CHAPTER III

THEORY

Catalytic oxidation can be categorized as complete oxidation and selective oxidation. Complete oxidation is the combustion of organic compound to the combustion products; CO_2 and H_2O [Thammanonkul (1996)]. It is a practicable method for elimination of organic pollutants in gaseous streams. While selective oxidation is the reaction between hydrocarbon and oxygen to produce oxygenates (such as alcohols, aldehydes, carboxylic acids which are produced from partial oxidation processes) or unsaturated hydrocarbons (such as ethane and propene which can be produced from oxidative dehydrogenation process) [Thammanonkul (1996)].

In studies on oxidative catalysis; commonly great attention is attached to the state of oxygen on the catalyst surface. A relative inert oxygen molecule is activated by interacting with the surface of oxide catalyst. The main parameter determining oxygen reactivity on the catalyst is energy of oxygen binding with the catalyst as a thermochemical characteristic. Correlation between rates of catalytic oxidation and oxygen binding energy on oxide catalysts have been established. The weaker the oxygen binding with the catalyst surface, the more efficient is complete oxidation with this catalyst [Satterfield (1991)].

With oxide catalysts, chemisorbed surface oxygen as well as lattice oxygen may play a role. The oxidation of propylene to acrolein on a $BiMo/SiO_2$ catalyst in a pulsed reactor showed by isotopic oxygen studies that surface chemisorbed oxygen as well as lattice oxygen could contribute to the overall reaction. It seem plausible that in many other cases chemisorbed oxygen would lead to a different set of products than lattice oxygen and both mechanisms could be significant. On the basis of other studies advanced the hypothesis that surface-adsorbed oxygen may in general lead to products of complete oxidation and the lattice oxygen is needed for partially oxidized products, but more study is need to teat this proposal [Satterfield (1991)].

3.1 Mechanism of oxidation reaction

The mechanisms of oxidation reaction on the catalyst surface were shown as follow:

1. Reaction between reactant and adsorbed surface oxygen species,

Reactant (fluid phase) → Reactant (surface species)
Oxygen (fluid phase) → Oxygen (surface species)
Reactant (surface species) + Oxygen (surface species) → Product (surface species)
Product (surface species) → Product (fluid phase)

2. Redox mechanism, reaction between reactant and lattice oxygen of metal oxide, was first proposed by Mars and van Krevelen in 1954.

Reactant + Catalyst (oxidized form) → Product + Catalyst (reduced form)
Oxygen (fluid phase) + Catalyst (oxidized form) → Catalyst (oxidized form)

3.2 Cobalt magnesium oxide catalyst

Cobalt oxide is an interesting material in the field of heterogeneous catalysis. Among the transition metal oxide Co_3O_4 shows the highest catalytic activity for the combustion of organic compounds, CO, diesel soot, NO, and ammonia. This is the reason why Co_3O_4 and Co-containing mixed oxides are normally included in the formations of catalysts for treatment of waste gases and are of interest in view of development of methane catalytic combustion technology for energy supply. In addition, it is also active for hydrogenation and hydrodesulphurization reaction [Busca *et al.* (1990)].

Co_3O_4 is a black material having the structure of a normal spinel; it is thermodynamically stable up to 900°C with respect to the lower oxide CoO. This implies that Co_3O_4 is the oxide stable under the conditions of catalytic oxidation. Both Co_3O_4 and CoO are readily reduced to the metal in the hydrogen flow near

300°C. The surface of Co_3O_4 shows Co^{3+} ions in excess. This surface is very reactive, even with respect to a stable molecule such as ammonia and methanol, which are readily decomposed at room temperature [Busca *et al.* (1990)].

For the gas-phase oxidation of hydrogen, ammonia, methane, ethylene, propylene, carbon monoxide, or toluene, the order of activity varied somewhat with the reactant, but the general pattern of activity found was [Satterfield (1991)].

$$Ti < V < Cr < \underline{Mn} > Fe < \underline{Co} > Ni < Cu > Zn$$

In almost all cases the most active catalyst was cobalt oxide and manganese oxide; the least active were the oxides of titanium or zinc.

MgO is white powder that usually obtained by dehydration of magnesium dihydroxide. Its catalytic interest lies in its essentially basic surface character, which makes it an effective catalyst support. Magnesium oxide is also interesting because it has the ability to stabilize metals in unusual oxidation states and to avoid sintering and evaporation of the metal atoms [Aramendia *et al.* (1999)].

3.3 Acidic and Basic Catalyst [Kirk-Othmer (1979)]

The correlation of catalytic efficiency with the strength of the acid or base is of considerable importance. The general theory of acid-base catalysis in which a proton is transferred from the catalyst to the reactant (acid catalysis) or from the reactant to the catalyst (base catalysis). The velocity of the catalyzed change is thought to be determined by a protolytic reaction between the reactant and the catalyst. The molecule, on receiving or giving a proton, is converted into an unstable state which immediately (or very rapidly, compared with the velocity of the protolytic reaction) leads to the reaction under consideration. Thus, acid catalysis of a basic reactant is represented by the general scheme $R+AH^+ \rightarrow RH^++A$, whereas $RH^++B \rightarrow R+BH^+$ represents basic catalysis of an acidic reactant.

3.4 Chemisorption at oxide surface [Bond (1987)]

On the basis of their electrical conductivities, solids are traditionally divided into four classes as shown in Table 3.1.

Table 3.1 Classification of solids by electrical conductivity

Class	Conductivity range (Ω cm^{-1})	Chemical class	Examples
Superconductors	up to 10^{35}	metals at low temperatures	-
Conductors	10^{4}-10^{6}	metals and alloy	Na, Ni, Cu, Pt etc.
Semiconductors	10^{3}-10^{8}	(a) intrinsic: semi-metals	Ge, Si, Ga, As etc.
		(b) extrinsic: oxides and sulphides of transition and post-transition elements	ZnO,Cu_2O, NiO, ZnS,MoS_2, NiS etc.
Insulators	10^{-9}-10^{-20}	Stoichometric oxides	MgO, SiO_2, Al_2O_3 etc.

There are two classes of semicondutors. Group IV elements such as silicon and germanium, and analogous Group III-Group V compounds like gallium arsenide, are termed *intrinsic* semiconductors because their conductivity is an inherent feature of their chemical structure. However, important as these substances are in solid state devices, they are not catalytically active and will not be considered further. Of greater interest are the oxides and sulphides whose conduction is due to their departure from precise stoichiometry: these substances are termed extrinsic or defect semiconductors. The more non-stoichiometric they are, the greater their conductivity. Another important general feature of semiconductors is that their conductivity increases with temperature according to a relation similar to the Arrhenius equation.

3.4.1 The Band Theory of solids

Let us consider the sequential condensation of atoms of sodium from the vapour; in the resulting crystal each sodium atom is surrounded by others in a body-centred cubic structure, and the atoms are held together by what are best described as resonating covalent bonds. In effect, the 3s valence electrons are not specifically attached to any sodium ion but form a collective electron 'sea' which permeates the array of sodium ions. In a crystal of molar size there will be 6×10^{23} of these indistinguishable 3s electrons. But now we encounter a difficulty: the Pauli Exclusion Principle states that not more than two electrons in an atom can have the same set of quantum numbers, and that these two must occupy different spin states. The sodium crystal is like a giant atom in which many cations are held together by the same number of electrons. This apparent dilemma was resolved in the late 1920s by assigning to each electron an energy infinitesimally different from that of all others, so that, in contrast to the free atom, in which each electron occupies an energy *level* determined by the quantum numbers, there is a *band* of permitted energy levels in which electrons can exist. This idea is shown schematically in Figure 3.1; the concept can also be developed on the basis of pairs of bonding and antibonding molecular orbitals formed in pairwise interactions of the atoms.

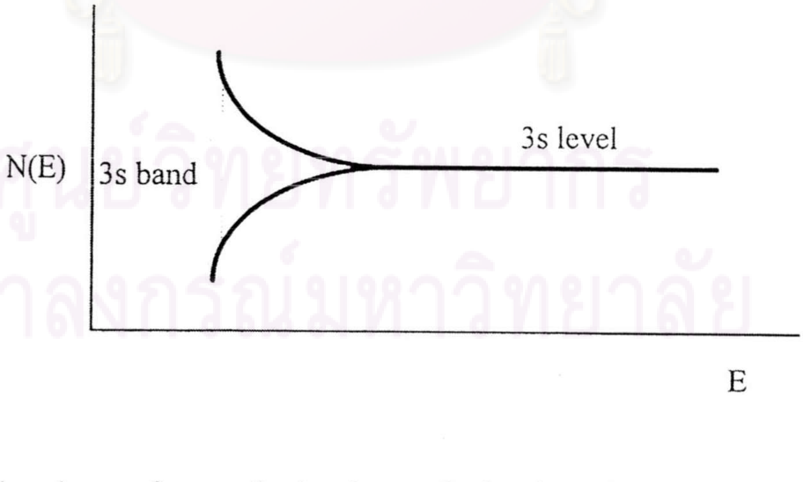

Figure 3.1 The change from a 3s level to a 3s band as the average interatiomic distance between sodium atoms decreases.

The valence electron in the free sodium atom is described as 3s^1; there is a corresponding 3s band in the solid which, like the orbital in the free atom, can accept one more electron of opposite spin for each ion present. This gives the electron configuration of magnesium, a crystal of which has a filled 3s band. Similarly metals having p, d or f valence electrons will have p, d or f bands. In the case of sodium and magnesium there will also be fills 1s, 2s and 2p bands lying at lower energies than the 3s band, but just as core electrons do not contribute to the chemistry of the elements so we can afford to ignore the corresponding bands and focus on those for the valence electrons.

The next question to arise is whether the *density* of electron levels is constant across the band: the electron level density *N(E)* is defined as the number of levels having energies between *E* and *E+dE*. The simplest theoretical model predicts that *N(E)* will increase as the square root of the energy, giving, at the absolute zero, band structures as shown for sodium and magnesium in Figure 3.2. For sodium, the 3s band is half-filled: for sodium-magnesium alloys, it will be between half and fully occupied depending on the composition of the alloy. It is important to appreciate that when electrons are added to a band, the lowest levels are occupied first, and the higher levels progressively. The highest energy level in the band that is occupied by electrons is termed the *Fermi level*.

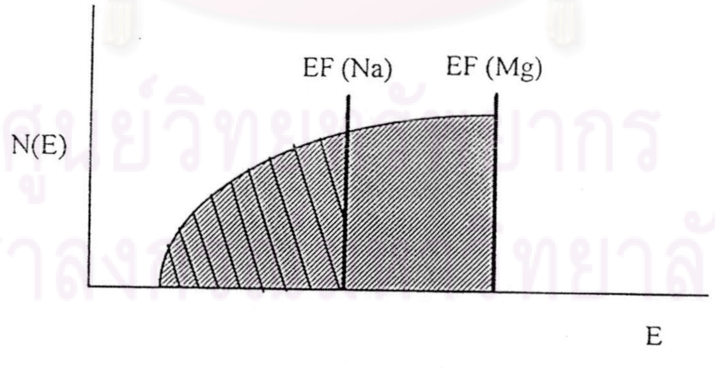

Figure 3.2 The density of electron energy level *N(E)* as a function of the energy *E* for the 3s band. E_F (Na) represents the Fermi energy of sodium and E_F (Mg) that of magnesium.

There is now one simple rule relating the electron occupation of bands to the electrical conductivity of the solid. It is this. *Conduction is only possible if the valence band is incompletely filled.* This may be understood qualitatively if we assume that an electron has to be excited to a slightly higher level in order to move: if there are no vacant levels. there can be no excitation. The first difficulty is that according to this rule magnesium should be an insulator, not a conducting metal, as it has a filled 3s band. The answer is that the filled 3p band overlaps with a vacant 3p band (see Figure 3.3). so that it has a partly-filled hybrid sp band, and hence does not violate the rule.

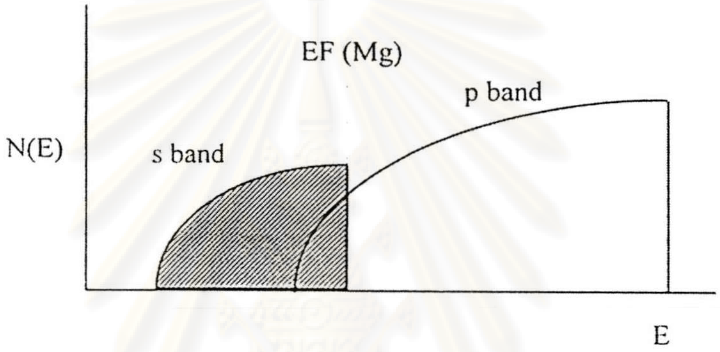

Figure 3.3 The overlap of the 3s and 3p bands in magnesium.

In an insulator such as magnesium oxide there will be filled 2sp valence bands corresponding to the Mg^{2+} and to the O^{2-} ions. There is a large forbidden energy gap between the top of these bands and the bottom of the empty 3s conduction band (see Figure 3.4). To obtain conduction it would be necessary to excite some electrons from close to the Fermi level into the conduction band, but the gap is too large for the usual thermal or radiative methods of excitation to be effective. This difficulty is connected with the great chemical stability of magnesia: indeed all insulators are thermally stable and are widely used in making ceramic ware. With intrinsic semiconductors the band gap is much smaller, and excitation by heating or by light is easily possible.

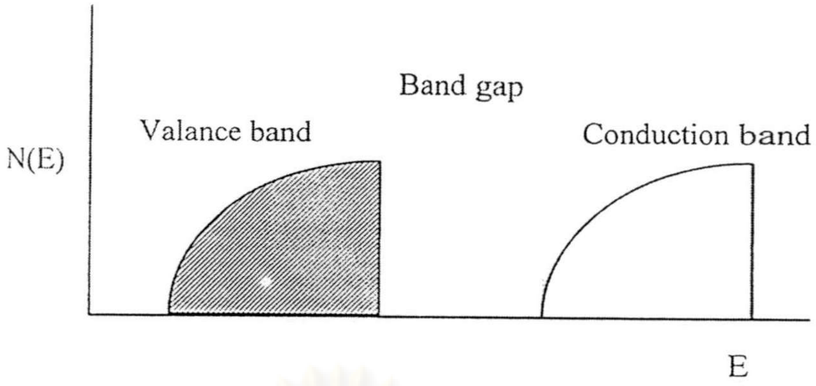

Figure 3.4 The Band Theory diagram for an insulator.

Finally we come to the interesting question of the defect semiconductors and will take zinc oxide and nickel oxide as our examples. Here it is easier to look at the chemistry first, and then find the equivalent Band Theory description. We have seen that nickel oxide when heated in air acquires additional oxygen; this is accompanied by the oxidation of a small fraction of the nickel ions from the 2+ to the 3+ state, i.e.

$$2Ni^{2+} + 1/2O \rightarrow 2Ni^{3+} + O^{2-}$$

For each oxygen molecule used, four Ni^{3+} ions have to be created: they are referred to as *positive holes* in the nickel oxide lattice. Now if an electron jumps from an Ni^{2+} ion to an Ni^{3+} ion, the positions of the ions are reversed, but there is no other effect: the jump however constitutes the mechanism of the electrical conduction. Conductivity thus depends on the concentration of Ni^{3+} ions in the lattice: this depends exponentially on temperature, and on oxygen pressure. The conduction mechanism is called *positive-hole conduction*, and compounds of this kind are *p-type* semiconductors. The Band Theory representation of this situation is shown in Figure 3.5. There is a large gap between the valence and conduction bands, but the Ni^{3+} ions constitute an *acceptor level* just above the Fermi level, so that electrons can easily jump from the top of the valence band into one acceptor level, thus creating the conditions for electrical conduction. Incidentally, the valence electrons of Ni^{3+} are assigned to a level rather than a band because their concentration is low and they effectively act as isolated, non-interacting species. The concentration of Ni^{3+} ions can be increased by *valence induction*: addition of a little lithium oxide generates additional Ni^{3+} ions in order to preserve the charge balance.

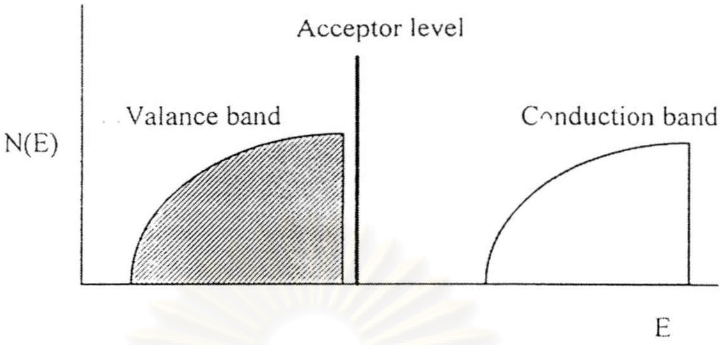

Figure 3.5 The Band Theory diagram for a p-type impurity semiconductor.

Zinc oxide loses oxygen on heating in air. This is accompanied by the reduction of some zinc ions to atoms according to the reaction

$$2Zn^{2+} + 2O^{2-} \rightarrow 2Zn + O_2$$

Electrical conduction is due to the electrons associated with the zinc atoms, and since they are negative species zinc oxide is said to be an *n-type* semiconductor. In Band Theory terms, the zinc atoms constitute a *donor level* situated just below the bottom of the vacant conduction band, so that excitation into the conduction band is relatively easy, and the conductions for electrical conduction are met (see Figure 3.6). Electrons attached to the zinc atoms are assigned to a discrete energy level, because (as with the Ni^{3+} ions above) their concentration is low and they do not interact. The concentration of zinc atoms can also be increased through valence induction by doping with ions having a charge greater than 2+.

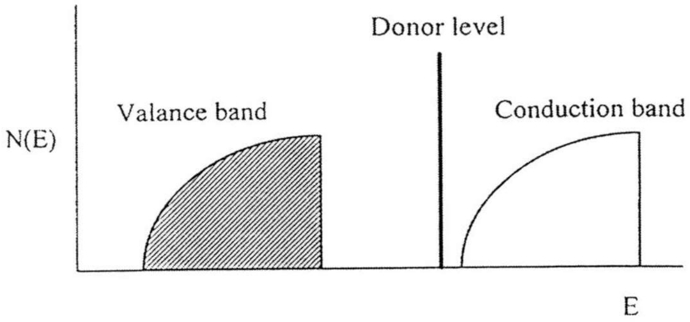

Figure 3.6 The Band Theory diagram for an n-type impurity semiconductor.

A useful generalization concerning the requirement for p-type semiconductivity is that the cation shall have an accessible higher oxidation state: thus cobalt(II)oxide and copper(I)oxide are also in this group. For n-type semiconductivity an accessible lower oxidation state (which may include the zero-valent state) is needed: thus cadmium oxide and iron(III)oxide fall in this group (see Table 3.2).

Table 3.2 Classification of semiconducting metal oxides

Effect of heating in air	Classification	Examples
Oxygen lost	Negative (n-type)	ZnO, Fe_2O_3, TiO_2, CdO, V_2O_5, CrO_3, CuO
Oxygen gained	Positive (p-type)	NiO, CoO, Cu_2O, SnO, PbO, Cr_2O_3

3.4.2 Chemisorption on semiconducting oxides

A qualitative understanding of the chemisorption of simple gases on semiconducting oxides follows simply from their chemistry. Reducing gases such as hydrogen and carbon monoxide are adsorbed strongly, but irreversibly: on heating, only water and carbondioxide respectively can be recovered. Hydrogen probably dissociates heterolytically on adsorption, viz.

$$H_2 + M^{2+} + O^{2-} \rightarrow HM^{+} + OH^{-}$$

The hydroxyl ion will decompose on heating to form water and anion vacancies, and an equal number of cations will be reduced to atoms.

Carbon monoxide usually chemisorbed first on the cation, whence it reacts with an oxide ion:

$$(CO) \cdots M^{+} + O^{2-} \rightarrow M + CO_2.$$

Here is the first stage of a process that can lead ultimately to the complete reduction of the oxide to metal. These steps are also similar to those involved in the catalyzed oxidation of these molecules.

The chemisorption of oxygen on p-type oxides occurs by a mechanism involving the oxidation of Ni^{2+} ions at the surface to Ni^{3+}:

$$2Co^{2+} + O_2 \rightarrow 2(O^{-} \cdots Co^{3+}).$$

High coverages by the O^- ion can result, and it is easy to see that this is the first step in the incorporation of excess oxygen, referred to above. When the n-type oxides (exemplified by zinc oxide) are exactly stoichiometric, they cannot chemisorb oxygen: when however they are oxygen-deficient, they can chemisorb just as much as is needed to restore their stoichiometry by refilling the anion vacancies and reoxidizing the zinc atoms.

3.4.3 Adsorption on insulator oxides

Since the cations of insulator oxides can be neither oxidized nor reduced, they cannot chemisorb oxygen to any significant extent; they cannot chemisorb hydrogen or carbon monoxide for the same reason. They can, and do, react with water and other polar molecules as:

$$M^{x+} + O^{2-} \xrightarrow{H2O} (HO^{-} \cdots M^{x+}) + OH^{-}$$

$$M^{x+} + O^{2-} \xrightarrow{CH3OH} (CH_3O^{-} \cdots M^{x+}) + OH^{-}$$

Indeed under normal circumstances the surface of oxides such as alumina and silica are covered by a layer of chemisorbed water: the surface is then said to be fully hydroxylated, and indeed these hydroxyl groups are very firmly bound. Their complete removal by heating is almost impossible. When the oxides are suspended in water the M-OH groups can dissociate either as acids or as bases, depending on the electronegativity of the cation, e.g.

$$\mathrm{Mg-OH} \rightarrow \mathrm{Mg^{2+} + OH^-}$$

$$\mathrm{Si-OH} \rightarrow \mathrm{SiO^- + H^+}$$

The variation of valence electron quantity causes the oxidation number change. These phenomenon leads to the electrical conductivity and acidity change (consider in case of Lewis acid).