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Preface

Metallic oxides: filling the gap between catalysis and surface science

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This special edition deals with the reaction of oxide surfaces with emphasis on model reactions of model surfaces for the understanding of catalytic reactions and catalytic processes. The issue includes 23 contributions covering a broad spectrum of surface science and catalytic investigations. Atomic imaging by STM and NC AFM of local sites on CeO_2, TiO_2, WO_3, Pd/SiO_2 and PdO are providing new insights into the role of surface cations and surface point (and cluster) defects for both adsorption and reactions. Kinetic parameters can now be obtained by following atomic motion on insulator oxides. By monitoring oxygen hopping on the surface of $CeO_2(1\,1\,1)$ single crystal, Namai et al. [1] have calculated the activation energy of the hoping process. The reaction of methanol on point/cluster defects of $CeO_{2-x}(1\,1\,1)$ was also studied by the same group who concluded that methanol adsorption occurs preferentially on these defects. Two complementary studies of low index anatase TiO_2 single crystal surfaces by two groups [2,3] are also presented. The presence/absence of point defects depending on the surface structure was tracked. For example, it was shown that the anatase $(1\,0\,1)$ TiO_2 surface does not reconstruct, and while it does contain two-fold bridging O atoms on the surface, these are stable; no evidence of formation of point defects (unlike on rutile TiO_2 single crystal surfaces). Evidence of surface reconstruction of the anatase $TiO_2(0\,0\,1)$ surface to (1×4) under UHV annealing is given by both groups. This surface, which contains under-coordinated Ti atoms, dissociates carboxylic acids to carboxylates very similarly to other rutile TiO_2 single crystal surfaces. In an ambitious study dealing with the common but still not well understood concept of metal–support interactions, Min et al. [4] have prepared ultra-thin well-ordered SiO_2 films on a $Mo(1\,1\,2)$ substrate and deposited Pd metal on top. The authors have shown (by STM and other spectroscopic tools) that oxygen vacancies as well as excess Si play a critical role in determining the strength of the metal–support interaction. In general, sintering is favored in those systems that show a weak metal–support interaction, whereas encapsulation and/or inter-diffusion and alloy formation occurs for the strongly interacting systems. The use of computational methods (primarily DFT that is now making impressive contributions to investigations of surface phenomena) is presented by the work of several groups: Calatayud et al. [5], Sensato et al. [6], Branda et al. [7], Wendt et al. [8], and Rodriguez [9]. In their work, the effects of acid–base properties of dopants, and of coordination are shown to be dramatic to catalytic reactions. Dissociative adsorption of methanol was computed by Branda et al. [7] using cluster DFT models and their results tend once more to indicate the crucial role of under-coordinated atoms on the surface for molecular adsorption. DFT periodic calculations for solid solutions of $Sn_xTi_{1-x}O_2$ were conducted by Sensato et al. [6] in order to understand the role of this solid solution in the enhancement of the photo-catalytic rate when compared to TiO_2 alone. Small extents of Sn substitution for Ti in rutile TiO_2, increase the photo-activity of the rutile by up to 15 times for the oxidation of acetone. The authors find that Sn substitution increases the oxidation–reduction potential of the oxide as well as causing the lowest energy transition to be indirect. These two effects are probably the key factors controlling the rate of photo-generated electron–hole recombination. In an

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extensive review by Calatayud et al. [5], the rich chemistry of adsorption and reaction on solid oxides is tied to the acid–base properties of unreduced oxides and explained from first principles. The correlation between the electronic and chemical properties of a series of different oxide materials (molybdates, perovskites, fluorites and rocksalt structures) was investigated by Rodriguez [9]. Particular emphasis was given to $DeNO_x$ and $DeSO_x$ applications. As stated by Rodriguez, electronic effects should be carefully considered when dealing with mixed oxide catalysts. For example, in an endeavor to understand the effect of doping of CeO_2 by Zr or Ca ions, it was shown that the structural perturbations in the lattice of ceria made it easier to remove oxygen atoms, resulting in the appearance of Ce 4f occupied states at about 2 eV above the CeO_2 valance band. These occupied states attributed to Ce^{3+} are now well positioned for bonding interactions with orbitals of adsorbates. The effect of promoters (Mo) on the oxidation of hydrocarbons on promoted iron phosphate was studied by Ai [10] who is proposing that the enhancement of the reaction is due to more efficient redox cycles in the presence of Mo.

In an interesting experimental work, Dohshi et al. [11] changed the coordination environment of Ti atoms by mixing TiO_2 with either SiO_2 or B_2O_3. Although the effect of the host materials is not well understood, there seems to be a correlation between tetrahedral/octahedral coordination of Ti atoms and their photo-catalytic properties. Using a similar idea, yet on a totally different system (perovskite materials), Bedel et al. [12] show that only the orthorhombic structure of $LaCo_xFe_{1-x}O_3$ is active for Fischer Tropsch synthesis while the rhombohedral structure is inactive. The authors explain the difference in terms of the capacity of the orthorhombic structure to accommodate large number of cation vacancies.

A synthetic approach for the design of specific sites on oxides was conducted by two groups. Xue et al. [13] have prepared an alumina material (with a very high density of Lewis acid sites) from an Al-alkoxide-amine adduct that resulted in enhancing the catalytic activity five-fold for the aminolysis of epoxide when compared to a more conventionally prepared alumina. The other study was conducted on manganese oxides with a tunnel structure (OMS-2) for the selective oxidation of alcohols by Makwana et al. [14]. It was shown that ion exchange by H^+ resulted in weakening of the Mn–O bond and this in its turn enhanced the oxidation reaction.

A nice example of bridging both the material and pressure gaps is a comprehensive study for the oxidation of CO, conducted by two groups [8,15] on RuO_2 single crystal and catalysts. The TON for CO oxidation over supported RuO_2 catalysts was found similar to that observed on a $RuO_2(1\,1\,0)$ single crystal. Moreover, DFT calculations combined with TPD and surface spectroscopy investigations have shown that on-top oxygen atoms (atoms adsorbed on the five-fold coordinated Ru) are mostly used to re-oxidize the surface and are not directly involved in the recombination with adsorbed CO–CO_2 (unlike bridging surface oxygen atoms).

In a fundamental study of N_2O reactions, Henderson et al. [16] have shown that by carefully creating surface oxygen defects on rutile $TiO_2(1\,1\,0)$ surface they could convert N_2O–N_2 at two temperature domains starting as low as 90 K. The authors attribute (based on results from ab initio computations [17,18]) the two channels observed for N_2 production from N_2O decomposition to two conformers of N_2O (linear and bridging). The oxidation of NH_3 over $Cu(1\,1\,0)$ surface in the presence of oxygen leads to the formation of a nitride or oxynitride phase as seen in the work of Louis-Rose et al. [19]. By a combined kinetic study and in situ FT-IRAS, the reaction between ammonia molecules and surface oxygen atoms was successfully tracked. The reaction of methanol over α-Cr_2O_3 $(1\,0\,\bar{1}\,2)$ single surface was also conducted by Mensch et al. [20]. They show that the O-terminated surface is completely inactive for the reaction. In contrast, upon preferential removal of terminal O atoms, methanol is oxidized on the surface once more due to the presence of under-coordinated Cr atoms. The reaction of H_2S was conducted on the surface of polycrystalline UO_2 surfaces by Wu et al. [21] (the presence of large stocks of uranium oxides and the need to find a more efficient de-sulfurization catalysts were the main reason behind the investigation) and it was shown that the presence of O vacancies is detrimental to both the adsorption and decomposition of H_2S.

Two groups have conducted a comparative study between polycrystalline and single crystal materials. In the first work, Vohs et al. [22] have shown that the reactivity of a high surface area, monolayer vanadia/ceria catalyst is paralleled by that of a 0.5 monolayer ceria film supported on the (1 1 1) surface of CeO_2 single crystal. Both materials were active for the oxidation of methanol to formaldehyde and the temperature at which adsorbed methoxide intermediates underwent dehydrogenation to produce formaldehyde during TPD was found to be a function of the oxidation state of the vanadium. On the other hand, Senanayake et al. [23] have studied the reaction of formaldehyde over UO_2(1 1 1) single crystals and UO_2 powder. While formaldehyde reacted to give a high yield of ethylene (by reductive coupling) on the single crystal, it gave mainly methanol on the powder. The discrepancy of the results between both materials once again shows that other challenges still remain to understand some systems. Sherrill et al. [24] have studied the reactions of acrolein over two types of surfaces of a TiO_2(0 0 1) single crystal. On the defect-containing surface, acrolein is reductively coupled to form C_6 olefins. The high reaction yield of ca. 80% shows the high activity of such surfaces for C–O bond dissociation (due to surface oxygen restoration as tracked by NEXAFS) and C–C bond formation to make olefins. On the stoichiometric surface (the one exclusively composed of acid–base sites), acrolein underwent condensation to give a C_6H_8O product tentatively identified as 2-methyl-2,4-pentadienal. Condensation reactions of acids and aldehydes to ketones were investigated, by Hendren and Dooley [25], on CeO_2 surfaces. The behavior of surface oxygen was also studied because of its potential role in the oxidation part of the reaction, and it was shown that the addition of water increased the production of the final ketone product because it supplies oxygen to the surface to generate the carboxylate intermediates.

The important role of surface oxygen and surface point defects could not be overstated in all the above studies. Clearly the dynamics of oxygen and oxygen vacancies, and of coordination number/local electronic charge associated with the counter-ions, are central to understand the foundation of catalytic reactions on metal oxides. Although the surface science of oxides has seen huge growth in the last decade, it is still faced with old and new challenges to understand the role of the catalytic materials. Previous concepts such as stabilization effects of dopants (important for several technologies such as automobile catalytic converters, for example) and acid–base sites (important for activation of hydrocarbons) are now being explained on the basis of local (atomic) models and probes. The next decade or so will see new inventions and associated with them, inevitably new directions. We do hope that this special edition will serve as a guidepost for future studies needed to understand the complexity of surface reactions on oxide catalysts.

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