CHAPTER II

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EXPERIMENTAL

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(1) MATERIAL AND METHODS

(1.1) **Preparation of Cation Exchanged and Adsorbed Samples**

The molecular sieve employed in this work is a synthetic material Hydrophilite resembling synthetic zeolite 4A. This material has been developed and marketed by Ras Enterprises, Bombay, as an effective desiccant useful in paints, coatings and other allied industries. It is available in white odourless powder form with different mesh sizes. The bulk material in powder form as supplied by Ras Enterprises was used in preparing various cation exchanged samples and their adsorbed derivatives.

Following Analytical grade chemicals were used for preparing the cation exchanged samples:

- Silver(I) sulphate (Ag₂SO₄)
- Mercurous(I) nitrate (Hg₂(NO₃)₂·2H₂O)
- Tetramethyl ammonium(I) iodide ((CH₃)₄NI)
- Vanadyl sulphate (VOSO₄·2H₂O)
- Cadmium(II) nitrate (Cd(NO₃)₂·4H₂O)
- Lead(II) sulphate (Pb(NO₃)₂)
- Beryllium(II) carbonate (BeCO₃·4H₂O)
- Nickel(II) sulphate (NiSO₄·7H₂O)
- Bismuth(III) nitrate (Bi(NO₃)₃·5H₂O)
- Cerium(III) sulphate (Ce₂(SO₄)₃)
- Zirconium(IV) nitrate (Zr(NO₃)₄·2H₂O)

Adsorbed samples with these cation exchanged forms of Hydrophilite were prepared by using gases like hydrogen sulphide, carbon dioxide and ammonia in the form of liquor ammonia (Specific gravity 0.888).
Fig. 1
Preparation of Cation Exchanged Derivatives from Hydrophilite

The original sample of Hydrophilite was directly used for preparing the cation exchanged derivatives. These derivatives were prepared as a rule by treating Hydrophilite with saturated solutions of appropriate electrolytes at room temperature. The arrangement used is shown in Fig. 1. The rate of flow of the solutions through the exchanger was adjusted to between 5 and 10 ml per hour by means of the water pump. This treatment was repeated a number of times in order to ensure the maximum exchange. The cationic form of Hydrophilite was then dried in the oven at 110°C and then allowed to equilibrate with the water vapour over a saturated aqueous NH₄Cl solution in a desiccator at room temperature. This procedure was necessary to ensure a constant content of zeolitic water and, therefore, constant composition for the samples. The water content of a zeolite is independent of the relative humidity of the surrounding atmosphere.

Preparation of Adsorbed Samples with Cation Exchanged Derivatives

Ammonia adsorbed samples with cation exchanged Hydrophilite were prepared in the following manner:

Cation exchanged samples of Hydrophilite were placed in a flask and mixed with 100 ml of liquor ammonia and kept for several days. The mixed mass was stirred from time to time for complete reaction. The liquor ammonia used was changed from time to time to add fresh aliquots. After filtering off the excess liquid, the samples were kept on filter-paper and air dried.
Cation exchange derivative of Zeolite (Hydrophilite)

Fig. 2
Hydrogen sulphide and carbon dioxide adsorbed samples with cation exchanged Hydrophilite were prepared by using a conical flask provided with an inlet and an outlet as shown in Fig. 2. Inlet was connected with gas generating apparatus and the air is evacuated by passing continuous stream of the gas. The adsorbents were placed in the flask and exposed to a continuous and steady flow of the gas. In order to ensure maximum adsorption, this process was carried out continuously for several hours.

(2) ANALYTICAL METHODS USED FOR INVESTIGATIONS

(2.1) Composition Studies

Composition studies of Hydrophilite and its derivatives have been carried out by simple gravimetric analysis and using atomic absorption spectrophotometer and flame photometer.

The following constituents have been determined:

I. SiO₂ : Weighed quantity of the sample was dissolved in concentrated hydrochloric acid, diluted, and the solution was dehydrated on water-bath. The dehydrated residue was hydrofluorised in a platinum crucible and the loss in weight was reported as silica.

II. CaO and MgO : Weighed quantity of the sample, after removal of silica, was aspirated in a varian Techtron atomic absorption spectrophotometer Model 575. The calcium was estimated by its absorption at 422.7 nm and magnesium by its
absorption at 285.2 nm. Lanthanum was added as an ion suppressor.

III. \( \text{Na}_2\text{O} \) and \( \text{K}_2\text{O} \): Weighed quantity of the sample was treated with perchloric and hydrofluoric acids in a platinum crucible and slowly heated to dense fumes in a fuming chamber. The contents in the crucibles were extracted and made up to a definite volume in a volumetric flask. From this solution, sodium and potassium were estimated using HEL flame photometer.

(2.2) Infrared Spectroscopy

The measurement of infrared absorption spectra of compounds is finding widespread use, since stable commercial spectrophotometers have become available. The infrared spectrophotometer is used for quantitative measurements of concentration and even for automatic control and recording. In addition, it is a valuable tool for detecting and identifying small amounts of impurities and for the elucidation of the structure of molecules. Infrared spectra arise from the different modes of vibration and rotation of a molecule. The pure rotational spectrum of molecules occurs at very long wavelengths i.e. in the microwave region well beyond the long wavelength limit of about 25 μ of most infrared spectrophotometer. At wavelengths below 25 μ, the radiation has sufficient energy to cause changes in the vibrational and of course also the rotational levels of the molecules.

Since many of the individual bands occurring in the infrared spectrum are more or less characteristic of specific
pairs or groups of atoms in the molecules, they give much information about the structure of a compound.

In recent years, a number of aluminosilicate minerals including tetrasilicate and clay minerals have been examined in a phenomenological sense by infrared spectroscopy\textsuperscript{1,2}.

A systemic investigation regarding structures of zeolites has been carried out in the 1300 cm\(^{-1}\) - 200 cm\(^{-1}\) region. For assignment of bands, it is necessary to know the basic structure of zeolites. Hence this method of investigation is complimentary to X-ray structure analysis\textsuperscript{3,4}.

The IR absorption bands in case of zeolites can be divided into two groups. The first group, which contains bands common to all zeolites, corresponds to vibrations within the tetrahedra. These vibrations are not sensitive to structural vibrations. The second group of vibrations are related to the linkages between the tetrahedra. They are sensitive to the overall structure and the joining of the individual tetrahedra in secondary structural units as well as their existence in the larger pore openings.

The first group of spectra that consists of the strongest vibrations found in all zeolites are noted between 950 cm\(^{-1}\) - 1250 cm\(^{-1}\) and between 420 cm\(^{-1}\) - 500 cm\(^{-1}\). The strong vibration near 950 cm\(^{-1}\) is assigned to a T-O stretch. The next strongest band in the 420 - 500 cm\(^{-1}\) region is assigned to a T-O bending mode.

Stretching modes involving mainly the tetrahedra atoms are assigned the region from 650 cm\(^{-1}\) to 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 tetrahedra aluminium atoms. The bending mode 420 cm\(^{-1}\) - 500 cm\(^{-1}\) is not as sensitive\(^5\)\(^-\)\(^9\). The positions of the IR bands are also sensitive to changes in the Al/Si ratio, the location of cations and the crystallinity of zeolites. The frequency of a number of the stretching vibrations decreases linearly with an increasing atom fraction of Al ions in the framework.

The second group of frequencies which are sensitive to the linkages between tetrahedra, the topology and the arrangement of secondary units in the zeolite structure occur in the regions 500 cm\(^{-1}\) - 650 cm\(^{-1}\) and 300 cm\(^{-1}\) - 420 cm\(^{-1}\). A band in the 500 cm\(^{-1}\) - 650 cm\(^{-1}\) region is related to the presence of the double rings (D6R and D4R) in the framework structures. The zeolites which do not contain the double rings or layer polyhedra units such as the cage, show only a weak absorption in this region of the spectrum. The 300 cm\(^{-1}\) - 420 cm\(^{-1}\) portion of the spectrum is related to the pore opening or motion of the tetrahedra rings which form the pore openings. The other bands attributed to the linkages of the primary structure units are found in the 750 cm\(^{-1}\) - 820 cm\(^{-1}\) region and the 1050 cm\(^{-1}\) - 1150 cm\(^{-1}\) region.

A linear relationship has been found between frequencies of certain absorption bands and reciprocal of the sum of the cation and framework oxygen radii\(^10\). The positions of the IR bands are also sensitive to changes in the Al/Si ratio, the location of cations and the crystallinity of zeolite. The
frequency of a number of the stretching vibrations decreases linearly with an increasing atom fraction of Al ions in the framework. Such correlation between frequency and composition can be used to determine the concentration of framework Al atoms in ultrastable and aluminium deficient zeolites\textsuperscript{11-13}. Since the hydroxyl groups present in both cation exchanged and hydrogen form of zeolites are responsible for many of the catalytic properties of the host, number of investigations have been made of the hydroxyl stretching region between 3750 cm\textsuperscript{-1} and 3500 cm\textsuperscript{-1} of the IR spectrum. These were reviewed by Yates\textsuperscript{14} and Basila\textsuperscript{15} and later by Ward\textsuperscript{16}, Breck\textsuperscript{18} and Kiselev and Lygin\textsuperscript{9}.

Water molecules associated with cation and framework oxygen ions of a zeolite depend upon the openness of the structure. For example, in zeolite NaX which is representative of the more open structure with large voids, water molecules are associated with the cation and to some degree are hydrogen bonded to the oxygen ions of the framework. This is evident by a sharp IR band at 3690 cm\textsuperscript{-1}; the latter being attributed to the hydroxyl group of water molecule bonded to a framework oxygen\textsuperscript{17}.

**Applications of Infrared Spectroscopy to the Study of Zeolites**

Infrared spectroscopic studies of various zeolite derivatives with different cations and adsorbents have helped in the elucidation of zeolite structure and the changes occurring in the structure as a result of the different types of interactions\textsuperscript{19-39}.
In the present investigation, the infrared spectroscopic studies between 5000 cm\(^{-1}\) - 650 cm\(^{-1}\) have been carried out with a view to record the structural changes in the original Hydrophilite as a result of cation exchange and adsorption. IR spectral analysis of samples were recorded before and after heating, using potassium bromide pellet phase on a Spektromom 2000 IR spectrophotometer. The spectra are shown in Figs. 1 to 24.

(2.3) Thermogravimetric Analysis

The roots of thermogravimetric analysis lie at the beginning of the 20th century. TGA involves the measurement of the weight of a sample either as a function of time at constant temperature or as a function of some parametric temperature as the system temperature changes. The sample may either lose weight to the atmosphere or gain weight by reaction with the atmosphere. The record is usually in the form of an integral curve with absolute weight (W) as the Y axis and time t or temperature (T) as the X axis. However, systems have been developed which record change in weight as a function of t or T. This produces a rate differential curve dw/dt or better dw/dT\(^{40-44}\).

The thermal analysis of zeolites helps to understand the effect of dehydration and lattice transformations as a consequence of heat treatment. From the thermograms of a series of modified chabazites, Barrer and Langlay\(^{45}\) found that the thermal stability of host lattice increased with increase in the size of the exchanged cations. The thermal stability increased with the Al/Si ratio\(^{46}\).
Most zeolites may dehydrate to some degree without major alternation of their crystal structure (viz. zeolites A, X, Y and chabazite). They may subsequently rehydrate, that is, adsorb water from the vapour or liquid phase. Such a behaviour is treated as reversible. Many zeolites when completely dehydrated, undergo reversible structural changes and suffer total structural collapse e.g. natrolite, socolait and mesolite. Zeolites that undergo dehydration reversibly and continuously do not show substantial change in the topology of the framework structure. Exchangeable cations are located in the channels and co-ordinated with water molecules (as in chabazite, faujasite and zeolite X) may migrate to different sites on the channel walls or other positions of co-ordination.

**Kinetics**

Equations with the thermogravimetric data can be derived for non-reversing reactions so that rate dependent parameters like the rate of reaction, activation energy and order of reaction may be calculated from a single experimental curve.

An excellent discussion of dynamic and isothermal methods has been given by Doyle. All methods suggested to date suffer more or less seriously from procedural and experimental errors. Energy of activation and reaction order from programmed TGA evidence should always be held in doubt until confirmed by other techniques.

In many cases, TG data are the only experimental facts available and must be used. To facilitate such calculations, the following two methods are given. These methods have the
advantage to simplicity of manipulation and relative freedom from error. In addition, if error is present, the result will be absurd.

The first method, reported by Broido, applies only to first order reactions. The weight loss at any given temperature is defined as:

\[ \alpha = \frac{(W_t - W_0)}{(W_0 - W_{oo})} \]

where, \( W_t \) is the indicated weight at time or temperature \( t \); \( W_0 \) is the initial weight and \( W_{oo} \) is the residual weight or weight at the end of the process under study.

In practice, a plot of \( \ln (1/\alpha) \) or the axis versus \( \frac{1000}{T} \) (where \( T \) is the temperature in kelvin) is made. This must yield a straight line if the data are accurate and the reaction is first order. The method is very sensitive to weighing errors, especially in \( W_0 \) and \( W_{oo} \). Proof has been offered that if the plot is linear over the total range of decomposition, the reaction must be first order\(^{51,52}\).

Coats and Redfern have proposed a method which gives reasonable values of \( T \) only if the assumed kinetics are correct. In practice, a plot \( \ln 2 \left[ \frac{1-(1-\alpha)^{\frac{1}{2}}}{T^2} \right] \) versus \( 1000/T \) is made as above. This must also yield a straight line\(^{53,54}\).

In solid state decomposition kinetics using thermal analysis, the activation energy is one parameter that is generally calculated. Several methods have been proposed for decomposition reaction to evaluate the kinetic parameters\(^{55-57}\). Among them empirical equation of Coats and Redfern has been widely employed\(^{58}\). Several investigations have shown the
difficulties in calculating meaningful activation energies from the dynamic method alone. Even with isothermal TG, the activation energy by any of standard techniques is rather tedious. It involves determining the proper mechanism of the reaction and then evaluating the appropriate $g(\alpha)$ (integral rate expression) and specific reaction rates. In the literature, use of induction period and the time of completion of the reaction has been suggested as alternatives to determine the specific reaction rates. However, in all of the techniques, an accurate knowledge of the time of inception of reaction is necessary.

The equation expressed in the most general form can be written as:

$$\log \left( \frac{g(\alpha)}{T^2} \right) = -\frac{E}{2.303 RT} + \log \frac{ZR}{BE} \left[ 1 - \frac{2 RT}{E} \right]$$

where, $B$ is the linear heating rate, $E$ is the apparent activation energy and $Z$ is the pre-exponential factor of Arrhenius equation.

In all the analysis of the TG curves, the linearity criterion of $\log \left( \frac{g(\alpha)}{T^2} \right)$ vs $\frac{1}{T}$ is taken as sufficient proof for the current form of $g(\alpha)$ and hence the model of the reactions mechanism proposed. However, Criodo and Morales based on their recent theoretical analysis, have concluded that this linearity of $\log \left( \frac{g(\alpha)}{T^2} \right)$ vs $\frac{1}{T}$ is necessary but not a sufficient criterion to assign an unequivocal $g(\alpha)$ function. They have shown that $g(\alpha) = -\log \left( 1 - \alpha \right)^{1/2}$ yielded about the same linear correlation between $\log \left( \frac{g(\alpha)}{T^2} \right)$ vs $\frac{1}{T}$ for $n = 1, 2$ or 3.
Applications of Thermal Analysis in the Study of Zeolites

Much work has been done using TG method for studying dehydration and desorption process for commercial molecular sieves in powder and pellet forms. The researches include the determination of kinetic parameters of the various thermal events involving various types of zeolite derivatives.64–78

Current interpretations of the nature of water in zeolites are based on the determination of the dehydration isobars and the ability of the dehydrated zeolite to completely rehydrate or adsorb gases and vapours. Thermogravimetric analysis has been useful in indicating the stability of zeolites towards dehydration.79–91

The thesis incorporates the TG plots of Hydrophilite and its cation exchanged and adsorbed derivatives. Samples were taken in platinum crucible and heated from room temperature to 800°C at 10°C/minute heating rate on a TG balance supplied by FCIL, Sindri. From the weight loss data at 2 minute (20°C) intervals, first and then g(\(\alpha\))^ were calculated to evaluate the kinetic parameters of thermal reactions for each sample studied. The TG plots are shown in Figs. 25 to 36 and the thermal data evaluated are tabulated in tables 1 to 48.

(2.4) X-Ray Diffraction

The field of X-ray diffraction owes its inception to a momentous discovery by Max Laue in 1913. Within two years of discovery, a most comprehensive theory explaining the basis of X-ray diffraction was developed by C.G. Darwin, who spent
the next several years expanding this theory.

The importance of X-ray diffraction to the development of modern science can be appreciated best by considering its widespread influence. First of all, X-ray diffraction confirmed the speculations of leading crystallographers and chemists that crystals were composed of atoms arranged in an orderly and periodic array. The basis of modern X-ray diffraction theory and its application is to the characterisation of crystals.\textsuperscript{92-97}

The zeolite structures have been also determined basically by the X-ray diffraction technique. Beside the unit cell constants, the position of cations in the zeolite crystals belonging to different symmetries have been reported\textsuperscript{98,99}.

\begin{equation}
T = C4\overline{3}d
\end{equation}

Most of the zeolite framework structures have been determined from single crystal study and are well established. However, closely related structures can be hard to distinguish from one another. Thus, Sherman and Benneth have shown that several natural and synthetic zeolites have almost identical X-ray patterns, although their framework topology is different\textsuperscript{100,101}.

Variations in lattice parameters and framework symmetry have been observed for many zeolite systems\textsuperscript{102,103}. Meier\textsuperscript{104} has shown by crystal structure analysis from powder data that removal of Al atoms during the ultrastabilization leaves tetrahedral vacancies which are subsequently filled by silicon atoms.

The random occupancy of T sites by Al and Si will cause displacement of adjacent O atoms but only the average position will be measured by X-ray spectroscopy. Hence chemical changes affecting stabilization of bonding orbitals cause chemical shift.
The X-ray diffraction has had limited application to the study of Si and Al distribution in zeolites because of scattering power of the two atoms is practically identical. Furthermore, since it only presents description of the average unit cell content, it is intrinsically unable to provide information concerning local order. However, cation sites in the various zeolites determined by the X-ray diffraction have been tabulated by Rees.\textsuperscript{105} Fisher\textsuperscript{106} has reviewed the work on refinement of crystal structure from X-ray data.

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

Because an X-ray diffraction diagram is characteristic of any given compound, this method has been used for qualitative determination of Hydrophilite and its cation exchanged adsorbed derivatives. The XRD studies of the Hydrophilite and its derivatives were carried out on a Philips PW 1140 Model X-ray unit, using copper radiation with 2 cm/min chart speed and 2θ/min scanning speed between 5° to 70°.

From 2θ values, the corresponding 'd' spacings were recorded. These along with intensities are tabulated in Tables 49 to 88. XRD plots are shown in Figs. 37 to 48.

(2.5) \textit{Electron Micrograph of Hydrophilite}

Electron microscopy is used extensively to study the habit and surface topography of synthetic zeolite.\textsuperscript{107} The crystal structures of synthetic zeolites are difficult to determine by X-ray analysis because of size of the variable crystals and the similar scattering power of Si and Al atoms. Electron diffraction can be advantageous to examine such crystals as well
ELECTRON MICROGRAPH OF HYDROPHILITE
as super lattice ordering if any. This thesis incorporates the electron microscopic studies of the original Hydrophilite. Particles of powder form Hydrophilite are very tiny, therefore, it is necessary to prepare specimen support membrane for grids from suitable membrane. Collodion solution was used for the preparation of support membrane. Crystalline Hydrophilite is not completely soluble in any volatile solvent. For grid preparation, sample was shaken with acetone and dropped upon the grids. Acetone evaporates very fast and the specimen remained on the grid in the form of a very thin uniform layer. The photograph shows the electron micrograph of Hydrophilite. This was obtained by using JEM 100 L Transmission type electron microscope with 4000 magnification.
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