

# Chapter - 1

## Structure, Composition, Classification of Zeolites and its Carbon Hybridized Nanocomposites

Mukesh Sharma, Biraj Das, Mitu Sharma, and Kusum K. Bania

*Department of Chemical Sciences,  
Tezpur University 784028,  
Assam, India*

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**Abstract**—A brief historical introduction of zeolites and their zeotypes materials are discussed in this chapter. An outline of zeolite-Y is also described along with its configuration and structure. The role of MWCNTs in designing zeolite-CNT-based nanocomposites materials is also discussed in the last section of this chapter. The advantages of such nanocomposites materials are also covered.

### Introduction

#### A Brief Overview of Zeolites

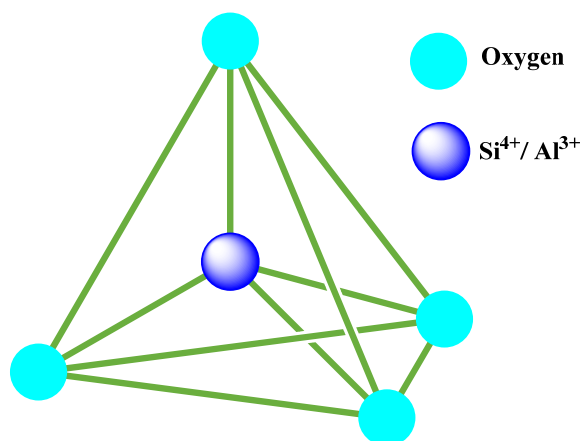
Zeolite was first used by a Swedish geologist, A. Cornstedt in 1756 when he described a mineral which released water upon heating, and could recover water reversibly at lower temperatures. Cornstedt had mainly used the mineral “stilbite” which is termed as one of the class of zeolites.<sup>1</sup> A timeline regarding the history of zeolite<sup>2</sup> has been provided:

1858      Eichorn points out the ion-exchange capability of zeolites.

- 1862 de St. Claire-Deville synthesized the first artificial zeolite, “Levynite”.
- 1876-1905 Studies on ion-exchange zeolites.
- 1930 Taylor reveals the structure of analcime.
- 1932 McBain introduces the term molecular sieves.
- 1938 Barrer presents a remarkable work on molecular sieving.
- 1940-1945 Reports on zeolite molecular sieves with different pore sizes.
- 1950-1972 Synthesis of zeolites A, X, Y, and ZSM-5.<sup>3</sup>

A zeolite is a crystalline aluminosilicate with a structure based on an open three-dimensional network which provides pores or channels, which in turn grants them very interesting properties. Zeotypes are the similar structures like zeolites but are made up of other materials like silicates or metalo-aluminates; that is,  $\text{Al}^{3+}$  ions have been replaced by ions such as  $\text{B}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Cr}^{3+}$ , and  $\text{Si}^{4+}$  has been replaced by  $\text{Ge}^{4+}$  or  $\text{Ti}^{4+}$ . Compounds such as aluminophosphates and silico-aluminophosphates are also called zeotypes.<sup>4-6</sup> The history of man-made zeolites started dates back to 1862 when de St. Claire-Deville synthesized “Levynite” in the laboratory. On the other hand, zeolite as it is known for (different pore sizes), synthesis commenced in the late 1940s and the work was done by Barrer and Milton.<sup>3</sup>

Zeolites are formed by oxide anions ( $\text{O}^{2-}$ ) forming tetrahedral structures. The  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  ions are situated at the centre of the tetrahedra formed by oxide anions as shown in Scheme 1.<sup>2</sup>



**Scheme 1.** Ball and stick model of zeolite.

The ratio between silicon and aluminium (Si/Al ratio) determines the framework charge of the overall matrix. Presence of aluminium ions derives a negative charge on the zeolites which are compensated by incorporating different cations at extra-framework positions, which confers the zeolites, its ion-exchange capability. The empirical formula of a zeolite is,  $M_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$ , where “M” represents the interchangeable cation and n represents its oxidation state,<sup>11</sup> and x will always be higher than or equal to 2, as proposed by Löewenstein’s rule.<sup>7</sup>

Löewenstein’s rule of “aluminium avoidance” states that; on forming the aluminosilicate zeolite framework there is a disinclination for tetrahedral units of alumina to exist adjacent to one another, forbidding formation of –Al-O-Al- linkages, and restricting the maximum Si/Al ratio of any zeolite to unity.

### **Classification of Zeolites**

Zeolites are broadly classified in two categories,

- Depending on their pore size, they are classified into four types. The four types of zeolites classified based on their pore size<sup>2</sup>, along with their examples, are tabulated below:

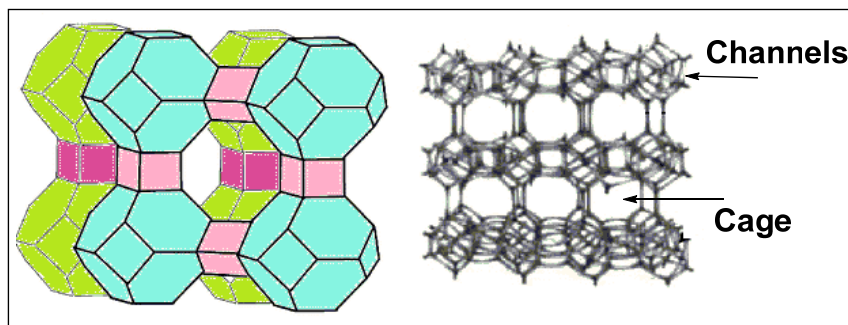
Zeolite type	No. of tetrahedral units forming the pore	Pore diameter, (nm)	Examples
Small pore	8	$0.3 < D < 0.5$	Erionite, A, SAPO-34
Medium pore	10	$0.5 < D < 0.6$	ZSM-5, ZSM-11
Large pore	12	$0.6 < D < 0.9$	Y, Mordenite, $\beta$ , $\Omega$
Extra-large pore	$\geq 14$	$D > 0.9$	AIPO <sub>4</sub> -8, VPI-5

- Depending on the content of silica (Si/Al ratio), zeolites are classified into three types. The three types of zeolites classified based on silica content<sup>8</sup>, along with their examples are tabulated below:

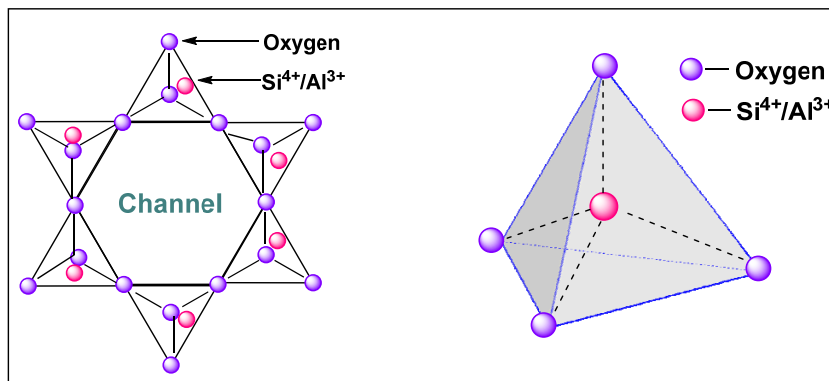
Zeolite type	Si/Al ratio	Examples
High silica	$> 5$	ZSM-5 (MFI), Zeolite- $\beta$ (BEA)
Intermediate silica	2-5	Chabazite (CHA), Faujasite (FAU), Mordenite (MOR), Na-Y (FAU)
Low silica	$\leq 2$	Analcime (ANA), Cancrinite (CAN), Na-X (FAU), Natrolite (NAT), Sodalite (SOD), Phillipsite (PHI)

The tetrahedra form a structural framework in zeolites with centrally located Si or Al atoms and corners occupied by O-atoms being shared between SiO<sub>4</sub> and AlO<sub>4</sub> units. These tetrahedra units are positioned such that the structural framework develops voids or pores in the form of cages and channels, as shown in Figure 1a. Single ring tetrahedron structure and

framework of a zeolitic mineral and a 3-D view of centrally located tetrahedral silicon or aluminium atoms demonstrated in dotted lines, Figure 1b.



**Figure 1a.** The schematic view of zeolites showing the cages and the channels.



**Figure 1b.** Building blocks of zeolite framework and 3D view of tetrahedra with centrally located Si or Al atoms.

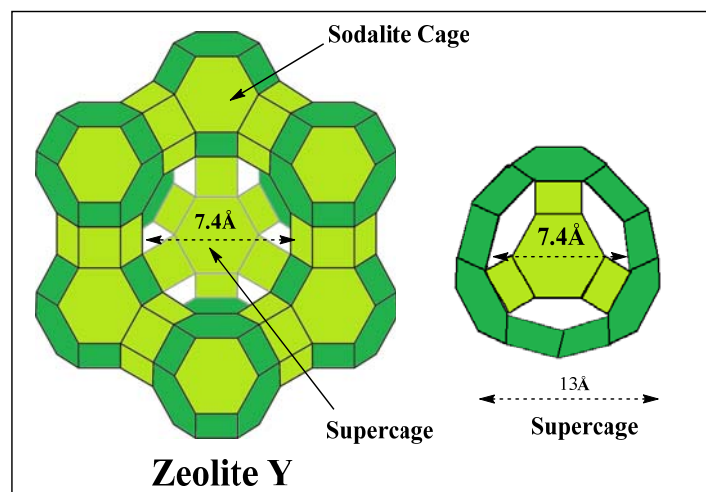
The synthetic zeolites hold some more key advantages than the natural one. Some synthetic zeolites type such as A, X, Y, P, and Na-P1 possesses more industrial uses than the natural zeolites.<sup>4,5</sup>

### **Zeolite-Y**

Zeolite-Y belongs to faujasite mineral group and is, basically, sodium aluminosilicates. The faujasite framework is made up of sodalite cages and connected by hexagonal prisms. The pore of the framework has a diameter of 7.4 Å and surrounded by 12 sodalite cages (Figure 1c). Depending on the Si/Al ratio of their framework, synthetic faujasite zeolites can be divided into two categories: zeolite X and zeolite Y. Zeolite-Y has two types of cages, namely, supercage and sodalite cage (Figure 1c). It can act as a molecular sieve and absorbs molecules depending upon their size and shape. It can be used in catalytic cracking petrochemical industries. Zeolite-Y has advantage over zeolite-X for its greater activity and thermal resistance. In general, high-silica Y zeolitic materials are prepared by elimination of some of the Al-sites from the zeolite-Y framework employing some chemical and thermal or hydrothermal approach.<sup>4-6</sup>

The name zeolite-Y also designates sodium aluminosilicates. In zeolite-Y, three-dimensional frameworks of  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedrons cross-links, by sharing of the oxygen atom. The charge balance of each tetrahedron containing aluminium is balanced by the presence of a cation such as an alkali metal ion in the aluminosilicate framework. Water molecules occupy the empty spaces in the framework. Zeolite-Y has the tendency to act as molecular sieves because it can selectively adsorb molecules based on their size and shape. Molecular sieves have its sorption site available at the inside of a large number of uniformly sized pores of molecular dimensions. With this arrangement, molecules of certain shape and size enters the

pores and get adsorbed, whereas larger or differently-shaped molecules are not adsorbed.<sup>18</sup> Additionally, zeolite-Y is mostly used as a cracking catalyst. In petroleum refinery catalytic cracking units, zeolite-Y is used in an acidic form to increase the production of diesel fuel and gasoline from crude oil feedstock by cracking heavy paraffins into gasoline grade naphthas. Zeolite-Y is also used in the hydrocracking units as platinum/palladium support to increase aromatic content of reformulated refinery products.<sup>4,5</sup>



**Figure 1c.** Pictorial representation of zeolite-Y and its supercage.

### **Zeolites / MWCNT-Hybrid Composites**

#### **Multi-walled carbon nanotubes (MWCNT)**

Sumio Iijima in 1991, using a high-resolution transmission electron microscope studied the soot created in an electrical discharge between two carbon electrodes, at the NEC Fundamental Research Laboratory in Tsukuba, Japan. He found that the soot was made up of several concentric tubes of carbon. A single sheet of graphite that has been rolled up into a

tube is called a single-walled carbon nanotube. A multi-walled carbon nanotube (MWCNT) is one which has several such tubes rolled one over the other resulting in concentric tubes of carbon. The diameters of MWCNTs are about 30 nm, and the number of concentric walls in them varies in the range of 6-25 or more.<sup>9</sup> Some of the properties of the MWCNTs<sup>1</sup> are given below.

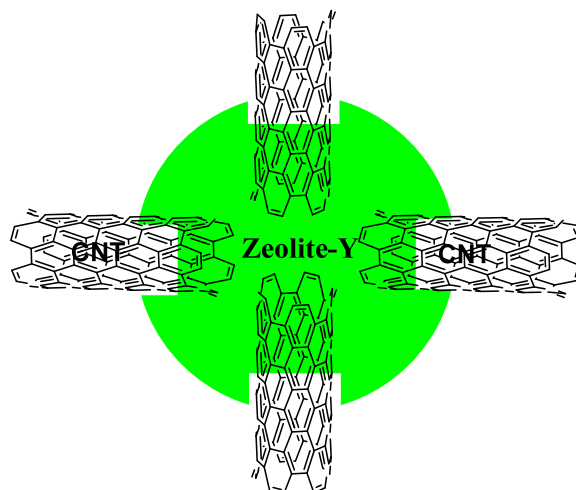
- MWCNTs are highly conductive when they are properly integrated into a composite structure. Only the outer wall is conducting, whereas the inner layers only provide mechanical support. However, all the layers can be made conducting if we can make electrical contact with all the layers.
- MWCNTs have a high aspect ratio (length/diameter ratio), typically more than 100. Their performance not only depends on the aspect ratio but the degree of entanglement and the straightness of tubes too.<sup>9</sup>
- MWCNTs have excellent tensile strength, about five times that of steel. When coupled with a composite, can significantly increase its strength. It also possesses a low specific weight.
- MWCNTs have high thermal stability of more than about 600°C.
- MWCNTs have high chemical stability and are an allotrope of sp<sup>2</sup> hybridized carbon, similar to fullerenes and graphite, and can be functionalized to enhance both the strength and dispersibility of composites.



The basic crystalline structure in zeolites generally originates the micropore structures in zeolites. Though the intrinsic nano-dimensioned pores and channels have many chemical applications, however, it sometimes suffers from the diffusion limitation of mass transfer leading to the pore blockages and ultimately decreases the catalytic activity.

Resasco *et al.* reported that their technique was advantageous in preserving the activity of zeolites in the polar medium by fabrication of the zeolites with MWCNT.<sup>10</sup> Similar advantage of this hybrid material were reported saying that upon incorporation of MWCNTs into NaY-zeolite, increases nucleation sites that resulted for the formation of smaller size NaY-zeolite crystals. This also led to an enhanced gas adsorption capacity with selectivity; due to increase of micropore volume.<sup>11</sup> Such hybrid material could be a promising substitute to traditional heterogeneous catalysts for the gas separation and purification processes. Further, zeolites are usually poor conductors of electricity, but on the incorporation of carbon materials, the composite becomes conductive.

Schimdt *et al.* synthesized carbon nanotube template zeolite-Y during the crystallization process. The limited scope due to low mass diffusion could be overcome by the synthesis of such hybrid materials.<sup>12</sup> The schematic representation of their findings is shown below in Scheme 2.



**Scheme 2** Schematic representation of CNT-hybridized zeolites.

### Conclusion

In conclusion, zeolite types, structures, and its composition have been described in this chapter. The role of MWCNTs in such nanocomposites has also been discussed.

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