CHAPTER II

THEORY

2.1 Heterogeneous catalysis

So far the most important catalysts used are the heterogeneous catalysts [42]. Heterogeneous catalysis takes place between two or several phases. Generally, the catalyst is a solid, and the reactants are gases or liquids. For supported catalysts the catalytically active substance is added to a support material that has a large surface area and that is usually porous.

Generally, in the heterogeneous catalysis, phase boundaries are always present between the catalyst and the reactants, while in the homogeneous catalysis, catalyst, reactants, and products are in the same phase. Homogeneous catalysts have a higher degree of dispersion than heterogeneous catalysts since each individual atom, in case of metal catalysts can be catalytically active. In heterogeneous catalysts only the surface atoms are active. Due to the high degree of dispersion, homogeneous catalysts exhibit a higher activity per unit mass of metal than heterogeneous catalysts. The major disadvantage of homogeneous transition metal catalysts is difficulty separating catalysts from the product. Heterogeneous catalysts are either automatically removed in the process, or they can be separated by simple method such as filtration or centrifugation. In case of homogeneous catalysts, more complicated process such as distillation, liquid-liquid extraction, and ion exchange must be often used [41, 45-47].

2.2 Molecular sieves

With the recent discoveries of molecular sieve materials [43] containing other elements in addition to, or in lieu of, silicon and aluminum, the casual interchange of the terms "molecular sieve" and "zeolite" must be reconsidered. In 1932 McBain proposed the term "molecular sieve" to describe a class of materials that exhibited selective adsorption properties. He proposed that for a material to be a molecular sieve, it must separate components of a mixture on the basis of molecular size and shape differences. Two classes of molecular sieves were known when McBain put forth his definition: the zeolites and certain microporous charcoals. The list now concludes the silicates, the metallosilicates, the metalloaluminates, the aluminophosphates ($AlPO_4$), metalloaluminophosphates (MeAPO), as well as the zeolites. The different classes of molecular sieve materials are listed in Figure 2.1. All are molecular sieves, as their regular framework structures will separate components of a mixture on the basis of size and shape differences. The difference lies in their elemental composition but not with in the structure of these materials, as many of them are structurally analogous. Therefore, all are molecular sieves though none but the aluminosilicates should carry the classical name zeolites.

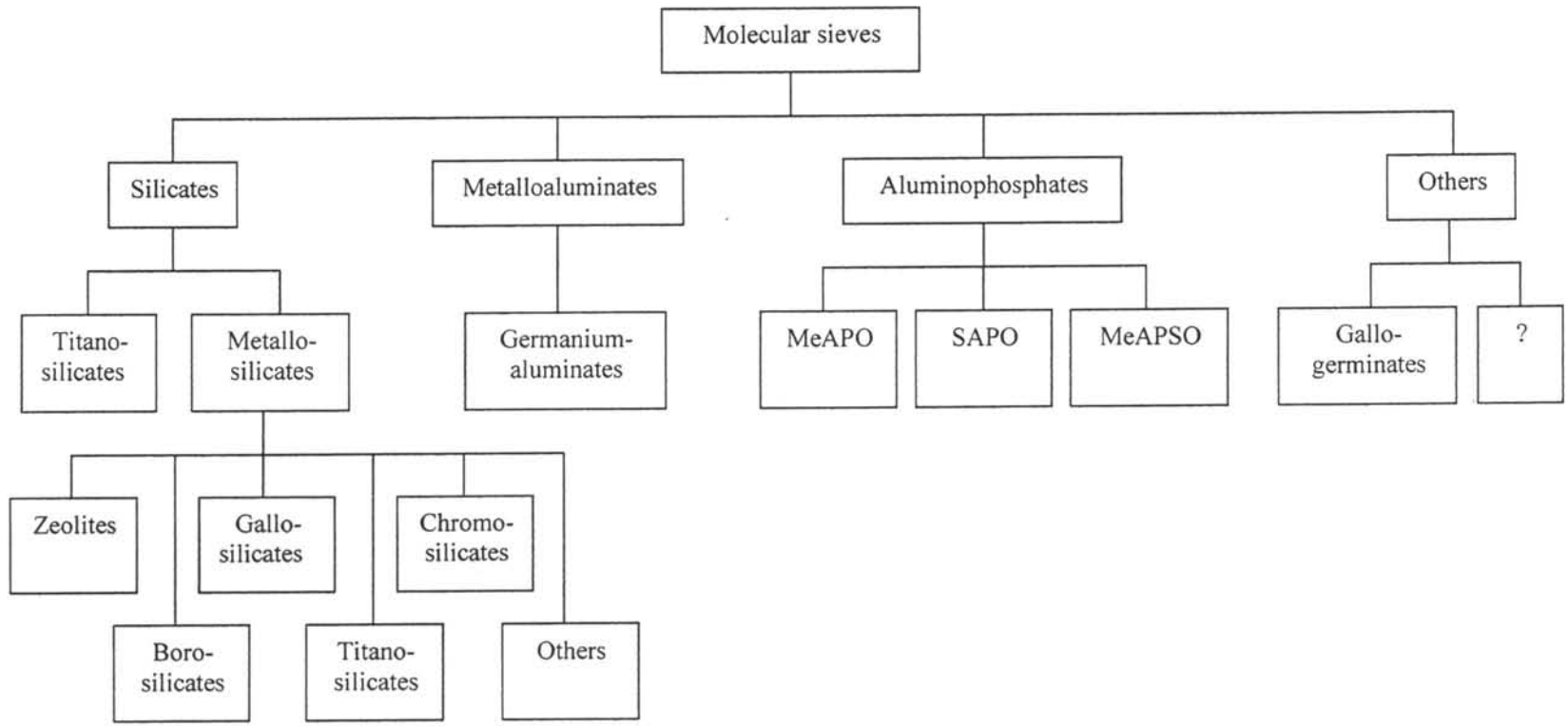


Figure 2.1 Classification of molecular sieve materials including the extensive variation in composition. The zeolites and titano-silicates occupy a subcategory of the metallosilicates [43].

2.3 Zeolites

Zeolites [43-44] are crystalline, hydrated aluminosilicates of group I and group II elements, in particular, sodium, potassium, magnesium, calcium, strontium and barium. Structurally, the zeolites are "framework" aluminosilicates, which are based on an infinitely extending three-dimensional network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing all of the oxygen as shown in Figure 2.3.

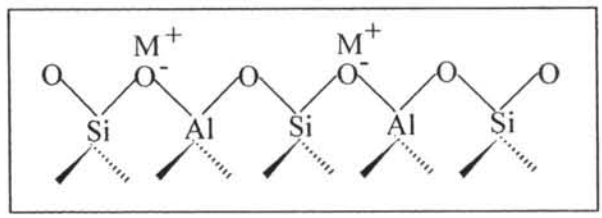


Figure 2.2 The structure of zeolites. [43]

The AlO_2^- tetrahedra in the structure determine the framework charge which is balanced by cations that occupy nonframework positions. The general formula for the composition of zeolites is

$$M_{x/n}\,[(AlO_2)_x\,(SiO_2)_y].\ w\ H_2O$$

Where M is the cation of valence n, generally from the group I or II ions, although other metals, nonmetals, and organic cations are also posible, w is the number of water molecules. Water molecules presented are located in the channels and cavities, as are the cations that neutralize the negative charge created by the presence of the AlO_2^- tetrahedral unit in the structure. Total number of tetrahedral atom, x+y, are specific for a structure. For example, the FAU structure has total number of x+y equal to 192 while MFI has number of x+y equal to 96.

2.4 Structures of Zeolites

The structures of zeolites consist of a three-dimension framework of the tetrahedral primary building units when tetrahedral atoms are silicon or aluminum. as shown in Figure 2.3. All zeolite structures have in common the primary building unit.

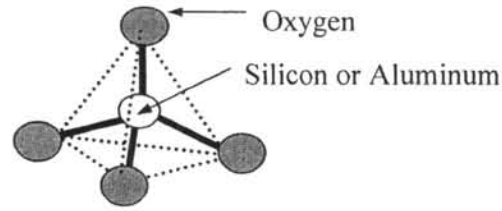


Figure 2.3 A primary building unit of zeolites.

Many zeolite structures are based on a secondary building unit (SBU) which consists of selected geometric groupings of these tetrahedra. There are nine such building units, which can be used for describing all of the known zeolite structures. The secondary building units consist of 4, 6 and 8-member single ring, 4-4, 6-6 and 8-8 member double rings, and 4-1, 5-1 and 4-4-1 branched rings as illustrated in Figure 2.4.

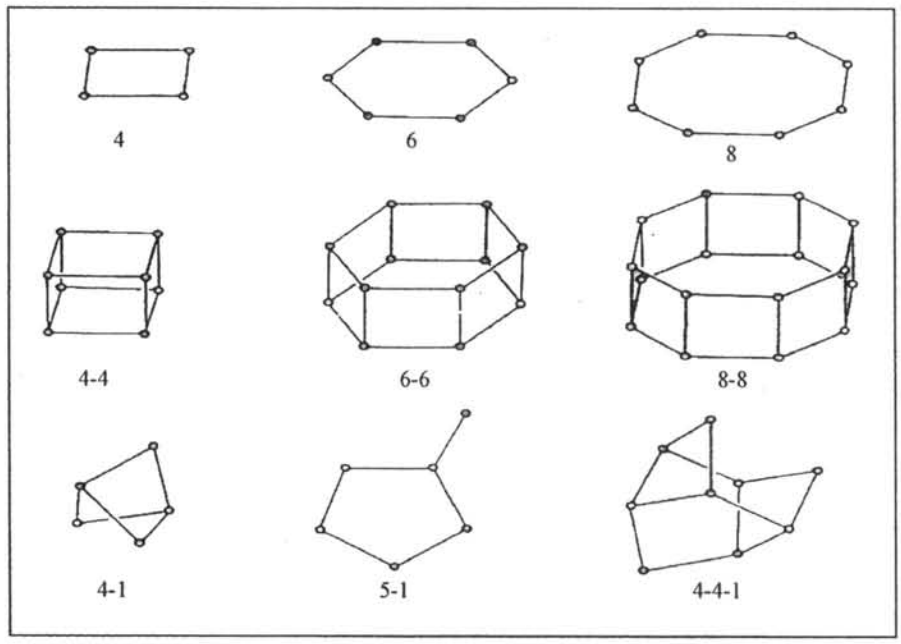


Figure 2.4 Secondary building units found in zeolite structures [43].

The different pore sizes found in zeolites were due to the different number of tetrahedral atoms defining the opening, as shown in Figure 2.5.

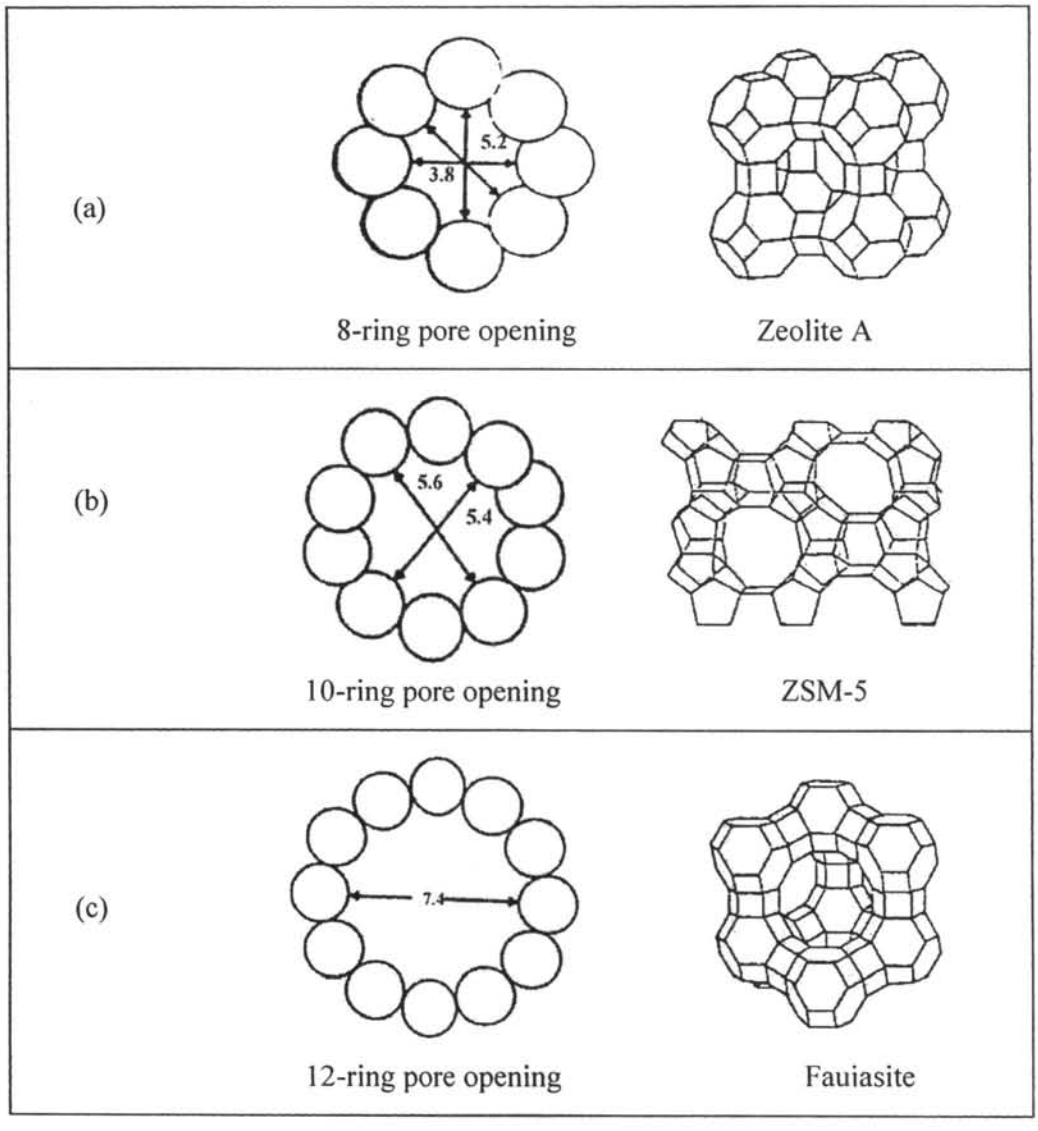


Figure 2.5 Examples of the three types of pore openings in the zeolite molecular sieves, (a) small pore zeolite, (b) medium pore zeolite and, (c) large pore zeolite [43].

2.5 Shape Selectivity of Zeolites

Shape selectivity [43] plays a very important role in zeolite catalysis. Highly crystalline and regular channel structures are among the principal features that zeolites used as catalysts offer over other materials. Shape selectivity is divided into 3 types: reactant shape selectivity, product shape selectivity, and transition-state shape selectivity. These types of selectivities are depicted in Figure 2.5.

Reactant selectivity [48] is observed when only a fraction of the reactant has access to the active sites because of molecular sieving effects, while product selectivity occurs when only some product species with proper dimensions (or shape) can diffuse out of the zeolite intracrystalline volume. Restricted transition-state selectivity will take place when certain reactions will be prevented as the transition-state necessary for them to proceed will not be reached due to steric and space restrictions.

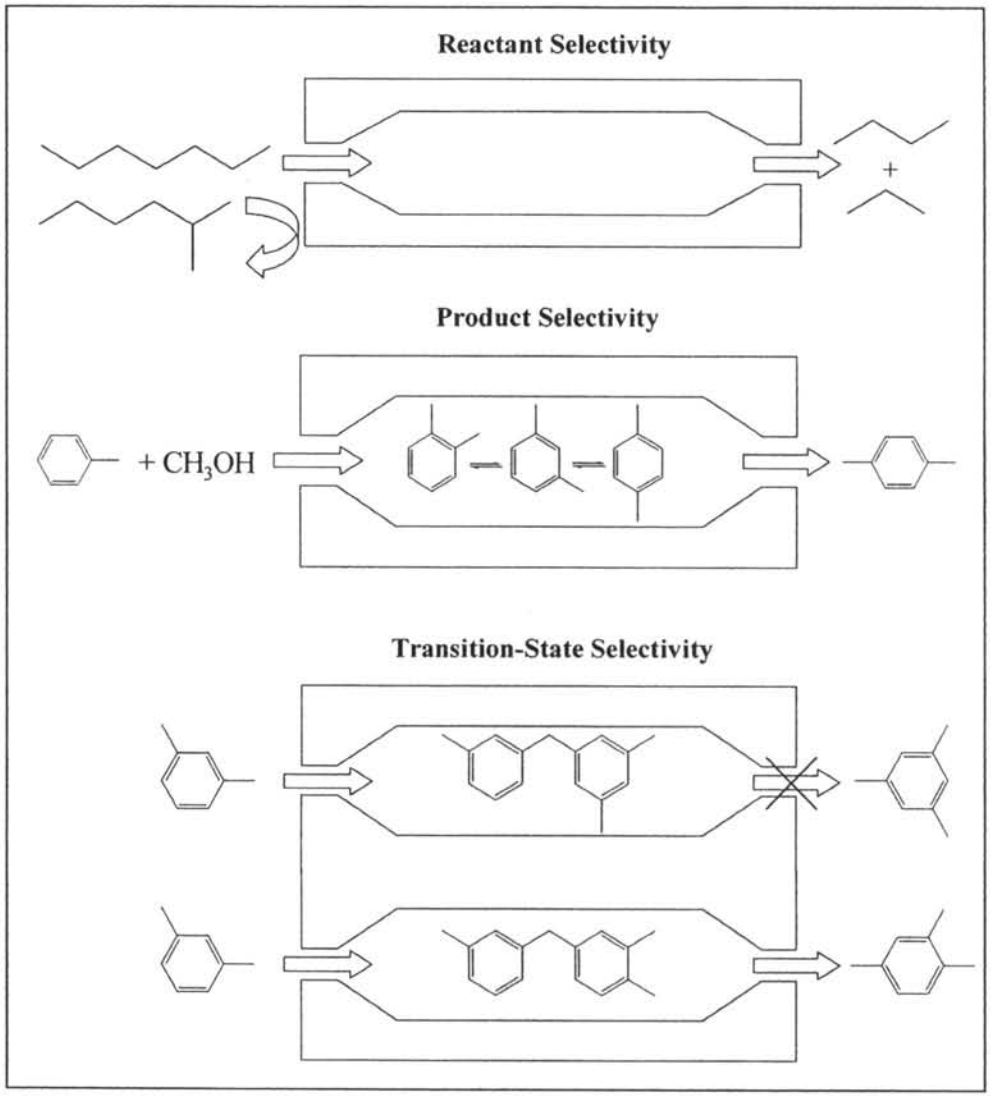


Figure 2.6 Three types of selectivity in zeolites: reactant, product and transition-state shape selectivity [43].

Diffusion will of course play a role of paramount importance. Those molecules with high diffusivity will react preferentially and selectively, while molecules which

are excluded from the zeolite will only react on the external non-selective surface of zeolite only, due to their diffusivity is zero. Products with high diffusitivity will be preferentially desorbed while the bulkier molecules will be converted and equilibrated to smaller molecules, which will diffuse out, or eventually to larger (partially dehydrogenated) species, which will block the pores. The later will lead to a progressive deactivation of the catalysts by carbonaceous residues laydown (*i.e.* coke).

A channel (or pore) opening consisting of 10-member oxygen rings which is intermediate between that of classical shape-selective zeolites (such as erionite, ferrierite, gemelinite, chabazite, or zeolite A) and that of large pore zeolites (such as faujasite, mordenite, and fault-free offretite) as shown in Figure 2.7. ZSM-5 accepts, by decreasing order of preference, normal paraffins, isoparaffins, other monomethyl-substituted paraffins, monocyclic aromatic hydrocarbons (eventually substituted by no more than three methyl groups), and to a much smaller extent dimethyl-substituted paraffins.

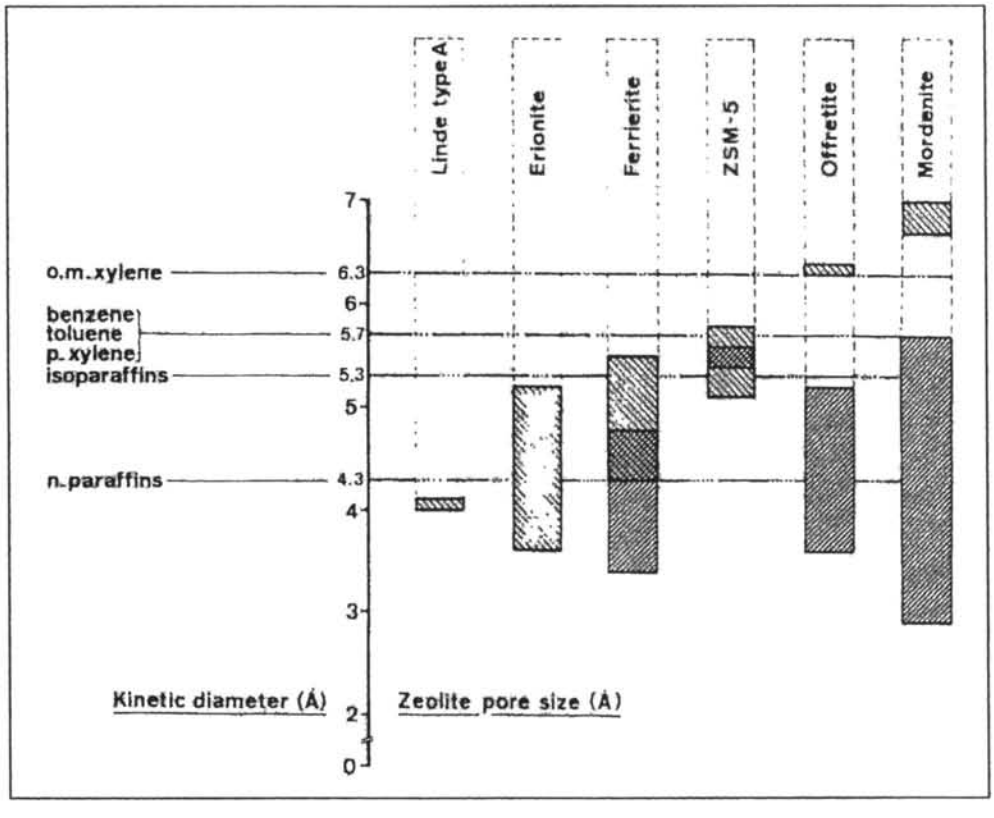


Figure 2.7 Correlation between pore size of various zeolites and kinetic diameter of some molecules [48].

The zeolites are classified according to the sizes of these apertures (Table 2.1). The table includes the number of oxygen atoms in the aperture of each molecular sieve (8, 10, 12, 18 or>18) and the aperture dimension (the smallest being about 0.4 mm for zeolite A and the largest being MCM-41 around 1.5-10 mm). The size of the aperture is also dependent on the sizes of the nearby cations, which may partially block it.

Table 2.1 Some representative molecular sieves and their pore dimensions [a] [49-50]

Zeolite	Number of Oxygens in the Ring	Aperture Dimensions, Å
Chabazite	8	3.6 × 3.7
Erionite	8	3.6 × 5.2
Zeolite A	8	4.1
ZSM-5 (or silicalite)	10	5.1 × 5.5; 5.4 × 5.6
ZSM-11	10	5.1 × 5.5
Heulandite	10	4.4 × 7.2
MWW[b]	10	4.0 × 5.5; 4.1 × 5.1
Ferrierite[c]	10	4.3 × 5.5
Faujasite (X,Y)	12	7.4
Zeolite L	12	7.1; 7.0
Mordenite	12	6.7 × 7.0
Beta	12	6.4 × 7.6
Offertite	12	6.4
VPI-5	18	12.1
MCM-41	>18	15-100

[a] The framework oxygen is assumed to have a diameter of 2.75 Å

[b] There are also apertures with twelve-membered oxygen rings in MWW.

[c] There are also apertures with eight-membered oxygen rings in FER.

2.6 Factors Influencing Zeolite Formation

Three variables have a major influence on the zeolite structure crystallized: the gross composition of the reaction mixture, temperature, and time [43] showed in table 2.2. There are also history-dependent factors such as digestion or aging period, stirring, nature (either physical or chemical) of the reaction mixture, and order of mixing.

Table 2.2 Factors influencing zeolite crystallization

- Gross composition
  1. SiO_2/Al_2O_3
  2. $[OH^-]$
  3. Cations
     (a) Inorganic
     (b) Organic
  4. Anions (other than $[OH^-]$)
  5. $[H_2O]$
- Time
- Temperature
  1. Ambient - ca. 25 to 60°C (natural zeolite formation)
  2. Low - ca. 90 to 120°C
  3. Moderate - ca. 120 to 200°C
  4. High - ca 250°C or higher
- History-dependent factors
  1. Aging
  2. Stirring
  3. Nature of mixture
  4. Order of mixing

2.6.1 Reaction Mixture Components

Each component in the reactant mixture contributes to specific characteristic of the gel and to the final material obtained. Table 2.3 provides a broad listing of individual components of the mixture and the primary influence each component has within that reactant mixture.

Table 2.3 The effects of selected variables of gross composition on the final crystalline product in zeolite synthesis

Variables	Primary influence
SiO_2/Al_2O_3	Framework composition
H_2O/SiO_2	Rate, crystallization mechanism
OH^-/SiO_2	Silicate molecular weight, OH^- concentration
Inorganic cation(s)/SiO_2	Structure, cation distribution
Organic additives/SiO_2	Structure, framework aluminum content

The SiO_2/Al_2O_3 mole ratio, the hydroxide content of the gel, and the presence of inorganic cations, also contribute to determining which structures would finally crystallize besides the organic additives as pore-directing agent or template. For example, ZSM-5 generally crystallizes in the TPA^+ (tetrapropylammonium cation) system at the ratio SiO_2/Al_2O_3 between 20 and infinity. However, at the ratio below 20 the mordenite phase appears, as impurity, no matter with or without the presence of the organic quaternary amine. The crystallization of a particular zeolite structure from the gel system containing these four components strongly depends on the SiO_2/Al_2O_3 ratio of the starting gel mixture. The inorganic or organic cations influence not only the structure crystallized but also other features of the final crystalline products produced, such as morphology and crystal size.

2.6.2 Temperature

Temperature influences several factors in zeolite synthesis; it can alter the zeolite phase obtained as well as change the induction period before the start of crystallization. This induction period decreases with increasing temperature. Conditions may favor formation of other phases when the temperature is changed. For any mixture as the temperature increases, the rate of crystallization increases. The

solubilities of aluminate and silicate species also increase, causing a shift in the concentration of the liquid phase. Loosen zeolites prefer crystallization at lower temperature while denser zeolites do at higher temperature.

2.6.3 Time

Time, as a parameter, can be optimized in the synthesis of many zeolites. In systems, which produce only one zeolite phase, optimizing maximum crystallization over a short span of time is important. Crystallization parameters must be adjusted to minimize the production of the other phase while also minimizing the time needed to obtain the desired crystalline phase.

2.7 Titanium-containing zeolites

Redox zeolites are one of the remarkable developments in the chemistry of zeolites and Molecular sieves of recent years. These zeolites contain small amounts of transition metal ions isomorphously substituted for Si^{4+} in a pure silica framework. The first example of such materials was Ti silicalite-1 (TS-1), developed by Enichem researchers [3]. TS-1, which has the structure of silicalite-1 (MFI) with Ti^{4+} in the framework, has been shown to possess unique catalytic properties which have been exploited in a variety of oxidation reactions. This discovery has initiated a new field of zeolite catalysis.

In 1987, the successful start-up of a new process was announced for the production of 10,000 tons/year of catechol and hydroquinone by the selective oxidation of phenol with H_2O_2 catalyzed by TS-1 (51).

Titanium containing materials have been investigated of various reactions, but selective oxidations with H_2O_2 as the oxidant have attracted the most interest. For these reactions, the formation of surface titanium peroxo compounds with H_2O_2 and the subsequent transfer of the peroxidic oxygen to the organic reactants have been proposed to explain the mechanism by which titanium participates in the catalytic cycle.

2.8 Structure of titanium-containing zeolites

2.8.1 TS-1

Taramasso et al. [3] first synthesized TS-1, in 1983 and its structure is MFI. The tetrahedral are linked to form the chain-type building block. Ring consisted of five oxygen atoms are evident in this structure; the name pentasil is therefore used to describe it. TS-1 is a medium-pore zeolite having an orthorhombic crystalline structure. The pore opening is composed of a 10-member ring. The MFI framework contains two types of intersection channels: one type is straight, has elliptical (5.1-5.5 Å) openings, and run parallel to the b-axis of the orthorhombic unit cell, while the other has near-circular (5.4-5.6 Å) openings, is sinusoidal (zigzag) and directed along the a-axis. Figure 2.8 exhibits structure of ZSM-5 and schematic of three-dimensional channel.

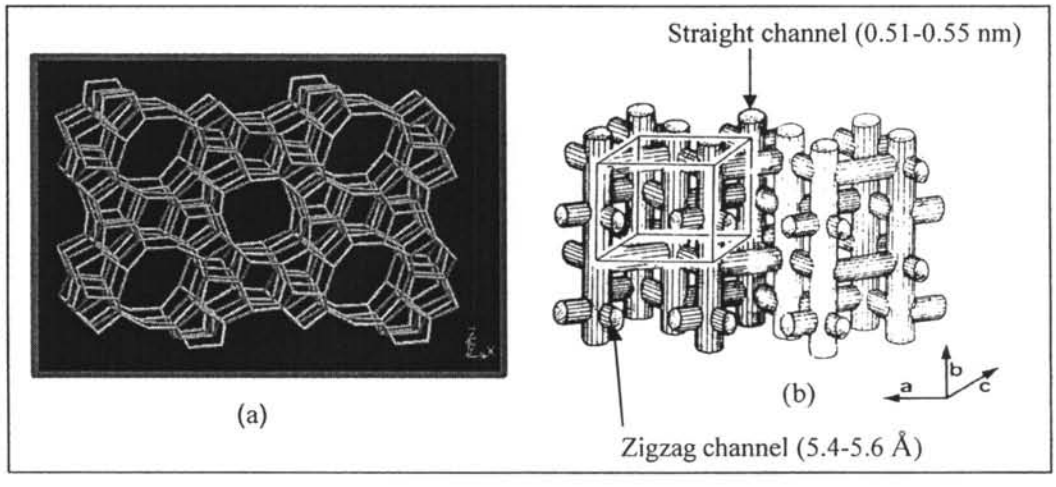


Figure 2.8 (a) Structure of TS-1 (MFI). View shows the straight channel. The sinusoidal channels run perpendicular to the straight channels [52]. (b) Schematic illustration of the three-dimensional channels in TS-1 [48].

A general procedure for the preparation of TS-l is given below: The procedure consists of the preparation of a solution of mixed alkoxides of titanium and silicon such as tetraethylorthosilicate (TEOS) and tetrabuthylorthotitanate (TBOT) followed by hydrolysis with alkali free solution of tetrapropylammonium hydroxide (TPAOH), distillation of the alcohol, and crystallization of the resulting gel at 175 °C [7]. The temperature at which the reagents are mixed and the rate of hydrolysis are critical.

2.8.2 Ti-MWW

A novel zeolite with MWW topology [6], having a unique and unusual crystalline structure, is expected to serve as such a candidate for preparing Ti-containing catalysts that are both highly stable and accessible. The MWW structure is constructed from a lamellar precursor undergoing dehydroxylation upon calcination between the layered sheets. The dehydroxylation causes a recrystallization to form crystals of hexagonal thin plates. Besides two-dimensional sinusoidal channels of 10-memebered rings (MR) (Figure 2.9(c)) running throughout the structure parallel to the *ab*-plane, one of these lies within the layer, and the second between the double layers. The MWW structure contains also an independent channel system which is comprised of large supercages (Figure 2.9(b)) (0.7 × 0.7 × 1.8 nm). The supercages turn to be pocket or cup moieties (0.7 × 0.7 nm) at the crystal exterior [53].

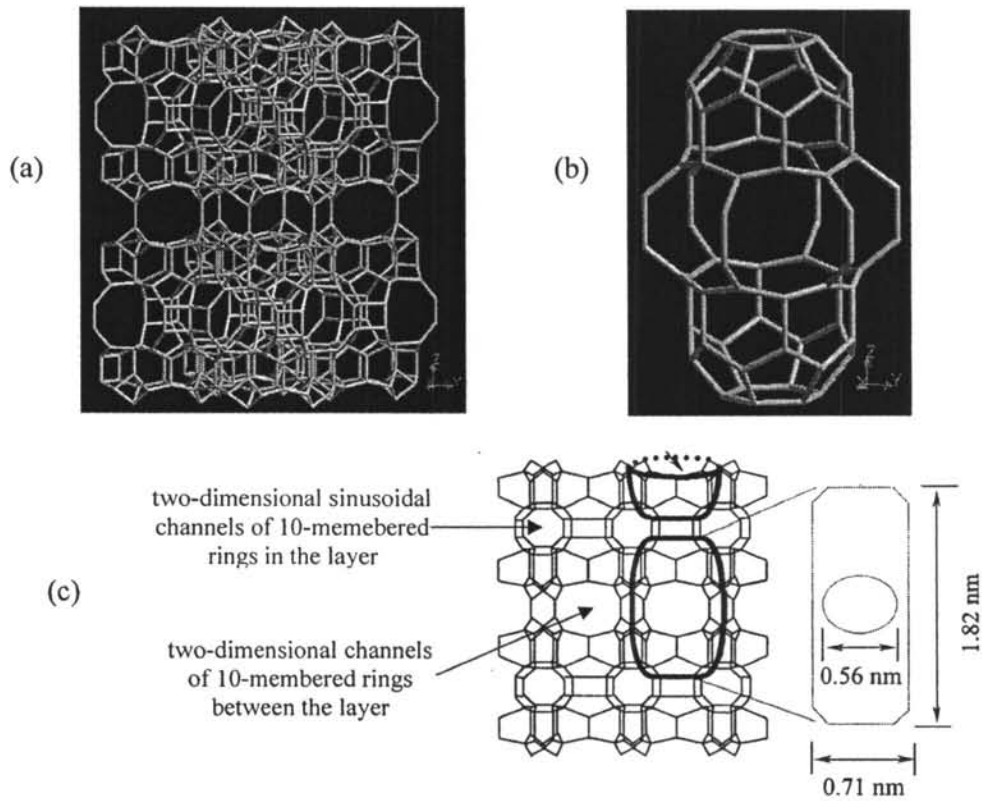


Figure 2.9 (a) Structure of Ti-MWW (MWW). (b) Large supercage of Ti-MWW (c) The two-dimensional channels of 10-member in Ti-MWW.

Ti-containing MWW precursor was synthesized using fumed silica, tetrabutyl orthotitanate (TBOT), boric acid, and deionized water, with piperidine (PI) or hexamethyleneimine (HM) as an SDA, and crystallization of the resulting gel at 403 K and then 423 K each for 1 day and further at 443 K for 5 days. To removed boron and extraframework Ti species, an acid treatment with HNO_3 solution was carried on the as-synthesized products at 373 K for 20 h, and then calcined at 803 K to burn off any residual organic species.

2.9 Catalytic Sites

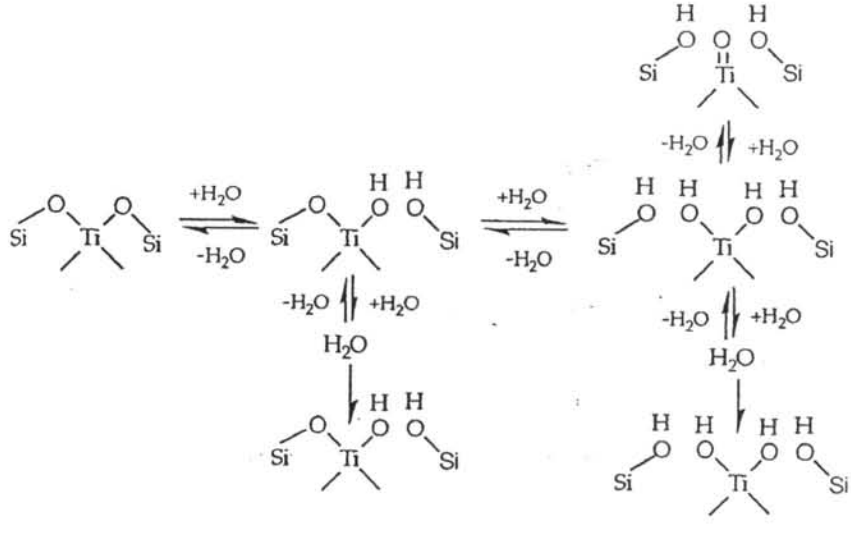
The catalytic activity of titanium silicates must be ascribed Ti^{IV} sites, because pure crystallinesilica are totally inactive. The Ti^{IV} is present in the crystalline structure randomly. Very likely, the random distribution that is obtained in the precursor reagents is maintained in the solid. Being dilute, each Ti^{IV} is expected to be surrounded by OSi^{IV} groups and isolated from Other Ti^{IV} ions by long O-Si-O-Si-O sequences. It has been proposed that Ti^{IV}, in this state of dispersion and tetrahedral coordination, has properties different from those of other materials having Ti^{IV} sites with octahedral coordination and are not isolated from each other. It has been proposed that isolated Ti^{IV} sites have a low activity for H_2O_2 decomposition [51]. However, isolation alone is not sufficient to explain all the observed properties. The hydrophobic environment prevailing inside the catalyst pores and the multiple Ti-O-Si bonds that allow interaction with reactants but prevent complete hydrolysis of the Ti^{IV} sites in titanium silicates must also play a role in stabilizing the dispersed Ti^{IV} sites. The addition of H_2O_2 to titanium silicates brings about the formation of a titanium peroxo complex, which, has been proposed as the active species for the transfer of oxygen from the oxidant to the reactant.

2.10 Reaction Mechanism of titanium silicate with H_2O_2

Investigation of mechanisms of reaction catalyzed by titanium silicates has been limited to oxidation reactions with H_2O_2 as the oxidant, as described below. As was previously discussed, elements different from titanium and silicon in the catalysts materials change their properties.

Mechanistic information is difficult to obtain when catalytically active titanium centers are present in a dilute matrix of silica. Only few techniques can be applied, and the available information does not allow discrimination between possible mechanisms. Consequently, it is necessary in this discussion to rely on analogies with the known chemistry of titanium compounds.

Once the crystalline structure and the distribution of titanium therein are established, one of the first issues that must be considered concerns the interactions of the isolated titanium sites with water, H_2O_2 and other reactants. Adsorption of a number of compounds on the titanium sites leads to an increase in the coordination of titanium which, as previously noted, is reversible. The moieties of, Ti-O-Si are hydrolyzed, forming TiOH and SiOH groups. The hydrolysis process cannot be extensive, because Ti^{IV} species separated from the matrix would undergo rapid sintering, as is observed for Ti^{IV} dispersed on amorphous silicates. Therefore, in titanium silicates the Ti^{IV} must maintain a number of bonds to the crystalline lattice [57]. To simplify the graphic presentation, hydrolyzed groups are indicated as TiOH and $Ti(OH)_2$. This latter group can be considered equivalent to a titanyl group, Ti=O. Spectroscopic properties of the $Ti(OH)_2$ and Ti=O may be different, but their chemical properties are substantially identical; therefore, their notation will be used interchangeably. The scheme shown in below indicates the hydrolysis of the Ti-O-Si bond and further interactions with water.



Scheme 2.1 The hydrolysis of the Ti-O-Si bond and further interactions with water on titanium silicate.

2.10.1 Acidity of Crystalline Titanium Silicates

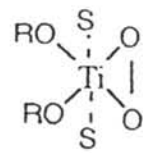
The TiO_2-SiO_2 was shown that no significant acidity is present in the SiO_2-rich region. This is very likely due to the fact that, in the presence of excess SiO_2, Ti^{IV} assumes a tetrahedral coordination with the consequence that no charge imbalance exists and no Brønsted acidity is created. The same is true for crystalline titanium silicates that contain small amount of Ti^{IV} and, assume tetrahedral coordination. The chemical behavior is as expected; many acid-sensitive compounds like the epoxides can be obtained in high yield without undergoing major hydrolysis or solvolysis. The fact that the limited solvolysis observed for propylene and allyl alcohol con be reduced by silanization or by the addition of controlled amounts of bases is consistent with the hypothesis that the solvolysis is due to silanol groups and disappears when they are transformed or neutralized. Further evidence comes from the observation that if the same epoxidation is carried out with titanium silicates containing traces of trivalent elements, hydrolysis takes place. Furthermore, TS-l is inactive for acid-catalyzed hydrocarbon reactions; but when Al^{+3} is present, TS-1 becomes active for xylene isomerization [58-59]. As for TiO_2-SiO_2, the adsorption of water, ammonia, pyridine, and pyrole indicates that Ti^{IV} in titanium silicates behaves as a Lewis acid: and the fact that these adsorbates are removed by simple evacuation leads to the conclusion that Ti^{IV} is a fairly weak Lewis acid [60-61]. The change in Ti^{IV} coordination that is observed as a result of adsorption has no effect as far as the development of protonic acidity is concerned, since the molecules that are coordinated are neutral. To produce the charge imbalance in the solid that is at the origin of acidity, charged O^{2-} groups are necessary.

Acidity in crystalline titanium silicates has been observed only when a titanium-containing zeolite interacts with H_2O_2 but this is due to the formation of peroxo compounds, as discussed below.

2.10.2 Titanium Peroxo Complex

The addition of H_2O_2 to titanium silicates brings about the formation of a titanium peroxo complex, which has been proposed as the active species for the transfer of oxygen from the oxidant to the reactant. From the chemistry of Ti^{IV} compounds in the liquid phase, it is known that H_2O_2 acts as a bidentate ligand and displaces other ligands to form the very stable side-bonded peroxo species I. Weakly bonded neutral molecules of the solvent S are also coordinated at the Ti^{IV} center. The

alkyl hydroperoxides from peroxo complexes displacing only one ligand to give the end-on hydroperoxo complex II. In some case, the alkyl hydroperoxo complex may adopt the side-bonded structure III, displacing a weakly bonded neutral molecule of solvent:



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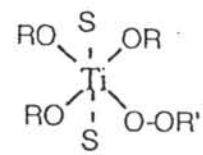

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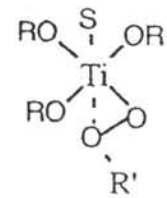
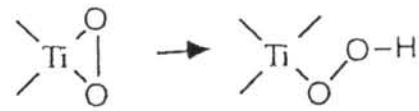


III

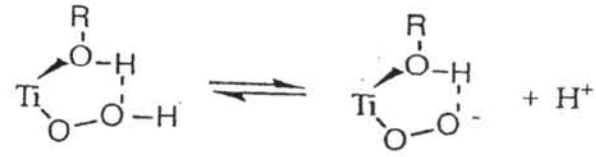
The stability of the peroxo complexes formed with H_2O_2 measured by the association constant, is much higher than the stability of hydroperoxo complexes. The strong repulsion between formally unshared electrons in planar H_2O_2 can be reduced by transition-metal ions such as Ti^{IV}, as they accept electron density from the filled antibonding orbitals of H_2O_2 interacting with the empty metal d orbitals of appropriate symmetry. It is for this reason that even hydroperoxo complexes may prefer the side-on configuration that can provide the added stability [62].

The formation of a peroxo complex between H_2O_2 and a titanium silicates has been demonstrated in several ways, the most convincing being the appearance of an absorption band in the UV-visible spectra at 26,000 cm^{-1} when H_2O_2 is added to a titanium silicate. A band at the same frequence is present in the UV-visible spectra of the peroxo complex $[TiF_5\ (O_2)]^3$, and the absorption has been attributed to a charge transfer process $O_2^{2-} \rightarrow Ti^{4+}$ [65]. The stability of these complexes is limited to a temperature of 333 K: they decompose rapidly at 373 K [63]. The thermal stability of the peroxo complex formed on TS-l is markedly increased in the presence of bases, the decomposition temperature being shifted to 523-673 K. Stable species and formed which have been characterization by both physical chemical methods and catalytic tests. Under carefully controlled conditions the ratio "active O"/Ti approaches unity, indicating that every Ti^{IV} site in the solid has been transformed to a peroxo complex. The increased stability of the titanium peroxo complex in the presence of bases could be the reason for the observed deactivation of these catalysts caused by alkalies [64].

In the $[TiF_5 (O_2)]^{3-}$ ion, the peroxo group is bonded to Ti^{IV} side-on, and therefore this could also be structure of the complex formed on titanium silicates. However, the possibility of a peroxo species bonded end-on cannot be ruled out, because the side-on structure requires a deeper degree of hydrolysis to give the Ti $(OH)_2$ group, whereas the hydroperoxo con form on a Ti (OH) group, which is more easily obtainable in a material resistant to hydrolysis. The two forms can be represented as follows:



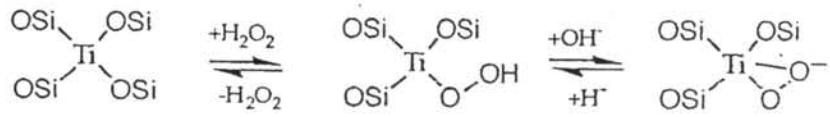
The titanium peroxo complex under neutual conditions oxidizes alkenes, giving the epoxides with no evidence of acid catalyzed reactions. But when the oxidation reaction is complete and the epoxides are exposed to an excess of H_2O_2, a hydrolytic reaction of epoxides is observed. The rate of this reaction is similar to the rate obtained when the same epoxides are exposed to 0.1 M formic acid. By contrast, silicalite-1 is inactive and unaffected by the presence of H_2O_2. The addition of NaOH reduces the hydrolytic activity of the system TS-1+ H_2O_2, indicating that an acidic species is responsible for the hydrolysis. The formation of protonic acidity by H_2O_2 has been ascribed to the interaction of the titanium peroxo complex with a donor hydroxyl moity of a molecule such as H_2O coordinated on Ti^{IV}, resulting in the formation of a cyclic structure. The stabilization provided by the cyclic structure would make the dissociation and the protonic acidity possible. When alcohols, and particularly methanol, are used as solvents, the coordinated OH group could be that of the alcohol [66] can be represented as follows:



The fact that the acidic properties and the hydrolysis reaction are absent during epoxidation must mean that other donor molecules like alkenes are more strongly coordinated at Ti^{IV} and prevent the formation of the complex responsible for generating protonic acidity can be represented as follows:.

The formation of an acidic species could therefore also be explained as the result of the transformation of a hydroperoxo group into a side-bonded peroxo group, which becomes possible when more strongly coordinating molecules are absent

This process would be stabilized by alkalies, and the overall process could be represented as follows:



In the presence of excess alkalies these reactions could by inhibited by the formation of Si-O-Na groups [67].

2.10.3 Mechanistic Proposals

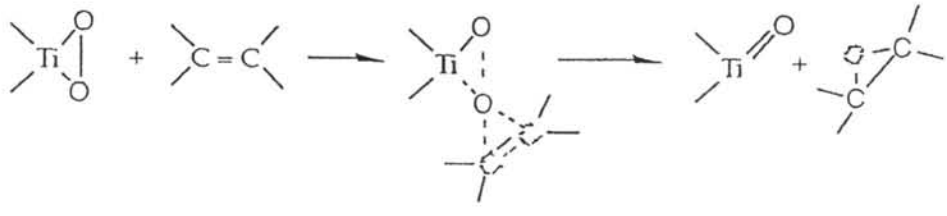
Many characteristics related to the particular structure of the material contribute to the final outcome of H_2O_2 oxidation reactions catalyzed by titanium silicates:

1. The resistance of the titanium center to extensive hydrolysis.
2. The thermal decomposition of the titanium peroxo compounds, with the consequence that different mechanisms can be operative at low and high temperatures.
3. The selective adsorption of reactants, owing to the hydrophobic nature of titanium silicates.
4. Reactant shape selectivity effects related to the dimensions of reactant molecules and catalyst pores, including restricted transition-state shape-selectivity effects as well as chemical and stereochemical selectivity.

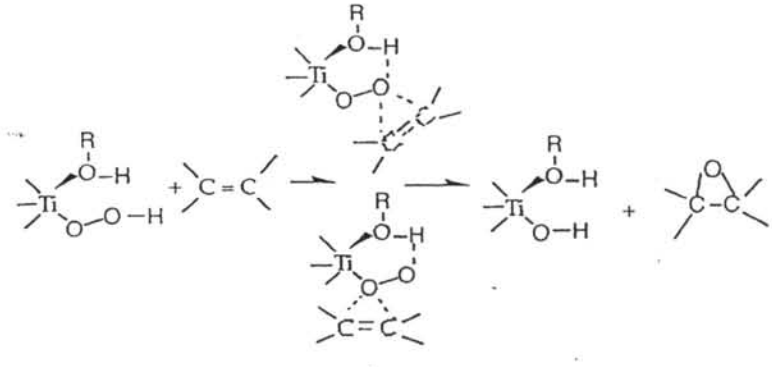
These effects were illustrated above.

The proposals advanced to give a representation of the mechanism by which the O is transferred from the titanium peroxo complex to the reactant molecules can be classified as concerted mechanisms and radical mechanisms.

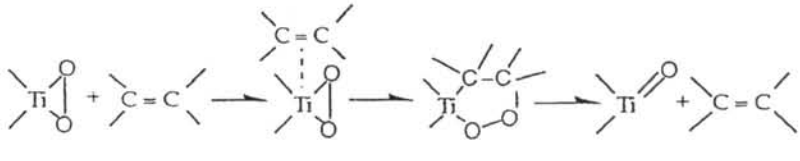
Concerted mechanisms have been proposed on the basis of work carried out with soluble Mo^{IV}, W^{IV} and Ti^{IV} peroxo compounds. The experimental evidence is consistent with the hypothesis that these compounds act as oxidants in stoichiometric epoxidations and that the reactions involve electrophilic attack of the peroxo compound on the organic molecule or, what is equivalent, a nucleophilic attack of the organic molecule on the peroxidic oxygen, in a "butterfly" transition state. The reaction product is formed and, after desorption, the peroxo compound is regenerated by reaction of Ti^{IV} with H_2O_2: this accounts for the catalytic nature of the reaction [68]. The same type of mechanism has been proposed for the surface titanium peroxo complex formed on titanium silicates [51]. In this case of alkene oxidation, the mechanism of oxygen transfer from the titanium peroxo complex to the alkene would be as follows:



A modification of the mechanism that involves the hydroperoxo titanium complex and one solvent molecule has been proposed that involves the formation of a stable cyclic titanium peroxo complex (81-2). In this case, the two peroxo oxygens are not equivalent, and thus two intermediates would be possible: (Eq. A. B).



(A)

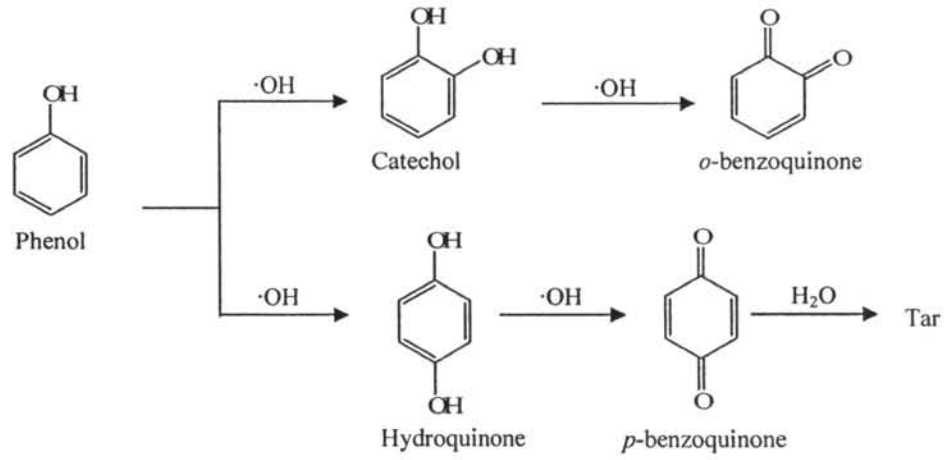


(B)

2.11 Phenol Oxidation

Hydroxylation of phenol with H_2O_2 in the presence of a catalyst is the most desirable method for producing hydroquinone and catechol. The reaction mechanism for the oxidation of aromatic compounds employing transition metals has been previously studied [55]. The reaction path proposed for the present study shown in Scheme 2.2. The interaction catalysts and H_2O_2 yields HO• and HO_2• species, via a redox mechanism. Hydroquinone and catechol are subsequently obtained in parallel processes, by the attack of HO• radicals to the aromatic ring, benzoquinone can be formed by the consecutive oxidation of hydroquinone. In addition, a little tar was formed during the procedure of phenol hydroxylation due to over-oxidation of BQ. Oxygen and water are formed in side reactions by the decomposition of H_2O_2.

This can be achieved through homogeneous catalyst or heterogeneous catalyst. Homogeneous catalysts such as mineral acids, metal ions and metal complexes are difficult to be separated and recovered from the reaction mixture, which prevents their practical utilization. Therefore, numerous heterogeneous catalysts such as metal oxides, supported metal complexes, metallosilicalites, hydrotalcite-like compounds, metal-bearing, mesoporous materials, metal hydroxylphosphates, and heteropoly compounds have been attracting research interest recently [56].



Scheme 2.2 Reaction path for the hydroxylation of phenol [55].

2.11.1 Reaction mechanism for the hydroxylation of phenol on TS-1 catalyst [37].

The coordination of protic solvent molecules results in an increase of the size of the active titanium site. This narrows the TS-1 channels, leading to a geometric constraint for an approaching phenol molecule. Hydrogen bonds of the phenolic OH with solvent OH groups will make the phenol molecule more bulkier. Phenol, hydrogen-bonded to the solvent OH groups, will approach the bulky titanium site with the OH group pointing away from the titanium site (Scheme 2.3) yielding hydroquinone. Additionally, the presence of coordinated protic molecules close to the peroxo group could lead to hydrogen bond formation with the active site (species (a) and (b) in Figure 2.10), destabilizing H-bonding with the phenol molecule assisting in *o*-hydroxylation (as shown in Schemes 2.4(a) and 2.4(b)). Thus, the existence of titanium sites without protic molecules coordinated is proposed (Figure 2.10, species (c)). In that case another reaction pathway is opened, i.e., the conversion via pentacoordinated (trigonal bipyramidal) Ti site, involving coordination of phenol to Ti peroxo species yielding catechol (Scheme 2.4(a)). This will be the case in aprotic solvents, such as acetone. Protic solvents will compete with phenol, so that this pathway is not dominant in these solvents. Formation of catechol without coordination of phenol to the active titanium site takes place via a six-membered transition state involving phenol (see Scheme 2.4(b)).

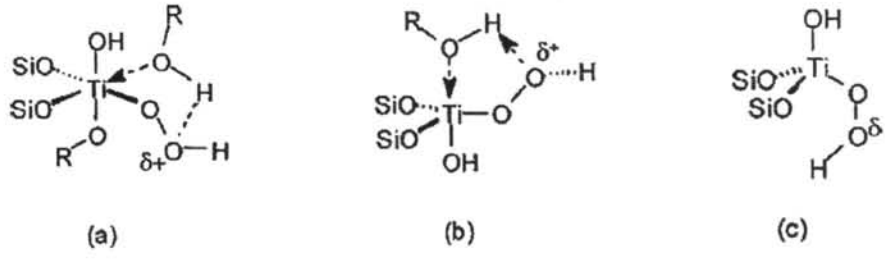
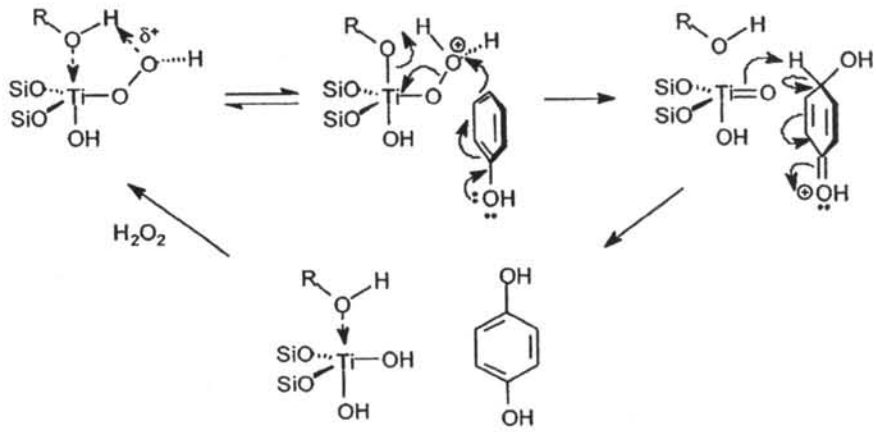
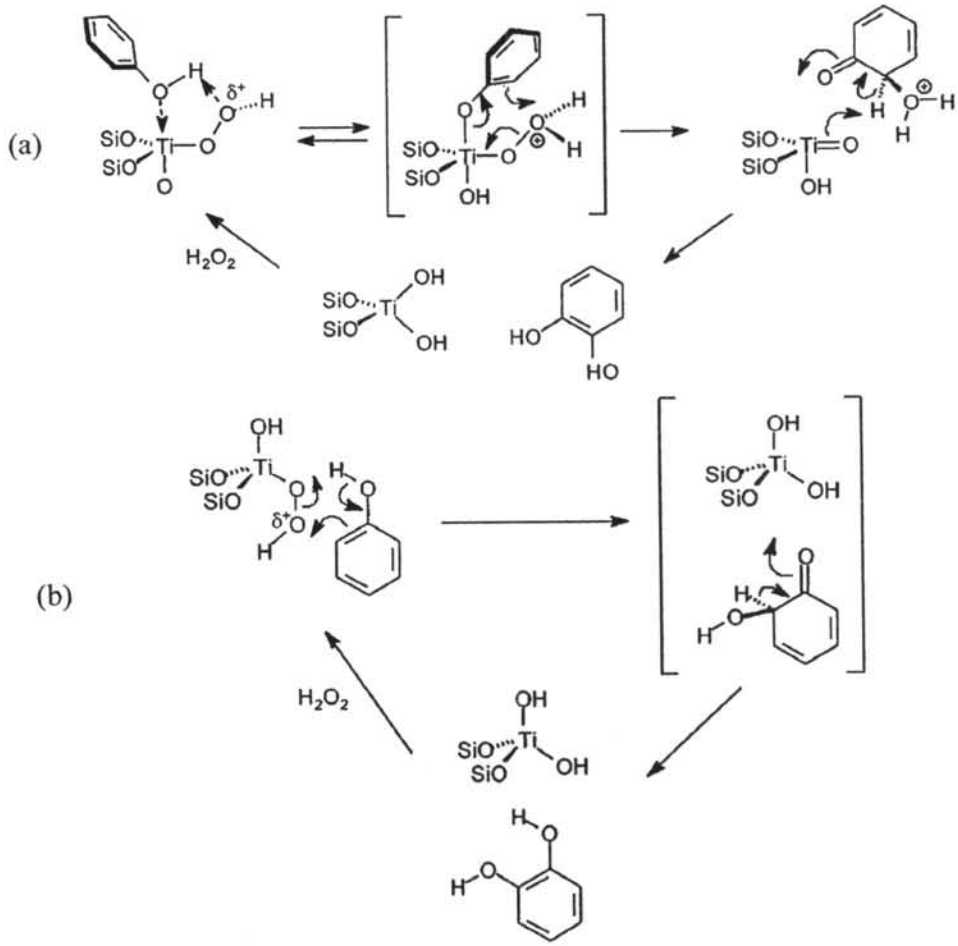


Figure 2.10 Possible configurations of the hydroperoxo-titanium active site of TS-1: (a) hexacoordinate octahedral, (b) pentacoordinate trigonal bipyramidal, and (c) tetracoordinate tetrahedral.



Scheme 2.3 Proposed reaction mechanism for the formation of hydroquinone in phenol hydroxylation.



Scheme 2.4 Proposed reaction mechanism for the formation of catechol in phenol hydroxylation.