CHAPTER III
THEORY

Selective oxidation processes using air or oxygen are used to manufacture a variety of chemicals, and complete catalytic oxidation is a practicable method for elimination of organic pollutants in gaseous streams. In the manufacture of organic chemicals, oxygen may be incorporated into the final product, as in the oxidation of methane to formaldehyde; or the reaction may be an oxidative dehydrogenation in which the oxygen does not appear in the desire product, as in the conversion of propane to propylene. The desire reaction may or may not involve C-C bond scission.

It has been reported that maximum selectivity is associated with an optimum degree of oxygen mobility. For an optimum selectivity combination of activity and selectivity there should be matching between the difficulty of oxidizing the reactant and the ease of removal oxygen from the catalyst. High mobile oxygen should result in a high activity catalyst, but one that is nonselective [Satterfield (1991)].

Conventional selective oxidation catalysts discriminate between reactants and products primarily on a bond strength basis. This means that the weakest bond in a reactant or mixture of reactant and selective oxidation products is activated preferentially. The best selective oxidation catalysts are capable of discriminating in favor of activation of a bond in a reactant provided that the bond dissociation enthalpy of the weakest C-H bond being activated ($D^oH_{C\text{-}H\ reactant}$) is not more than 30-40 $kJmol^{-1}$ stronger than that of the weakest bond in the selective oxidation product ($D^oH_{C\text{-}H\ or\ C\text{-}C\ product}$). This value (30-40 $kJmol^{-1}$) effectively defines the discriminating capacity of active sites in conventional selective oxidation catalysts [Batiot *et al.* (1996) and Cassidy *et al.* (1998)].

The multiple selectivity-conversion plots were then used to evaluate the optimum selectivity at a conversion of 30% that has been reported for each of the full set of reactions shown in figure 3.1. The observed correlation shows that there is a

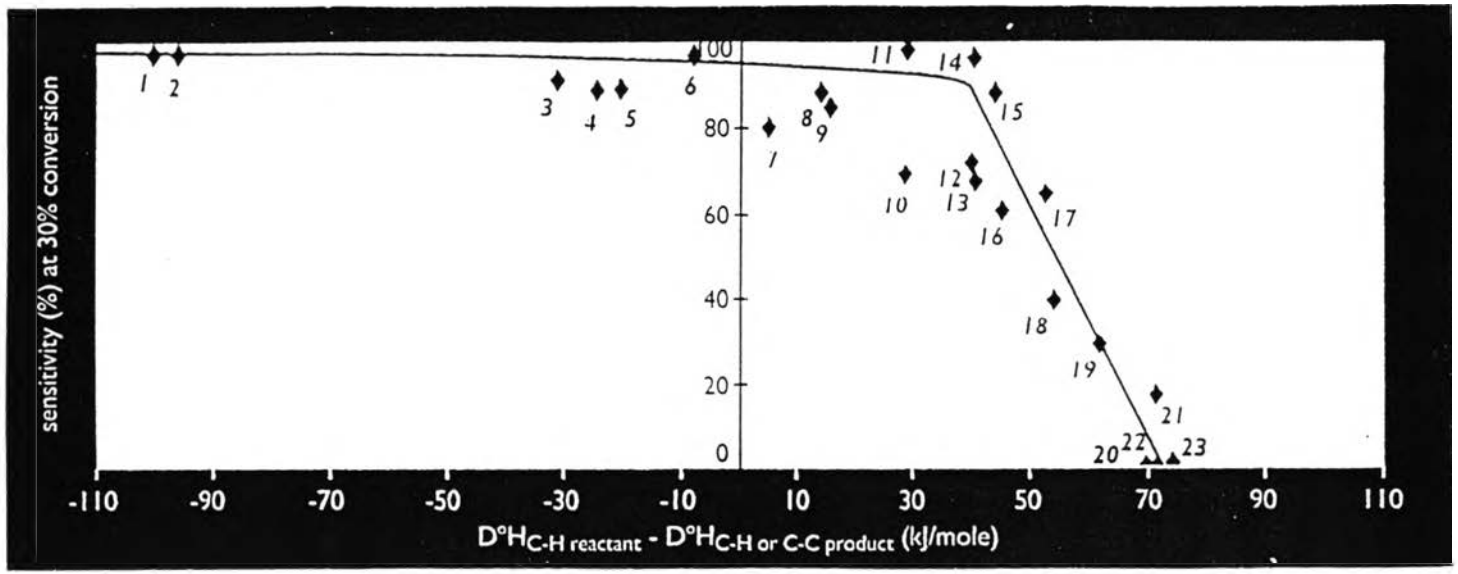


Figure 3.1 Selectivity at 30% conversion for the reactions indicated as a function of $D^{o}H_{C\text{-}H\ reactant} - D^{o}H_{C\text{-}H\ or\ C\text{-}C\ product}$ [Cassidy *et al.* (1998)].

1. Ethylbenzene to Styrene
2. 1-Butene to 1-3-Butadiene
3. Acrolein to Acrylic acid
4. Ethane to Ethylene
5. N-butane to Maleic anhidride
6. Benzene to Phenol
7. Toluene to Benzaldehyde
8. Propene to Acrolein
9. 1-Butene to 2-Butanone
10. Isobutane to Isobutene
11. Methanol to Formaldehyde
12. Methacrolein to Methacylic acid
13. Propane to Propene
14. Ethanol to Acetaldehyde
15. Isobutene to Methacrolein
16. N-butane to Butene
17. Benzene to Maleic anhydride
18. Propane to Acrolein
19. Methane to Ethane
20. Ethane to Acetaldehyde
21. Isobutane to Methacrylic acid
22. Methane to Formaldehyde
23. Isobutane to Methacrolein

clear relationship between limiting selectivities and the nature of the weakest C-H or C-C bonds in the reactants and products.

Selective oxidation of small-saturated hydrocarbons such as ethane and propane is a key challenge of current catalysis research. However, low yields in the desire product were frequently observed and, in almost all cases, the productivity of these processes was far from that of industrial interest. The main reasons are the free-radical nature of these processes, the high exothermicity, and the fact that oxygen attacks partially oxidized products more easily than the starting hydrocarbon, resulting in overoxidation [Sun *et al.* (1997)]. Therefore, there is an idea to use other chemicals such as alcohols as reactants for selective oxidation reaction.

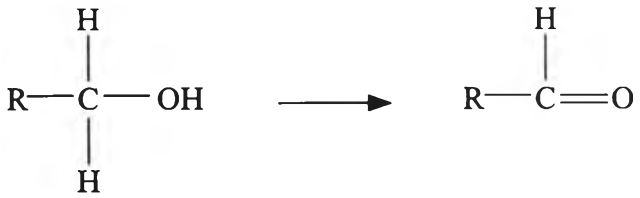
3.1 Reactions of alcohols

Reactions of an alcohol can involve the breaking of either of two bonds: the C-OH bond, with removal of the -OH group; or the O-H bond, with removal of -H bond. Either kind of reaction can involve substitution, in which a group replaces the -OH or -H, or elimination, in which a double bond is formed.

3.1.1 Oxidation

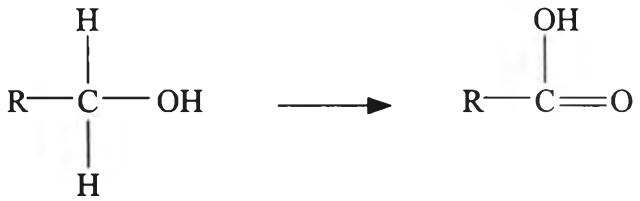
The oxidation of an alcohol involves the loss of one or more hydrogens (α-hydrogens) from the carbon bearing the -OH group. The kind of product that is formed depends upon how many of this α-hydrogens the alcohol contains, that is, upon whether the alcohol is primary, secondary, or tertiary.

A primary alcohol contains two α-hydrogens, and can either lose one of them to form an aldehyde,



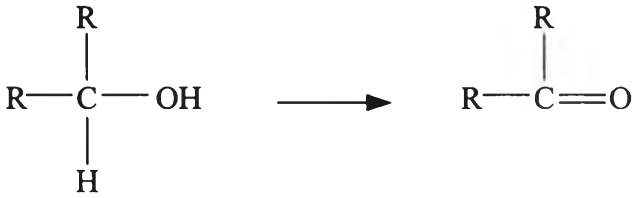
A 1°alcohol An aldehyde

or both of them to form a carboxylic acid.



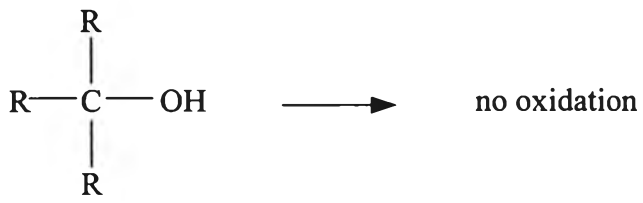
A 1° alcohol A carboxylic acid

A secondary alcohol can lose its only α-hydrogen to form a ketone.



A 2° alcohol A ketone

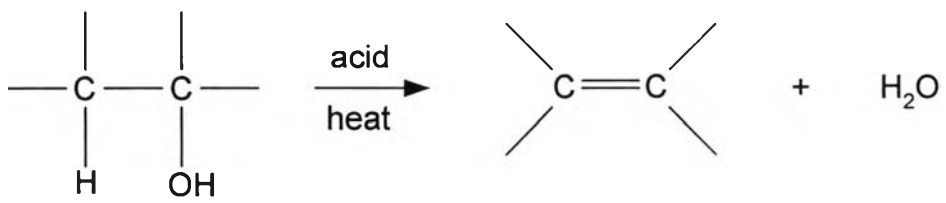
A tertiary alcohol contains no α-hydrogen and is not oxidized. (An acidic oxidizing agent can, however, dehydrate the alcohol to an alkene and then oxidized this).



A 3° alcohol

3.1.2 Dehydration

Dehydration requires the presence of an acid and the application of heat. It is generally carried out in either of two ways: (a) by heating the alcohol with sulfuric or phosphoric acid; or (b) by passing the alcohol vapor over a catalyst, commonly alumina (Al_2O_3), at high temperature. An alcohol is converted into an alkene by dehydration (elimination of a molecule of water).



Alcohol Alkene Water

The various classes of alcohols differ widely in ease of dehydration, the order of reactivity being

Ease of dehydration of alcohol $3^\circ > 2^\circ > 1^\circ$

3.2 Redox mechanism

The behavior of most oxidation catalysts can be interpreted within the framework of a redox mechanism. This postulates that the catalytic reaction comprises two steps [Mars van Krevelen (1954)]:

1. Reaction between catalyst in an oxidized form, Cat-O, and the hydrocarbon, R, in which the oxide becomes reduced:

$$\text{Cat-O} + \text{R} \longrightarrow \text{RO} + \text{Cat}$$

2. The reduced catalyst, Cat, becomes oxidized again by oxygen from the gas phase:

$$2\text{Cat} + O_2 \longrightarrow 2\text{Cat} + \text{O}$$

Under steady-state conditions the rates of the two steps must be the same.

3.3 Cobalt oxide catalyst

Cobalt oxide is an interesting material in the fields 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. 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.

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 (1980)].

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

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

3.4 Effect of support on catalytic performance

Many researches found that the catalytic performance of catalyst depending on the type of support. Suitable support not only improves catalytic activity, but also increases the thermal stability and therefore the lifetime of the catalyst. For the oxidative dehydrogenation of propane, MgO was used as support for V_2O_5 catalyst that showed high catalytic performance in the oxidation of propane. It is suggested that the loading of V_2O_5 catalyst on metal oxide having solid-base properties or the formation of complex metal oxide between V_2O_5 and basic metal oxides, reduce the strong oxidation ability of V_2O_5 to attain higher selectivity to oxidative dehydrogenation [Chaar *et al.* (1988)].

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)].

3.5 Surface reducibility and basicity

A general agreement is that the reducibility of the catalyst plays an important role in the reaction course on the activation of propane [Gao *et al.* (1994)]. In V-Mg-O catalysts, where one V atom is replaced by one Mg atom, the involved lattice V-O-M oxygen atom is less mobile and thus the catalyst surface is less reducible: these catalysts led to dominant propylene selectivity [Corma *et al.* (1993)]. For that reason, it may be possible to postulate the role of reducibility V-Mg-O systems to cover Co-Mg-O catalyst to explain the behavior of the selective oxidation reaction of alcohols.