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Research Paper

ANALYSIS OF APPLICATION OF OXIDE SURFACE AS ENVIRONMENTAL INTERFACE

Aadarsh Mishra[1]*

*Corresponding Author: Aadarsh Mishra, ✉aadarshm9@gmail.com

In the expanding area of research environmental molecular surface science has been of great interest. This paper focusses at the molecular level of oxide surfaces. These oxide surfaces are used as catalysts in the remediation of environment. In troposphere oxide particles adsorb and catalyze the reaction of trace gases thereby causing the chemical balance of the atmosphere. The pollutant molecules are adsorbed and catalyzed by the reactions which occur when mineral oxides come in contact with the ground water. For understanding the molecular level information a lot of study has to be done on surface science which involves environmentally relevant conditions, adsorbate-surface interactions, surface reaction mechanisms, structure-reactivity relationships and an overall understanding of these processes on the molecular level.

Keywords: Oxide surface, Environmental interface, Rock salt

INTRODUCTION

Oxide surfaces play a very significant role in controlling the environmental processes which includes environmental catalysis and bioremediation. Oxides surfaces range from catalysts in industry to natural interfaces in soil. Oxide surface in each case exhibit a different role in different ambient condition. However the composition and chemical properties of oxide surface differ even if the chemical composition of bulk oxide is same. The surface of oxide at a particular temperature and pressure exhibits the property such that there is a minimum amount of water vapor present. The surface of an oxide in thepresence of water vapor on the order of a few Torr will most likely be terminated with hydroxylgroups and coated with a layer or two of adsorbed water which will have an effect on its surfacereactivity (Blesa *et al.*, 1994; and Stumm, 1992). The nature of few layers of water has a significant effect to determine the reactivity of an oxide. Oxides surface depend on the environment for their composition. In case of ionic compounds cations and anions are held in a crystal lattice by the columbic interactions (Masel, 1996).

[1] Department of Mechanical Engineering, Manipal Institute of Technology, Manipal University, Manipal, Karnataka 576104, India.

The description of structure of oxide crystals is based on the array of closed pack oxygen anions with metal cations occupying interstitial site (Henrich and Cox, 1996). Octahedral and tetrahedral interstices are present in face centered cube and hexagonal closed packing both of which are classified under closed pack arrays. By filling the octahedral sites with cations in an oxygen anion face centered cube array we get the structure of a rock salt. Almost two third of the octahedral sites are occupied by the cations in the hexagonal closed pack oxygen array. Similarly if half of the octahedral sites of the hexagonal closed pack oxygen anion array are filled it results in rutile structure. Spinel structure can be regarded as one of the most complex structure of oxide. Rock salt is having the simplest structure amongst all of the oxides. Oxides consists of some the common phases like alpha phase or corundum and gamma phase. These phases are stable under the ambient conditions. Depending on the surface area one phase has dominant over the other. Iron oxide exists in four different types of phases out of which Hematite (Fe_2O_3) and magnetite (Fe_3O_4) are the most common and stable phases. Rutile, anatase and brookite are the three phases of titanium dioxide which are stable at room temperature/ atmospheric pressure.

Silicon dioxide differs from other oxides as it has covalent bonding instead of ionic. Quartz, tridymite and crystobalite are the crystalline forms of silicon dioxide. Quartz is stable at temperatures below 1143 K, tridymite is stable at higher temperatures between 1143 and 1743 K and crystobalite exists at temperatures above1743 K. Transition from alpha to beta phase takes place at each temperature range

Figure 1: Unit Cell of Titanium for TiO_2

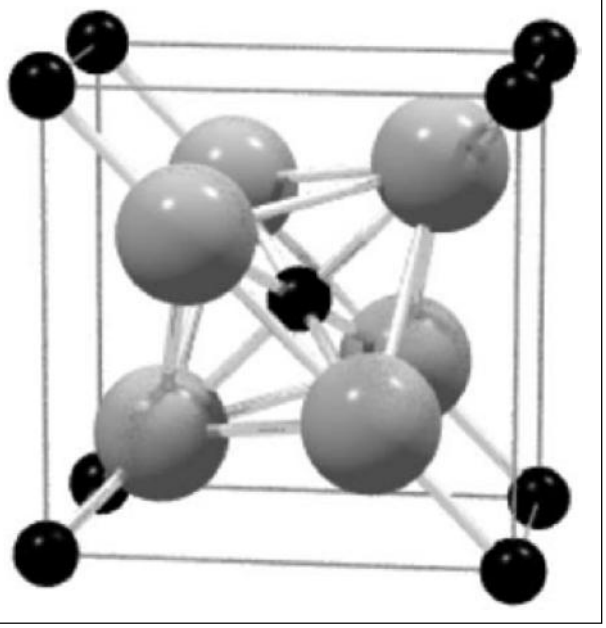
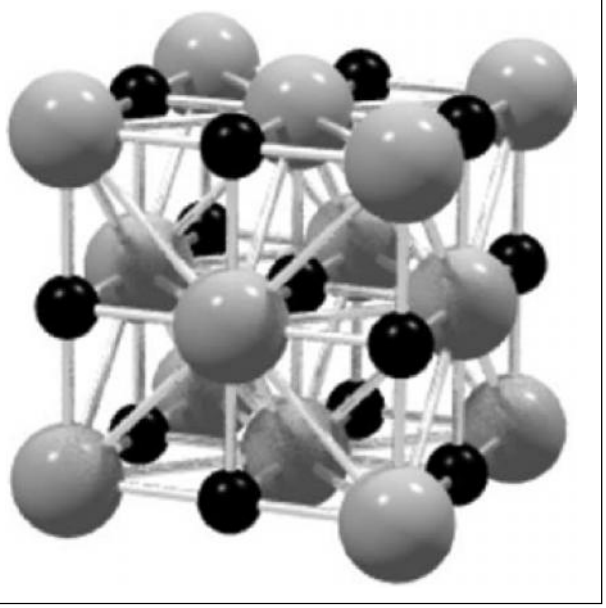


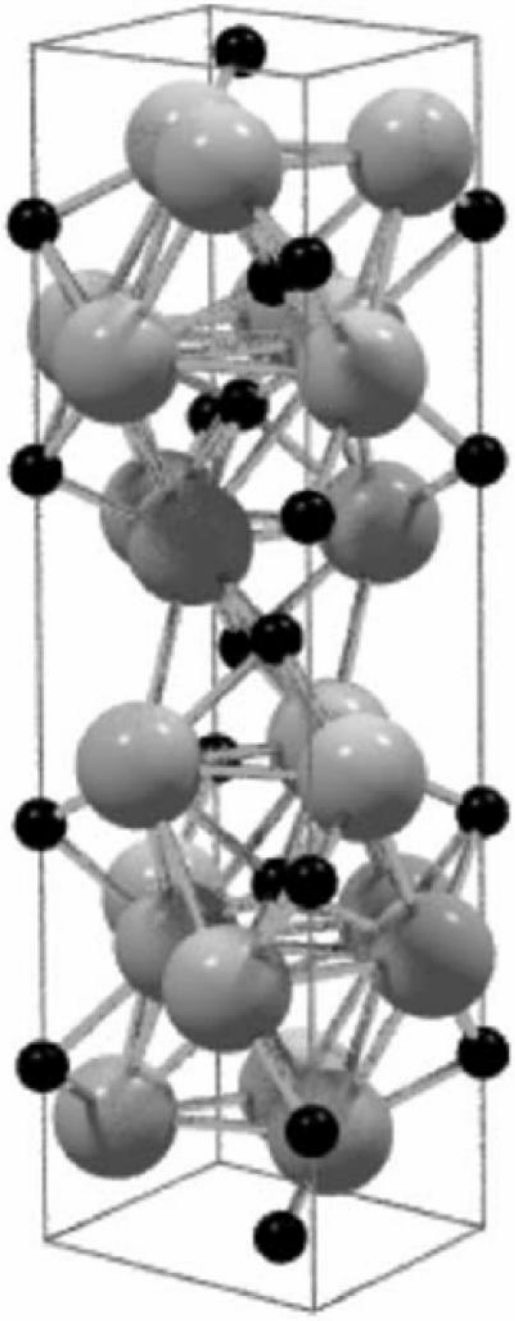
Figure 2: Unit Cell of Magnesium for MgO



while transition occurs at 846 K for quartz. Quartz has the densest structure among all other crystalline forms.

Since the lowest energy surface planes terminates the bulk crystalline structure, growth of naturally occurring minerals take place. The

Figure 3: Unit Cell of Alpha Phase of Al_2O_3



positions of surface ion differ from the bulk structure when the crystal is cleaved along a particular crystallographic planes. To obtain a thermodynamically stable surface the Gibbs energy is minimized by the newly created surface. In order to minimize the free energy, reconstruction of surface ions take place. In case if the energy barrier for reconstruction is too high metastable surface structures exists. To compare the stabilities of different surfacestructures, the factors considered are degree of coordinative unsaturation and surface polarity.

EXPERIMENTAL STUDIES

Titanium oxide due to its photo catalytic process is regarded as an important oxide (Helz *et al.*, 1993; Schaar-Gabriel *et al.*, 1996; and Brinkley and Engel, 1998). Mineral TiO_2 (rutile) occurs in nature and it cleaves preferentially along its naturally grown face, the (1 1 0) plane. Other low Miller index surfaces include the (0 1 1) and (0 1 0) planes. The most studied surface plane of TiO_2 is the (1 1 0) plane (Linsebigler *et al.*, 1995). The surface plane can be regarded as non-polar due to bridging oxygen rows resulting in five and six coordinated cations (Henrich and Cox, 1996). The (1 1 0) surface is unreconstructed and undergoes slight relaxation (Charlton *et al.*, 1997; and Renaud, 1998). Less common surfaceplanes of TiO_2 such as the (0 0 1) and (1 1 1) planes can be grown on a single-crystal metalsurfaces (Chambers, 2000).

Many experimental studies have been conducted on single crystal quartz surface. Some LEED studies on the alpha-quartz (0 0 0 1) surface can be found in the literature (Janossy and Menyhard, 1971; and Bart and Gautier, 1994). Calculationsof the structure and stability of the (0 0 0 1) and other surface planes of alpha quartz have been done using first principle ab initio methods (Rignanese *et al.*, 2000) and atomistic simulation techniques (Leeuw *et al.*, 1999).

RESULTS AND DISCUSSION

The mineral corundum occurs in nature and exhibits a wide range of naturally grown faces (Henrich and Cox, 1996). The (0 0 0 1) surface (or the c plane) of the alpha phase of aluminum oxide is the most studiedsurface plane (French and Somorjai, 1970; Coustet and Jupille, 1994; Gorb *et al.*, 1995; Ahn and Rabalais, 1997; Nygren *et al.*, 1997; Puchin *et al.*, 1997; Toofan and Watson, 1998; and Eng *et al.*, 2000). This surface also easily grows on a variety of metal substrates (Goodman, 1996; and Chambers, 2000). Theoretical studies (Puchin *et al.*, 1997; Wittbrodt *et al.*, 1998; and Hass *et al.*, 2000) conclude that the Al-terminated surfaceis electrostatically more stable than the O-terminated surface since the surface possesses a netzero dipole when terminated by Al cations.Surface structure calculations using quantum mechanical methods have demonstratedthat the (0 0 0 1) surface is stabilized by hydroxylation and that the actual surface may consist ofa different oxide from the bulk material (Leeuw *et al.*, 1999). Hematite crystalsdo not readily cleave and the (0 0 0 1) basal planes of hematite are the predominant naturally grown faces (Henrich and Cox, 1996).

CONCLUSION

Due to the unique catalytic andadsorptive properties of oxide surfaces. There are many defect sites that are present on nearly all surfaces including steps, kins and impurity atoms. Due to electron bombardment and annealing at high temperatures vacancies are produced. Moreover oxygen vacancies are far more than metal cation vacancies. Reduction on screening between surface cations occurs due to the oxygen vacancies and they have a significant effect on the electronic energy levels.

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