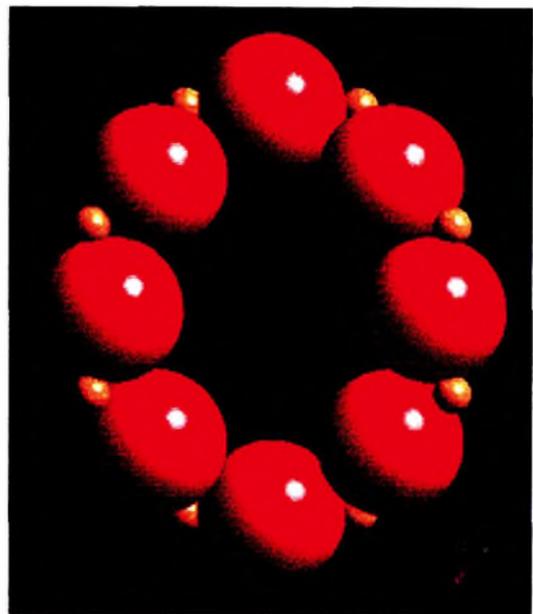
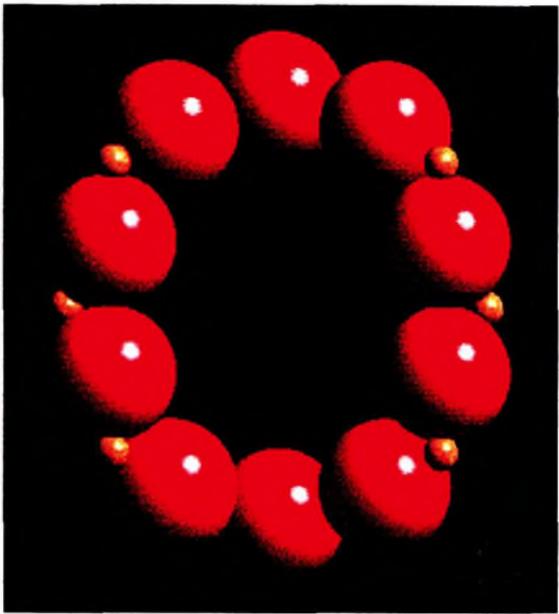


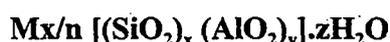
# *Chapter I*



## *General Introduction*

## 1.1 General introduction:

Zeolites, a class of crystalline, microporous, hydrated aluminosilicate molecular sieves have been extensively studied<sup>1-8</sup>. Structurally, they possess a framework based on an indefinite extending three dimensional network formed by  $[\text{SiO}_2]^{4-}$  and  $[\text{AlO}_4]^{5-}$  tetrahedra linked through oxygen atoms in such a way that no two alumina tetrahedra exist adjacent to one another. The negative charge on the alumina tetrahedra is compensated by cations (alkali metal, alkaline earth metal or organic cations) resulting in a neutral framework. Thus, zeolites are represented by the general formula:



where **M** is the charge compensating cation with the valency **n**. **M** represents the exchangeable cations (viz. group II or I or an organic cation). The ratio  $x/y$  can have the value 1 to  $\infty$ . According to Lowenstein's rule no two aluminum tetrahedra can exist adjacent to one another, hence, the Si/Al molar ratio corresponds to the acid sites in the zeolites. **z** represents the number of water molecules, which can be reversibly adsorbed or desorbed in the pores. Zeolites are also popularly known as '*molecular sieves*' due to their ability to differentiate between molecules of different shapes and size.

Zeolites have found widespread application as adsorbents, ion exchangers, detergent builders and catalysts, especially in petroleum refining and petrochemicals as Fluidized Cracking Catalysts (FCC)<sup>7</sup>. Furthermore, recently zeolite functionality has also been compared with catalytic antibodies<sup>9</sup> and metalloenzymes<sup>10</sup>.

The chief characteristic features of zeolites, which make them effective catalysts, are:

- high surface area and adsorption properties. The latter can be controlled and varied from hydrophobic to hydrophilic type materials,
- active sites i.e. acid sites, can be generated in the framework and their strength as well as concentration can be tailored for a particular application,
- shape selectivity (due to uniform pores and channels),
- easy regeneration &
- high thermal stability.

## 1.2 Historical background:

Axel Fr. Cronstedt<sup>11</sup> (1756), a Swedish mineralogist, observed that certain rock minerals, when heated sufficiently appeared as were boiling. He named them '*Zeolites*' (*zeo* means to boil and *lithos* means stone). Damour<sup>12</sup> observed that zeolites could be reversibly dehydrated without alteration in the structure or morphology. The role of water as a mineralizing agent, aided by alkaline conditions, drew the attention of mineralogist towards hydrothermal reactions and synthesis. The first claim to have synthesized a zeolite named levynite was made by St. Claire Deville and Thompson in 1862<sup>13,14</sup>. In 1962, the commercialization of natural zeolites namely chabazite, erionite, mordenite and clinoptililote started for a number of applications<sup>15</sup>. McBain introduced the term *Molecular Sieves* to describe a class of materials that exhibited selective adsorption properties<sup>16</sup>. Molecular sieves separate components of a mixture on the basis of molecular size and shape differences. However, Barrer<sup>17</sup> was the first to demonstrate the molecular sieve behavior of zeolites and their potential in separation techniques. Since, 1940 systematic studies on zeolites were undertaken. ZK-5<sup>18</sup> was the first known synthetic zeolite (no natural counterpart) crystallized under hydrothermal conditions. Hydrogen forms of zeolites were also made for the first time in the year 1949 by heating ammonium-exchanged forms of mordenite<sup>19</sup>.

## 1.3 Nomenclature:

Although, there is no systematic nomenclature developed for molecular sieve materials, the Structure Commission of International Zeolite Association and IUPAC have assigned structural codes to synthetic and natural zeolites<sup>20,21</sup>. Designations consisting of three capital letters have been used to identify structure types. The codes for zeolite identifications have generally been derived from the names of the type species, and do not include numbers and characters other than roman letters. Structure type codes are independent of chemical composition, distribution of various possible T atom, (e.g. Si<sup>4+</sup>, Al<sup>3+</sup>, P<sup>5+</sup>, Ti<sup>4+</sup>, etc.), cell dimension or crystal symmetry for e.g. FAU (faujasite, X and Y), MFI (Mobil Five, ZSM-5), MEL (Mobil Eleven, ZSM-11), MOR (mordenite), FER (ferrierite, ZSM-35, ZSM-21), MCM's (Mobil Carbon Materials), etc.

## 1.4 Classification:

Zeolites have been classified in accordance with morphologies<sup>22</sup>, crystal structure<sup>1,3,23</sup>, chemical composition<sup>24</sup> and effective pore diameter<sup>25,26</sup>. On the basis of morphology alone zeolites can be classified as **fibrous** (when the tetrahedra are linked more numerous in one crystallographic direction), **lamellar** or open framework materials (when zeolites have structural linkages more numerous in one plane and are characterized by a platy cleavage). The **framework** structures have similar bonding strength of their tetrahedra in all directions. Smith<sup>27</sup>, Fischer<sup>28</sup> and Breck<sup>29</sup> have structurally classified zeolites on the basis of differences in the secondary building units, which were grouped as shown in table 1.1. Flanigen<sup>24</sup> also classified zeolites according to their chemical composition as shown below:

low silica zeolites	Si/Al = 1- 1.5	A, X, sodalite, etc.
intermediate silica zeolites	Si/Al = 2.0 - 5.0	erionite, chabazite, mordenite, X,Y,L, Ω, etc.
high silica zeolites	Si/Al = 5 - 500	MFI, FER, BEA, etc.
pure silica zeolites	Si/Al = ∞	Si-MFI (silicalite-1), Si-MEL (silicalite -2), Si-TON, Si-MTW, Si-ZSM-48, Si-NCL-1, Si-FER, Si-UTD-1, etc.

The thermal stability increases from low silica zeolites to high silica molecular sieves. The high silica molecular sieves are hydrophobic in nature while low silica zeolites are more hydrophilic. The acidity tends to increase in strength with increase in Si/Al ratio. The cation concentration and ion exchange capacity (which is directly proportional to the aluminum content) decreases with the increase in Si/Al ratio. Structurally, low silica zeolites are formed predominantly with 4-, 6- and 8- rings of tetrahedra while in case of intermediate silica zeolites there is an onset of 5- rings for example in case of omega and mordenite. In case of high silica zeolite 5-ring tetrahedra predominates in the structure.

Zeolites are also classified according to their effective pore diameter, which is dependent on the number of tetrahedra resident in the ring aperture, which circumscribes

**Table 1.1: Classification of zeolites on the basis of differences in the secondary building units [Ref 28]:**

	species	crystal system and space group	secondary building blocks
1.	<b>Analcime group:</b> Analcime	Cubic Ia3d	interconnected 4- and 6- membered rings
2.	<b>Natrolite group:</b> Natrolite Thomsonite Edingtonite	orthorhombic Fdd2 orthorhombic Pnn2 orthorhombic P2 <sub>1</sub> 2 <sub>1</sub>	chains of tetrahedra with 6.6 Å repeat distance.
3.	<b>Chabazite group:</b> Chabazite Erionite levynite Gmelinite cancrinite hydrate sodalite hydrate	trigonal R3m hexagonal P6 <sub>3</sub> /mmc trigonal R3m hexagonal P6 <sub>3</sub> /mmc hexagonal P6 <sub>3</sub> cubic P43n	approximately parallel 6- membered rings or double 6- membered rings
4.	<b>Phillipsite group:</b> phillipsite Gismondine Barrer's P	orthorhombic B2mb monoclinic P2 <sub>1</sub> /C cubic Im3m	approximately parallel 4 membered rings
5.	<b>Heulandite group:</b> Heulandite Brewsterite Stilbite	monoclinic Cm monoclinic P2 <sub>1</sub> /m monoclinic C2/m	characteristic configuration with 4- or 5- membered rings
6.	<b>Mordenite group:</b> Mordenite  Ferrierite Dachiardite Epstilbite Bikitaite	orthorhombic CmCm orthorhombic Immm monoclinic C2/m monoclinic C2/m monoclinic P2 <sub>1</sub>	each tetrahedron of the framework belongs at least to one 5-membered ring.
7.	<b>Faujasite group:</b> Faujasite Linde A ZK-5 Paulingite	cubic Fd3m cubic Fm3C cubic Im3m cubic Im3m	framework based on polyhedral cages of cubic or near cubic symmetry

the pore. Barrer<sup>25</sup> has made such a classification of zeolites into five groups. Sand<sup>26</sup> modified the classification into three groups, as shown in table 1.2. In 1988, Davies *et al.* discovered a very large pore aluminophosphate molecular sieve VPI-5 containing 18 membered ring pore openings<sup>30</sup>. Recently, an extra large pore gallophosphate molecular sieve containing 20 membered ring pore opening called cloverite has been synthesized<sup>31</sup> and a 14- membered ring structure called UTD-1 has also been reported<sup>32</sup>.

**Table 1.2: Classification of zeolites on the basis of the effective port diameter [ref 26]**

Small pore (8 MR)	Medium pore (10 MR)	Large pore (12 MR)
Li-A	dachiardite	cancrinite
MTN	epstilbite	Linde X,Y, L.
NU-1	Ferrierite (FER)	gmelinite
bikitaite	heulandite	mazzite
brewsterite	laumontite	mordenite
chabazite	ZSM-5 (MFI)	offeritite
clinoptillolite	ZSM-11 (MEL)	ZSM-12 (MTW)
edingtonite	EU-1 (ZSM-50)	omega
erionite	stilbite	beta (BEA)
gismondine	ZSM-23	
ZK-5	theta-1 (ZSM-22)	
Levynite	ZSM-48 (EU-2)	
Linde A		
merlonite		
natrolite		
Paulingite		
phillipsite		
Rho		
thomsonite		

### 1.5 Hydrothermal synthesis of zeolites:

In nature, zeolites occur in vesicles of basaltic lava in specific types of rocks subjected to moderate geological temperature, pressure and in altered and reacted volcanic ash deposits. The formation of these natural zeolites from volcanic glass and saline water as reactants must have occurred in the temperature range 300-350 K and at  $\text{pH} \geq 13$ , requiring several years for crystallization<sup>33,34</sup>.

Morey and Ingerson<sup>35</sup> have already documented reports of zeolite synthesis up to 1937. Barrer<sup>36</sup>, in 1940 initiated systematic study in hydrothermal synthesis of zeolites

followed by major demonstration of separations using molecular action and sorption by zeolites.

Zeolites are synthesized under hydrothermal conditions by reacting certain basic oxides (e.g.  $K_2O$  and  $Na_2O$ ) with silica and alumina. Zeolites with a various structures as well as varied compositions and properties can be synthesized by varying the reactants. Zeolite crystallization is mainly a nucleation-controlled process, occurring in homogenous alkaline aqueous gels, in the temperature range of 348 to 523K. A number of silica and alumina sources<sup>1</sup> can be utilized in gel formulation and the final product is generally source dependent.

Inorganic cations (like alkali / alkaline earth metals) play a major role in directing a particular structure. Zeolite structural sub-units such as double four membered ring (D4R), double six membered ring (D6R) and cancrinite, gmelinite and sodalite cages are thought to be formed by way of clathration of an alkali cation with silica and alumina<sup>1,37,38</sup>. Sodium and hydrated sodium ions were suggested to be responsible for the formation of D4R, D6R, gmelinite and sodalite cages<sup>1,39</sup>. Potassium, Barium and Rubidium ions were believed to be responsible for directing cancrinite cages<sup>1,39</sup>. R.M. Barrer compiled a list of various zeolite types showing the cations, which are preferred of, or preferentially direct the formation of each type of zeolite. Barrer thus came to the following conclusions:

- Sodalite, cancrinite hydrates gismondine types (Na-P), gmelinites, faujasites and zeolite A are all favored by sodic environments.
- Mordenite, analcime, edingtonite and phillipsite type zeolite can be synthesized in a variety of cation environments, the later favoring sodic, calcic and strontium containing environments.
- In potassic environments chabazite and zeolite L are favored. Lithic environments favor zeolite Li-ABW and Li-H. Alkaline earth metal cations were the constituents in the gel from which thomsonite, epistillbite, heudandite, ferrierite, yugawaralite, Ba-J and Ba-K were formed.

Certain zeolites prefer the presence of two or more cations in the system e.g. zeolite EAB, offeritite and mazzite were formed in a binary cation system which in this case is sodium and TMA<sup>39</sup>.

The major drawback of the above synthesis procedures was that the zeolites with high silica to alumina ratios could not be synthesized using inorganic cations alone. Furthermore, these materials possessed low thermal stability.

Introduction of organic ammonium cations (e.g. tetramethyl ammonium cation) in zeolite synthesis led to a major breakthrough in zeolite science and as a result more siliceous materials i.e. zeolites with high silica to alumina ratios could be crystallized.

### **1.6 Role of organic additives in zeolite synthesis:**

The utilization of quaternary ammonium cation and their inherent capacity to “template” the formation of zeolite structures had two major impacts on zeolite science. The first impact relates to larger size of the organic cation. Template cations being larger cannot be placed as close together in zeolite pore system as their alkali / alkaline earth counter parts. Preservation of charge neutrality, therefore, forced the anionic aluminum sites to be equivalently spaced at larger intervals and hence zeolites with higher silica to alumina ratios could be synthesized. Furthermore, it led to the synthesis of ultrastable species.

The second major attribute of the addition of quaternary ammonium and other organic ions to hydrothermal synthesis was that the structure directing functions contributed by these ions could such influence the silica polymerization procedure that many unique zeolite structure types were found to crystallize in presence of certain organic bases and in combination of alkali and / or alkaline earth salt<sup>1</sup>.

The structure-directing role of a quaternary ammonium compound appears to influence the variety of SBU's (secondary Building Unit) present in the hydrothermal

magma. The result of this is that a particular organic base does not lead to the formation of specific zeolite structure type but rather a variety of structure types, which can be compiled from the various combinations of secondary building units. An example of this is evident in the systems employing TMA as quaternary amine e.g. gismondine, sodalite, zeolite P, N-A, NU-1, ZSM-5, Ferrierite, etc. while certain zeolite structures tend to be preferentially crystallized in the presence of certain organic bases as reported by Lok *et al*<sup>40</sup>. Furthermore, the structure directing role of mixed amines / salts appeared in early 1980's.

The next generation of molecular sieves was the synthesis of  $\text{AlPO}_4$  molecular sieves wherein phosphate substitutes silica. More than 20 unique three dimensional aluminophosphate molecular sieve structures could be crystallized from more than 45 amines and quaternary ammonium ions<sup>40</sup>. Furthermore, substituted aluminophosphates<sup>41,42</sup> and zinc (or beryllio-) phosphates (or arsenates)<sup>43,44</sup> have also been reported. Tetrahedrally coordinated atoms in some of these structures can be substituted by other metal ions, which give rise to other families of structures such as gallophosphates<sup>45,46</sup>.

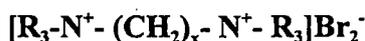
Although zeolites have desirable catalytic properties they become inadequate when the reactants with sizes above the pore diameter have to be processed. As a result scientists diverted their efforts towards synthesis of mesoporous type materials using large template molecules (e.g. surfactants). This family was termed as M41S and had large channels from 1.5 to 10 nm ordered in a hexagonal (MCM-41), cubic (MCM-48) and lamellar (MCM-50) with surface areas above  $700 \text{ m}^2/\text{g}$ <sup>47-56</sup>. Isomorphous substitution of heteroatoms such as  $\text{Ti}^{4+}$ ,  $\text{V}^{4+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Cr}^{3+}$  etc. in M41S type materials is now well known<sup>57</sup>.

In addition to the above, recently a number of di-quaternary ammonium salts also have been used as templates for the synthesis of high silica molecular sieves (Table 1.3).

**Table 1.3: Diquaternary ammonium salts and zeolite structure relationship.**

No.	diquaternary ammonium salt	R-grp	-(CH <sub>2</sub> ) <sub>x</sub> -	Zeolite	Ref.
1.	trimethylene bis (trimethyl ammonium bromide)	-CH <sub>3</sub>	3	ZSM-39, EU-1	58 59
2.	tetramethylene bis(trimethyl ammonium bromide)	-CH <sub>3</sub>	4	EU-1	58
3.	pentamethylene bis(trimethyl ammonium bromide)	-CH <sub>3</sub>	5	EU-1	60
4.	hexamethylene bis(trimethyl ammonium bromide)	-CH <sub>3</sub>	6	ZSM-48 EU-1	61 62
5.	heptamethylene bis(trimethyl ammonium bromide)	-CH <sub>3</sub>	7	ZSM-23 MCM-10	63 64
6.	octamethylene bis(trimethyl ammonium bromide)	-CH <sub>3</sub>	8	ZSM-23	63
7.	nonamethylene bis(trimethyl ammonium bromide)	-CH <sub>3</sub>	9	EU-2	61
8.	decamethylene bis(trimethyl ammonium bromide)	-CH <sub>3</sub>	10	NU-87	58
9.	tetramethylene bis(ethyl dimethyl ammonium bromide)	-C <sub>2</sub> H <sub>5</sub> -CH <sub>3</sub>	4	ZSM-12	65
10.	hexamethylene bis(ethyl dimethyl ammonium bromide)	-C <sub>2</sub> H <sub>5</sub> -CH <sub>3</sub>	6	ZSM-12	66
11.	hexamethylene bis(dimethyl Benzes ammonium bromide)	-C <sub>2</sub> H <sub>5</sub> -CH <sub>3</sub>	6	ZSM-12	66
12.	hexamethylene bis(triethyl ammonium bromide)	-C <sub>3</sub> H <sub>7</sub>	6	ZSM-5	67
13.	hexamethylene bis(tributyl ammonium bromide)	-C <sub>4</sub> H <sub>9</sub>	6	ZSM-5	68
14.	pentamethylene bis(triethyl ammonium bromide)	-C <sub>2</sub> H <sub>5</sub>	5	ZSM-57	60
15.	hexamethylene bis(triethyl ammonium bromide)	-C <sub>2</sub> H <sub>5</sub>	6	NCL-1	68,69

The di-quaternary salts may be represented by the general formula:



Where **R** may be methyl, ethyl, propyl, butyl, benzyl or a mix of thereof and **x** may have values in the range 3 to 10. In the case of bis quaternary ammonium cations, both the chain length and terminal alkyl group determine the particular structure that may be

crystallized. By systematically increasing the chain length in bis quaternary salts and keeping their terminal alkyl groups constant e.g. methyl, a number of zeolite structures can be crystallized. Recently, a high silica, large pore, ZSM-12 zeolite has been synthesized using mixed alkali quaternary salt of the formula:  $[(C_2H_5)(CH_3)_2-N^+-(CH_2)_6-N^+(CH_3)_2(C_2H_5)]2Br^-$  and  $[(CH_3)_2(C_6H_5CH_2)-N^+-(CH_2C_6H_5)(CH_3)_2]2Br^-$ <sup>66</sup>. Recently, a novel, high silica zeolite, NCL-1 has been synthesized using a new di-quaternary ammonium salt<sup>68,69</sup>.

### 1.7 Mechanism of zeolite crystallization:

The actual mechanism of zeolite crystallization is yet a mystery due to the complex interactions occurring in the hydrogel. Sand<sup>70</sup> in brief has described the reactions that can occur during the synthesis as follows:

1. precipitation of a gel phase,
2. dissolution of the gel,
3. nucleation of zeolite,
4. continued crystallization and crystal growth of the zeolite,
5. dissolution of the initial meta stable phase,
6. nucleation of the more stable metaphase phase or phases,
7. continued crystallization and crystalline growth of the new crystalline phase while the initial crystals are dissolved,
8. dissolution of the metastable phase,
9. Crystallization and crystal growth of the final crystalline phase.

Two mechanisms have been suggested for the zeolite formation. Kerr<sup>71,72</sup> postulated crystal growth from solution for zeolite A and X. McNicol *et al.*<sup>73</sup> suggested that the nucleation and crystal growth of zeolite take place within the gel phase. It was evidenced for example by crystallizing zeolites from clear solutions under hot conditions with the help of microscope<sup>74</sup>, the nucleation and subsequent crystallization can occur readily in the solution. Culfaz and Sand<sup>75</sup> proposed that the nucleation occurs at solid liquid interphase wherein it was suggested that nucleation, mass transfer of species by diffusion and zeolite crystallization occur in the boundary layer at the solid-liquid

interface. There are other physical variables such as order of mixing, rates of addition of aluminate to silicate solution and vice-versa and also agitation rate.

## **1.8 Modification of zeolites:**

Properties of zeolites can be modified either by isomorphous substitution or by cation exchange, metal loading or dealumination.

### ***1.8.1 Isomorphous substitution:***

Modification of zeolites by isomorphous substitution imparts additional properties of zeolite, which may lead to interesting catalytic properties. Goldsmith<sup>76</sup> for the very first reported isomorphous substitution of  $\text{Si}^{4+}$  by  $\text{Ge}^{4+}$  in the lattice. This was followed by isomorphous substitution of  $\text{Si}^{4+}$  or  $\text{Al}^{3+}$  by elements such as  $\text{B}^{77-79}$ ,  $\text{Fe}^{78,78a}$ ,  $\text{Ga}^{78,78b}$ ,  $\text{Ti}^{80}$ ,  $\text{V}^{81}$ , etc. It has been well established<sup>82</sup> that isomorphous substitution of Si and Al by P, Ge, B, Ga and Al modify the acid strength and catalytic properties of various zeolites. This was followed by synthesis of a number of new aluminophosphate molecular sieves containing  $\text{Al}^{3+}$  and  $\text{P}^{5+}$  in lattice. Furthermore, isomorphous substitution of  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Be}^{2+}$ ,  $\text{B}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Si}^{4+}$  and  $\text{Mo}^{3+}$  in AIPO structure is also established<sup>82,84</sup>.

Barrer<sup>83</sup> classified four types of isomorphous substitution in zeolites namely, (i) cation exchange, (ii) framework substitution, (iii) isomorphous substitution of isotopes and (iv) substitution of intracrystalline salts and molecular water. Isomorphous substitution can be achieved by direct hydrothermal synthesis or by post synthesis methods. Characterization techniques such as XRD, IR, MASNMR, ESR, UV-VIS, XPS and by catalytic test hydrocarbon conversion reactions the tetrahedral occupancy of the substituted metal cation can be verified.

### ***1.8.2 Cation exchange:***

The ion exchange capacity of a zeolite is dependent upon the amount of aluminum present in the framework of zeolite. Majority of the zeolites synthesized, are in their

cationic forms, wherein, positively charged cations neutralize the charge on the framework. These extra framework cations are exchangeable and the degree of cation exchange depends on:

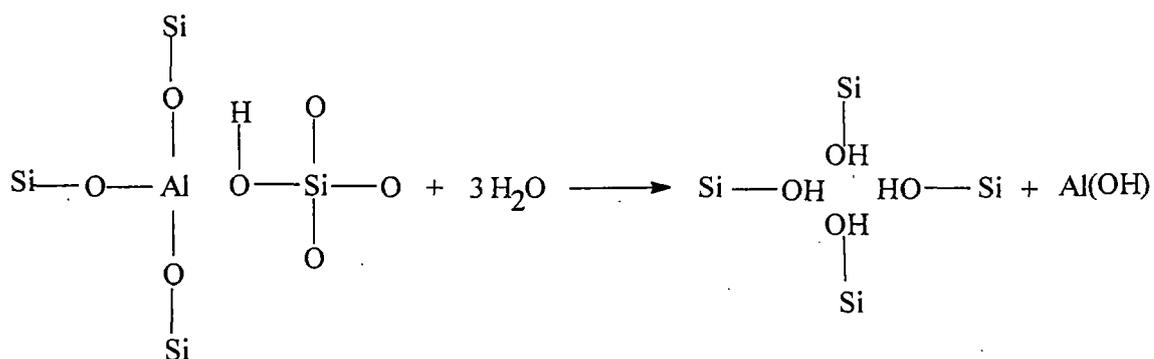
1. The type of cation being exchanged, its size as well as its charge.
2. The nature, size and strength of any cation coordination complex.
3. The temperature of the ion-exchange treatment.
4. The thermal treatment of zeolite before and after exchange.
5. The structural properties of the zeolites and its silica to alumina ratio.
6. The location of the cations in the zeolite structure.
7. The concentration of the cation exchange solution
8. The previous treatment of the zeolite.

### ***1.8.3 Metal Loading:***

In certain reactions, consider for example hydrogenation or oxidation type reactions wherein it is necessary to have additional components in the catalyst to perform the total or partial catalytic functions. Such components are mainly metals, their oxides or sulphides similar to those used in non-zeolite amorphous catalyst systems. Loading may be achieved by ion exchange (solution), impregnation, adsorption from the gas phase (silylation) or co-mulling during the catalyst formation of the solid metal component in its solution. Ni, Pt, Co, Pd, Ag, W etc. are the metals, which are generally loaded on a zeolite.

### ***1.8.4 Dealumination or steaming:***

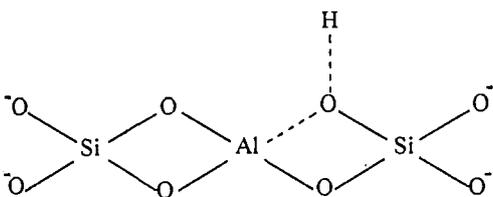
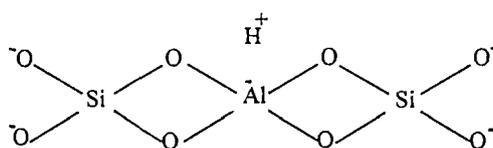
Dealumination or steaming generally involves removal of some surface and framework aluminum to make the zeolitic material more stable. Dealumination can be done by a number of techniques for example steam treatment, acid treatment, EDTA treatment or chemical vapor deposition (silylation). The dealumination process is generally represented as follows:



### 1.9 Acidity in zeolites:

When the cationic form of any zeolite is converted into its H-form or proton form the zeolite is said to be active or acidic. Acidity is dependent upon the number of  $\text{Al}^{3+}$  present in the framework or in other words zeolites with low silica to alumina ratios are highly acidic and their acidity decreases with increase in silica to alumina ratio. Substitution of trivalent metal atoms such as  $\text{Ga}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{B}^{3+}$ , etc. modify the acidity within the zeolite.

When hydrogen (proton) of the zeolite framework exhibits the property to act as a proton donor it is referred to as Brønsted acid<sup>84-86</sup>.





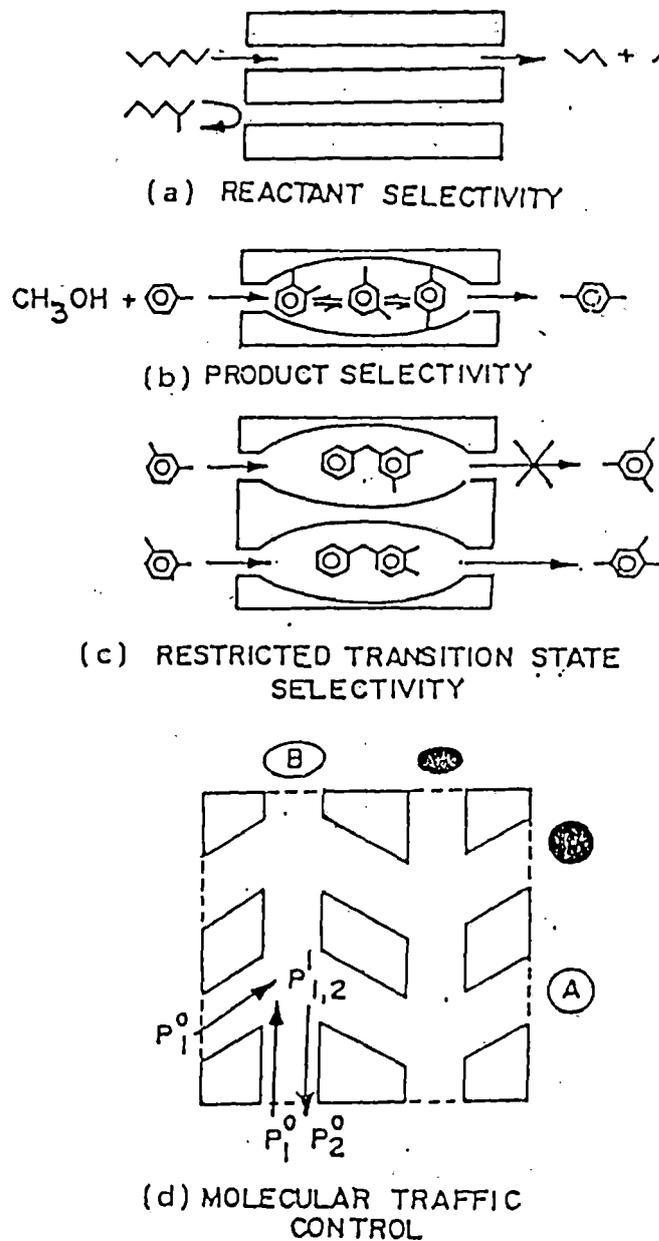


Figure 1.1 Types of molecular shape selectivity

### **1.10.2 Product shape selectivity :**

When certain compounds formed or produced within the zeolite pores during a reaction are too bulky to diffuse out as products, these bulky products will either be converted to smaller products and diffuse out or they may block the pores resulting in the deactivation of the catalyst. Consider for e.g. in xylene isomerisation, p-xylene is the major product in modified zeolites as compared to bulky o- and m- isomers due to pore diameter restrictions (Figure 1.1b).

### **1.10.3 Restricted transition state shape selectivity:**

This type of shape selectivity is observed when certain reactions are prevented because corresponding transition state requires more space than available in the zeolite pores. Diffusion of reactants and products in this situation are not hindered nor are the reactions involving smaller transition state (Figure 1.1c).

### **1.10.4 Molecular traffic control:**

Derouane and Gabelica<sup>90</sup> proposed a new type of shape selectivity in zeolites containing intersecting channel of different diameters. According to them, in cases where zeolites contain more than one type of intersecting channels, the reactants preferentially enter through one set of channels and the products diffuse out through the other, thus minimizing counter diffusion (Figure 1.1d).

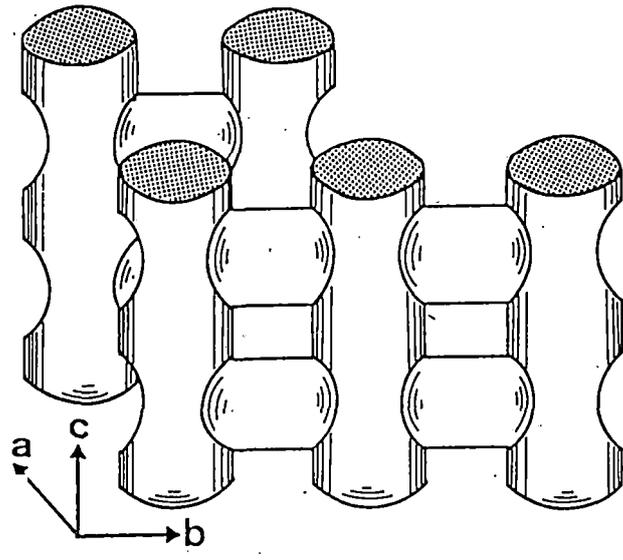
Several model reactions viz. constraint index<sup>91</sup>, refined constraint index<sup>92</sup>, spacious index<sup>93</sup>, o-p index<sup>94</sup>, DEB distribution in EB disproportionation<sup>95</sup> have been used to determine the shape selectivity of the zeolites quantitatively.

## **1.11 Structural features of Ferrierite:**

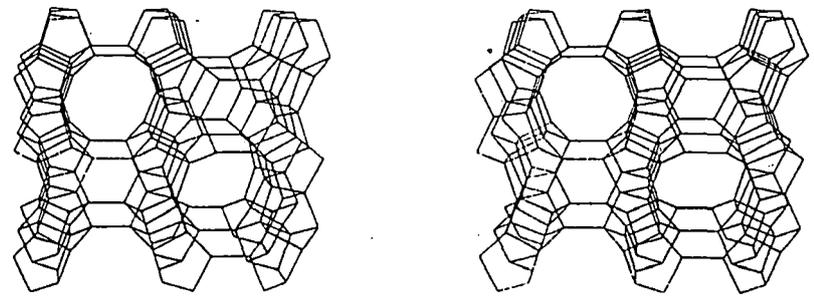
Ferrierite (FER) is a natural zeolite mineral, which occurs near Kamloops Lakes, British Columbia. Staples<sup>96</sup> in 1955 reported the unit cell content approximately as



Vaughan<sup>97</sup> and Kerr<sup>98</sup> solved its crystal structure. Breck<sup>99</sup> classified ferrierite zeolite in Group 6 together with mordenite, dachiardite, epistilbite and bikatite.



FERRIERITE



framework viewed along [001]

10-ring

8-ring

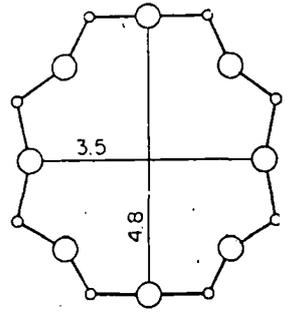
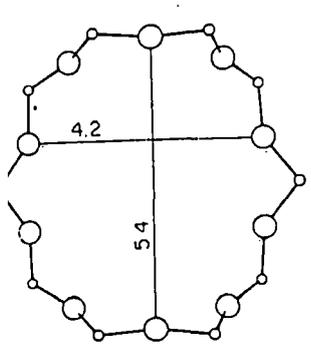


Figure 1.2 Structure of Ferrierite type Zeolites

Synthetic ferrierite is a medium pore, high silica zeolite. The FER framework is based on the chains of 5 rings, which are linked to give  $[5]^4$  polyhedral units (Figure 1.2). There are two types of perpendicular channels in the structure, which intersect one another. The main channels are parallel to orthorhombic 'c' axis of crystal and are outlined by elliptical 10 membered rings (4.3 x 5.5 Å) while the side channels parallel to 'b' axes are formed by 8 membered rings (3.4 x 4.8 Å). The ferrierite structure type is abbreviated to FER and its crystal has orthorhombic (Figure 1.2) symmetry with  $a = 1.92$ ,  $b = 1.41$  and  $c = 0.75$  nm<sup>97,100</sup> as unit cell dimensions. The unit cell contains 36 T atoms<sup>100</sup>.

### **1.12 Physico-Chemical Characterization of zeolites:**

X-ray powder diffraction and adsorption measurements are the essential means to identify zeolites. Infrared spectroscopy, Ultra violet spectroscopy, Nuclear Magnetic Resonance spectroscopy, Mössbauer spectroscopy and Electron resonance spectroscopy have also been applied in obtaining structural information about molecular sieves.

#### ***1.12.1 X-ray diffraction:***

Among the various spectroscopic techniques employed for structural evaluation of zeolites, x-ray diffraction is one of the most important and useful technique to identify zeolite structure<sup>101</sup>, phase purity, percent crystallinity, unit cell parameters, crystallite size and understanding the kinetics of crystallization. As the powder pattern is the finger print of the individual zeolite structure, phase purity and percent crystallinity of the synthesized zeolite can be ascertained by comparing with the standard pattern for the zeolite under investigation. Isomorphous substitution of a heteroatom in zeolitic framework results in changes in the unit cell parameters, unit cell volume. This is one way of confirming isomorphous substitution<sup>102</sup>.

#### ***1.12.2 Infrared spectroscopy:***

Infrared spectroscopy can yield information about the structural details of the materials. In addition, it can be used to confirm acidic characteristics and isomorphous substitution as well as aid in relating different zeolite materials by their common

structural features. Flanigen<sup>103</sup> and Ward<sup>104</sup> discussed IR studies in the hydroxyl group region. Maroni *et al.*<sup>105</sup> and Janin *et al.*<sup>106</sup> have used different probe molecules to study the acidity of zeolites by diffuse reflectance and transmission techniques. Baker *et al.*<sup>106</sup> studied the extraframework cations by far IR spectroscopy. The IR spectrum in the range 200 - 1300  $\text{cm}^{-1}$  is used to characterize and to differentiate various zeolite framework structures. The framework vibrations can be classified as *structure sensitive* (vibrations related to the external linkage of  $\text{TO}_4$  units in the structure) and *structure insensitive* (internal vibrations of framework  $\text{TO}_4$ ). No distinction can be made between the  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedral vibrations because the masses of the two T atoms are the same. Flanigen reported the general zeolite infrared assignments for the structure insensitive (internal tetrahedra) and structure sensitive (external tetrahedra) vibration, they are:

<b><i>Internal tetrahedra:</i></b>	
asymmetric stretch	1250 - 950 $\text{cm}^{-1}$
symmetric stretch	720 - 650 $\text{cm}^{-1}$
T—O bend	420 - 500 $\text{cm}^{-1}$
<b><i>External linkages:</i></b>	
double ring	650 - 500 $\text{cm}^{-1}$
pore opening	300 - 420 $\text{cm}^{-1}$
symmetric stretch	750 - 820 $\text{cm}^{-1}$
asymmetric stretch	300 - 420 $\text{cm}^{-1}$

Shifts in the band positions in the symmetric and asymmetric stretching vibrating models can be observed with change in silica to alumina ratio in the material though no distinct band can be assigned to either group.

Isomorphous substitution of the metals ions such as B, Fe, Ga, etc for Al and Ti, Ge, V etc. for Si also lead to a shift in band position or an additional band at 960  $\text{cm}^{-1}$  may be observed (viz Ti or V substituted zeolites). The IR bands around 3600 - 3700  $\text{cm}^{-1}$  confirm the presence of the silanol group<sup>107,108</sup> and or bridged hydroxyl groups in the zeolites and their Brönsted acidities can be compared. IR spectroscopy has also been used to determine the crystal purity of the samples of ZSM-5. Contamination with amorphous

silica can be evaluated by comparing the optical density ratio of 550 and 450  $\text{cm}^{-1}$  bands. A ratio of 0.8 for samples containing pure ZSM-5 materials has been suggested<sup>109-111</sup>.

### ***1.12.3 Nuclear Magnetic Resonance:***

Lipmaa *et al.*<sup>112</sup> were the first to demonstrate the use of  $^{29}\text{Si}$  MAS-NMR (Magic Angle Spinning Nuclear Magnetic Resonance) spectra in determining the nature and chemical environment of the atoms. Since then this technique was found to be very useful in understanding the structural and physicochemical properties of the zeolites. Nagy and Derouane<sup>113</sup> reported the application of a number of NMR nuclei to study zeolites. Mainly attention had been focused on  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS-NMR spectra which provided information on Si/Al ordering<sup>114</sup>. Crystallographic equivalent and non-equivalent Si and Al ions in various sites<sup>115,116</sup>, framework silica to alumina ratio<sup>117</sup>, coordination of Si and Al<sup>118,119</sup>, spectral correlation with Si—O—T bond angles<sup>120</sup> and Si—O bond lengths<sup>121</sup>.

Solid state MAS-NMR spectroscopy for  $^{29}\text{Si}$  and  $^{27}\text{Al}$  can prove tetrahedrally coordinated atoms in the zeolite lattice<sup>114,115</sup> and also show octahedral Al which may be present in the pores of the zeolites. Thirteen more NMR nuclei have been utilized in obtaining information on structural features of zeolites<sup>122,123</sup>.

### ***1.12.4 Thermal Analysis:***

Generally zeolites are thermally stable, but heating at elevated temperatures may lead to structure breakdown and therefore decrease in crystallinity. Thermal analytical data obtained from TG, DTA and DTG study are useful in evaluating the thermal properties of zeolites<sup>124</sup>. The shape and splitting of the endotherms (low temperature) helps to identify the location of water molecules and also helps in studying kinetics of dehydration of water molecules. Zeolites are known to possess high thermal stability, which increases with increase in silica to alumina ratio<sup>125,126</sup>. Ferrierite zeolite is found to be stable up to 1000 K.

### ***1.12.5 Sorption and Diffusion properties:***

As zeolites are microporous with channels and cavities they are able to selectively sorb certain molecules. Generally in zeolites, intracrystalline surface area is higher and constitutes to about 97 % of the total surface area. Damour (1846) demonstrated that

water could be reversibly removed from a zeolite without altering its structure. Later on a number of reports on sorption of gases and vapors by dehydrated zeolites started appearing<sup>127,128</sup>. Furthermore, Barrer and his co-workers studied sorption of various gases and vapors on natural as well as synthetic zeolites<sup>129,130</sup>. The selective adsorption of molecules depends on molecular size of adsorbate, polarizability and polarity of the adsorbate, organophilicity and hydrophilicity of the host zeolite structure, degree of unsaturation of organic adsorbate and polarizing power of the host cation. Sorption studies on zeolites can provide information about their void volumes, pore size, percentage crystallinity, crystal size, acidity, diffusion properties and crystal blockage if any.

Low temperature (77 K) nitrogen sorption isotherms help in determining pore volume, pore size distribution as well as the surface area of zeolite under study<sup>131,132</sup>. Adsorption and diffusion properties of zeolite play an important role on the rate of chemical reaction at the active sites. Barrer *et al.*<sup>133</sup> studied in detail the diffusion process in zeolites. Diffusion in zeolites has been categorized as Configurational, Knudsen and Bulk diffusion.

#### ***1.12.5.1 Configurational diffusion:***

Configurational diffusion is the one, which occurs in situations where the structural dimensions of the pores approach those of the molecules. In this diffusion regime, even a subtle change in the dimensions of a molecule can result in a large change in its diffusivity.

#### ***1.12.5.2 Knudsen Diffusion:***

Knudsen diffusion occurs when the mean free path of the molecule is comparable to the pore diameter, such conditions being usual in gas phase reaction on catalyst with pore diameters in the range of 30 - 1000 Å.

### **1.12.5.3 Bulk Diffusion:**

Bulk diffusion is observed when the mean free path of the molecule is much smaller than the pore diameter, and molecular collisions are more frequent than collisions with the walls, the rate of diffusion under such conditions being independent of the pore radius.

### **1.13 Catalysis over zeolites:**

Zeolites offer advantages over conventional catalysts in acid, acid-base, oxidation and reduction reactions. The major properties of the zeolite (molecular sieves) such as well defined structure, high thermal stability, high total surface area, easy regeneration, well defined micropore system (enhances selectivity), etc make them very useful as heterogeneous catalysts.

The catalytic sites for acid catalyzed reactions in aluminosilicate zeolites are mainly the Brønsted acid centres associated with protons. The as-synthesized form of zeolite can be converted into catalytically active protonic form (H form) by a number of techniques. The first and the simplest one being ion exchange of cations by protons from acidic solution. However, presence of acid leads to dealumination and finally may result into structural collapse, hence the above method is not feasible. The second method involves the replacement of cations (e.g. Na) by ammonium ions, from a solution containing ammonium salts followed by thermal decomposition of ammonium form to produce protonic form of the zeolite. The strength and the concentration of the acidic sites can also be modified by isomorphous substitution of trivalent Al and tetravalent Si by other metal ions.

Zeolites act as excellent catalysts in petrochemical and petroleum conversion processes<sup>133,134</sup>. Processes like selectofforming<sup>136</sup>, M-forming<sup>137</sup>, M-2 forming<sup>138</sup>, Cylar<sup>139</sup> and Aromax<sup>140</sup> have been developed using zeolite catalyst and commercialized by Mobil Oil Co. and British Petroleum Co. A list of commercial processes based on zeolites is given in Table 1.4.

Zeolite catalyst also plays important role in the synthesis of organic intermediates and a number of reviews on applications of zeolite catalysis in organic synthesis have been

demonstrated<sup>141-143</sup>. The utility of zeolites as catalysts in organic reactions like alkylation<sup>144-147</sup>, isomerization<sup>148-153</sup>, electrophilic substitution of arenes<sup>154,155</sup>, cyclization reactions (including hetrocyclic ring formation), nucleophilic substitution and addition<sup>156</sup> is well documented.

Ferrierite exhibits excellent selectivity for the skeletal isomerization of 1-butene. In addition, cobalt-exchanged ferrierite is reported to be active for the selective reduction of  $\text{NO}_x$ , which remains a serious environmental problem<sup>157,158</sup>.

**Table 1.4: Industrial processes based on shape selective zeolite catalyst:**

Name of the process	Purpose
selectoforming	octane boosting
M-forming	octane boosting
catalytic cracking	octane boosting
MDDW	Distillate dewaxing
MLDW	Lube dewaxing
M-2 forming CYLAR	gas to aromatics
MOGD	light olefins to gasoline and distillate.
MTG	methanol to gasoline
MTO	methanol to olefins
MVPI, MLPI, MHTI	xylene isomerization
XYLOFINING	xylene isomerization
MTDP	toluene disproportionation
ALBENE	ethylbenzene synthesis
para selective reactions	<i>p</i> -xylene synthesis
	<i>p</i> -ethyltoluene
	<i>p</i> -diethylbenzene
	<i>p</i> -cumene
	<i>p</i> -diisopropylbenzene

### 1.14 Conclusion:

As evident from the literature survey on zeolite, it can be seen that zeolites science developed very rapidly in the past decade. However, it can be observed that although a large number of zeolites are synthesized, only few (Na-Y, ZSM-5, etc.) have been applied on the commercial scale. Number of other zeolites and related molecular sieves are likely to be commercialized, in future.

In subsequent chapters, systematic study on a medium pore zeolite, Ferrierite, has been described.

### 1.15 Aim of the present work:

Zeolite ferrierite (FER) belongs to high silica medium pore class of zeolites. The silica to alumina ratio is in the range 15 - 60. These zeolites are thermally stable and acid resistant. Isomorphous substitution of  $\text{Al}^{3+}$  by  $\text{Fe}^{3+}$  and  $\text{Si}^{4+}$  by  $\text{Ti}^{4+}$  modifies the physico-chemical as well as catalytic properties of the zeolite. The aim of the present work was to synthesize Al, Fe and Ti analogs of ferrierite (FER) type zeolites by hydrothermal methods followed by their characterization and evaluation of their catalytic properties. The present study includes:

- Hydrothermal synthesis of Ferrierite zeolite in (a) absence of template; (b) presence of templates such as pyrrolidine, tetramethyl ammonium hydroxide and propyl amine; (c) to study influence of promoting media (pyrrolidine template) and (d) synthesis in presence of surfactant like sodium bis-(2 ethyl hexyl) sulphosuccinate (AOT). Modifying the zeolite by impregnation and dealumination.
- Study on kinetics of crystallization of aluminum ferrierite in presence of promoting media.
- Isomorphous substitution of  $\text{Fe}^{3+}$  for  $\text{Al}^{3+}$  and  $\text{Ti}^{4+}$  for  $\text{Si}^{4+}$  in the ferrierite topology.
- Physico-chemical characterization of Ferrierite as well as its Fe and Ti analogs.
- Modification of the above synthesized sample (Al) by impregnation and dealumination to study the catalysis.
- To study the catalytic properties (viz. acid reactions and mild oxidations) and their comparison.

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