

Surface Science

Room: 611 - Session SS2-WeA

Oxide Surface Structure I

Moderator: R.L. Kurtz, Louisiana State University

1:40pm **SS2-WeA1 Diffusion of Bridge-bonded Oxygen Vacancies on TiO₂(110)**, *Z. Zhang*, Pacific Northwest National Laboratory, *Q. Ge*, Southern Illinois University, *S.-C. Li*, University of Texas at Austin, *B.D. Kay*, Pacific Northwest National Laboratory, *J.M. White*, University of Texas at Austin, *Z. Dohnálek*, Pacific Northwest National Laboratory

Since oxygen atom vacancies play a central role in the behavior of oxide materials, determining their properties is widely pursued both experimentally and theoretically. Rutile TiO₂(110) has become a model system for the studies of lattice oxygen defects - bridge-bonded oxygen vacancies (BBO_V's). Despite that, surprisingly little is known about the spatial distribution and/or mobility of these BBO_V sites. As a function of temperature between 340 and 420 K, we report here the first measurements and calculations of the intrinsic mobility of BBO_V's on a rutile TiO₂(110) surface. Under conditions where interference by adsorbates was negligible, isothermal atomically-resolved scanning tunneling microscope images that track individual vacancies in real time show that vacancies migrate along bridge-bonded oxygen (BBO) rows. The hopping rate increases exponentially with increasing temperature with experimental activation energy of 1.15 eV. Density functional theory calculations are in very good agreement giving an energy barrier for hopping of 1.03 eV. In agreement with the theory, the BBO_V distribution determined by analysis of the STM images indicates short-range repulsive interactions between vacancies on a given BBO row. The research described here was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

2:00pm **SS2-WeA2 Probing the Structures of CeO₂(111) Thin Films and Ceria-Supported Metal Particles with Scanning Tunneling Microscopy**, *J. Zhou*, *A.P. Baddorf*, *V. Meunier*, *S.V. Kalinin*, *S.H. Overbury*, *D.R. Mullins*, Oak Ridge National Laboratory

Ceria oxide and ceria-supported metal nanoparticles are important heterogeneous catalysts. They exhibit unique chemical reactivity dependent on Ce oxidation state as revealed by our previous XPS and TPD studies. To elucidate the nature of their reactivity, we investigated their structure and morphology using STM. Reducible (111) oriented thin films were grown in situ on Ru(0001) under ultrahigh vacuum conditions. Our data demonstrate that surface structures of ceria films are dependent on the film thickness and the degree of ceria reduction. Hexagonal superlattice structures consisting of five CeO₂ unit cells coincident with seven Ru unit cells can be produced when the films are two or three layers thick and disappear with the increase of film thickness. DFT calculations were performed to explain the origin of these superlattice structures. Fully oxidized CeO₂(111) film exhibits a fairly low density of point defects due to the formation of O vacancies. However, the number of surface defects increases as the ceria film is reduced. Metal particles (Pd and Rh) were vapor-deposited onto ceria thin films at 300 K. The growth of metal particles was investigated by STM as a function of metal coverage, post-deposition annealing temperatures, as well as Ce oxidation state. The research is sponsored by DOE BES Division of Chemical Sciences, Geosciences, and Biosciences.

2:20pm **SS2-WeA3 Structure and Stability of Cerium Oxide Surfaces in an Oxidizing Environment from First-Principles**, *M. Fronzi*, *A. Soon*, The University of Sydney, Australia, *B. Delley*, Paul Scherrer Institut, Switzerland, *E. Traversa*, University of Rome "Tor Vergata", Italy, *C. Stampfl*, The University of Sydney, Australia

Because of its peculiar and desirable properties, cerium oxide, has been the object of intense interest in relation to solid oxide fuel cells (SOFC) as well as to heterogeneous catalysis, e.g., it can effectively reduce NO_x emissions as well as convert harmful carbon monoxide to carbon dioxide. Since it behaves as a good ionic transporter, and at the same time as a good catalyst, cerium oxide finds application both as an electrolyte and as an anode support in SOFCs. In anode reactions, it plays an active part in the catalysis of the fuel cell, and thus it is important to investigate the properties of the oxide surfaces exposed to an anodic fuel cell gas environment (e.g. methane, CH₄). Furthermore, for a particular subclass of fuel cells (single

chamber) the anodic side is exposed to oxygen as well as the fuel. For this reasons it is of high importance to understand the behavior of cerium oxide in varying oxygen environments. Using density-functional theory as implemented in the DMol³ code,¹ we investigate the structure and stability of CeO₂ surfaces under realistic conditions using the approach of ab initio atomistic thermodynamics.² From calculation of the surface free energy, we obtain the pressure-temperature surface phase diagram. This allows us to identify and predict stable, and potentially catalytically important, structures and stoichiometries under varying pressure and temperature conditions. We investigate many different geometries for the low index (100), (110), and (111) surfaces, including structures containing defects. For a wide range of the oxygen chemical potential we find that the thermodynamically most stable surface is CeO₂(111). For increasingly more reducing conditions, surfaces with oxygen vacancies become more stable, followed by a structure which through significant atomic relaxation, exhibits an interesting morphological transformation into a structure with a Ce₂O₃(0001)-like surface.

¹B. Delley, J. Chem. Phys. 92, 508 (1990); ibid. 113, 7756 (2000).

²K. Reuter, C. Stampfl and M. Scheffler, in Handbook of Materials Modeling, Volume 1, Fundamental Models and Methods, Sidney Yip (Ed) (2005).

2:40pm **SS2-WeA4 Revealing Atomic Structures on Oxide Surfaces with the Dynamic Force Microscope**, *M. Reichling*, Universität Osnabrück, Germany **INVITED**

Nanostructures on oxides are most important in numerous fields of science and technology. One of the most prominent ones is chemical catalysis where oxides play a major role as support, storage material and in providing catalytically active centres. Dynamic scanning force microscopy (SFM) operated in the non-contact mode is the method of choice for the atomic scale characterisation of oxide surfaces and nanostructures on surfaces. The state of the art in highest resolution dynamic SFM on oxide systems is illustrated for structures on CeO₂(111), TiO₂(110), and Al₂O₃/Ni₃Al(111). Individual atoms and atomic arrangements can be imaged and in some cases a quantitative understanding of atomic contrast formation can be obtained with the help of atomistic simulations. Defects are revealed to play a major role in surface chemical reactions studied at the atomic scale while the dynamic SFM also facilitates the manipulation of molecules on oxide surfaces.

4:00pm **SS2-WeA8 The Use of High-Field Nuclear Magnetic Resonance Spectroscopy to Study the Surface Structure of Poorly Crystalline γ -Al₂O₃ Surfaces**, *J.H. Kwak*, *J.Z. Hu*, *D.H. Kim*, *J. Szanyi*, *C.H.F. Peden*, Pacific Northwest National Laboratory

γ -alumina, one of the metastable 'transition' alumina structural polymorphs, is an important catalytic material both as an active phase and as a support for catalytically active phases, with widespread applications ranging from petroleum refining to automotive emission control. As such, the bulk and surface structure of γ -Al₂O₃, and its formation and thermal stability have been and continue to be the subject of a considerable amount of research, including attempts to prepare model surfaces via the controlled oxidation of NiAl alloy single crystals. However, due to the low crystallinity and very fine particle size of γ -Al₂O₃, it is very difficult to apply well-established analytical techniques for determining its surface structures. Of particular importance for understanding the catalytic properties of γ -Al₂O₃, relating its surface structure to the origin of Lewis acidity has been of considerable interest and has been studied by FTIR and solid state NMR spectroscopies, and most recently by theoretical calculations. In this presentation, we report the first use of very high field (21.1T) NMR to identify and quantify surface Al species thought to be responsible for imparting Lewis acidity to the γ -Al₂O₃ surface. In particular, a peak in the NMR spectrum at ~23 ppm with relatively low intensity, can be assigned to 5-coordinated Al³⁺ ions, and can be clearly distinguished from the two other peaks representing Al³⁺ ions in tetra-, and octahedral coordination sites. Spin-lattice ²⁷Al relaxation time measurements clearly show that these penta-coordinated Al³⁺ sites are located on the surface of the γ -Al₂O₃ support. Furthermore, we report the first observation of preferential anchoring of an impregnated catalytic phase onto these penta-coordinated Al³⁺ sites by noting that BaO deposition onto γ -alumina resulted in the loss of intensity of the 23 ppm peak, and that the intensity loss observed was linearly proportional to the amount of BaO deposited. Thus, the results of this study strongly suggest that, at least for BaO, these penta-coordinated Al³⁺ ions are the nucleation sites. The implications of these results, especially with respect to the recent and extensive use of theoretical calculations for determining the γ -Al₂O₃ surface structure, will be discussed.

4:20pm **SS2-WeA9 Ab Initio Studies of Adsorption and Diffusion Processes on α -Al₂O₃ (0001) Surfaces**, E. Wallin, J.M. Andersson, E.P. Munger, V. Chirita, U. Helmersson, Linkoping University, Sweden

Alumina, Al₂O₃, is one of the technologically most important ceramic materials. Due to the existence of a variety of different polymorphs, it finds use in a wide range of applications. Consequently, alumina thin film growth has been studied intensely in the past. However, the mechanisms behind the formation of different phases and microstructures are still poorly understood, especially for physically vapor deposited films. An increased atomic scale understanding of alumina surface processes would thus be an important step towards a more complete understanding and control of the deposition process. In the present work, density functional theory based methods were used to study the adsorption of Al, O, AlO, and O₂ on differently terminated α -alumina (0001) surfaces. The results show, e.g., that several metastable adsorption sites exist on the O-terminated surface, providing a possible explanation for the difficulties in growing α -alumina at lower temperatures, where the energy available for adatom diffusion to the bulk site might be insufficient. Moreover, the results show that Al adsorption in the bulk position is unstable or considerably weakened for completely hydrogenated surfaces, indicating that hydrogen, e.g. stemming from residual water in vacuum systems, might hinder crystalline α -alumina growth. Furthermore, energy barriers for different surface diffusion processes were investigated using the nudged elastic band method, showing, e.g., that the Al surface diffusion barrier is 0.7 eV on the Al-terminated (0001) surface. This is lower than what might be expected for a phase where synthesis at low temperatures is difficult (which is the case for α -alumina), supporting previous experimental studies suggesting the nucleation step of growth to be of crucial importance (see, e.g., Andersson et al., J. Vac. Sci. Technol. A 22, 117 (2004)). The computational results are discussed in the context of alumina growth and provide important insight into how different factors influence the growth and how deposition processes can be optimized in order to synthesize alumina films with desired properties.

4:40pm **SS2-WeA10 Iron Oxide Thin Films on Pd(111) and Pt(111)**, L.R. Merte, J. Knudsen, H.H. Sørensen, R.T. Vang, University of Aarhus, Denmark, M. Mavrikakis, University of Wisconsin-Madison, F. Besenbacher, University of Aarhus, Denmark

The Water Gas Shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) plays an important role in the production of clean hydrogen from fossil fuels by reducing the concentration of CO in the reformed gas mixture and increasing the yield of hydrogen. The catalysts currently available necessitate a two-stage WGS process, where a high-temperature reactor is used to obtain sufficient turnover rates and a low-temperature reactor is used to push the equilibrium of the exothermic WGS reaction towards CO₂ and H₂ and thereby achieve higher overall conversion. Proposed systems for on-board hydrogen production to power, for example, vehicle-mounted fuel cells would require a WGS catalyst that is sufficiently active at low temperatures and is robust against degradation and poisoning under intermittent operating conditions. Development of such catalysts is therefore important if this technology is to be implemented. Iron-doped palladium based catalysts have been shown to be interesting candidates in this regard¹, and our goal has been to expand our current understanding of the basic processes occurring in the Fe/Pd system, among which is the formation of iron oxide under WGS conditions. In this study we have synthesized different model systems consisting of thin iron oxide films on Pd(111) and, for comparison, Pt(111) and have shown through scanning tunnelling microscopy (STM) measurements that the morphology of these films depends strongly on the preparation conditions. Furthermore, we have studied the interaction of these films with hydrogen and the structural changes occurring upon reduction. We have also used thermal desorption spectroscopy (TDS) to examine the interaction of CO with these model systems in order to identify any chemical properties unique to the Fe/Pd system that may be relevant for the WGS reaction.

¹ Zhao, S. and R. J. Gorte (2004). "The activity of Fe-Pd alloys for the water-gas shift reaction." *Catalysis Letters* 92(1-2): 75-80.

5:00pm **SS2-WeA11 Factors Affecting Polarization Dependent Adsorption on Ferroelectric Oxide Surfaces**, D.B. Li, J. Garra, A. Kolpak, A. Rappé, D.A. Bonnell, University of Pennsylvania

Domain specific chemical reactivity has been demonstrated for ferroelectric surfaces in ambient and aqueous environments. To understand the factors that affect polarization dependent adsorption on ferroelectric surfaces, in situ studies in UHV were carried out on BaTiO₃ and lead zirconate titanate (PZT) surfaces. Polarization was oriented in situ with a metal coated scanning probe microscope (SPM) tip, surfaces were exposed to CO₂ at various dosages, and adsorption was monitored through its effect on local surface potential. Using SPM, we poled the ferroelectric substrates such that sub-micron meter sized out-of-plane domains terminate the surfaces. Surface potentials of these positive and negative domains were then

measured by frequency modulation scanning surface potential microscopy (FM-SSPM). The influence of domain polarization on molecular adsorption was examined by comparing surface potential variation as a function of CO₂ dosages. Positive and negative domains exhibited quantitatively different variations in surface potential. The differences are discussed in terms of possible adsorption mechanisms. The effect of the magnitude of the polarization is examined by comparing results on PZT and BaTiO₃ with first principles calculations of surface relaxations and associated adsorption energies. The effect of defects is examined by comparing results on BaTiO₃ single crystals before and after UHV annealing to produce oxygen vacancies.

Authors Index

Bold page numbers indicate the presenter

— A —

Andersson, J.M.: SS2-WeA9, 2

— B —

Baddorf, A.P.: SS2-WeA2, 1
Besenbacher, F.: SS2-WeA10, 2
Bonnell, D.A.: SS2-WeA11, 2

— C —

Chirita, V.: SS2-WeA9, 2

— D —

Delley, B.: SS2-WeA3, 1
Dohnálek, Z.: SS2-WeA1, 1

— F —

Fronzi, M.: SS2-WeA3, 1

— G —

Garra, J.: SS2-WeA11, 2
Ge, Q.: SS2-WeA1, 1

— H —

Helmersson, U.: SS2-WeA9, 2

Hu, J.Z.: SS2-WeA8, 1

— K —

Kalinin, S.V.: SS2-WeA2, 1
Kay, B.D.: SS2-WeA1, 1
Kim, D.H.: SS2-WeA8, 1
Knudsen, J.: SS2-WeA10, 2
Kolpak, A.: SS2-WeA11, 2
Kwak, J.H.: SS2-WeA8, 1

— L —

Li, D.B.: SS2-WeA11, 2
Li, S.-C.: SS2-WeA1, 1

— M —

Mavrikakis, M.: SS2-WeA10, 2
Merte, L.R.: SS2-WeA10, 2
Meunier, V.: SS2-WeA2, 1
Münger, E.P.: SS2-WeA9, 2
Mullins, D.R.: SS2-WeA2, 1

— O —

Overbury, S.H.: SS2-WeA2, 1

— P —

Peden, C.H.F.: SS2-WeA8, 1

— R —

Rappe, A.: SS2-WeA11, 2
Reichling, M.: SS2-WeA4, 1

— S —

Soon, A.: SS2-WeA3, 1
Sørensen, H.H.: SS2-WeA10, 2
Stampfl, C.: SS2-WeA3, 1
Szanyi, J.: SS2-WeA8, 1

— T —

Traversa, E.: SS2-WeA3, 1

— V —

Vang, R.T.: SS2-WeA10, 2

— W —

Wallin, E.: SS2-WeA9, 2
White, J.M.: SS2-WeA1, 1

— Z —

Zhang, Z.: SS2-WeA1, 1
Zhou, J.: SS2-WeA2, 1