



CHAPTER II

THEORY

2.1 General feature of titanium silicalite (TS-1) [Notari (1989)]

Titanium silicalite (TS-1) is an interesting material obtained by isomorphic substitution of trivalent metals or tetravalent metals in the framework of crystalline aluminosilicates or silicates. TS-1 is member of the pentasil family, rings consisting of O atoms, isomorphous with ZSM-5 and silicalite-1. The two well known molecular sieves of MFI type are silicalite-1 and ZSM-5 (Figure 2.1) shows a MFI – crystal. This type of linking results in the formation of two intersecting channels in MFI with 10-membered ring openings. One is elliptical with cross section 0.51 nm 0.53 nm and the other one is circular with a cross section of 0.55 nm. The cavities formed in ZSM-5 (MFI) by these intersecting channels are equivalent to a maximum diameter of 0.9 nm (shown in figure 2.2). The theoretical channel length in ZSM-5, obtained from crystallographic data, is 8.8 nm.

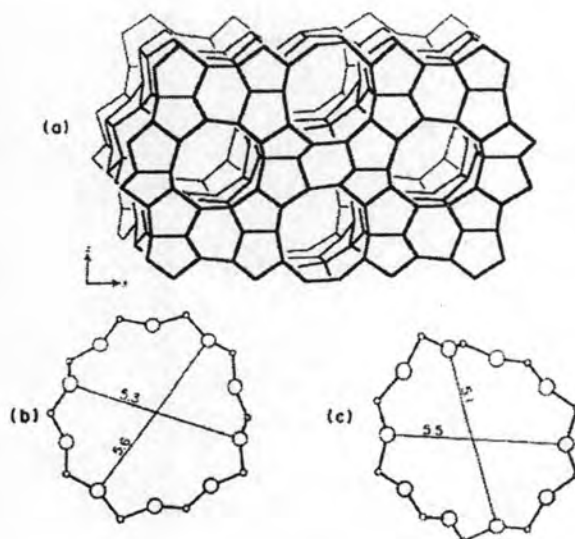


Figure 2.1 Structure of MFI a) The MFI framework topology b) 10-ring viewed along [010] (straight channel) and c) 10-ring viewed along [100] sinusoidal channel.

Titanium has a stable valence of 4 and in an oxidizing medium it is very likely that this valence is maintained. An examination of the chemistry of Ti^{4+} compounds immediately shows that Ti^{4+} has a strong tendency to assume a high coordination

number: with oxygen, six groups in octahedral coordination form a stable and very frequently observed configuration, but to do this Ti^{4+} must have near neighbours capable of increasing their coordination number to satisfy at the same time titanium valency of four and coordination of six. When bulky groups are linked to Ti^{4+} , tetrahedral coordination is also observed. Coordination of seven in a pentagonal pyramidal arrangement like in peroxo compounds and of eight like in $Ti(NO_3)_4$ are also observed.

From the crystalline structure and the regular change in unit cell parameters which are consistent with isomorphous substitution of Si^{4+} with Ti^{4+} it seems justified to represent TS-1 as a silicalite in which few Ti^{4+} have taken the place of Si^{4+} . The interpretation of the catalytic activity of TS-1 must take into consideration the role played by these few Ti^{4+} : in fact pure silicalite is totally inactive, and other phases containing Ti have not been identified. Due to the fact that TS-1 crystallizes from a homogeneous solution, it is reasonable to assume that the distribution of Ti^{4+} in the crystal lattice is at random; since the Si/Ti ratio is in the range 40 - 90 in typical preparations, most Ti^{4+} must be isolated from each other by long sequences of -O-Si-O-Si-O-. If Ti^{4+} replaces a Si^{4+} it should be tetrahedrally coordinated by O^{2-} : However, the presence of a band at 980 cm^{-1} closely corresponds to the band observed in other titanium compounds containing the $\begin{matrix} \diagup \\ \text{Ti} = \text{O} \\ \diagdown \end{matrix}$ group, whose stretching frequency is 975 cm^{-1} with bond distances of $1.66 - 1.79\text{ \AA}$; furthermore, hydroxyl groups are present at the surface as shown by the increase in selectivity which is obtained upon silylation.

Finally, near neighbour positions of Ti^{4+} are occupied by Si^{4+} which in a field of O^{2-} is stable only in tetrahedral coordination. A simple representation of the sites where substitution has occurred which takes into consideration the various pieces of experimental evidence could be

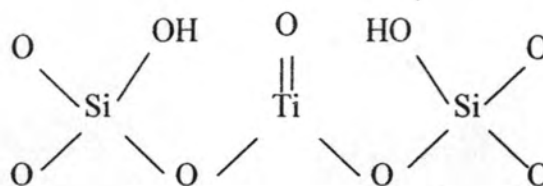


Figure 2.2 Framework of TS-1.

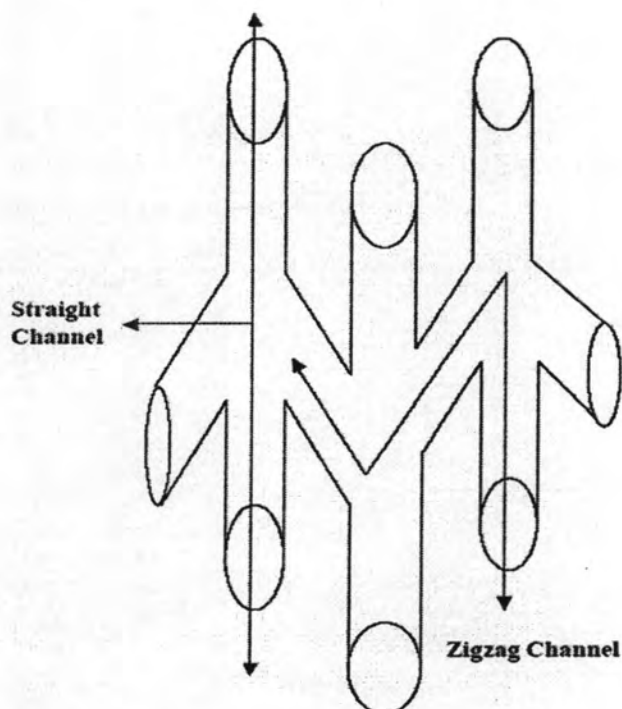


Figure 2.3 Pore and channel structure of TS-1.

High coordination ability of Ti^{4+} sites associated to the hydrophobicity of silicalite structure, spatial selectivity and random distribution of Ti^{4+} sites are responsible of this remarkable and unusual catalytic activity. Moreover, this catalyst also has important features such as run at less than $100^{\circ}C$, high selectivity ($> 80\%$), easy catalyst regeneration. Since its discovery TS-1 has been using in several chemical reactions, some of them also applied at industrial scale. Frequently TS-1 catalysis has completely opened new chemical ways replacing older technologies suffering from several drawbacks like wastes by product production as well as stronger reaction conditions.

The unique performances of the TS-1 catalyst are due to the specific features of isolated Ti active sites, able to efficiently promote activity and selectivity in several oxidation reactions with hydrogen peroxide, while not isolated Titanium, such as segregated TiO₂ "Anatase like" phase, is inactive for these reactions.

2.2 Catalyst properties

It was mentioned that catalyst properties can be classified as physical, chemical and dynamic.

2.2.1 Physical and mechanical properties

Physical properties of catalysts include particle size, density, pore volume, porosity, pore size and pore size distribution, BET surface area, active site concentration (catalytic surface area), and dispersion. Mechanical properties included crush strength and attrition resistance.

2.2.2 Chemical and mechanical properties

Chemical properties of catalysts include acidity (Brönsted and Lewis), composition (surface and bulk), oxidation state (surface and bulk) of the catalyst phase, and structure (surface and bulk).

2.2.3 Dynamic (catalytic) properties

Dynamic or catalytic properties focus on the behavior during reaction, i.e. catalytic properties including activity, selectivity and stability.

2.3 Parameters affecting the synthesis of TS-1 catalysts

Basically all synthesis parameters, some of which are fixed and some which are variable, influence the quality of the catalysts. Usually the synthesis of catalyst to have specific properties is desired. These properties could be the nature of the phase formed, chemical composition, purity, particle size, surface area, pore sizes, pore

volumes, and many more, including the demands which are imposed by the reaction conditions (activity, selectivity and conversion), catalyst compositions, metal dispersion and types of inorganic supported used. It is therefore necessary to optimize the parameters in order to produce the desired material. Figure 2.4 summarizes the parameters which can be adjusted in the synthesis of catalyst and the properties which are mainly influenced by these parameters. The following discussion attempts to give some general guidelines concerning the influence of certain parameters on the preparing catalyst. It should, however, be stressed, that the stated tendencies are only trends which might vary in special cases. The exact choice of synthesis parameters are usually the result of physical properties, chemical properties and catalytic behavior of catalyst.

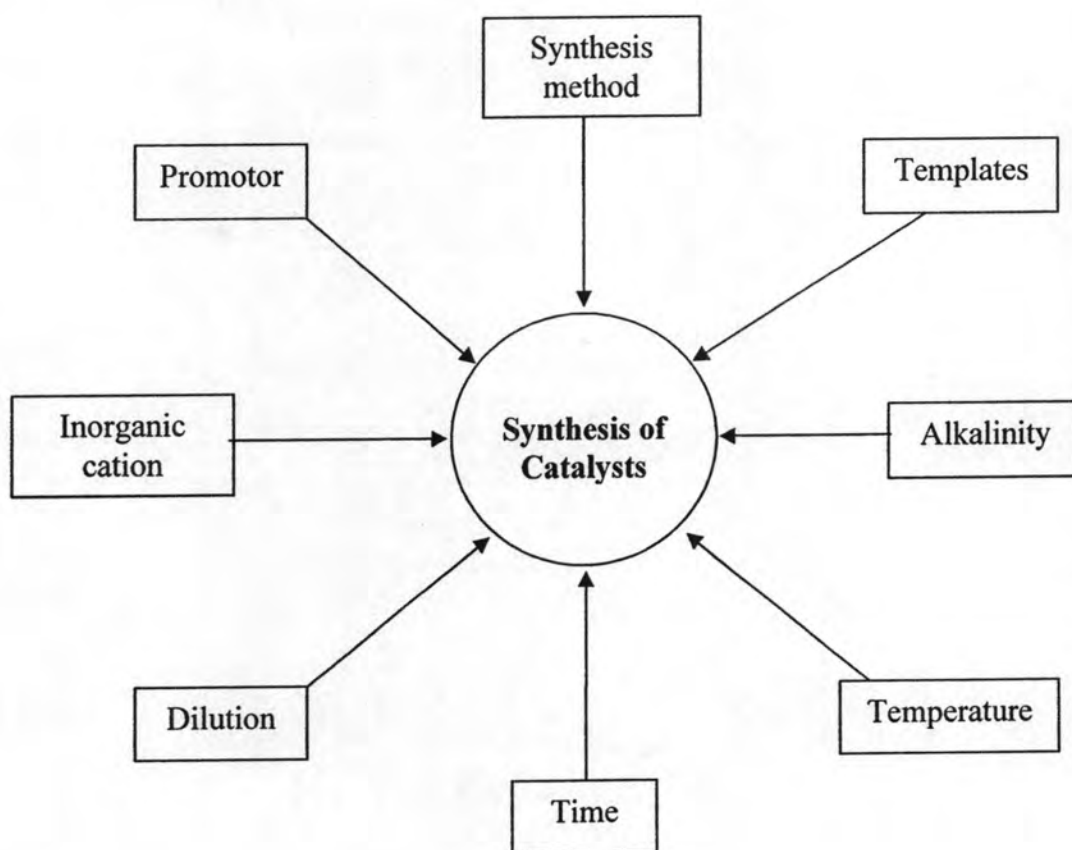


Figure 2.4 Parameters affecting the properties of catalyst.

2.3.1 Catalyst Synthesis Method

Richardson et al., (1989) has introduced the concept of a catalyst design triangle (Figure 2.5) and discussed how catalyst design is a careful optimization of physical/ mechanical, chemical and catalytic properties. For example, activity is increased by increasing porosity reactants and surface area decreases with increasing porosity. Thus, a clear understanding of these intricate relationships is necessary to optimize activity, stability and strength of the catalyst.

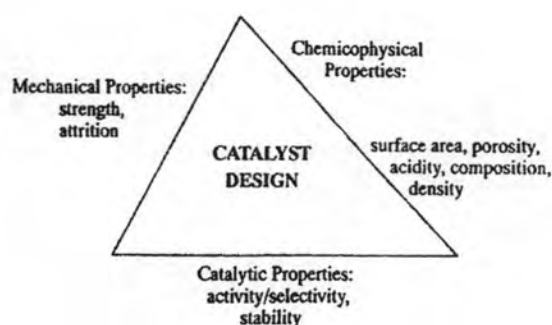


Figure 2.5 Triangle concept for catalyst design. Catalyst design is an optimized combination of interdependent mechanical, chemicophysical and catalytic properties (adapted from Richardson et al., 1989).

- *Hydrothermal synthesis*

This method involves heating the reactants in water/steam at high pressures and temperatures. The water has two functions, as a pressure-transmitting medium and as a solvent, in which the solubility of the reactants is P, T-dependent. The method is quite simple; reactants and water are placed inside a Teflon-lined cylinder or 'bomb' which is either sealed or connected to an external pressure control. The bomb is then placed in an oven, usually at a temperature in the range 100-500°C. Pressure is controlled either externally or by the degree of filling in a sealed bomb, by making use of the P/T "phase diagram". Figure 2.6 (a);

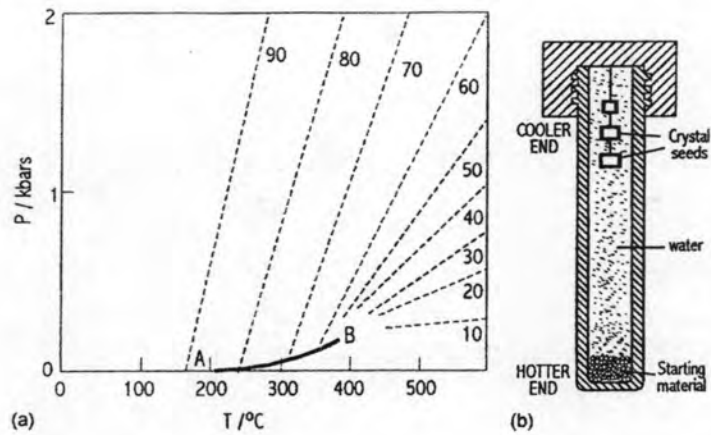


Figure 2.6 (a) Pressure-temperature relations for water at constant volume. Dashed curves represent pressures developed inside a closed vessel; numbers represent the percentage degree of filling of the vessel by water at ordinary P, T. (After Kennedy, 1950). (b) Schematic hydrothermal bomb used for crystal growth [West, (1984)].

Curve AB is the *saturated steam curve* and separates water (above) from steam (below); at temperatures above 374°C , point B, the water is in the *supercritical* condition and there is no distinction between liquid and vapour states.

Hydrothermal methods have a wide range of applications:

(a) For zeolite synthesis, the final stage is to heat aluminosilicate gels hydrothermally to crystallize the zeolites.

(b) Single crystals, are grown hydrothermally in a temperature gradient using the arrangement shown in Figure 2.6(b). The solubility of SiO_2 in NaOH solution increases with temperature; effectively, therefore, SiO_2 dissolves at the hot end, is transported to the cooler end by convection and crystallizes on the suspended seeds. In this reaction, NaOH acts as a *mineralizer*: SiO_2 is only sparingly soluble in H_2O , but solubility increases greatly when NaOH is dissolved in H_2O . Use of NaOH solution instead of pure H_2O greatly speeds up the growth of quartz crystals by hydrothermal treatment.

- *Comparison of different methods*

For each crystalline substance, there are optimum conditions for satisfactory crystal growth. In preparing to grow crystals of a new material, much preliminary work, perhaps lasting several months, is needed in order to find suitable growth conditions. The quality of the resulting crystals therefore depends very much on the experimenters' skill. In addition, the various techniques that are available have certain intrinsic advantages and disadvantages; these are summarized in Table 2.1.

High pressure and hydrothermal methods are finding increasing applications in materials science and solid state chemistry. They are technologically important, both as an important method of crystal growth and for the synthesis of new materials with useful properties. They are also interesting scientifically since the use of high pressures provides an additional parameter or lever for obtaining fundamental information on the structures, behavior and properties of solids.

In most high pressure methods, the sample is effectively squeezed between the laws of opposed rams or anvils. Hydrothermal methods differ in that water under pressure is present inside the reaction vessel.

Table 2.1 Comparison of crystal growth methods [West, (1984)].

Method	Advantages	Disadvantages
Melt growth (Czochralski, Bridgman-Stockbarger, Verneuil)	Rapid growth rates, giving large crystals; simple apparatus	Crystal quality may be poor with inhomogeneities and large defect concentration
Solution growth (water crystallization, flux growth, hydrothermal method)	Isothermal conditions with slow growth rates give quality crystals of low defect concentration	Slow growth rates; problems of contamination by container or flux

- *Incorporation method*

The incorporation method is used to improve the catalyst because this method is easy to prepare. Since titanium atom can be loaded into TS-1 framework, therefore, principal of second metal selection for this study is that the second metal should have atomic and ionic radius nearly to that of titanium. Both of titanium atoms and second metals are loaded directly into the framework simultaneously with SiO₂ framework forming in one step by hydrothermal method.

2.3.2 Effect of templates

These are organic molecules, generally, organic amines or organic quaternary ammonium salts. They usually contain a hydrophobic part (hydrocarbon chain) and a hydrophilic part (amine or quaternary ammonium moiety). The hydrophobic part of the template molecule polarizes the hydrophilic water envelope around the various building units and reorganizes them in a particular orientation. These molecules are usually known as structure directing agents as well as void filler. Depending on the nature of the template, zeolites with different morphologies are obtained. Templates may help the formation of zeolite either by kinetically or thermodynamically or both. Chemically they help TO₄ units to pack around themselves in a preferred orientation and thereby providing it with nucleus on which further nucleation followed by crystallization can occur. Thermodynamically it may help by lowering the chemical potential of the lattice formed upon the inclusion of the templates during nucleation. Tetrapropylammonium cation in the form of hydroxide is the most commonly employed template for the synthesis of TS-1. Although tetrapropylammonium hydroxide is most commonly used, tetrapropylammonium bromide is also used in presence of different amines such as ammonia, hexane diamine, etc.

2.3.3 Alkalinity

Alkalinity of the solution plays a key role in the hydrothermal synthesis of zeolites. This is known as mineralizer or mobilizing agent. It solubilizes both silicon and aluminium sources and brings them in a homogeneous solution with sufficient

number of soluble precursors for the zeolite synthesis. A supersaturated solution is reached which contains sufficient number of T-atoms in tetrahedral position with condensable ligands. Through condensation of these T atoms from the supersaturated solution, nucleus of the zeolite is formed which due to further nucleation leads to the formation of zeolite crystal. However, the alkalinity of the solution has a marked influence on the crystal size as well as the solid yield of the TS-1. At high OH⁻ concentration multiple nucleation takes place which leads to the formation of irregularly shaped crystals. The solubilization of different silicate precursors leads to a decrease in the yield of TS-1.

2.3.4 Temperature

The rate of nucleation increases with increase in temperature helping crystallization in zeolite synthesis. It can again determine the type of products that will crystallize from the solution. At high temperature, the water molecules, which normally fill up the pores of the porous solids, will be evaporated and dense packed structure is expected. Similarly if the pores are filled up with the high boiling liquid, then even at high temperature open porous structure is formed. However, TS-1 synthesis is dependent on temperature. It has both a lower limit and an upper limit. Beyond these limiting values, formation of extra-framework titanium species is facilitated.

2.3.5 Time

The crystallinity of a zeolitic material usually increases with time up to a certain extent, after that the phase transformation in zeolites follows the Ostwald rules of successive transformation. The least thermodynamic product will form first. This is then successively transformed to most stable product through meta-stable phase. TS-1 also follows the general rule that with time the crystallinity of the sample increases.

2.3.6 Dilution

Dilution also has an effect in the nucleation and crystallization process in the synthesis of TS-1. Increase in the water content leads to the dilution of the reactive zeolite precursors. Therefore, increased dilution prevents supersaturation and retards nucleation. Besides, increase in dilution forms a thicker sphere of hydration around both the silicate/titano-silicate species. Before these reactive species condense, they have to strip off their hydration sphere. So increased dilution may lead to an increase in nucleation time and may retard crystallization.

2.3.7 Inorganic cation

The presence of inorganic cations (Na^+ , K^+ , Cs^+ , etc) has a tremendous role in the synthesis of TS-1. In general, inorganic cations (Na^+ , K^+ , Cs^+ , etc) as well as organic strongly perturb the hydrogen bonding among the water molecules and orient them in a particular pattern around them. The smaller the size of the cation, greater is the charge density, greater the perturbation of the hydrogen bonded water molecules. Depending on whether these cations can organize the water molecules or not, they are defined as structure breaking and structure making. The small cations such as Li^+ , Na^+ , K^+ , etc, are called structure making as they can reorganize the water molecules. Large cations like Cs^+ , NH_4^+ , etc are called structure breaking, as because of their low charge density they are not able to reorganize the water molecules. The silicate can replace these organized water molecules and aluminate species and cage like structure can be obtained. However, alkali and alkaline earth metals have a negative effect on the synthesis of TS-1. The presence of alkali cation prevents the incorporation of the Ti^{4+} in the silicalite lattice and favors the formation of extra-framework titanium species.

2.3.8 Promoter (Farrauto and Bartholomew, 1997).

There are two kinds of promoters such as textural and chemical promoters. Textural promoters are used to facilitate the dispersion of metal phase during preparation and/or reaction conditions. Chemical promoters are used to enhance the activity and/or selectivity of catalysts. Generally, noble, alkali and alkaline earth

metals are considered to be chemical promoters, which play important roles on catalyst performance to date.

The effects of promoters such as Ru, Re, Rh, Pt and Pd on Co catalysts were studied. They reported that these metal promoters can increase the reducibility and dispersion of Co, preserve the activity by preventing the formation of coke, exhibit cluster and ligand effect and act as a source for hydrogen spillover.

2.4 Catalytic activity

The catalytic activity in zeolite and porous materials is governed, mainly, by diffusion process. The main processes governing the catalytic activity are,

- Transport of the reactant to the zeolite surface followed by diffusion of the reactant to an active site inside the pore / channel.
- Adsorption of the reactant to an active site.
- Chemical reaction of the adsorbed reactant to form adsorbed product(s).
- Desorption of the adsorbed product(s).
- Diffusion of the adsorbed products from interior active site to the outer surface of the catalyst.
- Transfer of the product(s) away from the zeolite surface.

2.4.1 Shape selectivity

One of the interesting features of the heterogeneous solid catalysts is the shape selectivity of the reactions. Three types of shape selectivity are mainly observed in zeolite catalysis. The reactant shape selectivity, product shape selectivity and restricted transitionstate shape selectivity. The reactant shape selectivity arises because of the different dimensions of reactant molecules. When more than one reactant is involved in a reaction, that reactant, the molecular dimension of which fits the pore diameter/channel dimension of the zeolite, can enter and react. This is known as reactant shape selectivity. This type of shape selectivity is utilized in petrochemical chemistry where linear alkanes are cracked preferentially leaving aside the branched alkanes. When a number of products are formed inside the

pores/channels of a zeolite, those products will diffuse out whose sizes are within the range of the pore diameter/channel dimension of the zeolite. The remaining heavy products will either break down to smaller molecules and will come out or they will deactivate the catalyst. This is known as product shape selectivity. Not all transition states are allowed to form inside the zeolite pore/channel. Only those transition states whose molecular dimension is within the dimension of the zeolite pore channel will be selectively formed. This is exhibited in the subsequent product distribution pattern. This is known as transition state shape selectivity.

2.4.2 Catalytic sites in TS-1

TS-1 behaves as a unique oxidation catalyst in the presence of aqueous hydrogen peroxide in a variety of reactions. Therefore, naturally, the emphasis on is to find out the reactive species in variety of oxidation processes involving TS-1 and aqueous H_2O_2 . By different characterization techniques it was proved that Ti- ion, in TS-1, was in +4 oxidation states and is in tetrahedral environment. There are several evidences that the active Ti sites in framework are responsible for catalytic oxidation. But, however, the nature of the tetrahedral titanium species as well as the nature of the active species involved in the oxidation, still, has been the matter of discussion and debate. Zecchina et al. (2004) have shown with the help of the EXAFS studies that there are at least two different kinds of tetrahedral framework titanium species in TS-1.

2.5 Reaction of alcohols

Reaction of an alcohol can involve the breaking of either 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 replace the -OH or -H, or elimination, in which a double bond is formed.

2.5.1 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 can lead to aldehydes, ketones or carboxylic acids, depending upon the reaction conditions and the degree of substitution on the alcohol (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

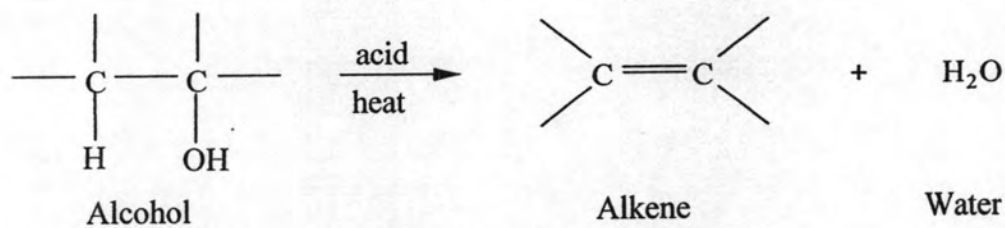
A tertiary alcohol contains no α -hydrogen and is not oxidized. (An acidic oxidizing agent can, however, dehydrate the alcohol to an alkene and then oxidized this).



A 3° alcohol

2.5.2 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

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

2.5.3 Combustion

The combustion is the burning of any substance, in gaseous, liquid, or solid form. In its broad definition, combustion includes fast exothermic chemical reactions, generally in the gas phase but not excluding the reaction of solid carbon with a gaseous oxidant. In combustion, the reactant will burn in oxygen, producing a limited number of products. When a hydrocarbon burns in oxygen, the reaction will only yield carbon dioxide and water. When a hydrocarbon or any fuel burns in air, the combustion products will also include nitrogen. When elements such as carbon, nitrogen, sulfur, and iron are burned, they will yield the most common oxides. Carbon will yield carbon dioxide. Nitrogen will yield nitrogen dioxide. Sulfur will yield sulfur dioxide. Iron will yield iron(III) oxide. It should be noted that complete combustion is impossible to achieve. In reality, as actual combustion reactions come to equilibrium, a wide variety of major and minor species will be present. For example, the combustion of methane in air will yield, in addition to the major products of carbon dioxide and water, the minor products which include carbon monoxide, hydroxyl, nitrogen oxides, monatomic hydrogen, and monatomic oxygen. Generally, the chemical equation for stoichiometric burning of hydrocarbon in oxygen is as follows:



For example, the balanced chemical equation for combustion of acetone is:

