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A Study on the Surface Properties of Transition Metal Oxides

***Muralidhara K, Dr. Prabhunath Misra** (Guide)*
Prof. of Physics
Bundelkhand University

ABSTRACT

Transition metal oxides show many interesting phenomena from high-T_c superconductivity to colossal magneto-resistance and multi-ferroicity, triggering intensive studies. However, we have barely tapped into their potential for applications. Oxides, often considered as synonymous with ceramics, bring terms such as china dishes or pottery to mind. However, oxides with transition metals that straddle the subtle boundary between covalent, ionic and metallic bonding show copious physical phenomena, ranging from high-$T_c$superconductivity in layered cuprates, colossal magnetoresistance (CMR) in perovskite manganites, to the coexistence of magnetism and ferroelectricity — termed multiferroicity.

INTRODUCTION

Transition metal oxides are compounds composed of oxygen atoms bound to transition metals. They are commonly utilized for their catalytic activity and semi-conductive properties. Transition metal oxides are also frequently used as pigments in paints and plastics, most notably titanium dioxide. Transition metal oxides have a wide variety of surface structures which affect the surface energy of these compounds and influence their chemical properties. The relative acidity and basicity of the atoms present on the surface of metal oxides are also affected by the coordination of the metal cation and oxygen anion, which alter the catalytic properties of these compounds. For this reason, structural defects in transition metal oxides greatly influence their catalytic properties. The acidic and basic sites on the surface of metal oxides are commonly characterized via infrared spectroscopy, calorimetry among other techniques. Transition metal oxides are also able to undergo photo-assisted adsorption and desorption to control their semiconductivity. One of the more researched properties of these compounds is their response to electromagnetic radiation, which makes them useful catalysts for redox reactions, isotope exchange, specialized surfaces, and a variety of other uses currently being studied.

SURFACE STRUCTURE AND STABILITY

There is very little known about the surface structures of transition metal oxides, but their bulk crystal structures are well researched. The approach to determine the surface structure is to assume the oxides are ideal crystal, where the bulk atomic arrangement is maintained up to and including the surface plane. The surfaces will be generated by cleavages along the planes of the bulk crystal structure. However, when a crystal is cleaved along a particular plane, the position of surface ions will differ from the bulk structure. Newly created surfaces will tend to minimize the surface Gibbs energy, through reconstruction, to obtain the most thermodynamically stable surface. The stability of these surface structures are evaluated by surface polarity, the degree of coordinative unsaturation and defect sites.

BULK STRUCTURES

The oxide crystal structure is based on a close-pack array of oxygen anions, with metal cations occupying interstitial sites.[1] The close-packed arrays, such as face-centered-cubic (fcc) and hexagonal-close packed (hcp), have both octahedral and tetrahedral interstices. [1]

MONOXIDES

Many compounds from first row of transition metal monoxides (MO), from TiO to NiO, have a rocksalt structure. The rock salt structure is generated by filling all octa-hedralsites with cations in an oxygen anion fcc array

DIOXIDES

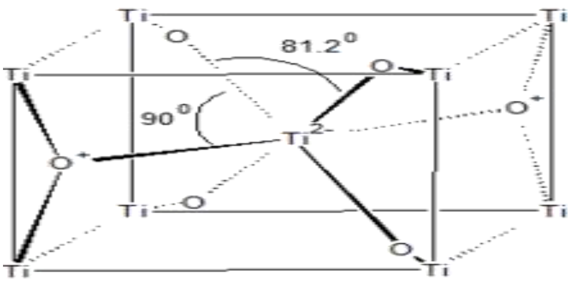
The majority of transition metal dioxides (MO_2) have the rutile structure, seen to the right. Materials of this stoichiometry exist for Ti, Cr, V and Mn in the first row transition metal and for Zr to Pd in the second. The rutile structure is generated by filling half of the octahedral sites with cations of the hcp oxygen anion array.

TRIOXIDES

Few transition metals can achieve the +6 oxidation state in an oxide, so oxides with the stoichiometry MO_3 are rare.

TERNARY OXIDES

The structure of binary oxides can be predicted on the basis of the relative sizes of the metal and oxide ions and the filling of holes in a close packed oxide lattice. However, the predictions of structure are more difficult for ternary oxides. The combination of two or more metals in an oxide creates a lot of structural possibilities. Also, the stoichiometry of ternary oxide may be changed by varying the proportions of the two components and their oxidation states. For example, at least twenty ternary oxide phases are formed between strontium and vanadium including SrV_2O_6, $Sr_2V_2O_5$, $SrVO_3$ and Sr_2VO_4.[5] The structural chemistry of ternary and more complex oxides is an extensive subject, but there are a few structures that are widely adopted by ternary oxides, such as the perovskite structure.



Rutile

PEROVSKITE STRUCTURE

The perovskite structure, ABO_3, is the most widespread ternary phase. The perovskite structure is frequently found for ternary oxides formed with one large (A) and one small cation (B). In this structure, there is a simple cubic array of B cations, with the A cations occupying the center of the cube, and the oxide atoms are sited at the center of the 12 edges of the simple cube.

SURFACE STABILITY

Since very little is known about the surface Gibbs energy of transition metal oxides, polarity of the surface and the degree of coordinative unsaturation of a surface cation are used to compare the stabilities of different surface structures. Also, defect sites can have a huge impact on the surface stability.

POLARITY OF THE SURFACE

When a crystal of a binary oxide is cleaved to generate two new surfaces, each solid’s charge remains neutral. However, the structure of the two newly created surfaces may or may not be the same. If the structures are identical, the surface will be dipoleless and is considered a nonpolar surface. If the structures are different, the surface will have a strong dipole and is considered a polar surface. Examples of nonpolar surfaces include the rocksalt (100) surface, the rutile (100), (110) and (001) surfaces and the pervoskite (100) surface. An example of a polar surface is the rocksalt (111) surface. In general, a polar surface is less stable than a nonpolar surface because a dipole moment increases the surface Gibbs energy. Also, oxygen polar surfaces are more stable than metal polar surfaces because oxygen ions are more polarizable, which lowers the surface energy.

THE DEGREE OF COORDINATIVE UNSATURATION OF A SURFACE CATION

The degree of coordinative unsaturation of a surface cation measures the number of bonds involving the cation that have to be broken to form a surface. As the degree of coordinative unsaturation increases, more bonds are broken and the metal cation becomes destabilized. The destabilization of the cation increases the surface Gibbs energy, which decreases the overall stability. For example, the rutile (110) surface is more stable than the rutile (100) and (001) surfaces because it has a lower degree of coordinative unsaturation.

EXTENSION OF ACID/BASE THEORIES TO SOLIDS

The surface of a metal oxide consists of ordered arrays of acid-base centres. The cationic metal centres act as Lewis acid sites while the anionic oxygen centres act as Lewis bases. Surface Hydroxyl groups are able to serve as Brønsted acid or base sites as they are able to give up or accept a proton.[10] The surface of most metal oxides will be, to some extent, hydroxylated under normal conditions when water vapor is present. The strength and the amount of Lewis And Brønsted acid-base sites will determine the catalytic activity of many metal oxides. Due to this there is a great need to develop standard methods for the characterization of the strength, concentration, and distribution of surface acid-base sites.

The concepts of Lewis acid-base theory and Brønsted-Lowry acid-base theory may be applied to surfaces, however there is no general theory that serves to determine surface acidity or basicity. The qualitative treatment of Brønsted acid base theory is based on the thermodynamic equilibrium constant (K_a) of acid-base reactions between individual molecules in homogeneous systems. This treatment requires measurement of equilibrium concentrations of reactants and products. The presence of two phases also provides a problem for the quantitative acid-base determination of solids. When an acid or base is adsorbed on to an oxide surface it will perturb neighbouring acid-base sites. This perturbation will inevitably influence the relaxation of the surface and make it impossible to have acid-base reactions at the surface which only involve a single surface site.

STRUCTURAL RELATION TO SURFACE ACIDITY/BASICITY

For metal oxides acidity and basicity are dependent on the charge and the radius of the metal ions as well as the character of the metal oxygen bond. The bond between oxygen and the metal is influenced by the coordination of the metal cations and the oxygen anions as well as the filling of the metal d-orbitals. The surface coordination is controlled by the face that is exposed and by the surface relaxation. Structural defects can greatly contribute to the acidity or basicity as sites of high unsaturation can occur from oxygen or metal ion vacancies.

METHODS OF DETERMINING SURFACE ACIDITY/BASICITY

INDICATOR METHOD

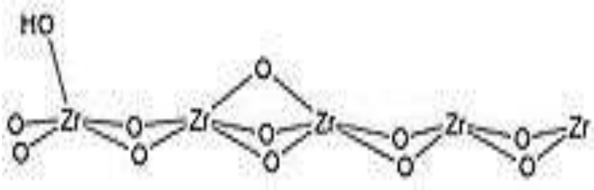
Adsorption of an indicator molecule was first proposed by Hammett for ordering the strength of solid acids and bases. This technique is only applicable to surface Brønsted sites on metal oxides. According to Hammett, the strength of a Brønsted surface site can be determined by the Hammett acidity function,

$$H_o = pK_{BH+} - log\frac{[BH^+]}{[B]}$$

where B is the basic indicator molecule. The concentration of Brønsted acid sites can be determined by titrating a suspension of the oxide with an acid/base indicator present. However, this method is subject to many problems. For instance only Bronsted acid sites can be quantified with this method. Metal oxide surfaces can have both Brønsted and Lewis acid sites present at the same time which leads to a nonspecific interaction between the oxide and the indicator. Also, as outlined in the theory section, the perturbation of neighboring sites upon adsorption of indicator molecules compromises the integrity of this model.

CASE STUDY OF SURFACE ACIDITY/BASICITY

ZrO_2



Zirconia exists in the monoclinic, tetragonal or cubic crystal system depending on the temperature. The surface acidity and basicity of the oxide is dependent on which phase is present and which crystal face is showing. The surfaces of Zirconia have hydroxyl groups, which can act as Brønsted acids or bases, and coordination-unsaturated $Zr^{4+}O^{2-}$ acid base pairs which contribute to its overall acid-base properties. Adsorption studies have shown that monoclinic zirconia is more basic than tetragonal, as it forms stronger bonds with CO_2. Adsorption of CO shows that the tetragonal phase has more acidic Lewis acid sites than the monoclinic phase, but that it has a lower concentration of Lewis acid sites.

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