Experimental Methods for Characterization OF ZEOLITE

Dr.V.P.Deshpande

Abstract— **Zeolites are microporous alkaline hydrated aluminosilicate crystals, which include both natural and synthetic varieties. Natural zeolites can grow in cavities of igneous rocks from natural hydrothermal solutions. The idea that zeolite crystals have potential applications in numerous areas of scientific, industrial and agricultural technology has provided impetus for research and development programs that have been carried out in several countries. Experimental methods for characterization of zeolite includes, X-ray diffraction, Infrared spectroscopy (IR), Chemical analysis, Scanning electron microscopy (SEM), Nuclear magnetic resonance spectroscopy (NMR) etc.**

Index Terms— **XRD,IR ,Chemical Analysis ,SEM, NMR**

I. INTRODUCTION

In any solid porous body, various pores can be differentiated depending upon their sizes: micropores, mesopores (Transitional pores) and macropores (1). The micropores are smallest, average radii being less than 15 – 16 A° . Pores with radius less than 15 A° but not less than 5 – 7 A° are called supermicropores.

In mesopores, the effective radii are from 15 A° to 2000 A°. The intensity of the adsorption interaction is less than that in microspores (2).

Macropores are characterized by the radii greater than 2000A°. Micro and mesopores are responsible for adsorption.

Natural zeolites are characterized by micro porosity. The micro porosity results from the specific crystalline structure of the zeolite particles which in turn depends upon it's composition. Existence of apertures of fixed diameters causes the molecular sieving action of zeolites. Under ideal conditions some molecules can pass through the apertures to the internal structure filling the available adsorptive space. Others (of larger size) cannot enter and remain on the outer surface of the zeolites grain.

Zeolite is an alkaline hydrated aluminosilicate with a skeletal structure (3) containing voids occupied by ions and molecules of the water having a considerable freedom of movement that leads to ion exchange and reversible dehydration.

Information about different experimental techniques used that provide structural, compositional and physicochemical information about zeolites is covered in this chapter. This includes, X – ray diffraction (XRD) studies, chemical analysis, IR studies, Scanning Electron microscopy, Nuclear Magnetic Resonance (NMR), etc.

II. X- RAY DIFFRACTION STUDIES

X- ray diffraction is one of the most powerful and useful tool which has been employed to understand the mechanism of crystallization (4,5). The X – ray structure analysis is based on the phenomenon on diffraction of X- rays by a substance. If a beam of x-rays falls on a crystal, whose dimensions are of the same order of magnitude as its wavelength, diffraction can occur.

Powder method

X – ray powder diffraction method is commonly used for the structural investigations of the synthetic and natural zeolites. The lattice parameters, cation distribution in the zeolites have been studied using X- ray diffractograms (7,8,9). This crystallographic technique is used when single crystals of reasonably large size are not available.

The essence of this method is that a beam of monochromatic X- radiation is incident on a powder sample. If the Bragg's law is satisfied i.e. $2d \sin\theta = n\lambda$, diffraction can occur.

In X-ray diffractometry it is a common practice to insert thin nickel foil in the primary X-ray beam to remove the K_β lines from the spectrum while transmitting K_α- lines.

In counter diffractometers the diffracted radiation is detected by the counter tubes, normally located at greater distances which move through angular range of reflections. The intensities of diffracted radiations are recorded on synchronously advancing strip charts.

Making use of the fact that a crystalline substance can be identified by the 'd' spacing and relative intensities of the reflections in its diffraction pattern, identification of several substances in a mixture is possible. The powder pattern of a substance effectively serves as a finger print by which it can be identified.

The X-ray diffractograms were recorded between 2θ values ranging from 5° to 50° with a chart speed of 1°/min,on a Phillips X-ray diffractometer(Model PW 1710) and Ni filtered CuKα radiation, of wavelength 1.54056 A° in continuous scan.

III. CHEMICAL ANALYSIS

Chemical analysis is one of the important tools to characterize natural as well as synthetic zeolite. The standard products for it are reported by several workers (10,11).

3.1 Preparation of Main Solution

The solution was prepared by adding 3 ml of dilute Sulfuric acid and 15 ml of Hydrofluoric acid (40% WIV) to the residue as obtained in loss on Ignition and evaporated on the low flame burner. After drying the contents, it was ignited. This

was then cooled and weighed. The process of the Hydroflurization, drying and weighing was repeated till the constant weight is obtained and was fused with 1gm of the Sodium Carbonate and the melt was extracted in 15 ml of dilute hydrochloric acid. By filtering and washing with the hot water, the filtrate has been made to 250 ml and preserved in a flask.

3.2 Loss on Ignition

By heating the known quantity of zeolite sample at high temperature in platinum crucible for 2 hours, constant weight was obtained. From the difference in the weight, loss on ignition was calculated which was used for getting the analysis on dry basis. Repeated heating, cooling and weighing till constant in weight of the sample was secured. Then decrease in its weight represents the loss on ignition.

3.3 Determination of Silica

About 0.3 to 0.4 gm of sample was weighed accurately in 250 ml of beaker. To it about 30 to 40 ml of concentrated HCL was added and boiled for 2 hours. Then the solution was filtered and the residue was washed several times with hot water and then it was ignited for getting SiO_2.

3.4 Determination of Alumina

For the estimation of alumina from the zeolite Sample, 3 ml of concentrated Nitric acid was added in exactly 200 ml of main solution and then boiled Mixed oxides were precipitated from the boiling solution by adding concentrated Ammonium

Hydroxide. The Alumina content was determined by recording the difference in weight of mixed oxides and silica.

IV. INFRARED SPECTROSCOPY

IR technique is based upon the simple fact that a chemical substance shows marked selective absorption in the infrared region. After absorption of IR radiations the molecules of a chemical substance vibrates at many rates of vibration, giving rise to close – packed absorption bands called IR absorption spectrum which may extend over a wide wavelength range. Various bonds will be present in IR spectrum, which will correspond to the characteristics bond present in a chemical substance. The infrared radiation refers broadly to that region of electromagnetic spectrum, which lies between visible, and microwave region that ranges from 2.5 to 25µ (microns) or 4000 to 400 wave numbers. This range gives important information about the molecular structure of zeolites.

Infrared spectra are recorded with the help of Absorption spectrometers. Light of a range of wavelength from the source is passed through the sample. The wavelengths corresponding to allowed molecular transition are absorbed. The transmitted light passes through a prism, which resolves it into various wavelengths. It is then reflected from the mirror on to a detector. The response of the detector is recorded as the transmittances of radiation as a function of wave number and gives the absorption spectrum of the sample.
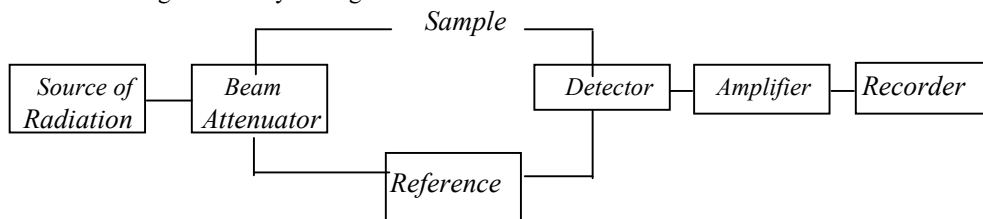
I. *FIG. 1 SCHEMATIC DIAGRAM OF A RECORDING SPECTROPHOTOMETER*

Infrared transmission spectra were obtained using Mull technique (12). In this technique, the finely ground solid sample is mixed with Nujol (mineral oil) to make a thick paste which is then made to spread between IR transmitting windows. This is then mounted in a path of infrared beam and the spectrum is run.

The most important feature of an IR spectrum is that the absorption or the lack of the absorption in specific frequency region can be correlated with specific stretching and bending motions and in some cases, with relationship of these group to the spectrum, it is possible to state that certain functional groups are present in the material, and that certain are absent. The applications of infrared spectroscopy has been covered by Kiseleve and Lygin (13) and Hair (14) to zeolites, and has been discussed by several authors (15 – 18).

The mid – infrared region of the spectrum contains the fundamental frame to work vibration of the $Si(Al)O_4$ groupings. In general, each zeolite structure has a characteristic infrared pattern; however, some common features are observed. Those vibrations include the asymmetric and symmetric stretch, double ring vibrations T-0

bending modes and possibly pore opening modes. The infrared spectrum can be classified into two groups of vibrations: (1) internal vibrations of the framework TO_4, which are insensitive to structural variation; and (2) vibrations related to the external linkage of the TO_4 units in the structure. The latter are sensitive to structural variation. No distinction can be made between the SiO_4 and AlO_4 related vibrations, as the similarity in the mass of the two T atoms precludes separation. The general zeolite infrared assignments for the structure insensitive (internal tetrahedral) and structure sensitive (external linkages) vibrations are given in table 2.1: Infrared structural studies of some natural and synthetic zeolite frameworks are reported (19).

A. Internal Tetrahedra	
Asym. Stretch	1250 - 950
Sym. Stretch	720 – 650
T – 0 bend	420 – 500
B. External Linkage	
Double Ring	650 – 500
Pore Opening	300 – 420
Sym. Stretch	750 – 820
Asym. Stretch	1050 – 1150

Table 1: Zeolite infrared assignments, cm^{-1}
The infrared spectra were recorded on a Perkin-Elmer-221 spectrophotometer in frequency range 400 – 4000 cm^{-1}.

5. SCANNING ELECTRON MICROSCOPY

The use of the wave properties of electrons in the electron microscope allows one to produce shorter wavelengths and thereby to sharply increase the resolving power of the microscope. The R.P. of microscope is $\delta = \lambda/2$, where λ is the De Broglie wavelength, which characterizes a beam of electrons moving at an accelerated velocity under the influence of potential difference U, is equal to

$$\lambda = 12.25 / \sqrt{u} \quad —$$

with an accelerating voltage of 100 KV, which is a typical of modern electron microscopes, the wavelength λ = 0.04 A°. The resolving power of the best modern electron microscope is, however practically lower by two orders and is 1- 5A°. The instruments put out serially usually have a resolving power of 5 A° and magnification of 2×10^5 to 2×10^6. The image of the micro object in the electron microscope seen with the aid of a special screen that becomes fluorescent under the impact of electrons. Usually the electron microscope is used to study the picture obtained when the electrons are passing through a thin layer (film) of a substance. The SEM has been operated in absorptive, emissive, reflective, transmission modes.

Electron microscopy can be used (20) rigorously to study particle size, morphology, crystallinity, stages of growth in case of the synthetic zeolites

6. DIELECTRIC STUDIES

The instrument used to measure the dielectric constants was a capacitance type. In it's most simple form, a capacitor is comprised of two oppositely charged parallel conducting plates separated by an insulator called a dielectric. Other capacitor geometries such as concentric cylinders are valid and frequently used. However for this study the most simple parallel plate model with an alternating current power supply is used. The frequencies used in the capacitance measurement are in the region 75 KHz to 30 MHz. The parallel plate capacitor used in this study as a mixture consists of two brass plate electrodes which are arranged parallelly and connected to an Hewlett – Packard model 4285 A° using thick copper wire.

To minimize undesirable fring field effect (21) the samples smaller than electrode size are used. Initially materials whose dielectric constants are known were tested. Very reliable results have been obtained.

7. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

This describes a form of spectroscopy in which, as a result of the magnetic properties of nuclei arising from their axial spin, radio frequency radiation is absorbed in a magnetic field. The method is called as the nuclear magnetic resonance (NMR) or nuclear spin resonance (NSR) spectroscopy. Spinning of nuclei about an axis resemble a minute bar magnet, the axis of which is coincident with the axis of spin. The angular momentum of the charge created by the spinning electrons can be described in terms of spin numbers I (in units of $h/2\pi$ where h is the Plank's constant). Spin numbers have integrals or Half integral values from $1/2$ to at least 9/2 for different nuclei; I=0 denotes no spin. Those have zero spin in which both the number of neutrons and number of protons is even e.g. C^{12}, O^{16} nuclei in this category do not give rise to an NMR signals.

Nuclei possessing nuclear spin values of ½ act as though they were spherical bodies possessing a uniform charge distribution which circulates over their surfaces. When a probing electrical charge approaches such a nucleus, it experiences an electrostatic field whose magnitude is independent of the direction of approach. The electrical quadruple moment is said to be zero these nuclei include H^1, F^{19} and P^{31}, the nuclei upon which most effort has been expended in NMR studies. As the electrical charges in a spinning nucleus describe an orbit about the nuclear axis (as a z – axis), the moving charges give rise to a magnetic field lying along the presumed axis of rotation. The resultant magnetic field may be represented by a nuclear magnetic moment, μ.

When a spinning nucleus is placed in a strong, uniform magnetic field H (in the z direction), the field exerts a torque upon the nuclear magnet and the nucleus tends to assume a definite orientation with respect to the external field. The torque is a vector with it's direction at right angles to the plane of μ and H. The net effect is a rotation of the nuclear axis around the direction of the external field, called processional motion. Each pole of the nuclear axis sweeps out a circular path in the xy – plane.

Each orientation of the nucleus corresponds to a different energy level or state. These energy revels are characterized by the magnetic quantum number m & take any values
I,(I-1) , (I-2), ------- (I-2), -(I-1), -I for a total of 2I+1 possible energy levels for nuclei.

For each isotope the energy revels are equally spaced, and the separation between adjacent energy revels is $\mu H/I$.

When an alternating radio frequency field, in the x – direction and super imposes over the stationary magnetic field, rotates at exactly the frequency at an energy levels the nuclear ensemble is brought into phase coherence, simultaneously, the nuclei will be provided enough energy to undergo a transition from a lower energy state to a higher energy state. The frequency ν of the radiation that will effect transitions between energy levels is derived by equating the Planck quantum of energy with the energy of reorientation of a magnetic dipole (22).

$\Delta E = h\nu = \mu H/I$

Absorption of the energy of the resonance frequency causes nuclei in a lower energy level to be " flipped " to the next higher energy level.

The frequency of the resonance absorption can be varied by altering the value of the applied magnetic field. The strength of the absorption signal is roughly proportional to the square of the magnetic field, large values of field strength lead to a large population difference and strong absorption signal. Considerations of magnet construction limit the applied field to approximately 23,000 gauss.

^{29}Si MAS NMR spectra were recorded in a 47,000 gauss field at frequency 59.628 MHz. With the pulse width 2 μs and repetition time 3s, on a Bruker – Physik (c x p – 200/300) solid state high resolution NMR spectrometers, equipped with a wide bore super conducting magnet and an Aspect – 2000 data system. Reference for ^{29}Si is taken to be TEOS (Tetraethyl or Silicate).

For ^{27}Al MAS NMR spectra reference is Aluminum Nitrate. The spectra were recorded at 78.205 MHz. The pulse length is 1 μs with repetition time 200ms.

CONCLUSIONS

For characterization of zeolite we used different experimental methodes such as X-ray diffraction, Infrared spectroscopy (IR), Chemical analysis, Scanning electron microscopy (SEM), Nuclear magnetic resonance spectroscopy (NMR) etc

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