played in transforming this field. In particular, obtaining critical information about the structure and composition of the active catalyst surface, the nature and quantity of dopant species that can act as poisons or promoters of catalytic reactions, and the identity and rates of the elementary steps of a catalytic reaction are all notable achievements of UHV surface science occurring in the last 30 years. These new results have led to new and refined concepts of surface reactivity and greatly improved understanding of catalytic reaction mechanisms, thereby providing meaningful targets for cata-

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lyst synthesis efforts as well as better defining optimum reactor operating conditions.

The progress just described has been obtained almost exclusively for catalysis by metals. Even for these materials, there is an important additional component of the actual catalyst; namely, the support material that is commonly composed of oxides such as silica, alumina, or titania. Of course, oxides themselves make up an important class of catalyst materials used for petroleum refining, commodity and specialty chemical production, and pollution prevention. Unfortunately, the application of UHV surface science methods to the study of oxide surfaces continues to be problematic [3,5–7]. Not only it is difficult to obtain single crystals of suitable size for these studies; even when they are available it can be quite challenging to mount, heat and cool the samples, and the lack of sufficient sample conductivity can prevent ready interpretation of the spectra obtained using charged particle probes. Furthermore, the ability to reproducibly prepare and characterize the surface of a single crystal oxide is by no means trivial [6,7]. For these reasons, it has been estimated that the understanding of oxide surface chemistry and physics lags at least a decade behind that of metals and semiconductors [6].

For surface science and catalysis studies, the development of coupled UHV surface analysis/atmospheric pressure catalytic reactors has been particularly useful [3]. Here again, these instruments have been used almost exclusively for studies of metal catalysts [2–4,8,9] with only a handful of papers published to date [10–13] that have measured moderate pressure reaction rates on well characterized oxide surfaces analyzed in UHV. Thus, in spite of their great practical utility as catalysts and catalyst support materials, a molecular-level understanding of the catalytic chemistry of oxide materials remains elusive.

In this paper, we describe our approach to circumventing many of the difficulties described above that are encountered in UHV surface science studies of oxides. In particular, we will present the results of efforts to grow and characterize thin-film, single crystal oxide surfaces using molecular-beam epitaxy (MBE) techniques for use as model catalysts. We have used these films to begin studies of oxide surface structure and chemistry. Specifically, we will discuss the adsorption and reaction of water on an $Fe_3O_4(0\,0\,1)$ film grown on an $MgO(0\,0\,1)$ substrate. Water/oxide surface chemistry is important to understand because water is ubiquitously present in reactant feed streams (either intentionally or inadvertently), is often a product of reaction, and as an adsorbed species in either molecular or dissociated (i.e., hydroxyl) form, is thought to play a critical role in the mechanisms of many oxide-catalyzed reactions. We have just begun to use these well-characterized model catalysts in a UHV surface analysis/atmospheric pressure catalytic reactor apparatus to perform rate measurements under realistic conditions. Instead of describing our initial experiments, we will summarize some of our previous studies [14–16] of a metal-catalyzed reaction, the CO oxidation reaction over single crystal Ru(0001), to illustrate some of the benefits of these experiments. In particular, we will address the possibility that this reaction can occur by a direct reaction of gas-phase CO with adsorbed oxygen, a so-called Eley–Rideal (E–R) mechanism [15]. We dedicate this latter discussion to the memory of Academician G.K. Boreskov whose work [17], published in the last year of his life, inspired our studies.

2. Experimental

2.1. Synthesis and characterization of model-oxide surfaces

As noted above, it is possible to avoid some of the difficulties of performing UHV studies of oxide surfaces by employing the techniques of epitaxial growth. By growing thin (≈10 nm), insulating films on conducting substrates [18–24], or by doping these epitaxial films to increase conductivity [25,26], it is possible to perform these measurements. In addition, epitaxial growth techniques have enabled crystalline materials to be synthesized in thin-film form with a level of structural quality and purity that is unprecedented in bulk crystal growth technology [27]. We are using plasma-assisted molecular beam epitaxy (MBE) techniques to grow oxide thin-films to use as model catalyst substrates. Many of the details of the custom-designed dual chamber UHV system [23] and the specific conditions used to grow the $Fe_3O_4/MgO(0\,0\,1)$ film [28] have been published elsewhere. Briefly, the MBE chamber is configured specifically for oxide epitaxy with metal evaporation sources and a

UHV-compatible electron cyclotron resonance (ECR) plasma oxygen source, as well as reflection high energy electron diffraction (RHEED) optics for real-time characterization of the growing film. Appended is a surface analytical chamber with capabilities for low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS) and diffraction (XPD). Films were grown with an oxygen partial pressure of 2×10^{-6} Torr, an Fe evaporation rate of ~0.6 Å/s, and an MgO(0 0 1) substrate temperature of 250°C, the relatively low substrate temperature being required to eliminate Mg diffusion outwards as this occurred at higher temperatures. The total film thickness was ~200 Å.

2.2. *UHV studies of oxide surface chemistry*

Studies of the surface chemistry of the Fe_3O_4/MgO(0 0 1) film were conducted in a stainless-steel ultra-high vacuum (UHV) system with a base pressure of 1.0×10^{-10} Torr. This system includes a single pass cylindrical mirror analyzer for Auger electron spectroscopy (AES), an ion sputtering gun, a quadrupole mass spectrometer (QMS) for temperature-programmed desorption (TPD), and LEED optics. The sample manipulator allows for sample temperatures from ~90 to ~750 K to be obtained by liquid nitrogen cooling and resistive heating, with sample temperatures monitored by a W/Re thermocouple spot-welded to a Ta ring in contact with the sample surface. The sample was cleaned by a number of 30–60 min cycles of annealing at T=523–573 K in 1.0×10^{-7}–1.0×10^{-6} Torr O_2 and in UHV. These values of temperature and oxygen pressure, which are close to those used to grow the Fe_3O_4(001) epitaxial film [28], were chosen to keep the required film stoichiometry (Fe_3O_4) and to prevent significant Mg diffusion from the MgO substrate into the film. During sample cleaning and all subsequent experiments, the surface stoichiometry and structure were monitored by AES and LEED, respectively.

In TPD experiments, pure D_2O was adsorbed at T=110 K by dosing through a leak valve, and then, while the sample temperature was linearly ramped at 2 K/s up to T=710 K, the signals of mass 4 (D_2) and mass 20 (D_2O) were monitored by the QMS. Because none of our experiments revealed any appreciable D_2 desorption, only TPD spectra of D_2O will be further considered here. The QMS is equipped with a custom stainless-steel cone, and during TPD measurements the center of the sample was placed within ~2 mm from the cone nozzle. Such an arrangement allowed for the detection of the desorption products primarily from the center of the sample. This eliminated, for the most part, the unwanted contribution due to water desorption from the Ta parts of the sample assembly. More details about the apparatus and experimental methods will be published elsewhere [29].

2.3. *Kinetic studies of model catalysts*

The CO oxidation experiments to be described below were performed in a custom built system which couples an UHV analysis chamber to a moderate pressure (<100 Torr) reactor, with the two being separated by a gate valve. The UHV analysis chamber is equipped with a wide array of analytical techniques. For this study we used primarily AES and LEED. The sample could be transferred from the reactor to the UHV analysis chamber within 5 min after reactor pumpdown with a typical base pressure of 10^{-9} Torr during spectroscopic analysis. The Ru(0 0 0 1), oriented to within ±0.5 degrees, was mounted on the transfer device using Ta wires spot welded to the edges of the sample for resistive heating, along with a W/Re thermocouple to monitor the crystal temperature. Sample cleaning was accomplished with previously published procedures [30].

Catalytic reactions were performed in a batch mode, with all products and reactants being measured by gas chromatography (GC). The experimental procedure for making a rate measurement was as follows: (1) the gate valves to the UHV analysis chamber and the reactor pump were closed; (2) the reactants were leaked into the reactor; (3) the sample was ramped to the reaction temperature; (4) held (±2 K) there for a specified time interval; (5) cooled to room temperature; finally, (6) the gases in the reactor were expanded into the evacuated GC sampling loops.

3. Results and discussion

3.1. *Synthesis of model oxide surfaces*

We have used plasma-assisted MBE to synthesize a number of oxide thin films [23–28] including MgO,

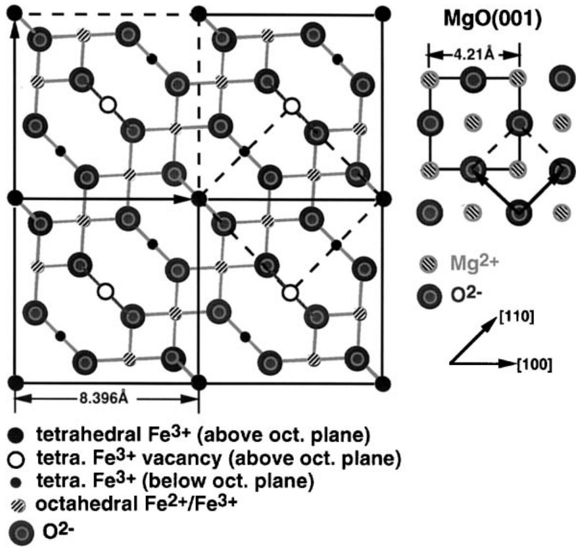

Fig. 1. Proposed surface structure of Fe_3O_4/MgO(001) – $(\sqrt{2}\times\sqrt{2})R45^\circ$, along with the known surface structure of MgO(0 0 1) [28].

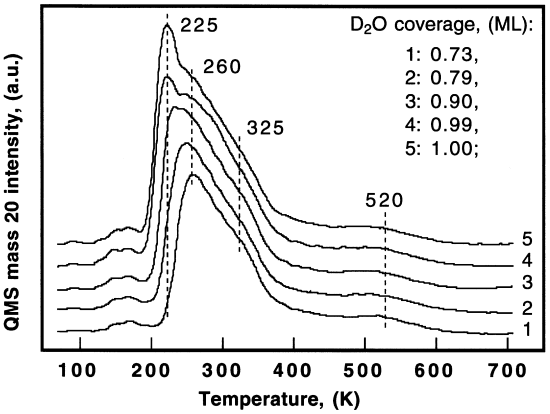

Fig. 2. Water desorption from a Fe_3O_4/MgO(0 0 1) surface at water coverages near one monolayer (ML). Adsorption was carried out below 100 K and the sample temperature was ramped at a rate of 2 K/s. Adapted from Ref. [29].

TiO_2 (pure and Nb-doped), and the oxides of Fe, and have used them to study oxide surface structure and reactivity. Here, we briefly give an example of this for the case of Fe_3O_4(0 0 1) grown on an MgO(0 0 1) surface (more details being given elsewhere [28]). This substrate was chosen because of good lattice and crystal symmetry matching. The Fe_3O_4(0 0 1) film must be grown at a relatively low substrate temperature of 250°C to avoid interfacial reaction and Mg diffusion outwards. The surface was found to display a $(\sqrt{2}\times\sqrt{2})$R45° reconstruction. A model proposed to explain the observed diffraction pattern, illustrated in Fig. 1, consists of a tetrahedrally coordinated Fe^{+3}-ion terminated surface with every other tetrahedral iron missing. These sites reside above a plane of iron (in octahedral coordination) and oxygen ions where every other iron ion is in either a +2 or +3 oxidation state. Thus, this surface can be expected to display a rich surface chemistry. We will discuss one example of this in the next section.

3.2. UHV studies of oxide surface structure and chemistry

We have recently been studying the adsorption and reaction of water and formic acid on a number of single crystal [31–35] and model thin oxide films [21,22,29] and have found that the surface chemistry of these species is strongly dependent on the atomic-level structure of the oxide surface. For example, the dissociation of water to hydroxyl groups on TiO_2 appears to require not only acidic cation adsorption sites, but also the close proximity of basic oxygen ions in order for water O–H bonds to break [34]. Similarly, TPD results obtained on the reconstructed Fe_3O_4(0 0 1) described above (shown in Fig. 2) contains three main chemisorbed states of water in the first monolayer, with TPD peak temperatures at saturation of 320, 280 and 225 K, respectively [29]. We also found that each state is approximately equally populated with concentrations of around 1/3 ML. Recall from above that the proposed surface structural model, consistent with LEED results, consists of three distinct cationic iron sites, tetrahedral Fe^{+3}, and octahedral Fe^{+2} and Fe^{+3} sites. For this reason, we have tentatively assigned the three TPD states to desorption of water from these three distinct cation iron sites on the surface [29].

Further identification of the adsorption sites responsible for each TPD state was obtained by adsorbing water subsequent to oxidation of the surface. Oxidation was carried out by heating the sample to 350 K during water exposure, resulting in a surface with a stoichiometry closer to Fe_2O_3; i.e., only Fe^{+3} sites in the surface region. TPD of water from this "fully oxidized" iron oxide surface showed only the high and low temperature peaks at 320 and 225 K, respectively [29]. Thus, it seems reasonable to assign the TPD peak at 280 K to the desorption of water from octahedral Fe^{+2} sites on the Fe_3O_4(0 0 1) surface.

3.3. *Kinetic studies of model catalysts*

The use of custom moderate-pressure catalytic reactor/UHV surface analysis instrumentation has provided significant new insights into the mechanisms of a number of metal-catalyzed reactions [2–4,8–16]. Some recent examples of this from our work will be briefly described in the following sections. However, we are aware of only a few recent efforts to apply such an apparatus to the study of the catalytic chemistry of oxide materials [10–13]. This is surprising considering the demonstrated utility of such systems to study metal-catalyzed reactions that are sensitive to surface structure. Due to the fact that the electronic structure of covalent and ionic insulators is highly localized in comparison with conductive metals, one might expect that the oxide catalytic chemistry would be rich with examples of structure sensitivity [5,36,37]. Correspondingly, metal oxides can be expected to show a much greater diversity of surface structures, including varied defect types and geometries, so that it will probably be more difficult to define structure/activity relationships in these systems. For these reasons, we have recently initiated studies of the photocatalyzed oxidation of small hydrocarbon molecules over model single crystal titania catalysts, using our catalytic reactor/UHV surface analysis system. The results to date are too preliminary in nature for this paper. Rather, in the following we present results from our previous studies of Ru-catalyzed CO oxidation to demonstrate the types of useful information that can be obtained in these experiments.

As mentioned above, Boreskov and co-workers [17] published in 1984 a study of the relative rates of CO oxidation carried out in UHV at pressures of $\sim 10^{-7}$ Torr over a variety of single crystal metal surfaces. These authors were able to correlate the rates of reaction with the relative heats of adsorption for oxygen on these various metals. For ease of comparison, some of their results are shown in Fig. 3. Also shown in the figure are results that we obtained subsequently at moderate pressures of $\sim$25 Torr [16]. What is perhaps most strikingly evident when comparing the relative rates obtained at low and high pressures is the behavior of Ru. At low (UHV) pressures, CO oxidation rates are lowest on Ru by over an order of magnitude when compared to other Group VIII precious metals, Pt, Pd, Rh, and Ir. On the contrary, reaction rates over Ru at moderate pressure were significantly greater than any of these other metals. These latter moderate pressure results were in quantitative agreement with rates measured over realistic supported catalysts under similar conditions, demonstrating the appropriateness of the model catalysts.

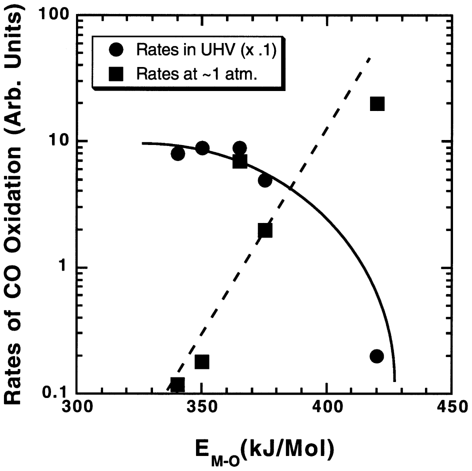

Fig. 3. Relative rates of CO oxidation obtained over various single crystal metal catalysts, plotted as a function metal-oxygen bond energy, E_{M-O}, at low (circles) [17] and moderate (squares) [16] pressures. Curves have been added as a guide to the eye.

We have previously speculated [15] that the reason for this apparent discrepancy between the moderate and low (UHV) pressure rate measurements may be due to an altered mechanism for the CO oxidation reaction over Ru at high pressures. At low pressures, the reaction has been shown to occur by a Langmuir–Hinshelwood mechanism between adsorbed CO and O. This reaction is particularly slow on Ru because oxygen is bound most strongly to the surface, as demonstrated in Fig. 3. At moderate pressures, Ru is uniquely able to stabilize a high coverage of oxygen under reaction conditions without a concurrent oxidation of the near surface region of the metal. Oxygen at this coverage, estimated to be equal to one monolayer (ML) in a (1×1) surface phase [14,15,38], is much more active than at lower coverages. For example,

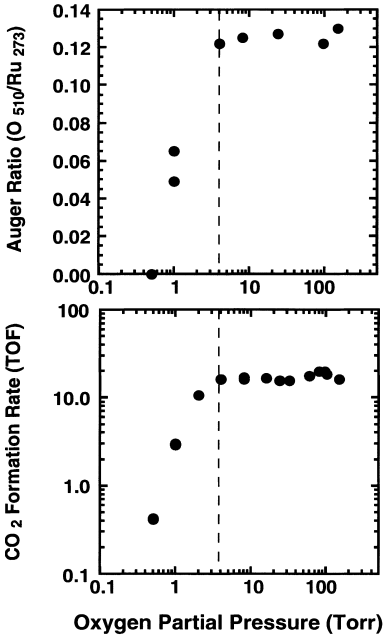

Fig. 4. A comparison of the effect of O_2 partial pressure on the rate of reaction and the level of surface oxygen detected following reaction by AES. Adapted from Ref. [14].

Fig. 4 shows the rates of CO oxidation and oxygen coverages obtained as a function of oxygen partial pressure [14]. In the O-(1×1) surface phase, CO would be sterically prevented from bonding directly to the Ru surface. In fact, in-situ FTIR spectra taken during moderate pressure reaction showed no evidence for adsorbed CO at reaction temperatures or after cooling the crystal to room temperature in the reactant mixture [15]. These and other results of our kinetic and spectroscopic studies are not readily interpreted by a simple Langmuir–Hinshelwood reaction mechanism between chemisorbed reagents. On this basis, we proposed that reaction could be occurring between gas-phase (direct or Eley–Rideal, E–R, mechanism) or weakly adsorbed CO and the O-(1×1)-Ru(0 0 0 1) surface [15].

From the apparent activation energy and rates of reaction determined in the medium pressure studies, it is possible to make estimates of the feasibility of an E–R route. If the E–R reaction is assumed to occur via translationally excited molecules surmounting a barrier equivalent in height to the apparent activation energy, E^*, then the flux of molecules impinging upon the catalyst surface and having this energy can be calculated using elementary statistical mechanics. In this way, it is easy to show that this flux, $J(E^*)$, is mathematically given by

$$J(E^*) = P(2\pi mkT)^{-1/2}\exp(-E^*/kT), \tag{1}$$

where m and P are the molecular weight of CO and its partial pressure in the reactor. Substituting our measured activation energy of 19.5 kcal/mol [14] into Eq. (1) yields a flux approximately 2000 times smaller than our measured turnover frequency. This demonstrates that the reaction cannot be occurring solely by a simple direct E–R mechanism in which the translational energy of the incoming molecule is responsible for surmounting the barrier. This conclusion is in good agreement with recent theoretical predictions for this reaction [39]. Thus, a detailed mechanistic understanding of the interesting phenomenological kinetics requires further study. As such, we plan to use molecular beam surface scattering techniques to probe this reaction in the near future.

4. Summary

A case is made for the need for fundamental studies of the physical and chemical properties of oxide surfaces in order to develop an improved understanding of their important catalytic behavior. This goal remains elusive due, in part, to the difficulty of performing electron spectroscopic measurements of these materials in UHV. We have described in the paper, our relatively new program to address these issues, including the growth and characterization of model oxide surfaces by MBE techniques. We have found evidence for variable reactivity of a particularly important molecule, water, with three distinct cationic sites on an Fe_3O_4(0 0 1) surface grown epitaxially on an MgO(0 0 1) substrate. Besides studies of the adsorption and reaction of important catalytic reagents with model oxide surfaces in UHV, we are also utilizing a moderate-pressure catalytic reactor/surface science apparatus. To demonstrate the utility of these latter experiments, we discussed some details of our previous work on the CO oxidation reaction over Ru(0 0 0 1) that continues to receive considerable attention [38,39]. These studies have helped to explain an interesting anomaly in the literature [16,17] concerning the relative rates of this reaction over a variety of transition metal surfaces when performed at low (UHV) or high (∼1 atm.) pressures.

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