CHAPTER II

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This chapter deals with the experimental work done in the studies of synthetic zeolites provided by Indian Petro-Chemicals Limited, Baroda and their derivatives.

**Materials and Methods :-**

**Materials used :-** The zeolites employed in this work are synthetic zeolites supplied by Indian Petro-Chemicals Limited, Baroda, available commercially.

The synthetic zeolites are available in white odourless powder and pellet forms. The synthetic zeolites used in this work are in the powder form.

The empirical formulae of synthetic zeolites are :-

Synthetic zeolite “one” : - Na$_{11}$ Ca$_1$ [Al$_{13}$Si$_{9.48}$O$_{45}$ ] .24H$_2$O

Synthetic zeolite “two” : - Na$_{17}$ Ca$_1$ [Al$_{19}$Si$_{17.42}$O$_{73}$ ] .51H$_2$O

For preparing cation-exchanged derivatives from these zeolites, the following analaR grade chemicals were used :-

(1) Lithium (I) Sulfate Li$_2$SO$_4$.H$_2$O

(2) Calcium (II) Chloride CaCl$_2$.6H$_2$O

(3) Ferric (III) Chloride FeCl$_3$.6H$_2$O

(4) Thorium (IV) Nitrate Th(NO$_3$)$_4$.12H$_2$O

Phosphatic derivatives with the synthetic zeolites together with their cation-exchanged forms were prepared using the following AnalR grade inorganic and organic sorbates in liquid state :-

(1) Phosphoric acid H$_3$PO$_4$

(2) Tricresyl phosphate TCP (CH$_3$.C$_6$H$_4$)$_3$.PO$_4$ and
(3) N- butyl phosphate n-BP \([\text{CH}_3\text{(CH}_2\text{)}_3\text{PO}_4]\)

**Preparation of cation -exchanged derivatives from synthetic zeolites**

The original samples of zeolites supplied by IPCL, Baroda in powder form were used directly for preparing cation-exchanged derivatives. The cation-exchanged derivatives of synthetic zeolites “one” and “two” were prepared by treating portions of the powdered zeolites “one” and “two” with the saturated aqueous solutions of appropriate electrolyte for 50 days. In order to achieve maximum exchange, the mixtures were heated upto 100°C on a water-bath with frequent stirring. After filtration, ion-exchanged samples were washed with distilled water until the anions were removed. Then, the samples were dried in an electric oven at 110°C and stored in air-tight bottles. The cation-exchanged derivatives are listed below:

- Li (I) exchanged zeolites “one” and “two”
- Ca (II) exchanged zeolites “one” and “two”
- Fe (III) exchanged zeolites “one” and “two”
- Th (IV) exchanged zeolites “one” and “two”.

**Preparation of phosphatic derivatives**

Phosphoric acid, tri-cresyl phosphate and n-butyl phosphate interacted samples of original zeolites and their cation-exchanged derivatives were prepared in the following manner:

Synthetic zeolites “one” and “two” and their cation exchanged derivatives (3 grams.) were placed in a flask and mixed with 50 ml. of appropriate phosphatic compounds. The mixed mass was shaken from time to time for maximum interaction. The process was continued for one month. After filtering off the excess liquid, the samples were kept on filter paper and air dried.
Analytical Methods Used for Investigating the Zeolite Samples:

Infra-red Spectroscopy:

Sir William Herschel discovered the method of infra-red spectroscopy in year 1800. After that infra-red spectroscopy has been proved to be one of the efficient physical tools available in the hand of chemists engaged in the determination of molecular structure of compounds with the presence as well as absence of functional groups in the molecule, their linkages and degree of concentration.

The spectral region between 400 cm\(^{-1}\) and 8000 cm\(^{-1}\) has been developed considerably in the past few years and hence is now useful both from academic and industrial point of view. The infra-red spectrum is characteristic of the molecule. It exhibits that certain groups of atoms give rise to bands at or near the same frequency regardless of the structure of the rest of the molecule. It is the persistence of these characteristic bands that permits the chemists to obtain useful information by simple inspection and reference to generalized charts of characteristic group frequencies\(^ {1-3} \).

Band positions in infra-red spectra are presented either as wavelengths or frequencies. The common unit of wavelength in infrared spectroscopy is the micron \(\mu\) 10\(^{-6}\) cm. equal to 10\(^{-3}\) mm. When the wavelength is in the microns, the wave number is:

\[
\bar{\nu} = \frac{1}{\lambda} \times 10^{4} \, \mu m
\]

Band intensities are expressed either as transmittance or absorbance. The measured variable is the transmittance of the substance under study as a function of wave numbers or the wavelength of the infra-red radiation. The result of measurement is plotted as a curve and is termed the infra-red spectrum.

Infra-red spectrum originates in transitions between two vibrational levels of the molecule in the electronic ground state and is usually observed as absorption spectrum in the infrared region 0.1 cm to 8000 Å. Molecular vibrations in a molecule can be divided into two groups:

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(I) Stretching vibration (II) Bending vibration.

A stretching vibration is a rhythmal movement along the bond axis such that the interatomic distance is increasing or decreasing. A bending vibration may consist of a change in bond-angles between bonds with a common atom, or the movement of a group of atoms with respect to the remainder of the molecule without movement of the group with respect to one another.

Only those vibrations that result in a rhythmal change in the dipole moment of the molecule are observed in the infrared spectrum. The alternating electric field, produced by the changing charge distribution accompanying a vibration, couples the molecular vibration with the oscillating electric field of the electromagnetic radiation, consequently even molecules which have no permanent dipole moment may also be IR active.

The frequency of vibration of molecule can be represented as :-

\[ \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \]

where, \( \pi \) - reduced mass of the molecule

\( k \) - force constant of the bond

There are two types of the infra-red spectroscopy :-

(i) Dispersive infra-red spectroscopy (ii) Fourier Transform infra-red spectroscopy

The fundamental limitations of energy by virtue of the use of slits in a dispersive spectrometer suggest an inefficient way to obtain a spectrum over a wide wave number range. An alternative approach was pioneered by Michelson and led to the method of Fourier Transform infra-red spectroscopy. In the FT-IR spectroscopic method, Michelson used interferometer named after him. The development of the technique for recording an interference pattern by scanning the moving mirror through a distance of \( \delta/2 \) produces a total path difference of \( \delta \).
The method of fast FT-IR spectroscopy overcome the disadvantages of the measurement of one resolution element at a time and the disadvantage of the energy entering and leaving the monochromator being limited by narrow slits.

Applications of the Infra-red Spectroscopy to the Study of Zeolites :

Infra-red spectroscopy has proved very useful for the examination of framework aluminosilicates and clay minerals\(^4\)-\(^6\). Earlier infrared spectra were reported on zeolite minerals\(^7\) upto about 670 cm\(^-1\) using wafer technique\(^8\). The mid-IR region of the spectrum is very useful for the study of zeolites as it contains the fundamental vibrations of the framework tetrahedra. Flanigen and coworkers investigated the framework structure of many synthetic zeolites in 200-1300 cm\(^-1\) region\(^9\). Each zeolite shows its characteristic infrared spectrum. The infrared spectra of several zeolite minerals belonging to same structural type and same structural group i.e. common subunit show general similarities. Several informations like the ratio of Si/Al\(^9\), structural changes during thermal decomposition, cation-movement upon dehydration and dehydroxylation\(^8\) can be found using infrared spectrum.

The infrared spectra for zeolites can be grouped into two classes :

(1) Those due to internal vibrations of the framework TO\(_4\) tetrahedra, the primary building unit of all zeolite structures and are not sensitive to other structural vibrations.

(2) Vibrations which are related to linkages between tetrahedra and are sensitive to the framework structure and the joining in secondary building units and their existence in the larger pore opening.

Specific AlO\(_4\) tetrahedra cannot be assigned by the infra-red method, however the vibrational frequency represents the average composition. T-O-T angle in zeolite frameworks ranges from 140° to 150° but the deviation from these values cannot be correlated with the infra-red values.
### Zeolite infrared assignments

#### Internal tetrahedra:
- Asymmetric stretch: 950-1250 cm\(^{-1}\)
- Symmetric stretch: 650-720 cm\(^{-1}\)
- T-O bend: 420-500 cm\(^{-1}\)

#### External linkages:
- Double ring: 500 - 650 cm\(^{-1}\)
- Pore openings: 300 - 420 cm\(^{-1}\)
- Symmetric stretch: 750 - 820 cm\(^{-1}\)
- Asymmetric stretch: 1050 - 1150 cm\(^{-1}\)

The first class of vibrations found in all zeolites are assigned to the internal tetrahedron vibrations consisting of two strongest bands. The strongest vibration at 950 - 1250 cm\(^{-1}\) is assigned to T-O stretch. The next strongest band in the 420 - 500 cm\(^{-1}\) is assigned to T-O bending mode. Stretching modes involving mainly the tetrahedral atoms are assigned in the region of 650 - 820 cm\(^{-1}\). The symmetric stretching mode involves the symmetric stretch of internal tetrahedra in the lower frequency region 650-720 cm\(^{-1}\) and symmetric stretch of external linkages in the higher region 750-820 cm\(^{-1}\). The stretching modes are sensitive to the Si-Al composition of the framework and may shift to a lower frequency with increasing number of aluminium atom.

The second group of frequencies occur in the region of 500-650 cm\(^{-1}\), 300-420 cm\(^{-1}\), 750-820 cm\(^{-1}\) and 1050-1150 cm\(^{-1}\) and sensitive to the linkages between tetrahedra and the topology and mode of arrangement of the secondary building units of structure in the zeolite.

An infrared band in the 500-600 cm\(^{-1}\) is related to the presence of the double ring in the framework structure of the zeolite and is a characteristic band for all the zeolites that contain the double four and double six ring.
The next main frequency, assigned to external linkages is between the range 300-420 cm\(^{-1}\) and is related to the motion of the tetrahedra rings which form the pore opening in the zeolites. It is a distinct band in the spectra of zeolites A, X and Y and intensity of this band is related to the symmetry of the structure, more prominent in cubic structure and decreases in prominence with a decrease in symmetry.

With the increase in the number of aluminium atoms in framework tetrahedral sites, decrease in frequency of IR bands has been reported,\(^9,^{11}\) i.e. 970-1020, 670-725 cm\(^{-1}\) which may be related to difference in mass of aluminium and silicon\(^4\) resulting in a decrease in force constant of the T-O bond.

In the hydrated zeolites, the three typical bands observed are the broad band characteristic of hydrogen-bonded -OH at about 3400 cm\(^{-1}\), the sharp band typical of isolated OH at 3700 cm\(^{-1}\) and the bending vibration of water at 1645 cm\(^{-1}\). In fully activated zeolite bending frequency at 1640 cm\(^{-1}\) is absent\(^{14}\).

Kiselev and other coworkers reported that the frequencies of the adsorbed water vibrations are a function of the exchanged cation and noted an approximate linear relationship between the -OH stretching frequency and the radius of the cation\(^{15-16}\). Szymanski et al. used mull technique and examined the spectrum of water adsorbed on a X-type zeolite at coverage below the 34% of the saturation value, a sharp band becomes obvious at 3550 cm\(^{-1}\) together with a weak band between 1600 and 1700 cm\(^{-1}\) which were earlier supposed to be due to surface hydroxyl groups\(^{17}\). The presence of surface hydroxyl groups on the molecular sieves was first definitely established by Carter and other coworkers in 1964\(^{18}\). According to Carter, three types of hydroxyl groups existed on the surface of the 13X except Li(I) exchanged 13X zeolite, the relative intensities of the -OH stretching frequencies have been found to vary considerably with changes in cations\(^{18}\). Infra-red studies have also explored the interaction of the hydroxyl groups with the adsorbed molecule\(^{19}\). Silanol group of the molecular sieve MCM-41 was investigated by infra-red spectroscopic method\(^{20}\). P-OH groups and Lewis acid sites are detected by IR.
spectroscopy in MCM-41 after silylation. IR studies by Sig Ko and Seung Ahn showed that IR bands are shifted to lower wave number as Fe\textsuperscript{3+} incorporation into the lattice increased and a new Si-O-Fe bond vibration was located near 668 cm\textsuperscript{-1} in Fe(III)-exchanged zeolite L. The incorporation of Co\textsuperscript{2+} in aluminophosphate molecular sieve leads to the formation of additional P-OH group studied by IR spectroscopy. The intensity of the 960 cm\textsuperscript{-1} band in the framework infrared spectra of V containing MCM-41 was increased with the concentration of vanadium. Infra-red spectroscopy is being used to study the surface acidic properties of different secondary synthetic FeY zeolite and catalytic activity appears to be directly related to the concentration of the Bronsted acid-sites. The transformation between different species in the synthesis and structural development of MCM-41 molecular sieve can be followed using the ATR-FTIR technique and the dehydroxylation of MCM-41.

In this work, the FT-IR spectra of derivatives were recorded on a Perkin-Elmer spectrometer in KBr pellets between 400 cm\textsuperscript{-1} and 4000 cm\textsuperscript{-1} IR region.

**X-ray Diffraction Method**

The most powerful method for structure elucidation of solids is X-ray diffraction method. A new and significant field of investigation was opened up when it was found that X-rays could be employed to investigate the interior of crystal. The important discovery that a crystal could behave as a three-dimensional grating led W. L. Bragg to the use of X-rays for the purpose of studying the internal structure of crystal.

**Diffraction by crystals**

In a crystal there are regular array of atoms in three-dimensions termed as crystal lattice. Every atom is able to scatter X-rays to an extent dependent on the number of external electrons and every atom-bearing plane in a crystal, that is every net plane or lattice plane behaves to X-rays, just as does a line in a diffraction grating to visible light. The position of the spectra when diffracted by a line grating depends on the distance...
between successive lines, similarly, the nature of the X-ray diffraction is determined by the spacing between successive planes. The essential condition for obtaining diffraction with any wavelength of light is that the spacing between the lines is of the same order as the wavelength of the light used. X-rays wavelength are roughly of the same magnitude as the separation of atoms in matter. A diffracted ray represents effect of many, scattering centres, and hence a reasonable perfection in structure is required.

For the formation of an intense and defined diffraction pattern in any direction, following conditions should hold:

(a) The angle of incidence should equal angle of reflection of the beam for the diffraction studied.

(b) \( n\lambda = 2d \sin\theta \)

\( n = \) is an integer and can have values of 1, 2, 3,……

\( \lambda = \) wavelength of X-rays used

\( d = \) distance between the lattice planes

\( \theta = \) angle between the crystal face and the incident as well as reflected X-ray beam.

This is the famed Bragg equation and is the fundamental relation underlying all X-ray diffraction measurement. Only for an angle of incidence such that \( \sin\theta = \frac{n\lambda}{2d} \) will X-rays be reflected. At all other angles destructive interference will occur.

Each set of plane is capable of producing an X-ray pattern. To identify the reflections, a method of indexing is employed similar to that used for lattice planes and crystal faces. The first order reflection from a (hkl) plane is described as hkl omitting the parentheses, the second order is represented by 2h, 2k, 2l and so on.

Several methods have been developed for the study of X-ray diffraction.
1) The method of Laue photograph, (2) Rotating crystal method, (3) Oscillating crystal method, (4) The powder method

**The Powder Method** :- This method was devised by P. Debye, P. Scherrer and A. W. Hull. The X-ray powder method has been mainly employed in the study of metals and alloys. Single crystals are difficult to obtain and it is fortunate, therefore that many of these substances belong to the cubic or hexagonal systems. The X-ray powder photograph is a characteristic property of a crystalline material and so has been employed as a method of identification and comparison.

Advantages of Powder Method Over Other Methods :-

(1) Most crystalline materials occur in nature as agglomerates. This means that such samples are already in powder form.

(2) Many technological processes deal with materials in a finely divided state or composites of small crystallites. The powder method enables us to study specimens in their normal state, avoiding perturbations which might otherwise arise from sample preparation.

(3) All the information can be recorded at one time on a single film, permitting rapid analysis.

(4) As little as 1 mg. of material is sufficient for study by the powder method.

(5) The technique involved in securing powder patterns is extremely simple.

(6) The interpretation of powder pattern is simple and straightforward.

**Interpretation of Powder Photograph**

From measurement of the position of a line on a powder photograph, only one parameter can be directly derived, the Bragg angle $\theta$ of the diffraction line. When the unit cell of the substance is known, indexing the lines is a straightforward matter, although...
calculations are rather lengthy for the systems of lower symmetry. When the unit cell is unknown, the problem of indexing is considerably more difficult, and trial and error procedures have to be used. With a simple cubic pattern, it is easy to index all the lines and to derive the length of the cell-side. With increase of the size of the unit cell, the complexity of the pattern increases, but cubic patterns are always easy to index\textsuperscript{39}.

**The Cubic System**: For the cubic system, the expression for \( \sin^2 \theta \) can be obtained by combining Bragg’s equation with the expression for \( d \):-

\[
\lambda = 2 \ d \ \sin \theta \quad \text{- Bragg equation}
\]

\[
d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}
\]

This gives :

\[
\sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2)
\]

The characteristics of the cubic system are that the values of \( \sin^2 \theta \) have a common factor. Expression for \((\sin^2 \theta)_{hk}\) is a simple function of \( h, k \) and \( l \). The values of \( \left(\frac{\lambda^2}{4a^2}\right) \) after multiplied with the possible values of \( (h^2 + k^2 + l^2) \) gives the values of \( \sin^2 \theta \), which are then compared with the values of \( \sin^2 \theta \) for the observed angles\textsuperscript{39}.

**Applications of XRD Method to the Study of Zeolites**: 

The zeolite structure has been determined basically by XRD technique. Besides the unit cell constants, the position of cations in the zeolite crystals belonging to different symmetries have been reported\textsuperscript{40-41}. Most of the zeolite framework structures have been determined from single crystal study and are well established. The location of extra framework cations can be directly determined by XRD method. The scattering power of atom depends on the number of external electrons, since the number of external electrons in silicon and aluminium are nearly same, the scattering powers of silicon and aluminium are practically identical. The X-ray diffraction method has a limited application to the
study of silicon and aluminium. An X-ray diffractogram can be taken as characteristic feature of any compound.

The application of X-ray crystallography has served to reveal certain broad principles upon which the structures of the silicates are based. The most frequently used method for determining the degree of crystallinity of zeolite is XRD method.

In 1930, Taylor made the first complete analysis of a zeolite analcime and followed both dehydration and replacement of sodium by silver by means of X-ray study\textsuperscript{42}. An X-ray investigation carried out by Taylor, Meek and Jackson simultaneously with chemical and optical investigations made by Hay and Banister which have done much to remove the confusion in the literature of these zeolites\textsuperscript{43-44}. Several natural and synthetic zeolites have almost identical X-ray diffraction patterns, although their framework topology is different\textsuperscript{45-46}. The crystal structure of mineral faujasite has been described by Nowacki and Bergerhoff\textsuperscript{47}. Its synthetic counterpart zeolites types X and Y have also been studied by XRD method\textsuperscript{41}. Powder X-ray patterns show the basic framework of faujasite and zeolites types X and Y to be similar. Positions of Mg, Ag, Ca, Ba, Zn in the sodium zeolite type A have been determined by X-ray powder diffraction method by Schoellner and other co-workers\textsuperscript{48}. X-ray powder diffraction study shows that aluminium substituted by boron atom in the framework led to a shrinkage in unit cell\textsuperscript{49}. An iron - containing hexagonal mesoporous silica molecular sieve material synthesized at room temperature for the first time and studied by XRD method confirmed the incorporation of iron (III) in the framework\textsuperscript{50}. The framework structure of MCM-41 molecular sieve has been recently studied by Gruner and Liu\textsuperscript{51-52}. A. V. Ramaswamy studied the crystal structure of large-pore Sn-b and aluminium free Sn-b molecular sieves\textsuperscript{53}. X-ray powder method is now used to observe the sequence of the formation of zeolite\textsuperscript{54-57}. Ermoshin studied the first solid-state transformation of an anionic aluminophosphate molecular sieve framework to an entirely neutral one using high temperature powder XRD method\textsuperscript{58-59}. The location and co-ordination of titanium in the titanosilicate mesoporous molecular sieve MCM-41 have
been studied by XRD powder method. The XRD results show isomorphous substitution of
titanium for silicon. The disintegration of the mesoporous structure in water has been
studied by powder XRD method supposed to be due to silicate
hydrolysis. Khouzami and coworkers carried out structural analysis of alumino-
phosphate using XRD method in both its as-synthesized and rehydrated forms. Silicon
was also shown to substitute partly for phosphorus in the framework and to give
catalysts with moderate acidic strength. Aluminophosphate, VPI-5 and AlPO4 have
been characterized by XRD method. The interaction of NH3 with template free silico-
alumino-phosphate namely SAPO-34 framework was studied by XRD powder method by
Vomacheld et al. In-situ X-ray powder diffraction experiments enable studies of
hydrothermal synthesis of zeolites reaction between solids and gas-phase at elevated
temperature and solid-state synthesis. Evaluation of zeolite crystallinity was carried out
using X-ray diffraction method and ZSM-5 analog zeolite by C. Anwar.

X-ray powder diffraction patterns of the derivatives discussed in this thesis were
recorded between 2θ angles 5° and 70° using Co radiation and Rigaca X-ray
Diffractometer.

**Thermal Analysis**

Thermal methods is a general term covering a group of related techniques
whereby the dependence of the parameters of any physical property of a substance on
temperature is recorded. Thermal methods such as thermogravimetric analysis (TGA) and
differential thermal analysis (DTA) are being employed increasingly in the investigation of
chemical reactions in the liquid and solid state at elevated temperatures. These techniques
involve the continuous measurement of change in a physical property such as weight and
heat capacity or energy as sample temperature is increased, usually at a predetermined
rate.
**Thermogravimetric Analysis (TGA)**

TGA is a technique in which the weight of a sample is measured as a function of temperature or time, whilst it is subjected to a controlled heating programme. The resulting curve is known as the thermolysis curve or thermogram or pyrolysis curve or thermoweighing curve.

The historical development of the modern thermobalance has been described by Gordon and Campbell\textsuperscript{73}, Duval\textsuperscript{74}, Wendlandt\textsuperscript{75}, Keat\textsuperscript{76}, Sait\textsuperscript{77} and others\textsuperscript{78-79}. Duval developed Chevenard thermobalance and studied the thermal properties of over 1,000 precipitates as well as the development of an automatic method of analysis based on this technique\textsuperscript{80}. Modern thermobalances facilitate studies in which a sample is subjected to conditions of continuous increase in temperature usually linear with time which is called dynamic thermogravimetry and is relatively recent (1923) compared to isothermal or static thermogravimetry\textsuperscript{81}.

TG curves which represent variation in the weight of the sample with temperature or time can be divided into various regions. From various regions, thermal stabilities of the original sample, the intermediate compounds and the final products can be determined. Thermogravimetry provides quantitative information on weight change processes and enables the stoichiometry of a reaction to be followed directly. TG curves are characteristic for a given compound or system because of the unique sequence of physicochemical reactions which occur over definite temperature ranges and at rates that are a function of molecular structure.

**Differential Thermal Analysis (DTA)**

Differential thermal analysis is a technique in which the difference in temperature between the sample and an inert reference material is measured as a function of temperature whilst it is subjected to a controlled heating programme. It is a technique developed by ceramists and mineralogists for studying the phenomena occurring when the
materials are heated. DTA was first employed by Le Chetelier in 1887 for identifying clays. The differential method in which the temperature of the sample is compared with that of the reference was conceived by Roberts-Austen in 1899. In 1952, R. L. Stone described dynamic gas atmosphere DTA apparatus which was the beginning of precision controlled atmosphere DTA. Commercial DTA equipments enabled investigators to obtain reproducible results and agreements with other workers around the world, if the pyrolytic conditions were identical. Vold has developed a new theory to describe the DTA curve.

The positions and profiles of the DTA peaks are characteristics of the sample being studied. The DTA curve may be thought of as a kind of thermal finger-print of sample under study. Experimental factors such as the size, packing, geometry, physicochemical history of the sample, electro-mechanical design of the instrumentation, gaseous environment, heating rate and the temperature (sample, reference or furnace) chosen for abscissa affect the shape of the thermal bands.

Applications of Thermal Methods to the Study of Zeolites

Thermal methods i.e. thermogravimetry and differential thermal analysis are useful in characterizing zeolites from their dehydration behavior. Based on dehydration behavior, the zeolites may be classified into two categories:-

(1) First category includes those zeolites which on dehydration do not show major structural changes and exhibit continuous dehydration curves. Examples are zeolite A, X, Y and chabazite.

(2) Second category includes those zeolites which undergo structural changes with dehydration and show steps or other discontinuities in the dehydration curves. Examples are natrolite, scolecite, mesolite etc.

The nature of water types present in zeolites and the ion content were postulated by using thermal methods by various investigators. The stability of the zeolites
increases with the increasing Si/Al ratio\textsuperscript{88} and size of the exchangeable cations as revealed by the thermal analysis.

Zeolites with closely related structures show entirely different dehydration behavior, stability behavior and their DTA curves are distinctly different\textsuperscript{89-92}. The characteristic dehydration behavior of each zeolite is evidenced by the dehydration curves and differential thermal analysis. The reversible dehydration of mineral chabazite was first observed by Damour in 1940\textsuperscript{93}. The mineral chabazite and its various cation-exchanged forms have been studied extensively in terms of their dehydration behavior and ability to rehydrate\textsuperscript{88,94-95}. Barrer and other coworkers studied a series of cation-exchanged forms of zeolite X by means of TGA\textsuperscript{86,96}, DTA and water absorption equilibrium measurements. Bolton in 1971 obtained the stoichiometry of rare earth exchanged zeolite by thermal analysis\textsuperscript{97}. Thermogravimetric data show that one molecule of hydroxyl water in the zeolite was associated with each rare earth cation. The temperature induced changes in the unit cell dimensions of synthetic Na A type zeolite are presented and changes of crystal types upon heating were discussed\textsuperscript{98}. Thermal methods are especially important in the study of adsorbed derivatives of zeolites\textsuperscript{99-103}.

Kornatowski made TGA measurements for the series of AFI, AEL and ATO type aluminophosphates molecular sieves substituted with various metals. It is found that DTG effects are proportional to the content of metallic substituents and can be taken as indication of metal incorporation into the molecular sieve framework\textsuperscript{104}. TG/DTA studies indicated the relative stabilities of the L-type zeolite and Fe-modified L-type zeolites\textsuperscript{105}.

TG/DTA analysis of SAPO-44 molecular sieve shows no structural collapse at > 1000°C\textsuperscript{106}. SAPO-11, SAPO-31, SAPO-41 molecular sieves synthesized using organic amine template have been characterized by thermal methods\textsuperscript{107}.
The zeolite samples used in this study were heated to a temperature range up to 900°C at a heating rate of 10°C per minute using SETARAM Thermal Analyzer in dynamic air.

**Compositional Studies:**

Compositional studies of synthetic zeolites “one” and “two” and their cation exchanged and phosphatic derivatives have been carried out by simple gravimetric analysis, AES-ICP and also using a flame photometer. The following constituents have been determined:

1. **Silicon**: Weighed quantity of the sample was dissolved in concentrated hydrochloric acid, evaporated to complete dryness on the water bath. The residue was heated for an hour at 110-120°C in an air oven to dehydrate silica. The residue was ignited in a platinum crucible at about 1050°C, cooled. The ignited residue is not usually pure SiO₂. The residue was treated with a little concentrated sulfuric acid and hydrofluoric acid to remove silica as silicon tetrafluoride. Loss in weight represents the amount of pure silica.

2. **Aluminium**: The aluminium was precipitated as the hydrated oxide by means of ammonia solution in the presence of ammonium chloride. The gelatinous precipitate was washed and the precipitate was ignited in a platinum crucible at 1000°C and weighed as alumina.

3. **Sodium**: Weighed quantity of the sample was treated with perchloric acid and hydrofluoric acid in a Teflon beaker. The contents were digested on a hot plate at 250°C till dense fumes were evolved. The contents were transferred in to 100 ml. volumetric flask, and made up to the mark. From this solution, sodium was estimated using a flame photometer.

4. **phosphorus**: The weighed quantity of the sample was dissolved in concentrated nitric acid and 48% hydrofluoric acid. To an aliquot concentrated nitric acid and ammonium
nitrate solution were added, followed by ammonium molybdate solution. Yellow precipitate of ammonium phosphomolybdate resulted. The precipitate was washed and dissolved in aqueous ammonia containing ammonium citrate. To this solution were added 10 ml. of magnesia reagent and then aqueous ammonia dropwise with vigorous stirring. The precipitate of magnesium ammonium phosphate was filtered, ignited and weighed as Mg₃P₂O₇.

**Calcium:** Inductively Coupled Plasma - Atomic Absorption Spectrometry has been used for the estimation of calcium present in original synthetic zeolites “one” and “two”. In this method plasma has the task of exciting the atoms to be measured. Plasma, in principle, is an electrically conductive fluid system, predominantly in gaseous matter. A plasma is produced by transferring electrical energy to a flow of gas. In the case of inductively coupled plasma, a high frequency generator with an induction coil is used to supply the energy for the ionization potential required.

A gas is fed through a system of quartz tubes whose shape facilitates flow and to the end of which a strong current of high frequency is applied. After ionization of the gas a homogeneous plasma of high thermal intensity is produced. Minutely atomized particles of solution are fed via an added carrier gas into the hot plasma core and ionized. This causes the element particles to emit spectra which can be recorded qualitatively and quantitatively with the usual spectrometric system. Each ICP system consists of a high frequency generator with induction coils, the plasma burner, and atomizer chamber, and an appropriate gas supply.

For preparing the solution, 200 mg of the sample was dissolved in 25 ml. of concentrated AnaLaR nitric acid and the contents were made up to 100 ml. The undissolved silica was filtered off carefully. This solution after standardization was subsequently fed into AES-ICP instrument of model LABTAM 8440 PLASMALABS.
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