

CHAPTER III

THEORY

A Large segment of the modern chemical industry is based on catalytic selective oxidation processes. Indeed, more than 60% of the chemicals and intermediates synthesized via catalytic processes are products of oxidation. Total catalytic oxidation is also becoming increasingly important as a method for destroying trace pollutants and contaminants in gaseous streams. One of the most important applications of selective oxidation catalysis is the functionalization of hydrocarbons. Today, catalytic oxidation is the basis for the synthesis of a large percentage of the monomers or modifiers used for the production of fibers and plastic [Centi (2001)].

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)].

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.

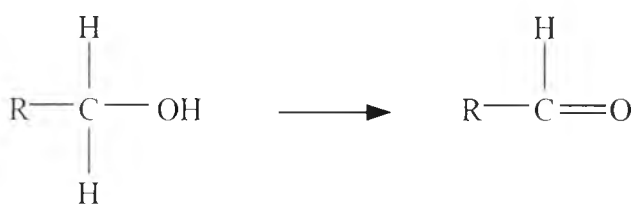
3.1 Reactions of alcohols

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.

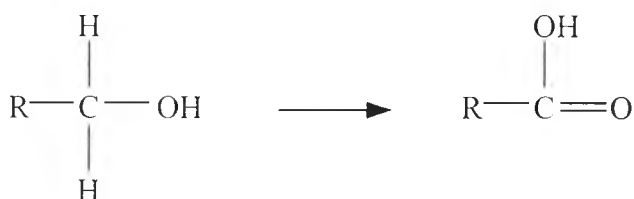
A primary alcohol contains two α -hydrogens, and can either lose one of them to form an aldehyde.



A 1° alcohol

An aldehyde

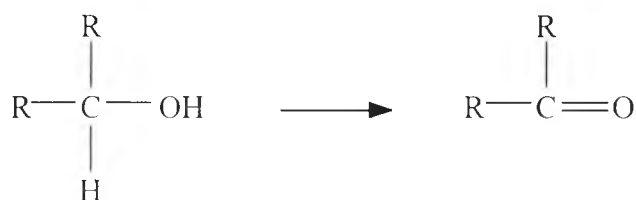
or both of them to form a carboxylic acid.



A 1° alcohol

A carboxylic acid

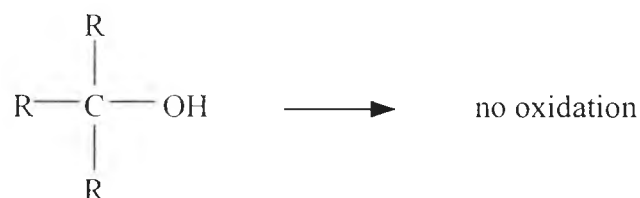
A secondary alcohol can lose its only α -hydrogen to form a ketone.



A 2° alcohol

A ketone

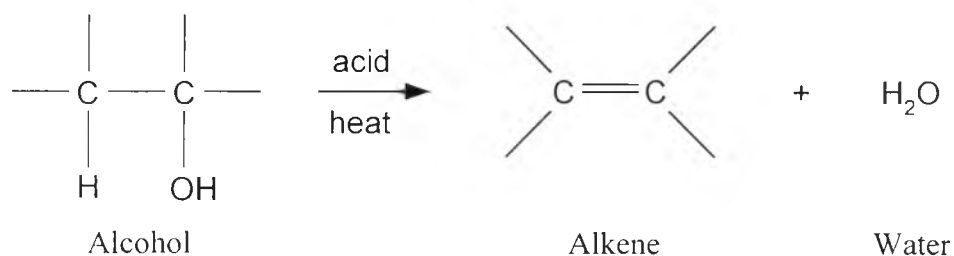
A tertiary alcohol contains no α -hydrogen and is not oxidized. (An acidic oxidizing agent can, however, dehydrate the alcohol to an alkene and then oxidized this).



A 3^o 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).



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



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:



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



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)].



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 V₂O₅ catalyst that showed high catalytic performance in the oxidation of propane. It is suggested that the loading of V₂O₅ catalyst on metal oxide having solid-base properties or the formation of complex metal oxide between V₂O₅ and basic metal oxides, reduce the strong oxidation ability of V₂O₅ 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.

3.6 Catalyst stability

A catalyst with good stability will change only very slowly over the course of time under operating conditions. Indeed, it is only in theory that a catalyst remains unaltered during reaction. Actual practice is far from this ideal. The importance of catalyst stability is often underestimated, not only in academia but also in certain sectors of industry, notably in the fine chemicals industry. In bulk chemicals production, chemists sometimes look upon the catalyst as a reactant: when it does not function anymore, it is disposed and new catalyst is added. So it is understandable that catalyst stability is not always a point of strong concern. With increasing environmental awareness this attitude will change. Some of things that lead to a progressive loss of activity and selectivity or mechanical strength are called catalyst deactivation.

3.6.1 Catalyst deactivation

A catalyst may lose its activity or its selectivity for a wide variety of reasons. The causes may be separated loosely into four types as follow [Satterfield (1991)]:

a) Poisoning

The activity of almost all catalysts is much reduced by the presence of small amounts of chemical species referred to as poisons. Atoms or molecules having electron lone pairs available for bonding to the surface tend to be strong poisons. Poisons are adsorbed on the catalyst much more strongly than the reactants, so effectively preventing their access to reaction centers. Only small amounts of poison are needed to deactivate catalysts [Pearce and Patterson (1981)].

b) Sintering

Sintering is an irreversible physical process leading to a reduction of effective catalytic area. It may consist of growth of metal crystallites on a support or of a decrease in area of a non-supported catalyst.

c) Fouling

In a number of processes catalysts are deactivated, not through sintering of the active phase or poisoning, but because reactants are physically prevented from reaching the catalyst. Fouling covers all phenomena where a surface is covered with deposit. In petroleum processing fouling is a major concern. In most of the catalytic processes in the petroleum refinery fouling by the deposition of 'coke' plays a major role. Coke is a term that is used in many meanings. Dependent on the conditions (temperature, partial pressure of stream, hydrogen, composition of the gas phase, etc.) several reactions can occur that lead to coke or in any case to carbonaceous material. At high temperatures poly-aromatic or even graphitic compounds are formed that deactivate catalysts. This coke is produced by unwanted polymerisation and dehydrogenation (condensation) of organic molecules present in the feed or formed as product. These reactions leave a layer of highly hydrogen deficient carbonaceous material on the catalyst surface, making the active sites inaccessible [Moulijn *et al.* (2001)].

d) Loss of active species

The particular active species may also be converted to another form less active or selective, as is the case with certain complex metal oxides used in partial oxidation reactions. A complex metal oxide crystal may also decompose into other compounds, sometimes caused by loss of a particular element via volatilization of a compound. A somewhat amorphous catalyst may crystallize, or a compound active in one crystal habit may be converted into a less active crystalline form. A supported metal catalyst may be reduced in activity or selectivity by becoming alloyed with a metallic impurity or by reaction with the support; for example, a nickel/alumina catalyst may be converted to a nickel aluminate.