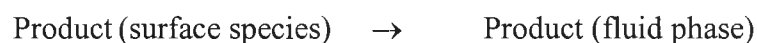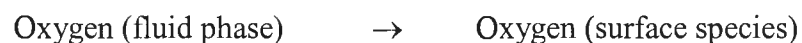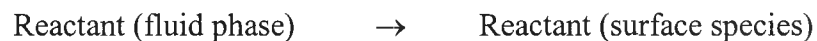# CHAPTER III

THEORY

Complete oxidation is the combustion of organic compound to the combustion products; CO_2 and H_2O. It is a method for elimination of organic pollutants in gaseous streams. However 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 [Satterfield (1980)].
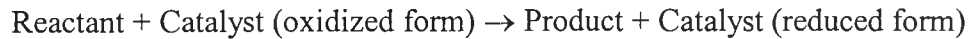
3.1 Mechanism of oxidation reaction

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) $\rightarrow$ Reactant (surface species)

    Oxygen (fluid phase) $\rightarrow$ Oxygen (surface species)

    Reactant (surface species) + Oxygen (surface species) $\rightarrow$ Product (surface species)

    Product (surface species) $\rightarrow$ 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 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.

## 3.3 Acid and base at surface of metal oxides [Sintarako (1998)]

Oxide catalysts are solid compounds of oxygen and one or more metal of semimetal elements. "True" metal oxides are composed by a metal and oxygen and are consequently characterized by an almost ionic bond. When pure, they are most commonly crystalline materials. The ideal surface of a metal oxide crystal is composed by crystal faces (exposed crystal planes), held together by corner and edges. The coordination of ions at the "ideal" surface is necessarily incomplete with respect to the coordination in the bulk. Even more incomplete is the coordination of atoms at corners or edges. Surface reconstruction certainly occurs in order to decrease the energy of the atoms exposed at the surface, but coordinative unsaturation will in part remain. The surface ions can also react with species from the environment, again to decrease the free energy. However, partly uncoordinated metal cations and oxide anions lie at the surface of metal oxide crystals, even in these conditions. These ions can act as acids and bases, respectively, according to the

Lewis definition. So that, Lewis acid sites (coordinatively unsaturated cations) and basic sites (oxide anions) are expected, and actually found, at the surface of ionic metal oxides [Sintarako (1998)].

The reversible interaction of water (always present in the environment) with such surfaces is in part dissociative, as shown below:

$$\blacklozenge M^{n+1}O^{2-} + H_2O \quad \leftrightarrow \quad HO^-M^{n+-}OH$$

Where $\blacklozenge$ indicates a coordinative unsaturation responsible for Lewis acidity, so that coordinatively unsaturated cations and anions can in part convert into surface hydroxy-groups. These groups are potentially BrÖnsted acidic, although they mostly behave as basic -OH groups, because the bond with which they are held to the metal cations is ionic (Figure 3.1).

O^- O^- $\square$ $O^=$ ^-OH $O^{..}$

M^{n+} M^{n+} M^{n+} M^{n+} M^{n+} M^{n+}
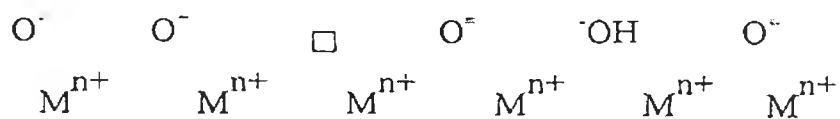
Inoic oxides
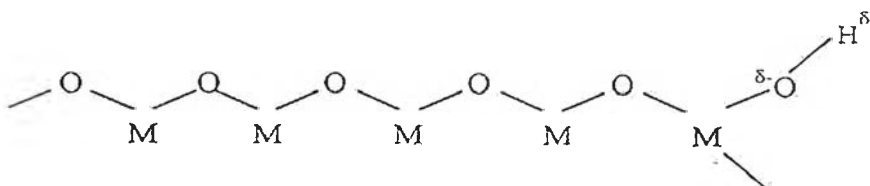
Covalent oxide *e.g.* SiO_2
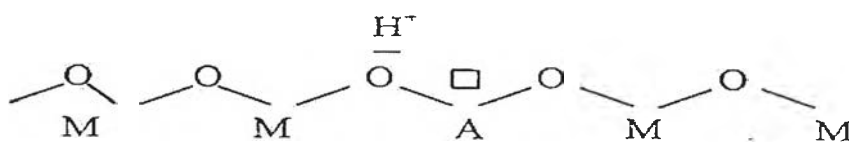
Silica-aluminas and protonic zeolites
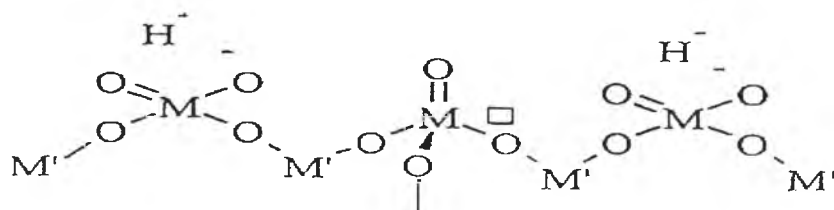
High-oxidation state metal oxides

$\square$ Vacant site

Figure 3.1 Structure of metal oxides

The oxides of semimetals, like silicon, boron, germanium, phosphorus, arsenic, and so on, are also solids active or useful in catalysis. In this case the bond is essentially covalent. These materials can also be crystalline but not unfrequently amorphous. The surface of these materials can also be crystalline but not unfrequently amorphous. The surface of these materials can be modeled on the basis of the structure of a crystal plane like the surface that is generated when a particle is ideally cut along a plane to form two smaller particles. This would generate again coordinatively unsaturated element and oxygen atoms (or ions). However, the reactivity of these element atoms is so strong that they cannot stay as such in "normal" conditions. The elements of water saturate almost irreversibly the coordinative unsaturations, so that in this case Lewis acidity completely disapperas and surface hydroxy-groups are formed, potentially responsible for BrÖnsted acidity.

In some cases, by "doping" covalent oxides with elements with lower valency (like Al in amorphous silica or crystalline silicate, giving rise to silica-alumina or ZSM-5 zeolite, respectively) a defect of charge is created, and this causes the formation of strong BrÖnsted acidity to balance it.

The oxides of metals in a high-oxidation state are also characterized by high covalency of the M-O bond, according to the high Sanderson's electronegativity of their ions. Accordingly, they show weak or no basicity. However, the cations tend to associate with some oxide ions giving rise to metal-oxygen "double-bonds" (vanadyl-, wolframyl-, molybdenyl-cations, etc.) whose coordination is very elastic. In spite of the covalency of metal-oxygen bonds, strong Lewis acidity can appear. The OH's are covalently bonded to the metal and the anion charge resulting from dissociation can be delocalized on terminal "doubly bonded" oxygen. Thus, medium to strong BrÖnsted acidity appears.

Knowledge of the structure of the surface vanadium oxide species in supported vanadium oxide catalysts is critical to the fundamental understanding of the surface vanadium oxide phase-support and surface vanadium oxide phase-reactant gas interactions. The structure of the surface vanadium oxide phase in supported vanadium oxide catalysts depends on both the particular gas and solid environment. Recent developments in the characterization of surface vanadium oxide phases with

the use of one or more of the characterization techniques have had a major impact on determining the molecular structure of the surface vanadium oxide species. The structure of the surface vanadium oxide species in supported vanadium oxide catalysts is discussed here with respect to the different environments experienced.

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$_2$O, NiO, ZnS, MoS$_2$, NiS etc.
Insulators	10^{-9}-10^{-20}	Stoichometric oxides	MgO, SiO$_2$, Al$_2$O$_3$ etc.

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.

A useful generalization concerning the requirement for p-type semi-conductivity 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

3.4.1 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.

$$H_2 + M^{2+} + O^{2-} \rightarrow HM^+ + OH^-$$
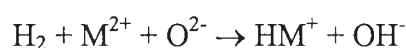
The hydroxyl ion will decompose on heating to form water and anion vacancies, and an equal number of cations will be reduced to atoms.

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

$$(CO) \cdots M^+ + O^{2-} \rightarrow M + CO_2.$$
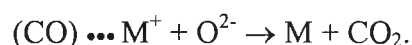
Here is the first stage of a process that can lead ultimately to the complete reduction of the oxide to metal. These steps are also similar to those involved in the catalyzed oxidation of these molecules.
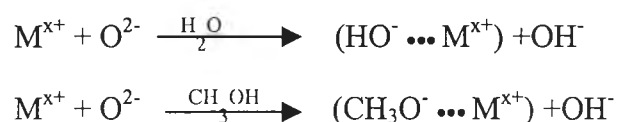
The chemisorption of oxygen on p-type oxides occurs by a mechanism involving the oxidation of Ni^{2+} ions at the surface to Ni^{3+}:

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

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.

3.4.2 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:

$$M^{x+} + O^{2-} \xrightarrow{\;\;H_2O\;\;} (HO^- \cdots M^{x+}) + OH^-$$

$$M^{x+} + O^{2-} \xrightarrow{\;\;CH_3OH\;\;} (CH_3O^- \cdots M^{x+}) + OH^-$$

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.

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

$$Si - OH \rightarrow SiO^- + H^+$$
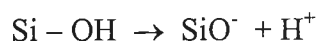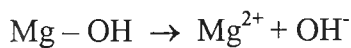
3.5 Stability of the surface vanadia monolayer

The surface vanadia monolayer is stable on many typical oxide supports (Al_2O_3, TiO_2, ZrO_2, Nb_2O_5 and CeO_2). The surface vanadia overlayer is also stable and not converted to crystalline V_2O_5 or vanadia species dissolved in the oxide support only after high temperature treatments that cause the collapse of the oxide support surface area, which reduces the number of available adsorption sites for the surface vanadia species [Wachs and Weckhuysen (1997)]. In the case of V_2O_5/TiO_2 (anatase) catalysts, high temperature treatments also transform the TiO_2 (anatase) phase to the TiO_2 (rutile) phase that can accommodate dissolved V^{4+} species in the rutile lattice [Bond (1991)]. The stability of the surface vanadia monolayer is reflected in the long life of such industrial oxidation catalysts [Wachs and Weckhuysen (1997)].

3.6 Molecular structures of surface vanadia species

The molecular structures of the surface vanadia species have been extensively investigated in the past few years with many different spectroscopies: Raman, IR [Wachs and Weckhuysen (1997)]. These studies revealed that the surface structures and oxidation states of the surface vanadia species are dynamic and are strongly dependent on the environment (oxidizing and reducing gases, moisture and temperature).

3.6.1 Dehydrated conditions

Dehydrated conditions are created by heating the supported vanadia catalyst to elevated temperature, 300-700°C, in a flowing oxygen-containing stream that does not contain any reducing gases. Such a treatment desorbs adsorbed moisture from the catalyst surface and maintains the surface vanadia species in the V(5+) oxidation state

- V$_2$O$_5$/(Al$_2$O$_3$, TiO$_2$, ZrO$_2$, Nb$_2$O$_5$ and CeO$_2$)

The dehydrated surface vanadia species on these oxide supports are primarily present as isolated and polymerized on VO$_4$ unit. The relative concentrations of isolated and polymerized surface vanadia species have not been quantified by the above Raman studies. Oxygen-18 isotopic labeling experiments demonstrated that these surface vanadia species only possess one terminal V=O bond. The molecular structures of these surface vanadia species are tentatively thought to consist of a terminal V=O bond and three bridging V-O support bonds for the isolated species, and a terminal V=O bond with one bridging V-O support and two bridging V-O-V bonds for the polymerized species. There may also be a minor amount of surface VO$_6$ units (octahedral coordination) present at monolayer coverages.

- V$_2$O$_5$/MgO

Unlike the above supported vanadia catalysts, the magnesia supported vanadia catalyst system cannot form a complete close packed surface vanadia monolayer because of acid-base reaction between acidic vanadia and basic magnesia. The strong interaction between vanadia and magnesia results in the formation of a mixed metal oxide compound rater than a stable surface vanadia overlayer on the magnesia support [Deo *et al.* (1992)]. The vanadia coordination in bulk V-Mg-O mixed metal oxide catalysts consists of VO$_4$, VO$_5$ and VO$_6$ units. Thus, the magnesia supported vanadia catalyst system possesses both surface and bulk vanadia species.

3.7 Acidity of surface vanadia species

The oxide supports only possess surface Lewis acid sites and the relative strength of these sites is Al$_2$O$_3$>Nb$_2$O$_5$>TiO$_2$>ZrO$_2$, and no surface Lewis acid sites are detected for SiO$_2$. In contrast to the oxide supports, unsupported V$_2$O$_5$ crystalline powders possess both surface BrÖnsted and surface Lewis acid sites [Busca (1989)]. The formation of the surface vanadia species on the oxide supports is accompanied by a decrease in the number of surface Lewis acid sites and an increase in the number of surface BrÖnsted acid sites. Only a very small fraction of the surface vanadia species

is also surface BrÖnsted acid sites since the concentration of surface BrÖnsted acid sites, measured by pyridine adsorption, corresponds to only 5-10% of the surface vanadia at monolayer coverage. Several in situ IR studies have assigned on OH vibration of dehydrated titania supported vanadia catalysts to BrÖnsted V-OH sites. The acidic characteristics of the surface vanadia overlayer are influenced by the specific oxide support ligand, but the molecular structural characterization studies reveal that the same dehydrated surface vanadia species are present on all the oxide supports (with the exception of silica). This suggests that the surface BrÖnsted hydroxyls may be located as bridging V-OH- support sites, but no direct spectroscopic evidence is currently available to support any assignment for the location of the surface BrÖnsted acid sites which are only present for the oxidized V(5+) surface vanadia species. Thus, probing surface acidity with reducing probe molecules will alter the surface BrÖnsted acidity properties of the supported vanadia catalysts.