Introduction

1-1. General Introduction

The metal oxides constituent a diverse class of materials whose properties cover the entire range from metals to insulators. The environmental degradation of high T_c superconductors, bonding between grains of alumina in sintered ceramics, the passivity of metal surfaces against corrosion, catalysts for the partial oxidation of hydrocarbons, solid state gas sensors for pollution monitoring and control, the failure of dielectric materials because of surface conductivity, the stability of electrode-electrolyte interfaces in fuel cells, all of these are dependent upon the properties of metal oxide surface or the interfaces between meta oxides and other materials. Several research groups have devoted their attention to study the properties of well-characterized metal oxide surfaces, both experimentally and theoretically.(1) However, there are different types of oxides including single, mixed and supported metal oxides. Titanium oxides are ones of the oxides which used recently in many applications.

1-2. Structures of Titanium Oxides:

Titanium oxides exist in many different phases:(1)

Ti_2O

The oxygen atoms being randomly distributed in the octahedral interstices of the titanium lattice.(2)

TiO

The TiO phase has a wider range of composition, extending from $TiO_{0.64}$ to $TiO_{1.25}$. X-ray parameter and density measurements have shown that a third of the oxygen sites are vacant in $TiO_{0.7}$ and a quarter of the titanium sites are vacant in $TiO_{1.25}$. Moreover, even in stoichiometric TiO about 15% of both sites are vacant. Above 1263 K, the vacancies are arranged randomly so that diffraction patterns typical of the cubic NaCl structure are formed; the lattice parameter is 4.18A.

Ti_2O_3

The sesquioxide has a narrow range of homogeneity extending from $TiO_{1.49}$ to $TiO_{1.51}$. It has the corundum structure in which the Ti-O bond lengths are slightly less than those in the monoxide.

Ti_3O_5

The compound is dimorphic. Above 450 K, it has a structure of the anosovite type (a slightly distorted pseudo-brookite structure). This form has Ti-O distances ranging from 1.91 to 2.10 Å and can be stabilized at room temperature with a small amount of iron. The oxides Ti_4O_7 and Ti_5O_9, of the Ti_nO_{2n-1}series, are built of slabs of rutile structure, infinite in two dimensions and respectively four and five octahedra thick, joined by sharing octahedron faces (compare corundum).

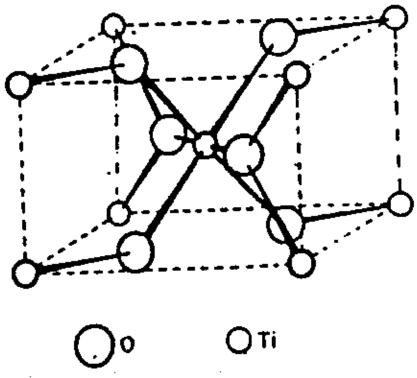
TiO_2

Titanium dioxide can be formed in three crystalline forms stable at atmospheric pressure, namely rutile, anatase, and brookite, all occur as minerals. These three polymorphs, together with the high-pressure form with the α-PbO_2 structure, are all built of octahedral coordination groups.

The crystal structure of rutile and anatase:

In both crystal lattices, every titanium(IV) ion is surrounded by six oxide ions arranged octahedrally (slightly distorted), and each oxide ion by three titanium(IV) ions. Rutile is the thermodynamically stable phase; it has tetragonal structure (Fig. 1-2.a). The structure consists of chains of TiO_6 octahedra, in which each octahedron shares a pair of opposite edges (Fig. 1-2.b), which are further linked by sharing vertices to form a 3D structure of 6 : 3 coordination. With the above coordinates each O has three coplanar neighbours. Ti has six octahedral neighbours, and all Ti-Ti distances (between centers of octahedra along a chain) are equal. The rutile structure is not close packed, but the Ti^{4+} ions may be considered as forming a considerably distorted body-centered cubic lattice and the O atoms represents a considerable distortion of hexagonal closest packing.

In less dense anatase, each $[TiO_6]$ octahedron shares edges with four adjacent $[TiO_6]$ octahedra (Fig. 1-2.c) which form spiral chains round each four-fold axis. It follows from the above structural consideration that the formation of linear polynuclear species containing bidentate oxo or hydroxo bridges between titanium(IV) ions will give rise to rutile nucleation, while nonlinear ones must pass into anatase nuclei.(3) The oxides are insoluble in water. M^{4+} ions do not exist in solution, but MO^{2+} ions are formed, giving basic salts such as titanyl sulphate $TiO.SO_4$. Either TiO^{2+} ions or $[Ti(OH)_2]^{2+}$ are present in solution, but in solid they polymerize into oxygen bridged $(MO)_n^{2+}$ chains.



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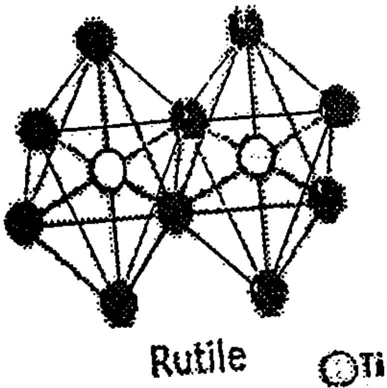

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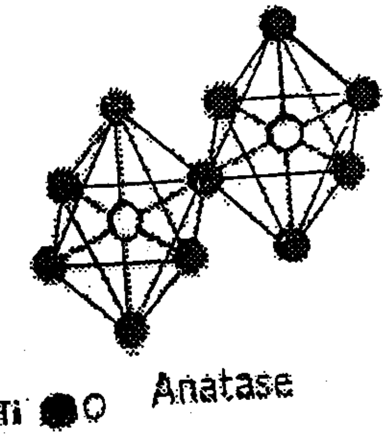

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