CHAPTER I

INTRODUCTION

1.1 Porous Materials

Porous materials are solids consisting of interconnected network of pores or voids [1]. The pore size, pore shape, surface area, pore volume (porosity), and surface chemical nature, \textit{i.e.}, whether hydrophilic or hydrophobic determine the properties of porous materials. According to the recommendations of the International Union of Pure and Applied Chemistry, the pores are classified on the basis of their size, as micropores (< 2 nm), mesopores (2-50 nm) and macropores (> 50 nm) [2]. Ceramics, filters, honeycombs, and foamed ceramics are macroporous materials. Porous glasses have pore sizes tuneable over a wide range and therefore they can be categorized as both mesoporous and macroporous materials. Zeolites, activated carbons, and pillared layer compounds (clays) are well-known microporous materials. The terms “microporous” and “mesoporous” can also be represented as “nanoporous” to indicate the nanometer-scale pores [3, 4].

The porous materials have shape and size selective adsorption or ion exchange of the molecules or ions with diameter smaller than the pore size. It can either discriminate or “sieve” molecules by its shape and size [5]. The term “molecular sieve” was advocated by McBain [6] to define porous materials. Zeolites are aluminosilicate members of the family of nanoporous solids which are classified under the category of molecular sieves.
1.2 Zeolites: Basic Concepts

The term “zeolite” was originally coined by the Swedish mineralogist Cronstedt during the 18th century [7]. Zeolite has a three dimensional framework consisting of nanometer sized channels and cages which impart high porosity and a large surface area to the material [7]. The basic structural unit of all zeolite frameworks consists of a silicon or aluminium atom tetrahedrally coordinated to four oxygen atoms (Fig. 1.1). Silicon and oxygen containing zeolites are neutral, but replacing the Si$^{4+}$ by Al$^{3+}$ creates a negative charge on the framework. All such frameworks are neutralized by cations (generally one of the alkali or alkaline earth metal ions) that reside within the zeolite pores, where they can move freely and get exchanged against other cations. This leads to the ion exchange property of these materials. In general, the zeolite composition can be described as follows [8]:

$$\frac{M_{n/m}^{m+}}{\text{Extraframework cation}} \cdot [\text{Si}_{1-n} \text{Al}_n \text{O}_2] \cdot n\text{H}_2\text{O}$$

Framework Sorbed phase

The amount of aluminium in the zeolite framework can vary over a wide range, with Si/Al ratio $\geq 1$, where the completely silicon containing framework being polymorphs of SiO$_2$. The lower value of Si/Al ratio of a zeolite framework arises because the arrangement of adjacent AlO$_4^-$ tetrahedra is not favoured due to the electrostatic repulsion between the negative charges. As the Si/Al ratio of the framework increases, the hydrothermal stability as well as the hydrophobicity increase [7].

1.3 Natural (Mineral) and Synthetic Zeolites

About 40 naturally occurring zeolites are known and 150 types of zeolites have been synthesised [8]. Many of the natural zeolites have lower Si/Al ratios. Analcime,
Fig. 1.1 A two dimensional representation of zeolite framework
bikitaite, cancrinite, natrolite, wenkite, chabazite, faujasite, ferrierite, heulantite, clinoptilolite, mordenite and offretite are some of the natural zeolites [9, 10]. Zeolite A, zeolite X, zeolite Y, sodalite, ZSM-5, MCM-41 and zeolite β are some examples of synthetic zeolites [10].

The syntheses of zeolites by hydrothermal method were reported during 1950’s by Barrer [11] and Breck et al. [12]. The procedure involves the hydrothermal crystallization of hydrated aluminosilicate gels or sols in a basic medium. The gels are prepared from aqueous solutions, reactive solids, colloidal sols, or reactive aluminosilicates. The gels are crystallized in a hydrothermal system at temperatures varying from room temperature to about 150 °C. The duration required for crystallization varies from a few hours to several days [7, 13-15]. The properties of the products depend on reaction mixture composition, pH of the system, operating temperature, reaction time and the templates used [15].

Suitable silica sources used for the preparation of zeolite are hydrated silicates, precipitated silica powders and colloidal silica sol. The aluminium sources are aluminium salts, aluminium oxides and metal aluminium. The alkalinity is maintained by alkali hydroxides, alkaline earth hydroxides, and organic bases. The organic amine used in the preparation is not only to maintain the alkalinity, but also to act as void filler, charge balancer, template and structure directing agent [7, 13, 14].

The commercial zeolites exist as micrometer sized crystals or crystal aggregates. Recently, the synthesis of nanozeolites has attracted considerable interest [16, 17]. In the synthesis of nanostructured zeolites also, conventional hydrothermal technique can be used, but the crystallization conditions have to be carefully controlled to initiate the nucleation instead of crystal growth. For example, synthesis at low temperature favours
the nucleation over crystal growth [18]. Silicalite-1 [19-22], MFI [23-26], EDI [27], mordenite [28], faujasite [28-33], A [34-37] and β [38] types of nanostructured zeolites have been synthesised using different experimental conditions.

Synthetic zeolites have some important advantages over natural zeolites, in terms of uniform and desirable structures with high purity. Since the starting materials used to prepare zeolitic materials are silica and alumina compounds, which are among the most abundant minerals on earth, it is possible to prepare unlimited quantity of zeolites for various commercial applications. The time required to prepare a synthetic zeolite (in days) is much less than the time required for the formation of a natural zeolite (in years). But, it may be very difficult to prepare zeolite crystals with dimensions comparable to natural zeolites [7, 8].

1.4 Building Units of Zeolites

The fundamental unit of zeolite is a tetrahedral complex consisting of a small cation (Si$^{4+}$) in coordination with four oxygen atoms. The Al$^{3+}$ is tetrahedrally as well as octahedrally coordinated with oxygen atoms in silicates. Zeolites have a common subunit of structures which is a specific array of (Al,Si)O$_4$ tetrahedra. For example, the two simplest units are the rings of four tetrahedra (4-ring) and six tetrahedra (6-ring) as found in many aluminosilicates. These subunits have been called as secondary building units (SBU) (Fig. 1.2) [39]. The primary building units are the SiO$_4$ and AlO$_4$ tetrahedra. The single ring indicates the tetrahedral (T) Si and Al atoms connected through shared oxygen atoms, whereas double ring indicates the positions of T atoms only. The rings containing tetrahedra are the n rings. The most common rings contain 4, 5, 6, 8, 10, or 12 tetrahedra, but zeolites with rings of 14, 18 and up to 20 tetrahedra have also been prepared [40-43].
Fig. 1.2 Various sizes of n-rings and secondary building units (SBU) of zeolites (D4R: Double 4-ring; D6R: Double 6-ring; D8R: Double 8-ring)
Materials with rings of 3, 7 or 9 tetrahedra are very rare [44-46]. In the double \( n \) ring, the most common rings are 4, 6 and 8.

Cages are obtained by constructing larger building units from \( n \) rings giving rise to a diverse and interesting set of structure. It is usually considered that 6-rings are the limiting ring size to form a cage. The cages of different shape and geometry can be built by connecting rings of different sizes [47]. For example, the sodalite cage is formed by connecting 4- and 6-rings in different arrangements (Fig. 1.3 A & B).

Cavities are polyhedral units which differ from cages by the fact that they contain windows that allow the passage of molecules in and out of the cavity [48]. It should not be infinitely extended and should be distinguished from other units such as pores and channels. For example, cavities of in zeolite A and faujasite type zeolites are shown in Fig. 1.3 C & D.

A channel is a pore that is infinitely extended at least in one dimension with a minimum aperture size (\( n \) ring) that allows guest molecules to diffuse along the pore [49]. The dimension of the pore is one of the significant properties of zeolite since it determines the maximum size of a guest molecule to allow its passage. It is important to note that the guest molecules or ions which are present inside the zeolite channels and cavities have contact with oxygen atoms of the framework in the form of van der Waals interaction. These guest molecules do not interact with T atoms of the framework, which are sterically shielded by the four surrounding oxygen atoms [50].
Fig. 1.3 Cages (A&B) and cavities (C&D) commonly found in zeolites. (A) α-cage; (B) sodalite cage (β-cage); (C) cavity of zeolite A type and (D) cavity of faujasite type zeolite
1.5 Classification of Zeolites: Based on Si/Al ratio

1.5.1 Low - Silica or Aluminium - Rich Zeolites (Si/Al ≤ 2)

The best example for the low-silica or aluminium-rich zeolites are X and A type, that were synthesised by Breck et al. [51, 52]. Both zeolites have the Si/Al ratio of 1, *i.e.* the zeolite framework is nearly saturated with aluminium. As a result, they contain the maximum number of cation exchange sites balancing the framework aluminium, and thus the highest cation contents and cation exchange capacities. These zeolites are highly selective for water, polar and polarizable molecules that serve as the basis for many of their applications in drying and purification.

1.5.2 Intermediate Silica Zeolites (2 < Si/Al ≤ 5)

Zeolite Y is the suitable example for the intermediate silica zeolite. It was synthesised by Breck with a Si/Al ratio varying from 1.5 to 3.0 [53]. Zeolite Y type has the framework topology which is similar to X type and the rare zeolite mineral faujasite. Zeolite Y type plays a major role in the important catalytic applications involving hydrocarbon conversion, *i.e.* cracking, hydro-cracking and isomerization. Another commercially important synthetic zeolite, mordenite was introduced by Sand [54], which has the Si/Al ratio of 5. Also some of the zeolite minerals such as erionite, chabazite and clinoptilolite have the intermediate Si/Al ratio of 3 to 4.

1.5.3 High-Silica Zeolites (Si/Al > 5)

The best known example for the high-silica zeolite is ZSM-5 with a Si/Al ratio of 10 to 100 or higher [55]. The framework structures of high-silica zeolites are suitable for the organic mediated reactions; because of their hydrophobic selectivity, organic (non-
polar) molecules have strong interaction whereas water and polar molecules have weak interaction. ZSM-11, ZSM-12, ZSM-21, ZSM-34, sodalite and MCM-35 types of zeolites belong to high-silica zeolites [9].

1.6 Classification of Zeolites: Based on Framework Structure

The classification of zeolites can be based on the framework topology by which the structures of zeolites are identified [7]. Based on their structures, zeolites are classified into seven groups. The zeolites within a group will have common SBUs.

1.6.1 Zeolites of Group 1

The zeolites of group 1 have the single 4-ring (S4R) SBU in their framework structure [39]. In the 4-ring, “4” denotes the positions of tetrahedral (T) silicon and aluminium atoms, and the oxygen atoms are located in between T atoms. The diagrammatic representation of a single 4-ring is shown in Fig. 1.2. The zeolite minerals namely analcime, wairakite, viseite, and kehoeite belong to group 1.

Analcime is a naturally available zeolite. Its crystal structure was determined by Taylor in 1930 [56]. The typical unit cell content of analcime is Na_{16}[(AlO_2)_16(SiO_2)_32] 16 H_2O. The aperture diameter of main channel is 2.6 Å [7]. The three dimensional (3-D) framework structure of analcime is shown in Fig. 1.4. The framework type code (FTC) for analcime is “ANA”. It has 3-D channel systems with the ring sizes of 8, 6 and 4. In hydrated form, the Na^+ ions are coordinated with the distorted 4-ring oxygen atoms and two water molecules. The Na^+ ions present in the zeolite framework can be exchanged by Li^+, K^+, NH_4^+, Ag^+, Ca^{2+} and Mg^{2+} at 225° C [57].
Fig. 1.4 Framework structure of analcime (zeolite of group 1)
1.6.2 Zeolites of Group 2

The zeolites of group 2 have the single 6-ring (S6R) SBU in their framework structure [39]. The diagrammatic representation of S6R is shown in Fig. 1.2. The following zeolites belong to group 2: erionite, offretite, levynite, zeolite T, omega and zeolite HS. Among the list of zeolites, the first three belong to natural zeolites.

The typical unit cell content and the main channel aperture size of erionite are (Ca, Mg, K₂, Na₂)₄.₅ [(AlO₂)₉(SiO₂)₂₇] 27 H₂O and 3.6 × 5.2 Å, respectively [7]. The 3-D structure of erionite is shown in Fig. 1.5. The FTC for erionite is “ERI”. Erionite has 3-D fibrous structure and it is highly stable in anhydrous form. In general, K⁺ and Ca²⁺ are the main cationic species, which are considerably present in the framework. The sedimentary variety of erionite containing K⁺ has considerable resistance to ion exchange which implies that the K⁺ ions are trapped within the pores. So, the ion exchange capacity of erionite is very poor. The erionite is one of the siliceous zeolites having the Si/Al ratio of 3 [7].

1.6.3 Zeolites of Group 3

The group 3 zeolites have the double 4-ring (D4R) SBU in their framework structure [39]. The D4R unit is created by joining two S4R units. Zeolite A, N-A and ZK-4 belong to zeolites of group 3. Zeolite A is the synthetic zeolite which is having the unit cell content of Na₁₂[(AlO₂)₁₂(SiO₂)₁₂] 27 H₂O. The aperture diameter of main channel is 4.2 Å [7]. The 3-D view of zeolite A type is shown in Fig. 1.6. The FTC for zeolite A is “LTA”.
Fig. 1.5 Framework structure of erionite (zeolite of group 2)

Fig. 1.6 Framework structure of zeolite A (zeolite of group 3)
The building units of zeolite A are the double 4-ring, \( \beta \) cage (sodalite) and \( \alpha \) cage. The molecules can diffuse in all the three directions across the 8-ring windows that are connecting the cavities. Among the 12 sodium ions present in the hydrated zeolite A, 8 ions are located near the centre of the 6-rings on the 3-fold axis inside the \( \alpha \)-cage. The remaining 4 ions appear to be located with water molecules in the 8-rings [58].

### 1.6.4 Zeolites of Group 4

The zeolites of group 4 have the double 6-ring (D6R) SBU in their framework structure [39]. The D6R unit is created by joining two S6R units. The group 4 zeolites include the minerals chabazite, gmelinite and R type (chabazite family); and faujasite, zeolite X and Y (faujasite family). Among the two different families, the structures of the latter ones are of considerable interest.

The unit cell content and the aperture diameter of main channel of zeolite Y type are \( \text{Na}_{56}[\text{AlO}_2]_{56}(\text{SiO}_2)_{136} \cdot 250 \text{H}_2\text{O} \) and 7.4 Å, respectively [7]. The 3-D view of zeolite Y type is shown in Fig. 1.7. The FTC for faujasite type structure is “FAU”. Zeolite X and Y have a Si/Al ratio of 1.25 and 2.3, respectively [59]. These synthetic materials (X and Y) are isostructural with the rare mineral faujasite. The three important building units responsible for the formation of FAU type of zeolite are double 6-ring, the sodalite (\( \beta \)) cage and a very large cavity with four 12-ring windows. The cavity is in tetrahedral symmetry and it is known as the supercage. The connectivity of this cage allows molecules to diffuse in all the three directions of the crystal interior. A unitcell contains 8 supercages, 8 sodalite cages and 16 double 6-ring units [49].

The 12-ring windows, with a free diameter \( \sim 7.4 \) Å, are perpendicular to the 111 directions, but because of the tetrahedral symmetry of the cavity there are no straight
Fig. 1.7 Framework structure of faujasite (zeolite of group 4)
channels along this direction. Molecules larger than water or ammonia can access only the supercages and cannot pass into the empty space inside the sodalite cage. Hence, all reactions of most molecules are confined to the supercages. In the dehydrated zeolite Y, Na$^+$ ions present in the unit cell occupy three different sites. Nearly 7.5 Na$^+$ ions are occupying site I (16-fold site located in the centre of the double 6-ring i.e., hexagonal prism), 30 Na$^+$ ions are in site II (single 6-ring outside of the β-cage and lies within the large cavity) and 20 Na$^+$ ions in site I’ (inside of the β-cage adjacent to D6R) [60].

1.6.5 Zeolites of Group 5

Pauling [61] and Taylor [56] established the structural characteristics of group 5 zeolites during 1930. These types of zeolites are sometimes called fibrous zeolites, because the morphology is explained by the long chains present in the framework. The group 5 zeolites have the complex 4-1 T$_5$O$_{10}$ SBU in their framework structure [39]. The complex 4-1 T$_5$O$_{10}$ refers to the unit of 5 tetrahedra for the 4-1 type of SBU. The diagrammatic representation of complex 4-1 T$_5$O$_{10}$ SBU is shown in Fig. 1.8.

There are three possible ways of cross-linking the above SBU to form three types of framework structure. The first way of cross-linking leads to the formation of natrolite, scolicicite, and mesolite. The second way of cross-linking leads to the formation of thomsonite and gonnardite. And the last way of cross-linking leads to the formation of edingtonite. The details regarding natrolite are explained here. The unit cell content and the aperture size of main channel of natrolite are Na$_{16}$[(AlO$_2$)$_{16}$SiO$_{24}$] 16 H$_2$O and 2.6 × 3.9 Å, respectively [7]. The framework structure of natrolite is shown in Fig. 1.9. The FTC for natrolite type structure is “NAT”.
Fig. 1.8 Complex 4-1 $\text{T}_2\text{O}_{10}$ secondary building unit

Fig. 1.9 Framework structure of natrolite (zeolite of group 5)
Introduction

Natrolite framework is formed by construction of chains of T₅ tetrahedral unit. The Na⁺ ions occupy as a cluster in natrolite channels, along with the water molecules i.e. the water molecules are clustered around cations. Na⁺ ion is undergoing coordination with four oxygens of the framework and two water molecules. The lattice dimension and framework structures undergo decomposition when it is dehydrated at very high temperature [7].

1.6.6 Zeolites of Group 6

The zeolites of group 6 have the complex 5-1 T₅O₁₆ SBU in their framework structure [39]. The SBU of 6 tetrahedra is called 5-1 unit. The diagrammatic representation of complex 5-1 T₅O₁₆ SBU is shown in Fig. 1.10. This SBU forms complex chains which are linked to each other in six different ways [62]. Mordenite, dachiardite, epistilbite, ferrite and bikitaite are some of the zeolites belonging to group 6.

The structural details regarding mordenite are explained briefly here. The unit cell content and the aperture size of main channel of mordenite are Na₈[(AlO₂)₈(SiO₂)₄₀] 24 H₂O and 6.7 × 7.0 Å, respectively [7]. The framework structure of mordenite is shown in Fig. 1.11. The FTC for mordenite type structure is “MOR”. The framework consists of chains, which are cross-linked by the sharing of neighbouring oxygen. Each tetrahedral unit belongs to 5-rings in the framework, and because of the large number of 5-rings, it is thermally stable. Mordenite has the Si/Al ratio of 5, which is the most siliceous zeolite mineral [63].

1.6.7 Zeolites of Group 7

The group 7 zeolites have the complex 4-4-1 T₁₀O₂₀ SBU in their framework structure [39]. The diagrammatic representation of complex 4-4-1 T₁₀O₂₀ is shown in
Fig. 1.10 Complex 5-1 $\text{T}_8\text{O}_{16}$ secondary building unit

Fig. 1.11 Framework structure of mordenite (zeolite of group 6)
Fig. 1.12. Heulandite, stilbite and clinoptilolite belong to the zeolites of group 7. Clinoptilolite is a naturally available sedimentary mineral, which is an isostructural variant of heulandite. The unit cell content and the aperture size of main channel of heulandite are $\text{Ca}_4[(\text{AlO}_2)_8(\text{SiO}_2)_{28}] 24 \text{ H}_2\text{O}$ and $4.0 \times 5.5$ Å, respectively [7]. The framework structure of heulandite is shown in Fig. 1.13. Because of the low bond density and strength in heulandite, the framework structure changes during dehydration [64]. Compared to heulandite, clinoptilolite is stable upon dehydration. The chemical compositions, like Si/Al ratio and exchangeable cations are significantly different for heulandite and clinoptilolite.

1.7 Salient Properties of Zeolites

1.7.1 Physical Properties

Zeolites are colourless in pure state. Synthetic zeolites are typically microcrystalline powders having particle size from 1 to 10 μm. The density of zeolites varies from 1.9 to 2.3 g/cm$^3$. They are thermally quite stable. For example, the decomposition temperature for low-silica and completely siliceous zeolites are about 700 and 1300 °C respectively. Low-silica zeolites are unstable in acid, whereas high-silica zeolites are stable in acids, but unstable in basic solutions. Low-silica zeolites are hydrophilic, whereas high-silica zeolites are hydrophobic. The internal surface area of the zeolite is greater than the total surface area of the zeolite. In general, the internal surface area of the zeolite is in the range between 300 and 700 m$^2$/g [7, 8].

1.7.2 Chemical Properties

Zeolitic materials have three outstanding properties, namely their molecular sieving behaviour (size, shape and charge selectivity), cation exchange capacity and the
Fig. 1.12 Complex 4-4-1 T_{10}O_{20} secondary building unit

Fig. 1.13 Framework structure of heulandite (zeolite of group 7)
inherent catalytic properties imparted by framework acid sites [7]. The Brönsted acidity in zeolites comes from the proton attached to oxygen atoms of the framework. The charge compensating cations or the trigonal Al atoms deficient in oxygen are responsible for Lewis acidity. These properties vary significantly with the Si/Al ratio. As the Si/Al ratio decreases, the cation content and ion-exchange capacity increases. Cation exchange capacities provide a measure of the selectivity of one ion over another. It also provides information regarding limitation of exchange capacity because of the exclusion of a cation. This is due to its large molecular size (ion sieving), or the cations occupy too much intrazeolitic volume (volume exclusion). Ion exchange capacities play a major role in the catalytic behaviour of zeolites [65].

Diffusion of ions in the zeolites can be either particle-controlled diffusion (rate limiting within the framework) or surface diffusion (in the zeolite-fluid boundary). Particle-controlled diffusion is governed by concentration gradients and also influenced by electrical potential gradients arising from the charge density differences of the exchanging ions [66].

1.8 Applications of Zeolites

The main uses of zeolites are due to their attractive characteristics, viz. molecular sieving behaviour, cation exchange capacity and the inherent catalytic properties. The following gives a summary of the important applications of zeolites.

Zeolite materials are used to adsorb a variety of molecules, and this includes the applications in purification and bulk separations [67]. The purification is based on the selectivity of the zeolite towards polar or polarizable molecules such as water, CO₂, sulphur compounds, etc. It plays a major role in the removal of heavy metal
contaminants and some other pollutants present in the aquatic system [68-70]. The bulk separations are entirely based on the molecular sieving behaviour. The ability to tune the size of the pores provides a means of shape selectivity like reactant selectivity, product selectivity and transition state selectivity in organic reactions [71]. It involves the separation of organic compounds [72] such as normal/iso-paraffin, xylenes and olefins, and also used for the separation of organic solvents [73]. Separation of gases [74] and amino acids [75] are some of the other important applications.

Zeolites are widely used as catalysts in several important reactions involving organic and inorganic molecules [76]. The most important organic reactions are cracking, isomerization, aromatization, hydrogenation, dehydrogenation and hydrocarbon synthesis. Some of the interesting catalytic reactions due to inorganic molecules are H₂S oxidation, CO oxidation and CO₂ hydrogenation. It can also be employed in acid-base and metal induced reactions [67]. The main industrial applications of zeolites are in petroleum refining and petrochemical production [7].

The counter cations present within the zeolite pores can readily undergo exchange with other cations and this property of zeolite is exploited for various applications. It leads to their application in water softening and detergents formulation [65]. In water softening processes, Ca²⁺ and Mg²⁺ present in water are removed by simple ion exchange. Zeolites can be used to remove radioactive and heavy metal ions from contaminated water [68-70]. They can also find applications in biomedicine [77].

Zeolitic materials have been used as a host for the synthesis of nanomaterials. The pores in the zeolites can be used as nanoreactors. For example, quantum dots (finely divided semiconductors) [78,79], noble metal particles [80] and conducting polymers [81] have been prepared within the nanopores of zeolites. This method has the advantage of
preventing any agglomeration or clustering of nanoparticles, and the size of a nanocluster is governed by pore diameter of the zeolite. The physical and chemical properties of the materials confined within the zeolite pores are different from the bulk materials. The absorption edge energy of cadmium sulfide quantum dots confined within a zeolite pores is higher than that of the bulk cadmium sulfide [82]. Such semiconducting nanoparticles have been found to show superior performance in solar energy conversion and photocatalysis [83]. Similarly metal nanoparticles incorporated zeolite materials are of great interest in heterogeneous catalysis [84]. Likewise, conducting polymer incorporated (molecular wire) zeolite materials can be used in molecular electronic devices. Silver entrapped zeolite materials are used in fluorescent probes, photographic processes, photographic imaging and optical data storage [85]. Above all, zeolites as modifier of electrode surfaces have led to a variety of applications in electroanalytical chemistry. The following gives a brief account of literature on the development of zeolite-modified electrodes (ZMEs) in electrochemistry.

1.9 Electrochemistry of ZMEs

It was Marshall who used zeolite minerals for the first time, in the electrochemical detection of some monovalent and divalent cationic species [86]. The major applications of zeolites in electrochemistry are in electroanalysis, electrocatalysis, charge and mass transport characterization, molecular recognition and power sources [87]. Potentiometry, amperometry and voltammetry techniques have been employed in the electroanalysis of various analytes using ZMEs. There are several comprehensive books and reviews on ZMEs [87-92].
1.9.1 Preparation of ZMEs

It has been a challenging task to modify an electrode by a zeolite, because of its microcrystalline nature and often special efforts are necessary in the preparation of ZMEs. A good ZME should have low resistance, low capacitance, high mechanical stability, long term stability and high reproducibility in terms of both fabrication procedure and electrochemical response [91]. Often, ZMEs are prepared using a conducting material like graphite with a binder like polystyrene to impart electronic conductivity, adhesion and mechanical stability to the modified layer [91].

Pellets of zeolite-carbon composite have been prepared by compression on a stainless steel [93], platinum [94,95] and gold grids [94]. Equal quantities of a zeolite and graphite powder (without any binding material) are used for the preparation of pellets. The pelletization does not affect the crystal structure of the zeolite. However, the mechanical stability of the pellets has been a major problem in their use as electrodes.

Zeolites have been coated on conventional solid electrodes using polystyrene as the binding material. The zeolite-polystyrene mixture dispersed in an organic solvent (e.g., tetrahydrofuran) is coated on various electrode surfaces including ITO [96-103], platinum [104,105] and glassy carbon [106-110] to get the zeolite-polystyrene composite film. The formation of voids due to the uneven distribution of zeolite and polystyrene is the major disadvantage of this procedure. In order to prepare a compact zeolite film, electrophoretic deposition procedures have been suggested. A binding material like Nafion is coated subsequently on the electrophoretically deposited zeolite film to get mechanically stable ZME [111,112]. However, a disadvantage of this methodology is the poor electronic conductivity of the film, which may significantly affect the electrochemical response.
In order to prepare a ZME surface with excellent conductivity and good mechanical stability, both graphite powder and polystyrene have been used. The zeolite-graphite-polystyrene mixture dispersed in THF can be coated on conventional electrode surfaces such as glassy carbon [113] and ITO [114-117], and it is called as zeolite-modified carbon paste electrode (ZMCPE). The performance (both stability and electrochemical response) of the zeolite-graphite-polystyrene modified electrode is better than zeolite-polystyrene modified electrode [118]. Instead of polystyrene, mineral oil or paraffin liquid can also be used to prepare ZMCPEs [119]. The zeolite-modified carbon paste can be packed at one end of glass [119,120] or polyethylene [121-129] or teflon [130-136] tube. The electrical connection is made through either stainless steel piston or copper wire. ZMCPE can also be prepared by screen printing technique [137]. The screen-printed ZMCPE gives better performance (in terms of peak current) than the corresponding ZMCPE in teflon tube [137].

ZMEs have also been prepared by covalent link between zeolite and electrode surface through a coupling agent. Tin oxide coated glass plate has been functionalized with silane coupling agent, which is then transferred to the suspension of zeolite Y particles to get a uniform zeolite film [138].

Nano ZMEs have been fabricated by layer-by-layer and secondary seed growth method on platinum or glassy carbon electrode (GCE) [139]. The platinum or GCE has been alternatively coated with three layers of anionic, cationic polyelectrolytes and negatively charged faujasite type nanozeolites to get a layer-by-layer nano ZME. In the secondary seed growth method, the zeolite seeded platinum or GCE has been treated in the synthesis solution at 80 °C for 1-8 h. The secondary seeded nano ZME is then washed.
in ammonia solution before doing the actual experiments. The performance of nano ZME prepared by layer-by-layer method is better than that by the secondary seed method.

The direct deposition of a compact and mechanically stable zeolite film on a GCE at slightly above room temperature has been reported [140]. An electrochemically-assisted preparation of self-assembled and highly oriented mesoporous silica film on various conducting supports has been recently reported. The method involves the use of a surfactant template and is akin to the electrochemical generation of sol-gel films [141].

As the present work is mainly concerned with the application of ZMEs in electroanalysis and electrocatalysis, the relevant literature is briefly summarized below.

### 1.9.2 Electroanalytical Applications of ZMEs

ZMEs have been mainly employed in the determination of various inorganic cations and organic molecules by potentiometry, indirect amperometry and voltammetry techniques [91].

#### 1.9.2(a) Inorganic Cations

The application of a natural zeolite membrane in the potentiometric detection of alkali and alkaline-earth metal ions for the first time by Marshall as early as 1939 revealed that the potentiometric response of the zeolite membrane was similar to that of the glass membrane electrode used in the determination of H⁺ activity [86]. A disposable screen-printed zeolite/sol-gel composite electrode was reported to give a stable response for H⁺ ions by potentiometric technique [142]. Similarly, platinum microparticle deposited on a conducting polymer (polypyrrole or polyaniline) blend containing zeolite particles was used as a pH sensor [143].
The detection of several alkali or alkaline earth metal ions by potentiometry [144-150] and indirect amperometry [117,124,134,151-153] techniques at ZMEs have been reported. Zeolite membranes or pellets were used in the potentiometric detection of cations. Polymeric materials including polythene, polystyrene and polymethylmethacrylate have been used in the preparation of zeolite membranes or pellets [144]. The size-selective detection of Na\(^+\) ion in the presence of size excluded tetraethylammonium ion using a zeolite A pellet impregnated with an inert polymer was reported [144]. Similarly, mordenite type zeolite pellets impregnated with low viscosity epoxy resin was employed for the detection of Cs\(^+\) ion in the presence of size excluded tetrabutylammonium ion. The linear response for the detection of Cs\(^+\) ion was from 3×10\(^{-5}\) to 10\(^{-1}\) M [145]. Copper ion exchanged A and X type zeolite / epoxy resin membranes were used for the detection of alkali metal ions [146]. Polydimethylsiloxane [147] and poly(tetrafluoroethylene-co-ethylene-co-vinylacetate) [148] were used to prepare stable zeolite (faujasite type) membranes for the potentiometric detection of Cs\(^+\) ion with ideal Nernst response. Likewise, poly(vinyl chloride)-stabilized ZME was also used to detect Li\(^+\), Na\(^+\), K\(^+\) and Cs\(^+\) ions [149]. The combination of clinoptilolite type zeolite with an ion-selective field effect transistor device showed linear potentiometric response down to the concentration of 10\(^{-8}\) M for ammonium ion [150].

It may not be possible to determine the alkali and alkaline earth metal ions (e.g., K\(^+\), Ca\(^{2+}\)) by either voltammetric or amperometric techniques using conventional electrodes directly, because their reductions occur at more negative potentials than that corresponding to water reduction [91]. However, a number of literature reports are available for the detection of alkali and alkaline earth metal ions by indirect amperometry using ZMEs [117,124,134,151-153]. For this purpose, the redox cations (e.g., Cu\(^{2+}\), Ag\(^+\)) exchanged zeolites were employed. The cations of the supporting electrolyte were of
molecular size greater (e.g., tetrabutylammonium ion, TBA\(^+\)) than the pore size of the zeolite. The ion exchange and electron transfer processes in the indirect amperometric detection can be described by the following equations [91]:

\[
E_{Z}^{m+} + mTBA_Z^+ \neq E_{S}^{m+} + mTBA_S^+
\]  

\[
E_{Z}^{m+} + mM_S^+ \Leftrightarrow E_{S}^{m+} + mM_Z^+
\]  

\[
E_{S}^{m+} + ne^- \Leftrightarrow E_{S}^{(m-n)+}
\]

where \(E^{m+}\) is the redox cation, \(M^+\) is the alkali or alkaline earth metal ions, and the subscripts \(Z\) and \(S\) refer to the zeolite and the solution phase, respectively. No redox response will be observed, when the voltammetric experiments are carried out using redox cation exchanged ZME in size-excluded electrolyte (TBA\(^+\)) solution, because the charge balance cannot be maintained (Eq. 1.1). On the other hand, if a trace amount of non-size-excluded cation (e.g., \(M^+\)) is added to the above electrolyte solution (TBA\(^+\)), redox response can be obtained due to the replacement of redox cations present within the zeolite cavity by non-size-excluded cation (Eq. 1.2).

Alkali metal ions, such as Li\(^+\), Na\(^+\), K\(^+\) and Cs\(^+\) ions were determined at the Ag\(^+\)-exchanged ZME in the TBA\(^+\) ion dissolved methanol/water mixture using faujasite [117,134,151] and mordenite [152] type zeolites. The peak current was directly proportional to the concentration of alkali metal cations. Also, the diffusion of Ag\(^+\) ion was directly related to the amperometric intensity. The NH\(_4^+\) ion has also been determined using Ag\(^+\)-exchanged zeolite Y-modified electrode [134,152].

Techniques like batch and flow injection analysis have been applied in the indirect amperometric detection of alkali and alkaline earth metal ions at ZMEs. In batch injection analysis, the analyte is injected through a microsyringe in close proximity to the ZME, whereas in flow injection analysis, a carrier electrolyte (TBA\(^+\)) from either
measurement cell or fresh electrolyte is used to carry the analyte to the ZME. Methyl viologen (MV²⁺) exchanged ZME was used to detect Li⁺, Na⁺, K⁺, Cs⁺, NH₄⁺, Mg²⁺ and Ca²⁺ ions by both batch and flow injection analysis [124]. The electrode response depended on both charge and size of the analyte. Batch injection analysis is applicable for direct detection of cations, whereas flow injection analysis is usually applied as a detector in ion chromatography. Similarly, Cu²⁺ or Ag⁺ ion exchanged A, X and Y type zeolites were employed in the detection of Li⁺, Na⁺, K⁺, Cs⁺, NH₄⁺, Mg²⁺ and Ca²⁺ ions [134,153]. The sensitivity of the electrode was higher for large pore zeolites. The selectivity of the analyte was independent of zeolite type; however, selectivity was related to the analyte size. So, the analysis of cation in the mixture required a separation step before analysis. A MV²⁺-doped zeolite Y modified carbon paste sensor was reported for the amperometric detection of Li⁺, Na⁺, K⁺ and Cs⁺ ions after their separation by ion chromatography [124,128]. Three types of zeolites (A, X and Y) exchanged with two different mediators (Cu²⁺, Ag⁺) were used to detect Li⁺, Na⁺, K⁺, Cs⁺, Ca²⁺, Mg²⁺ and NH₄⁺ ions. The peak current observed at Ag⁺-exchanged ZME was higher compared to Cu²⁺-exchanged ZME [134].

The redox active inorganic cations including Cu²⁺, Cd²⁺ and Pb²⁺ can be determined directly using ZME by voltammetric techniques [91]. In this method, the accumulation of analyte (redox cations) via ion-exchange on the ZME at open circuit and subsequent reduction by voltammetric technique has been followed. Lower detection limit and increased sensitivity can be achieved by this simple chemical preconcentration procedure prior to the electrochemical quantification [91]. The literature on the use of ZMEs for the detection of redox active inorganic cations following a preconcentration procedure is briefly summarized in Table 4.1. The first report on the voltammetric detection of cations using ZME was reported during 1987. A natural zeolite (from
Table 4.1 Detection of redox active metal ions using ZMEs

<table>
<thead>
<tr>
<th>Metal Ions</th>
<th>Zeolite Type</th>
<th>Supporting electrolyte</th>
<th>Technique*</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg$^{2+}$</td>
<td>Natural zeolite from volcanic rocks</td>
<td>KNO$_3$</td>
<td>CV</td>
<td>[121]</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>A</td>
<td>NaNO$_3$</td>
<td>DPV</td>
<td>[119]</td>
</tr>
<tr>
<td>Cd$^{2+}$ &amp; Pb$^{2+}$</td>
<td>Y</td>
<td>KCl</td>
<td>CV</td>
<td>[112]</td>
</tr>
<tr>
<td>Cd$^{2+}$ &amp; Pb$^{2+}$</td>
<td>Faujasite</td>
<td>NaNO$_3$</td>
<td>CV</td>
<td>[139]</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>Analcime</td>
<td>HNO$_3$</td>
<td>DPV</td>
<td>[154]</td>
</tr>
<tr>
<td>Cd$^{2+}$ &amp; Pb$^{2+}$</td>
<td>--</td>
<td>Acetate buffer</td>
<td>DPV</td>
<td>[155]</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>Mordenite</td>
<td>KCl</td>
<td>CV</td>
<td>[156]</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>Clinoptilolite</td>
<td>NaNO$_3$</td>
<td>DPV</td>
<td>[120]</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>13X</td>
<td>Phosphate buffer</td>
<td>SWV</td>
<td>[132]</td>
</tr>
<tr>
<td>Cd$^{2+}$, Cu$^{2+}$ &amp; Zn$^{2+}$</td>
<td>13X</td>
<td>Phosphate buffer</td>
<td>SWV</td>
<td>[126]</td>
</tr>
<tr>
<td>[Cu(NH$_3$)$_4$]$^{2+}$ &amp; [Hg(NH$_3$)$_4$]$^{2+}$</td>
<td>MCM-41</td>
<td>Aqueous ammonia</td>
<td>SWV</td>
<td>[157]</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>Y</td>
<td>KNO$_3$</td>
<td>ASV</td>
<td>[136]</td>
</tr>
</tbody>
</table>

* DPV-Differential pulse voltammetry; SWV-Square wave voltammetry; CV-Cyclic voltammetry; ASV-Anodic stripping voltammetry
volcanic rocks) was employed for the cyclic voltammetric determination of \( \text{Hg}^{2+} \) ion [121]. Wang and Martinez [119] reported that zeolite A showed high affinity towards \( \text{Ag}^+ \) ion for its differential pulse voltammetric detection. An electrophoretically deposited ZME was used for the detection of \( \text{Cd}^{2+} \) and \( \text{Pb}^{2+} \) ions by cyclic voltammetry. Zeolite Y type was found to give better sensitivity towards \( \text{Cd}^{2+} \) and \( \text{Pb}^{2+} \) ions compared to 4Å, 5Å and 13X types of zeolite molecular sieves [112]. Zeolites with large pore size, greater ion exchange capacity and lowest particle size give the maximum accumulation efficiency which leads to offer highest sensitivity and lowest detection limit in the determination of cations. An ultrathin nanozeolite (faujasite) film modified electrode was prepared by layer-by-layer and secondary seed growth methods for the detection of \( \text{Cd}^{2+} \) and \( \text{Pb}^{2+} \) ions. Between the two methods employed the ZME prepared by the layer-by-layer method was found to follow a better performance than the one prepared by the secondary seed growth method [139]. A separation and preconcentration procedure was proposed for determining trace amounts of \( \text{Cd}^{2+} \) ion in which a column of analcime zeolite modified with benzyltrimethyltetradecylammonium chloride and loaded with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol was used for retention of \( \text{Cd}^{2+} \) ion. The \( \text{Cd}^{2+} \) ion was recovered by using nitric acid for quantitative determination by anodic stripping pulse voltammetry at a hanging mercury drop electrode [154]. A preconcentration step was carried out at -1.2 V with stirring for the differential pulse stripping voltammetric detection of \( \text{Cd}^{2+} \) and \( \text{Pb}^{2+} \) ions using bismuth-modified zeolite doped carbon paste electrode. The \( \text{Cd}^{2+} \) and \( \text{Pb}^{2+} \) ions present in the tap-water and sewage water sample were determined using the above electrode [155]. A mordentie type ZMCPE was employed for the detection of \( \text{Cu}^{2+} \) ion in 0.1 M KCl by cyclic voltammetry [156]. A natural zeolite (clinoptilolite) was used for the the detection of \( \text{Cu}^{2+} \) ion by differential pulse cathodic stripping voltammetry [120]. The voltammetric peak current for \( \text{Cu}^{2+} \) ion was found to be
higher for 13X type compared to 3Å, 4Å and 5Å types of molecular sieve zeolite. The reduction of Cu$^{2+}$ ion depended on the pH of the medium [132]. The addition of ammonia in the detection medium was found to improve the detection of Cu$^{2+}$ ion, because the ammonia ligands were more efficient in facilitating the transfer of analyte (Cu$^{2+}$) out of the zeolite cavity for voltammetric reduction [126]. A mechanically stable zeolite-modified solid carbon paste electrode was prepared by incorporation of zeolite Y into the solid paraffin for the detection of Cu$^{2+}$ ion [135]. A MCM-15 type ZME was used for the detection of [Cu(NH$_3$)$_4$]$^{2+}$ and [Hg(NH$_3$)$_4$]$^{2+}$ ions in aqueous ammonia solution by square wave voltammetry [157]. The square wave voltammetry detection of Zn$^{2+}$ ion was reported using 13X and X type ZME in phosphate buffer and KNO$_3$, respectively [107,126].

1.9.2(b) Organic Molecules/Cations

ZMEs have also been exploited in the electroanalysis of some organic molecules. An ammonium ion sensitive field effect transistor (ISFET) based on a natural zeolite (clinoptilolite)-incorporated polymeric (siloprene) membrane was used to detect urea molecule. The urea was potentiometrically detected after functionalization of ISFET by the enzyme urease [158]. A thionine-exchanged mordenite type zeolite was incorporated into a poly(vinyl chloride) membrane for the potentiometric detection of ascorbic acid [159]. Zeolite-polydimethylsiloxane membranes were found to be suitable for the potentiometric detection of alkali metal ions [147] and were also used to detect the ionic surfactants including hexadecylpyridinium chloride and sodium dodecyl sulphate [160]. Stable potentiometric responses were obtained using pure zeolite membranes in the detection of tetraethylammonium ions in aqueous [161] and non-aqueous [162] solutions. The indirect amperometric detection of tetramethylammonium (TMA$^+$),
tetraethylammonium (TEA⁺) and tetrapropylammonium (TPA⁺) ions were reported using the Ag⁺-exchanged zeolite Y-modified electrode in water-methanol mixture [98].

The detection of phenol using a zeolite Y-modified carbon paste electrode (ZYMCE) in phosphate buffer by cyclic voltammetry has been reported [163]. Cyclic voltammetry, batch amperometric and flow-injection voltammetry techniques were employed to detect dopamine at a ZYMCE without any interference due to the ascorbate anion [130]. Similarly, the charge selective detection of dopamine using a faujasite-type zeolite film grown on GCE was also reported [140]. The square wave voltammetric detection of herbicides including paraquat (methylviologen) and diquat using screen-printed zeolite Y-modified carbon paste electrode (SPZME) in 0.1 M NaCl was reported [137].

1.9.3 Electrocatalytic Applications

Electrocatalysis at a chemically modified electrode can be accomplished by an immobilized redox substance acting as an electron transfer mediator between the electrode and the reaction substrate [164]. Cation-exchanged species or encapsulated metal complexes or metal nanoparticles within the zeolites have been employed in the electrocatalytic studies [90,91]. The electro-assisted oxidation or reduction of organic molecules and improved (either sensitive or selective) detection of organic molecules and biologically interesting molecules have been carried out using cation-exchanged species or encapsulated complexes containing ZMEs. However, metal nanoparticles encapsulated zeolites have been used in dispersion electrolysis [88].
1.9.3(a) Organic Molecules

The electrocatalytic reduction of benzyl bromide by cyclic voltammetry in acetonitrile using an encapsulated Co(salen)-Y ZME was reported. The enhancement of peak current for Co²⁺/Co⁺ reduction process with the concomitant disappearance of Co⁺/Co²⁺ oxidation process indicated that the [Co⁺(salen)]⁻ complex reacted with benzyl bromide in a chemical redox step to give an intermediate. Continuous consumption of the [Co(salen)] complex by reaction with benzyl bromide led the Co²⁺/Co⁺ process irreversible [165]. The electrocatalytic reduction of benzyl chloride using the Co(salen)-Y ZME was also reported [166]. A [Ni(bpy)₂]²⁺ complex encapsulated zeolite Y modified electrode was also used for the reduction of benzyl bromide and triphenylmethyl bromide in acetonitrile medium by cyclic voltammetry [95].

There are some reports on the electrocatalysis of oxygen reduction reaction using ZMEs. A Mn(salen) encapsulated zeolite Y has been used in the electro-assisted reduction of dioxygen leading to the formation of Mn-superoxo complex in the presence of a cocatalyst 1-methylimidazole. This kind of electro-assisted reaction can be applied to the biomimetic hydrocarbon oxidation process [167]. The Fe(phthalocyanine) encapsulated zeolite Y was also used for the reduction of oxygen [168]. Methylviologen exchanged zeolite Y was used for the reduction of dissolved oxygen [169]. Poly(phenosafranine) mediated oxygen reduction was carried out using L type zeolite. A decrease in reduction potential over 300 mV was observed with respect to unmodified electrode [170]. It is interesting to note that the detection of anionic ascorbic acid is possible by the use of a Fe³⁺-Y ZME [113]. Similarly, methylene blue incorporated mordenite type zeolite has been used in the amperometric detection of ascorbic acid [171].
A trinuclear ruthenium ammine complex \([((\text{NH}_3)_5\text{Ru}^{3+}-\text{O}-\text{Ru}^{4+}(\text{NH}_3)_4-\text{O-} \text{Ru}^{3+}(\text{NH}_3)_5)]^{6+}\) encapsulated ZYMCPE was used for the voltammetric detection of L-dopa (precursor of the neurotransmitter dopamine) in pharmaceutical formulations [172]. Copper-porphyrin incorporated ZME was employed in the detection of hydrazine with a fast response time of 1 s [173]. An electrochemiluminescence sensor was developed for the detection of heroin (diacetylmorphine) at a ZMCPE made of \([\text{Ru(bpy)}_3]^{2+}\) exchanged zeolite Y [174].

**1.9.3(b) Biological Molecules**

Enzyme based ZMEs show excellent sensitivity towards various biologically interesting molecules. For example, the immobilization of glucose oxidase on to a ZMCPE led to an improved amperometric detection of glucose [175]. In another study, a dealuminated zeolite Y displayed an adequate surface charge and an open structure large enough to accommodate glucose oxidase for the amperometric detection of glucose down to a concentration of 0.5 \(\mu\text{M}\) [176].

Certain mediators encapsulated within the zeolite cavity have been shown to enhance the sensitivity of detection of a number of analytes. Ferrocene [177] and ruthenium purple [178] containing zeolite Y were used as a mediators for the detection of glucose down to a concentration of 0.1 \(\mu\text{M}\). Also, the ferrocene incorporated zeolite Y displayed an enhanced electrocatalytic effect for the detection of NADH in comparison to the plain carbon paste electrode [129]. A cytochrome c immobilized within zeolite Y displayed a high affinity and sensitivity towards the detection of hydrogen peroxide. The detection limit was 0.32 \(\mu\text{M}\) [179]. A cytochrome c immobilized L type nanoZME prepared by layer-by-layer technique at ITO showed an enhanced detection limit down to a concentration of 0.0032 \(\mu\text{M}\) for hydrogen peroxide [180]. Similarly, a layer-by-layer
film of hemoglobin or myoglobin assembled with zeolite particles on Au surface was employed in the detection of hydrogen peroxide and nitrite ion [181]. A carbon paste electrode modified with methylene green immobilized on X type zeolite has been reported for the electrocatalytic detection of hydrogen peroxide [182]. The co-immobilization of horseradish peroxidase and methylene green on a ZME greatly improved the stability of electrode response [108].

The tyrosinase immobilized ZYMCPE was used for the detection of catechol and some phenolic compounds. As the dealumination of the zeolite Y increased, the enhancement in the electrode response became worse due to the increased hydrophobicity of zeolite Y upon dealumination [125]. A screen-printed methylphenazonium-zeolite Y-modified tyrosinase enzyme sensor was used in the detection of phenol down to a concentration of 0.25 nM [183].

A 2,4,6-triphenylpyrylium ion immobilized within the zeolite Y supercages exerted a remarkable catalytic effect towards the voltammetric detection of dopamine and norepinephrine in neutral aqueous media [184]. An electrochemical immunoassay was designed from the adsorption of an antibody within SBA-15 type zeolite and applied to the voltammetric detection of cardiac troponin I [185].

1.9.4 Electrode-Modified Zeolites

The practical disadvantages of using a high concentration electrolyte in electrochemical studies are the difficulty in separating the product from the electrolyte and the potential window being limited by electrolyte decomposition [90]. In order to overcome these problems, electrochemical reactions at low electrolyte concentration can be performed at microelectrodes because the charging current that flows at the
microelectrode is very small. However, these electrodes can not be useful in electrosynthesis due to the minute quantity of product formation. A zeolite-supported metal nanostructure can act as a nanoelectrode in electrochemistry which is designated as “electrode-modified zeolites” [88]. The use of feeder electrodes and dispersions of the metal incorporated zeolite offered an electrolysis whereby supported metal microstructures may function as electrode materials without a direct electrical contact. The dispersed zeolite-metal nanostructures can behave as an ensemble capable of effective electrochemical reactions [88].

Zeolite-metal nanostructures were electrically charged when they physically contact the feeder electrodes and so behave as dispersed electrodes, which obviate the need to individually wire each particle. Microheterogeneous dispersions of Pt-Y zeolite effectively electrolyzed water (without electrolyte) upon applying a dc voltage between two feeder electrodes. There was no significant water electrolysis occurring at the feeder electrodes in the absence of dispersed Pt-Y zeolite [186]. The dispersion of zeolite-metal nanostructures can also be used in controlled potential electrolyses. RuO₂ incorporated zeolite Y has been used in water electrolysis [187]. This technique can be extended to introduce minute quantity of an expensive electrocatalyst into an electroreactor [90]. The faradaic response of [Fe(CN)₆]³⁻ reduction at a reticulated vitreous carbon (RVC) feeder electrode in phosphate buffer was the same with or without zeolite-supported nanoelectrodes [90]. However, the addition of dispersed nanoelectrodes increased the rate of reaction. The electrolysis time decreased by 55% with dispersed 1wt % Pt-NaY and 26% with 5 wt % RuO₂-NaY as compared to electrolysis without dispersed nanoelectrode-modified zeolites. However, there was no improvement in the yield of product formation. This indicated that the zeolite supported Pt or RuO₂ nanoparticles
acted as electron transfer mediators rather than controlling heterogeneous electron
transfer surface [187].

1.9.5 Other Electrochemical Applications

ZMEs can also be used in batteries and fuel cell applications [91]. Zeolites were
employed to remove trace water from nonaqueous electrolytes [188]. They have been
used as gas-adsorbing material between the anode and cathode in lead-acid battery [91].
A zeolite membrane has been employed to separate the cathode and anode of a methanol
fuel cell, in order to prevent the escape of methanol into the atmosphere and also to
enable the fuel cell operation at high temperatures [91]. Ployaniline/zeolite-A composite
was used for the detection of CO in the concentration range between 16 and 1000 ppm by
electrical conductivity measurements [189]. An impedance based hydrocarbon gas sensor
was demonstrated using platinum doped zeolite film deposited onto an interdigitied gold
electrode, prepared by screen printing technique. A chromium oxide layer between gold
and zeolite was said to be responsible for the outstanding sensor effect [190,191].

1.10 Electron and Charge Transfer Mechanisms at ZMEs

In general, there are two basic requirements for an electroactive species ion-
exchanged in a zeolite framework to undergo electron or charge transfer reactions [91].
Firstly, the electroactive species should be in contact with a conductive electrode
material. The contact may be either physical, close enough to experience direct electron
transfer or mobile enough to freely diffuse to the electrode. Otherwise, the charge
transfers may be facilitated by appropriate mediator, which acts as a relay between
electrode and electroactive species (electrocatalysis). Electroactive species may itself
facilitate the self-exchange of electron between them (electron hopping). Secondly, the
reduction of electroactive species primarily exchanged in zeolite should require the migration of another cationic species from the bulk solution for charge compensation.

Shaw et al. [118] were the first to report on the electron transfer mechanism at ZME in late 1980’s. Subsequently, Dutta and Ledney [192] improved the electron transfer mechanisms proposed by Shaw et al. There are three types of charge and electron transfer mechanisms, which distinguish between the cations located at bulk and surface of the zeolite framework [72]. A brief description of the three mechanisms is given below:

Mechanism I: Intrazeolite

This type of mechanism demonstrates the charge and electron transfer reactions occurring at the interior of the zeolite cavity (Eq. 1.3) [118]:

\[ E^m_{Z} + ne^- + nC_{S}^+ \rightleftharpoons E^{(m-n)+}_{Z} + nC_{Z}^+ \] (1.3)

where \( E \) is the electroactive species with charge \( m^+ \), \( C^+ \) is the electrolyte cation, \( n \) is a number, and subscripts \( Z \) and \( S \) are zeolite and solution phases, respectively. The electroactive species present within the zeolite can undergo electron transfer in the zeolite pore itself. The charge balance is maintained by the electrolyte cation by entering into zeolite cavity. For example, the electrochemical reduction of \( \text{Ag}^+ \) [193], \( \text{Cu}^{2+} \) [106] and methyl viologen [194] exchanged ZME have been reported to follow an intrazeolite electron transfer mechanism (Eq. 1.3) in the presence of a supporting electrolyte containing bulky TBA\(^+\) cations.

Mechanism II: Extrazeolite

This type of mechanism explains the charge and electron transfer reactions occurring at the external surface of the zeolite (Eq. 1.4) [118]:
In this case ion-exchange of the electroactive species for the electrolyte cation prior to electrochemical reaction is taking place (Eq. 1.4a). The electroactive species egresses from the zeolite to undergo electrochemical reduction at the outer surface of zeolite framework. The electrochemical reduction of methyl viologen [120], and Ag$^+$ ion [99,100,114,115] exchanged ZMEs have been reported to follow an extrazeolite electron transfer mechanism (Eq. 1.4) when the non-size excluded cations like Na$^+$, K$^+$ and Cs$^+$ containing supporting electrolytes are used.

**Mechanism III: Surface Mediated**

This kind of mechanism deals with the charge and electron transfers occurring at zeolite framework which are facilitated by a mediator, M [91]. The surface-mediated mechanism distinguishes between the electroactive species present at the bulk and surface of the zeolite, and this mechanism can occur by three different pathways.

In the first case, the electroactive species present at the zeolite surface ($E_{Z,s}^{m+}$) can undergo electrochemical reduction easily, and the electrolyte cation ($C_s^+$) occupies the zeolite surface (Eq. 1.5a). Afterwards, the reduced electroactive species ($E_{Z,s}^{(m-n)+}$) acts as a mediator for the electrochemical reduction of those located in the bulk zeolite ($E_{Z,b}^{m+}$) (electron hopping) (Eq. 1.5b). The charge compensation is accomplished by the electrolyte present at the zeolite surface.

\[
E_{Z,s}^{m+} + mC_s^+ \rightleftharpoons E_{Z,s}^{(m-n)+} + mC_s^+ \quad (1.5a)
\]

\[
E_{Z,s}^{(m-n)+} + nC_s^+ + E_{Z,b}^{m+} \rightleftharpoons E_{Z,b}^{(m-n)+} + nC_s^+ + E_{Z,s}^{m+} \quad (1.5b)
\]
where $s$ and $b$ refer to the zeolite surface and bulk ion-exchange sites, respectively.

In the second case, the charge-transfer mediator ($M_S^{m^+}$) dissolved in the solution can facilitate the electrochemical reduction of electroactive species. Initially, mediators present in the solution ($M_S^{m^+}$) can undergo electrochemical reduction (Eq. 1.6a). Subsequently, the reduced mediators ($M_S^{(m-n)^+}$) assist the reduction of electroactive species present at the surface of zeolite ($E_{Z,s}^{m^+}$) (Eq. 1.6b). The charge compensation is achieved by the electrolyte present in the solution ($C_S^+$), and the charge and electron transfer mechanisms are given below.

$$M_S^{m^+} + ne^- \leftrightarrow M_S^{(m-n)^+} \quad (1.6a)$$

$$M_S^{(m-n)^+} + nC_S^+ + E_{Z,s}^{m^+} \leftrightarrow E_{Z,s}^{(m-n)^+} + nC_{Z,s}^+ + M_S^{m^+} \quad (1.6b)$$

In the third case, the mediator present at the surface of the zeolite can facilitate the electrochemical reduction of electroactive species. At first, the mediator present in surface of the zeolite ($M_{Z,s}^{m^+}$) undergoes electrochemical reduction, and electrolyte cations present in the solution occupy the zeolite surface (Eq. 1.7a). Then the reduced mediator present at the zeolite surface ($M_{Z,s}^{(m-n)^+}$) facilitates the reduction of electroactive species present in the bulk of the zeolite ($E_{Z,b}^{m^+}$) (Eq. 1.7b). The charge compensation is attained by the electrolyte present in the zeolite surface ($C_{Z,s}^+$), and the charge and electron transfer mechanisms are given below.

$$M_{Z,s}^{m^+} + ne^- + nC_S^+ \leftrightarrow M_{Z,s}^{(m-n)^+} + nC_{Z,s}^+ \quad (1.7a)$$

$$M_{Z,s}^{(m-n)^+} + nC_{Z,s}^+ + E_{Z,b}^{m^+} \leftrightarrow E_{Z,b}^{(m-n)^+} + nC_{Z,b}^+ + M_{Z,s}^{m^+} \quad (1.7b)$$
1.11 Scope of the Work

The present work is concerned with the development of robust zeolite-modified electrodes for some new electroanalytical and electrocatalytic applications.

Zeolites are microcrystalline solids, possessing several interesting properties like size, shape and charge selectivity, cation exchange capacity and catalytic behaviour. There are about one hundred and thirty five different framework types in zeolites. Thus, the zeolite family of materials possesses wide structural and chemical diversity.

The use of zeolites as both electrodes and electrolytes in electrochemistry is well documented in literature. The research groups of Baker, Bedioui, Calzaferri, Murr, Rolison and Walcarius have immensely contributed towards the progress in this field, especially during the past three decades. One of the major challenges in zeolite electrochemistry that remains to be tackled yet is the preparation of ZME surfaces with good reproducibility and stability. As a result, the complete exploitation of these novel materials in many electrochemical applications is yet to be realized.

The major goal of the present work is to develop some innovative procedures for the preparation of highly stable and reproducible ZMEs that can give reliable and consistent results. Towards this objective, procedures have been optimized to obtain a free-standing zeolite membrane, a ZMCPE on an ITO support and a zeolite-MWCNT composite electrode on glassy carbon surface. Free-standing zeolite membranes are often required for several industrial applications like catalysis, purification and bulk separation, petroleum refining, water softening and detergent formulation and are generally prepared by compaction of zeolite powders in the presence of a polymeric binder. Such pressed membrane discs are not suitable for electrochemical applications owing to the presence of
Introduction

pinholes/defects. In the present study, an attempt has been made to improve the coherence of the zeolite Na-Y pressed disc (without any polymeric binder) by adopting a new healing technique involving the use of tetrathylorthosilicate. The usefulness of the healed free-standing zeolite Na-Y membrane in electroanalytical application has been ascertained by the potentiometric sensing of Cd\(^{2+}\) and Pb\(^{2+}\) ions.

Electrochemistry at an interface between two immiscible electrolyte solutions (ITIES) has been of great interest not only to understand biomimetic processes but also due to its various practical applications in electroanalysis, electrocatalysis, phase-transfer catalysis and ion extraction. In the present study the free-standing zeolite Na-Y membrane is used to modify the liquid/liquid interface viz. water/1,2-dichloroethane interface for detailed investigation of size (tetrathylammonium and tetrabutylammonium ions) and charge (tetrafluoroborate and perchlorate ions) selective ion transfer processes using cyclic voltammetry.

There have been a number of reports on the incorporation of noble metal particles within zeolites by reduction at high temperature. In the present study, an attempt has been made to incorporate Pt nanoclusters within the zeolite Na-Y membrane by an electrochemical technique. The procedure developed in the present study can be used to replace the existing cumbersome practice of the high temperature decomposition of metal precursors and reduction with hydrogen. The stable electrochemical response of the Pt loaded zeolite Y membrane in oxygen reduction and methanol oxidation reactions suggests that it can be used in several other electrochemical applications.

In many of the reported electrochemical studies, ZMCPE is employed. The right quantities of zeolite, carbon powder and also a binder have to be used to obtain high quality films possessing a smooth texture and good electronic conductivity. In this work,
considerable efforts have been made to standardize a procedure for the preparation of reliable ZMCPEs using zeolite, graphite powder and paraffin liquid for routine electrochemical experiments. Considering the recent advances reported on the importance of CNTs as a new and viable electrode material of high surface area, an attempt has been made in the present study to use MWCNT instead of graphite in the preparation of ZMCPEs. A procedure is thus evolved to prepare zeolite-MWCNT nanocomposite modified glassy carbon electrode. The structural and morphological characterization of the free-standing membrane, ZMCPE and zeolite-MWCNT nanocomposite electrode have been carried out by using appropriate techniques like powder X-ray diffraction, solid state NMR and scanning electron microscopy.

Another objective of the present work is to investigate the scope for developing prototype electrochemical sensors for some heavy metal ions like Cd$^{2+}$, Pb$^{2+}$ and Cu$^{2+}$ ions, by exploiting the ion-exchange property of the zeolites. These metal ions are the major pollutants in water resources arising from various industrial processes. The metal pollutants produce severe ailments including mental retardation in living beings. So there is an urge to develop sensors, especially electrochemical sensors for environmental monitoring. Zeolites being cation exchangeable are highly suitable for this application and the heavy metal ions can be preconcentrated in zeolites by simple ion exchange. Preconcentration of the cations within the zeolite can lead to a several-fold enhancement in the electrochemical current for the reduction of the cations which will in turn help in improving the detection limit of the metal ion sensors.

The excellent size-selective cation exchange capacity combined with the preconcentration effects of zeolites can be expected to play a major role in the mediated electrocatalytic applications. In the present study, zeolite Y ion-exchanged with two
cationic mediators viz. MV$^{2+}$ and [Ru(NH$_3$)$_6$]$^{3+}$ are investigated for the electrocatalytic reduction of hydrogen peroxide at the zeolite-MWCNT nanocomposite modified glassy carbon electrode. The presence of MWCNT on the electrode surface can be expected to aid the electrocatalysis.

1.12 References


G. Kühl, in *Verified syntheses of Zeolitic Materials*, H. Robson (Ed.), Elsevier, Amsterdam, **2001**.


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