

PHYSICO - CHEMICAL AND CATALYTIC PROPERTIES OF ZEOLITES

COMPUTERISED

A THESIS
SUBMITTED TO
THE UNIVERSITY OF POONA

FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
(IN CHEMISTRY)

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661.183.6 (043)
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1980

ACKNOWLEDGEMENT

I feel great pleasure and affectionated in expressing a profound sense of gratitude to Dr.(Miss) S.B. Kulkarni, Scientist, National Chemical Laboratory, Poona-8, for her meticulous planning of this investigation, methodical guidance and encouragement which made this work possible.

I am thankful to all my firends and colleagues for their whole-hearted cooperation and for scanning the X-ray, infrared spectra, thermograms and X-ray photoelectron spectra of zeolite samples.

I express a deep sense of respect and sincere thanks to Dr. A.P.B. Sinha and Dr. P. Rathasamy for helpful discussions and encouragement.

I take this opportunity to thank the Director, National Chemical Laboratory, Poona-8, for allowing to submit this work in the form of a thesis for the Ph.D. degree.

Poona
May, 1980

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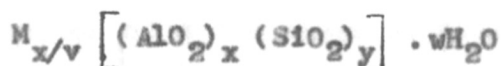
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CHAPTER - I : INTRODUCTION

The first chapter of the book is devoted to the study of the origin and development of the Indian economy. It deals with the various stages of economic growth and the role of different sectors in the development process. The chapter also discusses the impact of various factors such as population, technology, and institutions on economic growth. The chapter concludes with a summary of the main findings and a list of references.

INTRODUCTION

Zeolites are crystalline aluminosilicates with uniform porous structure, in which silica and alumina tetrahedra are linked through oxygens to form a rigid three dimensional framework. The negative charges on the alumina tetrahedra are compensated by exchangeable cations. The structural formula of a zeolite for the crystallographic unit cell is expressed as :



where M is the cation of valence v, w is the number of water molecules and the ratio (y/x) usually varies from 1-5 depending upon the structure. The sum (x+y) is the total number of tetrahedra in the unit cell. The square bracket represents the rigid zeolitic framework composition.

In 1756, Baron Cronstedt¹ discovered the zeolite minerals. Damour² observed reversible dehydration, and Weigel and Steinhoff³ observed that naturally occurring chabazite adsorbed methyl and ethyl alcohol and not acetone or benzene. To account for its selective adsorption capacity McBain⁴ coined the term "Molecular Sieves" for the

zeolitic minerals. The systematic pioneering investigations in zeolites were started by Barrer⁵⁻¹¹. The work on synthesis and sorption properties established the use of zeolites as dehydrants and in separation and purification of gases and liquids. Breck, Milton and others¹²⁻¹⁷ at the Union Carbide, U.S.A., synthesized zeolites, Linde A, X and Y. Synthetic zeolites were found to be extremely active for cracking, reforming oils and other reactions^{18,19} and this marked a new era in petrochemical industry. The interest and activity in zeolitic field was increased by the addition of a new class of zeolites named ZSM(5) by Mobile group²⁰⁻²³. ZSM(5) catalysts are of commercial value for alkylation reactions and are of great potential in the conversion of methanol/ethanol to gasoline.

1.1 CLASSIFICATION

Earlier, zeolites were classified according to morphological properties; three dimensional network, lamellar and fibrous zeolites were accordingly distinguished. Smith²⁴ classified zeolites on the basis of structure and composition which is still valid in an extended form. Breck has compiled²⁵ the information in detail on classification, synthesis, structure and properties of different zeolites. The classification with characteristic

composition is summarised in Table-1, which includes seven groups namely Analcime, Faujasite, Chabazite, Harmotome, Mordenite, Heulandite and Natrolite. The zeolites are distinguished on the basis of chemical composition, structure and their related physico-chemical properties.

Faujasites consist²⁵ of Linde A, X and Y types of zeolites, which are the most useful industrial catalysts. Further discussion is limited to Y zeolites, which is of our present interest.

1.2 UNIT CELL COMPOSITION

The (crystallographic) unit cell formula for NaY zeolite is expressed as:



In Y zeolites, the number of aluminum ions per unit cell is given by,

$$N_{\text{Al}} = \frac{192}{(1 + R)}$$

where $R = (N_{\text{Si}}/N_{\text{Al}})$. In Y zeolite N_{Al} varies from 76 to 48.²⁶ The corresponding (Si/Al) ratio, R varies from 1.5 to 3.

Table-1 : Properties of some important zeolites*

General formula : $M (AlO_2)_x (SiO_2)_y \cdot a H_2O$

Name	General formula				Symmetry	Void volume cc./gm.	Aperture size $\text{\AA}$
	M	x	y	a			
<u>Analcime group</u>							
Analcime	Na	16	32	16	Cubic	0.099	2.8
<u>Faujasite group</u>							
Zeolite A	Na	12	12	27	Cubic	0.30	4.2
Zeolite X	Na	86	106	264	Cubic	0.36	8.0
Zeolite Y	Na	56	136	264	Cubic	0.36	8.0
<u>Chabazite group</u>							
Chabazite	Ca	8	16	26	Rhombohedral	0.29	3.0 x 4.3
Erionite	Ca,Mg,Na	9	27	27	Hexagonal	0.21	3.6 x 5.2
<u>Harmotome group</u>							
Phillipsite	K,Na	5	11	10	Orthorhombic	0.22	4.0
<u>Mordenite group</u>							
Mordenite	Na	8	40	24	Orthorhombic	0.14	5.8 x 7.0
<u>Heulandite group</u>							
Stilbite	K,Na,Ca	10	26	28	Monoclinic	0.22	2.6
<u>Natrolite group</u>							
Natrolite	Na	16	24	16	-	-	-

* Ref. : J. Hopper, Ph.D. Thesis (1969), Louisiana State Univ., U.S.A.

1.3 STRUCTURE

The framework of Y zeolite²⁸⁻³⁰ consists of linked truncated octahedra which are joined tetrahedrally through the six membered rings. The linkage between two truncated octahedra is a double six-ring or a hexagonal prism; containing 12(Al,Si)-O₄ tetrahedra. The restriction on the arrangement of aluminum tetrahedra is the Loewenstein stability rule²⁷ which predicts that aluminum atoms do not share the same oxygen when in tetrahedral coordination. There are 16 hexagonal prisms in each unit cell. The void of Y zeolite is divided into supercage (α cage), sodalite cage (β cage, truncated octahedron) and hexagonal prism. The pore opening to supercage is 12 membered oxygen ring of nearly 8-9 Å diameter, while the pore-opening to sodalite is 6-oxygen ring of ~ 2.2 Å. The diameter of supercage is 11.6 Å while that of sodalite is 6.6 Å.

The saturation argon adsorption²⁶ volume is about 6700 Å³, as compared to the water adsorption volume which is 7900 Å³. About 1200 Å³ per unit cell is available more for water which corresponds to 150 Å³ for each truncated octahedron and agrees well with the calculated internal volume of 157 Å³ for this polyhedron.

The characteristic unit cell parameter is nearly 24.6 Å, which changes with the number of aluminum per unit

cell.²⁶ Breck and Flanigen²⁶ established a linear relationship between unit cell parameter, a , and aluminum per unit cell which is expressed as $a = 0.00868 N_{Al} + 24.191$. N_{Al} can be determined from chemical analysis and the relation of ' a ' to (Si/Al) is given by,

$$a = \frac{192 b}{1 + (N_{Si}/N_{Al})} + c$$

where b and c are the slope (0.00868) and intercept (24.191) respectively of the linear relation. Error in a determination estimated to be ± 0.005 .

1.4 CATION SITES

The exchangeable cations occupy electrostatically favourable positions in different cages. Smith³¹ has discussed different cation sites in case of X and Y type of zeolites which is in use since then. Figure 1 shows (a) structure of sodalite unit, and (b) Y zeolite, and also (c) different cation sites. Site I (16 per unit cell) is at the centre of each hexagonal prism, site II (32 per unit cell) is slightly displaced into the supercage from a hexagonal face shared by sodalite and supercage. Site I' is displaced into the sodalite from the hexagonal face shared by sodalite and hexagonal prism. Site II' is displaced into the sodalite from the hexagonal face shared by sodalite

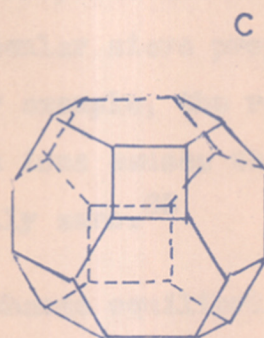
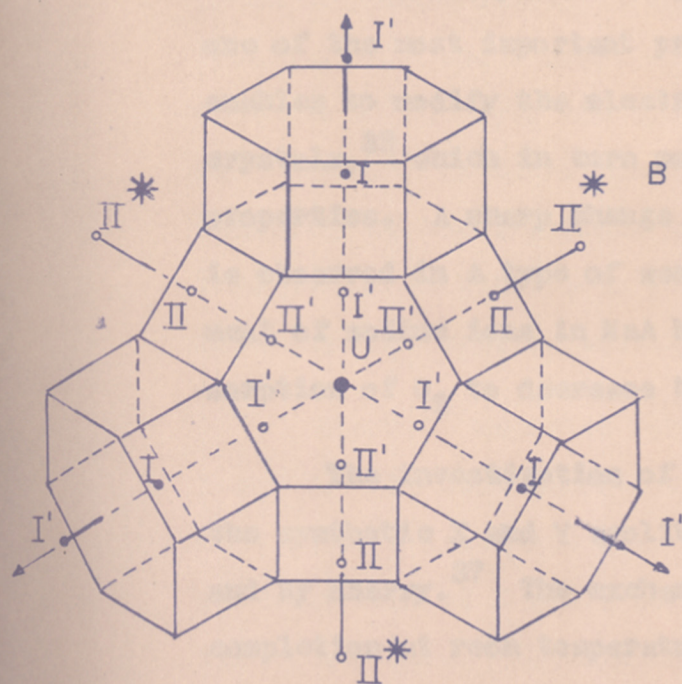
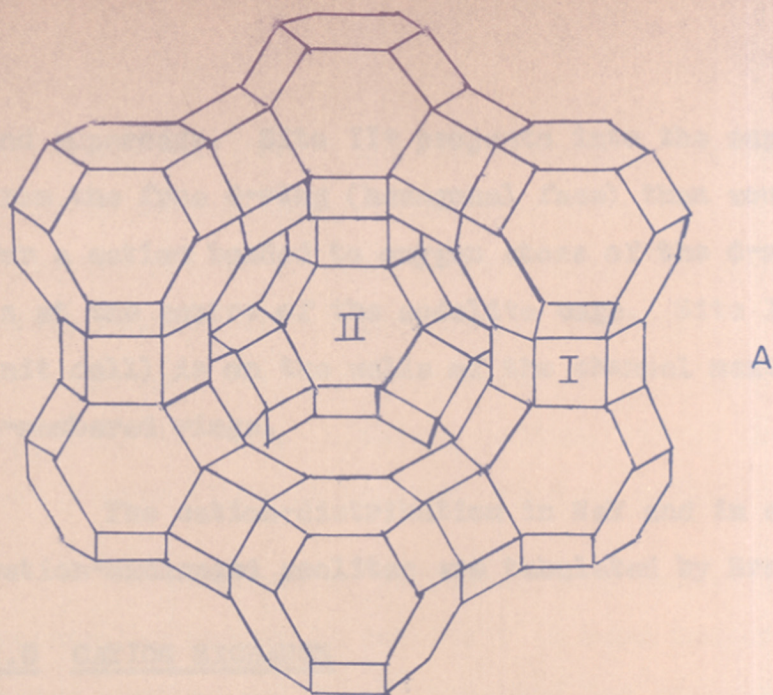


FIG. 1 : A - PERSPECTIVE VIEW OF PART OF THE FAUJASITE STRUCTURE.

I & II ARE THE CATION SITES (Ref: ²⁵13)

B - IDEALIZED PROJECTION OF SODALITE UNIT WITH CATION SITES (Ref: ³¹31)

C - SODALITE UNIT

and supercage. Site II* projects into the supercage away from the free 6-ring (hexagonal face) than would be expected for a cation bonded to oxygen atoms of the 6-ring. Site U is at the centre of the sodalite cage. Site III (48 per unit cell) is on the walls of the channel next to the 4-membered rings.

The cation-distribution in NaY and in some typical cation-exchanged zeolites are tabulated by Breck.^{25b}

1.5 CATION EXCHANGE

The ability to undergo reversible cation exchange is one of the most important properties of zeolites. It enables to modify the electric fields inside zeolite crystals,³² which in turn modifies the sorptive and catalytic properties. A sharp change in the molecular sieve properties is observed in A type of zeolites. For example, the replacement of sodium ions in NaA by potassium ions causes the sorption of O₂ to decrease to essentially zero.³³

The investigation of the ion exchange equilibria in the synthetic X and Y zeolites was done by Barrer and Rees³⁴⁻³⁶ and by Sherry.³⁷ The exchange reactions do not go to completion at room temperature, this indicates a different occupancy of cation sites in the hydrated form. The exchange with cesium, ammonium and thallium showed that about 16

sodium ions in site I are not exchanged indicating that the incoming cations are too large to penetrate the small hexagonal prisms at room temperature. The selectivity series changes with the degree of exchange. However, upto 68% exchange, the order decreases as $Tl > Ag > Cs > Rb > NH_4 > K > Na > Li$. Lithium, sodium, silver and potassium ions occupy sites in smaller cages as well.

The divalent or trivalent ions cannot completely replace the sodium in zeolite Y at room temperature.^{25b} Barrer, Davies and Rees³⁴ reported ion exchange in Y zeolite at 25°C. While Sherry³⁸ reported on alkaline earth ion exchange in X and Y zeolites over the temperature range of 5° to 50°C. Upto 82% ion exchange was reached for Ca^{2+} , Ba^{2+} and Sr^{2+} at 25°C. Sherry³⁸ has suggested that the inability of these cations to replace the last 16 sodium ions in NaY is kinetic in origin and results from an unfavourable exchange equilibria.

Sherry³⁹ reported rare earth ion exchange in zeolites X and Y. The most important point made in this work is that at 25°C lanthanum ions cannot replace 16 sodium ions per unit cell of X and Y zeolites, that is, the rate is infinitely slow. The lanthanum ion has a radius of $1.15 \text{ \AA}$ ⁴⁰ and should diffuse easily through the windows between the sodalite cages and supercages if potassium ion with a radius of $1.33 \text{ \AA}$ ⁴⁰ can do so. However, the radius of hydrated

lanthanum ion is $3.96 \text{ \AA}^{41}$. The water molecules must be stripped from the lanthanum ion if it is to pass through the window between the large and small cages. The enthalpy of hydration of lanthanum ion is about 900 to 1000 Kcal per gm. mole of ions and, although diffusion into the small cages of Y zeolites is slow at room temperature, it should be a highly temperature dependent process. Sherry³⁹ also demonstrated the electroselective effect which is operative when ions of different charges are exchanging that the zeolite preferentially selects the ion with the highest charge at low total normality and the ion with the lowest charge at high total normality. Above 90% ion-exchange may be achieved at higher temperature and repeating the ion-exchange procedure.

Theng, Vansant and Uytterhoeven⁴² reported the study of the exchange of ammonium ions and alkylammonium ions in zeolites X and Y. The maximum extent of exchange decreases with increasing molecular size of the incoming cations. If the aqueous solution of exchanging cation is highly acidic ($< 2 \text{ pH}$) which causes the destruction of zeolite, then ion-exchange should be carried out in non-aqueous media or in buffer solutions.

1.6 PHYSICO-CHEMICAL PROPERTIES

The X-ray studies^{24,29} established cubic $Fd3m$ type of structure for Y zeolites. Smith³¹ has reviewed the X-ray

studies on faujasites and discussed the positions of cations. The T(Si or Al)-O distances were determined and vary from $1.62 \text{ \AA}$ to $1.65 \text{ \AA}$ for Y zeolites depending on the cations present in the zeolite and the thermal treatment. The angles T-O-T fall mainly in the range of 130° - 155° with the hydrated forms yielding on average a smaller spread. Olson⁴³⁻⁴⁶ determined T-O distances, T-O-T angles and the distribution of cations in Na^+ , Ni^{+2} and Ce^{+3} faujasites by X-ray diffraction method.

Flanigen et al.⁴⁷ assigned the infrared bands to framework vibrations in the 200 - 1300 cm^{-1} region. With the increase of (Si/Al) ratio, the T-O bond strength increases and the corresponding shift in IR band towards higher frequency (cm^{-1}) is observed. Similarly, the effect of highly polarizable exchanged cation may broaden T-O frequency. Flanigen has reviewed the studies on IR in an excellent article.⁴⁸ Attempts⁴⁹⁻⁵³ have been made to discuss the applications of infra-red spectroscopy to zeolites. Ward^{54,55} has discussed the application of IR in the determination of acidity of various zeolites and correlation with the catalytic activity.

Depending upon the temperature of calcination and nature of cations, most of the alkaline earth, transition metal and rare earth cations show OH bands⁵⁵⁻⁶² at 3690 ,

3650 and 3540 cm^{-1} ⁵⁴ particularly. For Ca and ZnX^{59} , a band at 3750 cm^{-1} was also detected after evacuation at 450°C. The bands are attributed to different types of OH groups, e.g. to physically adsorbed water, cationic-hydroxyl groups, or Brønsted acidic OH groups. The question as to whether hydrogen on the surface of molecular sieves is mobile or localised has led to a number of investigations. ⁶³⁻⁶⁴ Most acidity studies have been made using basic molecules such as ammonia, pyridine and piperidine as probes. ^{57-59,65} These molecules have the property that their interaction with Brønsted acid sites, Lewis acid sites, cations and their hydrogen-bonding interactions give rise to different species detected by infrared spectroscopy. The adsorption on Brønsted acid sites give rise to ammonium, pyridinium and piperidinium ions with characteristic frequencies at 1475, 1545 and 1610 cm^{-1} respectively. Adsorption on Lewis acid sites - tricoordinated aluminum ions - occurs via a coordinate bond $\text{N} \cdots \text{Al}$ and gives rise to bands near 1630, 1450 and 1450 cm^{-1} . The interaction of zeolites with other molecules like CO, HCN etc. have been reported. ^{49,52,67,75} Eberly and Kimberlin ⁶⁶ related IR data with cumene cracking studies. The correlation of catalytic activity and acidic data obtained from IR have been discussed. ^{59,68}

The water-zeolite interaction and water desorption with respect to temperature have been studied ^{25c} by thermal

analysis, NMR, electrical conductivity measurements. The application of the thermal analysis to zeolites has been described by Barrer and Langley.^{69,70} The rate of dehydration, number of water molecules present at various temperatures and the destruction temperature of zeolite may be determined by thermal analysis. The proton and Na-23 resonance spectra (NMR) obtained on a dehydrated X zeolite containing varying quantities of water showed that the non-localised sodium ions form a cation solution in the water with the crystal lattice as the anion.⁷¹ The NMR studies of A and X^{72,73} zeolites revealed that the water molecules in supercages are highly mobile and the width of the NMR line varies with the amount of adsorbed water. Several studies⁷⁴⁻⁷⁷ established the application of NMR to zeolites.

1.7 ADSORPTION

Crystalline hydrates may be stoichiometric or non-stoichiometric in composition, in the non-stoichiometric group of hydrates water may be present as guest molecules in the host lattice as in zeolites. The adsorbed water molecules can be replaced by various other adsorbates depending upon the structure and sorptive properties of zeolites. A number of adsorbate molecules such as water,^{82,83} ethylene,⁷⁸ dimethylether, diethylether, benzene,⁷⁹

ammonia,⁸⁴ methanol, methylamine, carbon dioxide^{80,81} are strongly adsorbed on zeolites.

Coughlan and coworkers^{84,85} reported the adsorption of CO_2 and NH_3 on various modified A, X and Y zeolites. Egerton and Stone⁸⁶ showed that the Langmuir model gives a self-consistent description of the specific adsorption of CO on calcium exchanged Y zeolite. From stoichiometric consideration it was shown that the CO interacts with accessible calcium ions on a one-to-one basis.

Several investigators^{81,83,84} have related the type of exchange cations in zeolites with the specificity as determined by the heat of adsorption. Dzhigit et al.⁸³ showed that the differential heats of adsorption were determined to be due to the energy of interaction of water molecule with the exchange cations as well as with negative oxygen ions of the zeolite framework.⁸⁷ Isothermic heats of adsorption at zero coverage or loading were measured utilizing a gas-solid chromatographic method.⁸⁸ Initial heats of adsorption were determined from the measured retention times of various gases including O_2 , N_2 , CO, CH_4 , Xe and Kr. The change in the nature of adsorption isotherms and heats of adsorption was determined⁸⁹ using CO_2 which has a permanent electric moment, and Krypton which is non-polar. The isothermic heats of adsorption for CO_2 which were derived from the isotherms at various temperatures decreased with increasing removal of cation and framework charge.⁸⁹

Kiselev⁹⁰ has discussed molecular theory of adsorption with reference to various adsorbates and modified zeolites. Avgul et al.⁹¹ studied the heats of adsorption of ethane, ethylene and water on Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ exchanged X zeolites. Bezus et al.⁹² reported the adsorption of ethane and ethylene on X zeolites containing alkali metal cations. They have discussed the specific interaction of π -bond of ethylene with the zeolitic cations.

1.8 DIFFUSION

Comprehensive reviews of diffusion processes in zeolites have been presented by Barrer,⁹³ Timofeev⁹⁴ and Ruthven.⁹⁵ Diffusion coefficients depend mainly on the type and ionic form of the zeolite and the nature of adsorbate molecules.⁹⁶ The rate of the adsorption of argon and nitrogen on NaA zeolite decreased rapidly with decreasing temperature.^{25e} The diffusion of inert gases in KA zeolite at 300°C and above has been reported. At low temperatures most of these gases were not adsorbed by KA. The magnitude of diffusion coefficient, D_0 , increases with the increasing kinetic diameter of diffusing adsorbate.^{25e} A cooperative effect between potassium ions in A zeolite and ethane molecules was investigated. It was found that the formation of more uniform potential field resulted in a decrease in the activation energy for diffusion.⁹⁷

In one of the first studies of the kinetics of diffusion of hydrocarbons in zeolites, Barrer and Ibbitson⁹⁸ found that the apparent activation energy of diffusion in chabazite increased with the chain length of the hydrocarbon. Barrer and Peterson⁹⁹ compared the role of the aperture size in three zeolites, chabazite, erionite and CaA zeolite from the energy of interaction between the main 8-ring apertures and a normal paraffin hydrocarbon chain.

Adsorption kinetics for methane, ethane, propane and n-butane on CaA zeolite were studied gravimetrically by Ruthven and Loughlin.^{100,101} The counter diffusion characteristics of several liquid hydrocarbons in zeolites Y in Na^+ , Ca^{2+} , NH_4^+ and Ce^{3+} ion exchanged forms were measured.¹⁰² It was emphasized that the rates of diffusion processes can have a profound effect upon the apparent activity and selectivity of zeolite catalysts and upon such characteristics as dispersion and sharpness of separation in the use of zeolites in separation and purification processes.

1.9 THERMAL STABILITY

It is known^{25f} that the thermal stability of the zeolite structure increases with the Si:Al ratio. Upon calcination of ammonium zeolites, the structural stability

depends on the method of heat treatment and Si:Al ratio.¹⁰³ McDaniel and Maher¹⁰⁴ synthesized ultrastable Y zeolite and discussed their physico-chemical properties. The stabilizing effect of polyvalent cations has been related to their preferential location in the hexagonal prisms,¹⁰⁵ resulting in a more effective neutralization of those parts of the structure that have the highest charge density. The increased stability of polyvalent ion-exchanged faujasites, and therefore of the hydroxyl groups, has also been ascribed to the existence of Me-O-Me bridges filling up the sodalite cages and stabilizing them.^{49,105,106} Bremer et al.¹⁰⁷ studied the influence of cations on the thermal stability of Y zeolites. The role of aluminum in the hydrothermal treatment of ammonium-exchanged Y zeolite is discussed by Breck and Skeels.¹⁰⁸ It was reported that zeolites with low Si:Al ratio such as A and X zeolites lost their crystallinity at high percent ion-exchanges by polyvalent cations such as Ba^{2+} , Ni^{2+} , Fe^{3+} ^{25g} etc. due to extensive framework dehydroxylation. Zeolites, such as Mordenite, show high thermal stability and acid-resistance properties. Particularly, mordenite and modified ultra-stable Y zeolites are preferred for commercial use due to their high thermal stability.

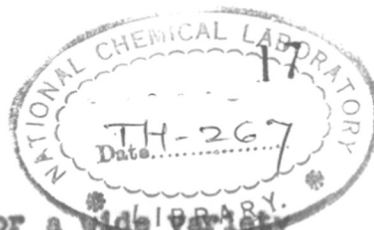
1.10 CATALYTIC PROPERTIES

Crystalline aluminosilicates are outstanding heterogeneous catalysts. Excellent reviews¹⁰⁹⁻¹¹³ have been

published on catalytic properties of zeolites.

Several studies¹¹⁴⁻¹¹⁷ on cation exchanged zeolites A, X, Y and mordenite have demonstrated the activity for C_1-C_6 n-alcohol dehydration and their dependence on cation size and valency. Bryant¹¹⁶ has demonstrated that kinetic effects in ethanol and n-butanol greatly favour olefin formation on a series of ionexchanged A zeolites and mordenite catalysts, while etherification is favoured in the corresponding X zeolites. Zeolites also show catalytic activity for displacement reactions¹¹⁸ like the gas phase conversion of ethanol and hydrogen chloride to ethyl chloride and water at temperatures from 150° to 270°C . The formation of ethylene from ethyl chloride was observed¹¹⁸ on X and Y zeolites at 260°C .

The hydrogen-transfer reactions have been observed for C_2H_4 and C_3H_6 over HY^{119,120} and for C_3H_6 and C_4H_8 over ReX¹¹⁹. In the isomerization of cyclopropane to propylene,¹²¹ a water promoted reaction, is also reported. Eberly¹²² has discussed the hydrogen transfer reactions of C_3-C_6 olefins leading to aromatic. Braun et al.¹²³ reported the isomerization of n-hexane and n-pentane over various modified zeolites. Zeolites actively catalyzed the polymerization of low molecular weight olefins.



Zeolites are versatile catalysts for a wide variety of alkylation reactions.^{119,126} The hydrogen and trivalent (rare earth) cation exchanged Y zeolites showed greater activity, as compared to the less active bivalent and monovalent cations in benzene alkylation with ethylene.¹⁰⁹ Within the bivalent cation-exchanged Y zeolites, the order $\text{Ca, Mg} > \text{Cd} > \text{Sr} > \text{Ba}$ has been observed¹⁰⁹ in benzene propylation at 250°-300°C.

In a reaction that involved fragmentation of the benzene ring, Frilette and Rubin¹²⁷ observed the formation of toluene and ethylbenzene when benzene alone was passed over H-mordenite at 400°C. The isomerization of o-xylene to m- and p-xylenes over H-mordenite at 200°-600°C and over REX at 177°-204°C has been reported.^{109,126} While trans-alkylation of polyethyl benzenes with benzene yields ethyl benzene.¹²⁶

Cumene dealkylation was studied over dehydroxylated Y zeolites,¹²⁸ and bivalent cation-exchanged X and Y zeolites.¹²⁹⁻¹³¹ The most important application of zeolites, (particularly rare earth exchanged ultrastable Y zeolite) is in the conversion of gas oil to gasoline¹³² of a high octane number.

High activity of A, X and Y zeolites has been discussed in the hydration of ethylene oxide to ethylene glycol.¹⁰⁹

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The activity of noble and transition metal zeolites has been studied in hydrogenation,¹¹⁵ hydroisomerization,¹³³ hydrodealkylation, hydrocracking and related processes.¹⁰⁹ Galich et al.^{134,135} have explored the use of zeolites as catalysts for the dehydrogenation of n-alkanes. Vemuto¹⁰⁹ has discussed various reactions including dehydrocyclisation, hydrogenation and other catalytic reactions. Jacobs¹³² has discussed bifunctional catalytic properties of zeolites at length. A few typical reactions are summarised in Table-2. Most of the reactions are catalyzed due to the acidic centers in zeolites. Few attempts¹³² have been made to explore the catalytic properties of metal dispersed zeolites. Lunsford¹³⁶ has reviewed the studies on the transition metal complexes in zeolites. However, no attempt has been made to use zeolite to heterogenise the homolytic reactions.

1.11 INDUSTRIAL PROCESSES

The industrial applications of zeolites are discussed in several articles.^{113,132,137-139} The use of zeolites as a highly versatile means of performing separations has become firmly established. The zeolites are used to remove CO₂ and H₂O from gas streams in cryogenic applications, from ethylene for high purity polymerization, to remove H₂S and low molecular weight mercaptans from natural gas, and for separation of normal paraffins, xylene separation, etc.

Table-2 : Applications of Zeolites*

Process	Probable zeolite catalysts	Competitive features
Catalytic cracking	X and Y	Improved yields. Reduced light gas and coke.
Isomerization	Y, Mordenite ZSM-5	High selectivity and resistance to high poisoning.
Catalytic reforming	Y, Mordenite	Activators unnecessary high selectivity.
Polymerization	Y	Noncorrosive
Alkylation	Y, HZSM-5	Noncorrosive, Feed treatment minimized.
Hydrodealkylation	X and Y	High activity and improved selectivity.
Hydrogenation	X and Y	Resistance to S poisoning.
Selective hydrogenation	A	Separation problems minimized.
Methanation	X and Y	High yields; resistance to poisons.
Dehydrogenation	X and Y	Improved selectivity.
Dehydration	A	Improved rates and yields.
Dehydrohalogenation	A	Molecular size selectivity.

* Ref. - P.E. Pickert, A.P. Bolton and H.A. Lanewala, Chem. Engn., 75(16), 133 (1968).

The other important industrial applications of zeolites are in catalytic cracking, hydroisomerization, selective forming, hydrocracking and transformations of aromatic hydrocarbons. In catalytic cracking (FCC), for the conversion of gas oil to gasoline, rare earth-H exchanged Y zeolite (ultrastable) is the most widely used catalyst with better performance.^{132,140} In hydroisomerisation reactions, noble metal dispersed zeolite is used. Zeolites are also being used in disproportionation of toluene to benzene and xylene, and in the isomerization of xylenes to p-xylene. Other industrial applications such as in alkylation (preparation of ethyl benzene) are at various stages of research and development.

It is well-known that transition metals in zeolites show catalytic activities in their cationic forms for a variety of reactions such as oxidation,^{141,142} cyclotrimerization of acetylene,¹⁴³ amination of chlorobenzene,¹⁴⁴ hydrogenation¹⁴⁵ and polymerization.¹⁴⁶ The catalytic activity of iron zeolites in ammonia synthesis^{147,148} and oxidation of CO¹⁴⁹ has been reported. It has been assumed that in catalytic oxidation of CO, the oxygen associated with the ferric ion takes part. In the cracking of n-hexane ferric zeolites were found¹⁵⁰ to be more active than ferrous; the Y zeolite being more active than the X type. Iron containing zeolites have also been used¹⁵¹ to adsorb H₂S evolved during the vulcanization of rubber.

Iron zeolite is reported¹⁵² to be an excellent oxygen carrier adsorbing 3.5 times the amount of oxygen held by haemoglobin. Due to the reversible oxidation-reduction behaviour of iron ions, the iron zeolites would be ideal for oxidation-reduction reactions. On account of the redox behaviour, their ability to form coordination complexes and special catalytic properties, we have prepared a series of ferric exchanged zeolites and studied their physico-chemical and acidic properties. We report the above data along with their catalytic activity for oxidative dehydrogenation reaction in this thesis.

CHAPTER - II : PHYSICO-CHEMICAL CHARACTERISATION

2.1 INTRODUCTION

Synthetic zeolites exchanged with Fe^{3+} ions are good acidic catalysts. However, the loss of crystallinity and thermal stability is reported for these zeolites. The difficulties in preparing ferric exchanged zeolites without breakdown were discussed in detail.^{153,154} Malashevich and coworkers¹⁵⁵ found that zeolites with low silica content, type A and X, retain their crystalline structure upto 15-17% substitution of sodium by ferric ions. Morrice and Rees¹⁵⁶ reported that exposure of zeolites to $\text{Fe}(\text{NO}_3)_3$ solution for a short time enabled Fe exchange without decomposition. Delgass et al.¹⁵⁷ reported that ferrous exchanged zeolites could be prepared without structure breakdown by first exchanging with FeSO_4 under a nitrogen stream and further oxidizing the Fe^{2+} to Fe^{3+} .

According to Malashevich and coworkers¹⁵⁵ ferric ion enters the zeolite cavity as $[\text{Fe}(\text{OH})_2]^{+1}$ at pH 7.6 while at pH 4 it enters as $[\text{Fe}(\text{OH})]^{2+}$. It appears that the distribution of such species depends on the temperature and influence the extent of structure breakdown. Badran et al.^{153,158} obtained ferric ion exchanged X and A zeolites using an ethereal solution of $\text{Fe}(\text{SCN})_3$ and buffer solutions. The loss of crystallinity appears to be dependent on both temperature and pH of the solution used for ion-exchange.

Attempts have been made to understand the structural aspects of iron exchanged zeolites, particularly by Mossbauer^{152,157,159} spectroscopy. Morice and Rees¹⁵⁶ observed a change in the oxidation state of iron ($\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$) upon dehydration in vacuum. Exposure of the sample to air caused reoxidation of ferrous ions to ferric ions, and gave a spectrum similar to that of the fresh Fe^{3+}Y sample. Goldanskii and coworkers^{160,161} also observed the change of oxidation state from Fe^{3+} to Fe^{2+} on thermal treatment. These authors further suggested that the adsorption process led to a localization of ferrous ions which were present in the zeolite in an unbound state before the adsorption.

Boudart and coworkers^{152,162} by Mossbauer and infra-red spectroscopy established the redox behaviour of iron in Y zeolite. They observed the oxidation of ferrous to ferric at higher temperatures in air, reduction of ferric to ferrous at 400°C by hydrogen and to ferric ions on adsorption oxygen at 400°C . They discussed the redox behaviour and dehydroxylation of possible $[\text{Fe}(\text{OH})]^{2+}$ species in the zeolites, and proposed the presence of $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{3+}$ inside the sodalite cages after the thermal treatment. The existence of $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{3+}$ is supported by a characteristic band for the linkage at 895 cm^{-1} in the infra-red spectrum of thermally treated iron Y zeolite.

Nesterov et al.¹⁶³ observed that the ESR spectra of fresh FeNaY specimen hardly differed from those of hydrated NaY while dehydrated FeNaY samples showed a line with $g = 4.31$, the intensity of which increased with the dehydration temperature upto 450°C . They concluded that after cation exchange, ferric ions are located in supercages in hexa-aquo form with octahedral symmetry. But with increasing dehydration temperature ($> 500^{\circ}\text{C}$) ferric ions penetrate into the small cavities. Bobrov et al.¹⁴⁹ studied the catalytic activity of iron zeolites in relation to carbon monoxide oxidation and characterised the catalysts by ESR and magnetic susceptibility methods. They concluded from the data that the main mass of iron in the zeolite is of paramagnetic nature and supported $\text{Fe}^{3+} - \text{O}^{2-} - \text{Fe}^{3+}$ linkages after heat treatment.

It was of interest to investigate the nature of aquocomplex of iron, the exact temperature at which the dehydroxylation of $[\text{Fe}(\text{OH})]^{2+}$ takes place, the cation site distribution in hydrated and dehydrated forms, migration of ferric ions and thermal stability of ferric exchanged Y zeolites with respect to different percent ferric exchanges, which we report in this Chapter.

2.2 EXPERIMENTAL

2.2A Preparation

Linde NaY zeolite, binder free, (SK-40, Lot No. 96805000) obtained from the Union Carbide, U.S.A., was used as the starting material for catalyst preparation. The Fe^{3+} exchanged zeolites were prepared by treating NaY with aqueous solutions of ferric acetate-acetic acid at about 4 pH at 27-30°C, with constant stirring. After cation exchange, zeolite was filtered, washed with distilled water several times till free of acetate ions and dried in the oven at about 120°C for about 20 hours, cooled and kept over saturated ammonium chloride solution in a dessicator at 25°C for a week. The highest exchange sample was prepared by carrying out the ion exchange process for three times at 80°C.

The lower exchanged Fe^{3+} Y were obtained within twenty minutes with appropriate concentrations of ferric acetate. Upto 75 % exchange, the samples were prepared in single ion exchange process indicating that the exchange of sodium ions present in supercages by ferric ions is thermodynamically favourable process. This is due to the fact that the hydration energy of Fe^{3+} ion is higher than that of sodium ion.

However it was difficult to exchange sodium in the zeolite above 82%, because bulky hydrated ferric ions do not enter into hexagonal prisms to replace sodium ions present at site I. Probably higher ($>82\%$) exchange can be achieved by heating the ferric exchanged sample above 400°C in air and subsequently carrying out ion exchange at higher temperature. Due to thermal treatment, dehydrated ferric ions enter into smaller cages and sodium ions come into supercages. A successful attempt was also made to prepare ferric exchanged Y zeolites in non-aqueous solutions. Ferric chloride or nitrate which forms highly acidic solutions in water, may destroy zeolite, therefore cannot be used for ion-exchange. Ferric exchanged Y zeolites were prepared by treating NaY with the ferric chloride ethanolic solution. The X-ray diffraction patterns showed that the zeolite samples prepared in non-aqueous media were highly crystalline.

2.2B Chemical analysis

The zeolite powder was treated with 1:1 hydrochloric acid and evaporated to dryness. After dehydration at 120°C the silica was first estimated by the conventional gravimetric method. To ensure complete removal of silica the filtrate was evaporated and the above procedure was repeated. From the filtrate some portion was used for sodium estimation

by flame photometry. The remaining filtrate was treated with 1N NaOH to separate out iron from aluminium. Aluminium will remain in solution as sodium aluminate. While iron precipitate was collected and iron was estimated by gravimetrically, volumetrically and by atomic absorption spectrometrically. The ion exchanged samples were also examined for dealumination. No dealumination was detected. The chemical compositions of ion-exchanged zeolites are summarised in Table-4.

2.2C X-ray diffraction

The X-ray powder diffraction patterns of hydrated zeolite samples were recorded on a Philips X-ray diffractometer Model PW 106000, using CuK_{α} radiation ($\lambda = 1.5405 \text{ \AA}$).

2.2D Thermal analysis

All thermograms were recorded under identical conditions on an automatic Hungarian derivatograph (Model - MOM-102) described by Paulik et al.¹⁶⁴ The thermograms were recorded under the following conditions:

1. Sample weight - 300 mg.
2. Heating rate - 6°C/minute
3. Sensitivity
 - (a) DTA - 1/1
 - (b) DTG - 1/3
 - (c) TGA - 300 mg.
4. Pressure - air suction

Pre-heated and finely powdered alumina was used as a reference material.

2.2E Infra-red spectra

The infrared spectra were recorded in the frequency range of $250-1300\text{ cm}^{-1}$ using Perkin-Elmer 221 spectrometer. The nujol mull or the KBr pellets of the hydrated samples were used for recording the spectra.

2.2F Visible spectra

The visible spectra were recorded at room temperature in the range of 200-800 nm using Specord UV-VIS, Carl-Zeiss Spectrometer. The KBr pellets of the hydrated samples were used for recording the spectra.

2.2G Thermal stability

To investigate the effect of thermal treatment, NaY, FeNaY(37) and FeNaY(82) zeolites were heated at 500°C for 2, 5 and 10 hours. The final temperature, 500°C , was achieved at a heating rate of 5°C per minute. After thermal treatment, the samples were cooled and kept over saturated ammonium chloride solution in a dessicator for a week and the X-ray diffractograms and DTA, TGA curves of the samples were obtained.

2.2H Electrical conductivity

The conductivity cell shown in Figure 2 was made up of silica tube. The conductivity measurements were performed using platinum electrodes of 1 cm diameter. All the pellets (1 cm. dia., ~ 0.4 mm thickness and 1 gm. weight) were prepared using a pressure of 20000 lbs./sq.inch. The silver paste was applied onto both the sides of the pellet for good electrical contacts. The temperature of the pellet was measured by chromel-alumel thermocouple placed near the pellet. The readings were recorded on a LCR-bridge at different temperatures in the range of 25° - 600° C. The reproducibility of the results was checked for different pellets.

2.2I X-ray photoelectron spectroscopy

The spectra were recorded on an ESCA-III V.G. Spectrometer. The exciting radiation was AlK_{α} with an energy of 1486.6 eV. The spectral resolution of the analyzer was ~ 0.50 eV. The binding energy of the electrons was determined within ± 0.2 eV. The pressure in the analyser chamber was 10^{-8} torr. For standardisation, the C 1s peak from condensed diffusion oil vapour was used. The value of binding energy for C 1s was taken to be 285.0 eV. $Au 4f_{7/2}$ 83.8 eV was also used as a standard

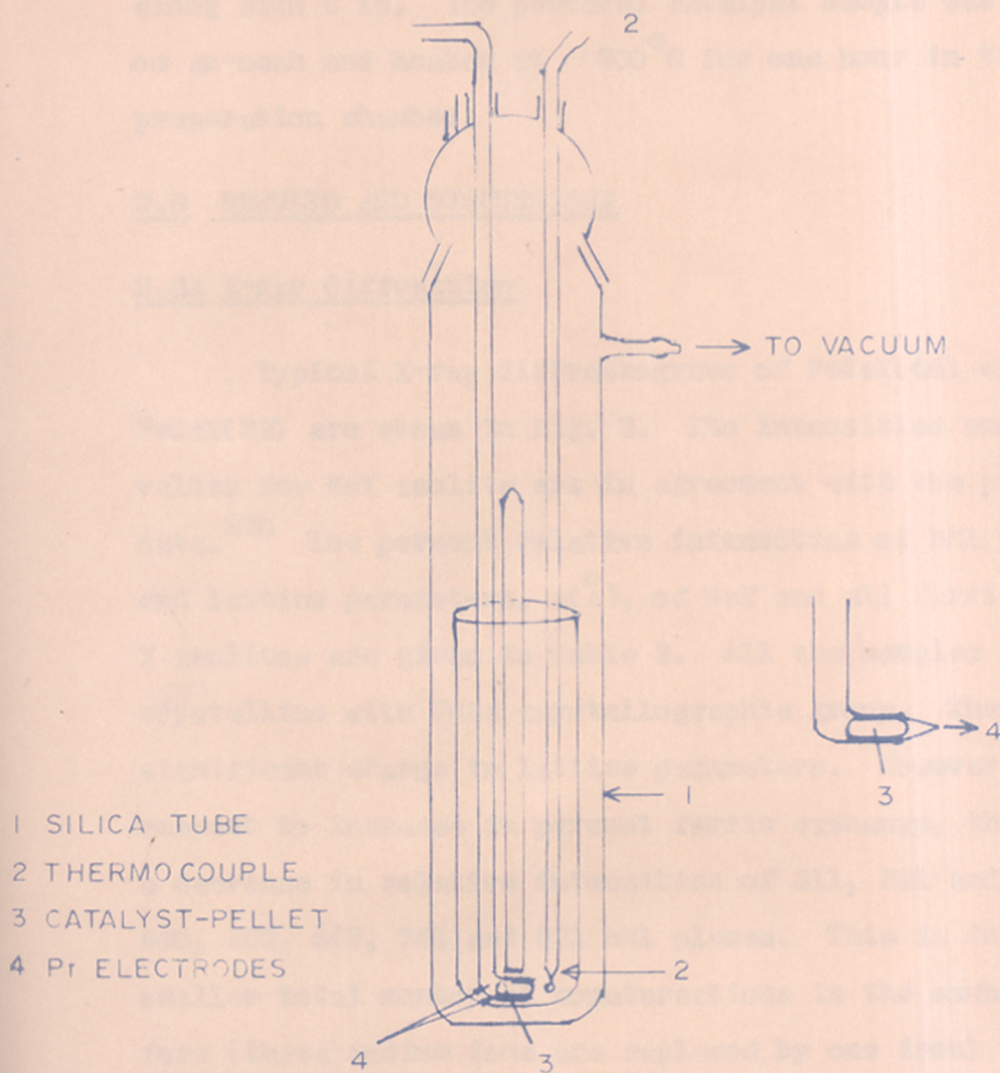


FIG.2 : SCHEMATIC DIAGRAM OF CONDUCTIVITY CELL.

along with C 1S. The powdered catalyst sample was pressed on Au-mesh and heated at $\sim 200^{\circ}\text{C}$ for one hour in the preparation chamber.

2.3 RESULTS AND DISCUSSIONS

2.3A X-ray diffraction

Typical X-ray diffractograms of FeNaY(44) and FeNaY(82) are shown in Fig. 3. The intensities and 2θ values for NaY zeolite are in agreement with the published data.^{25h} The percent relative intensities of hkl planes and lattice parameters, $a(\text{\AA})$, of NaY and all ferric exchanged Y zeolites are given in Table 3. All the samples are crystalline with Fd3m crystallographic group. There is no significant change in lattice parameters. However, with respect to increase in percent ferric exchange, there is a decrease in relative intensities of 311, 331 and 511, 440, 533, 642, 751 and 551 hkl planes. This is due to the smaller total number of counteranions in the exchanged form (three sodium ions are replaced by one iron) and to the fact that the ionic radius of Fe^{3+} is smaller than that of Na^{+} . From the changes in the relative intensities of the diffraction maxima it may be concluded that the replacement of Na^{+} by Fe^{3+} is not isomorphous. Considering 533 plane which is least affected by ion-exchange with

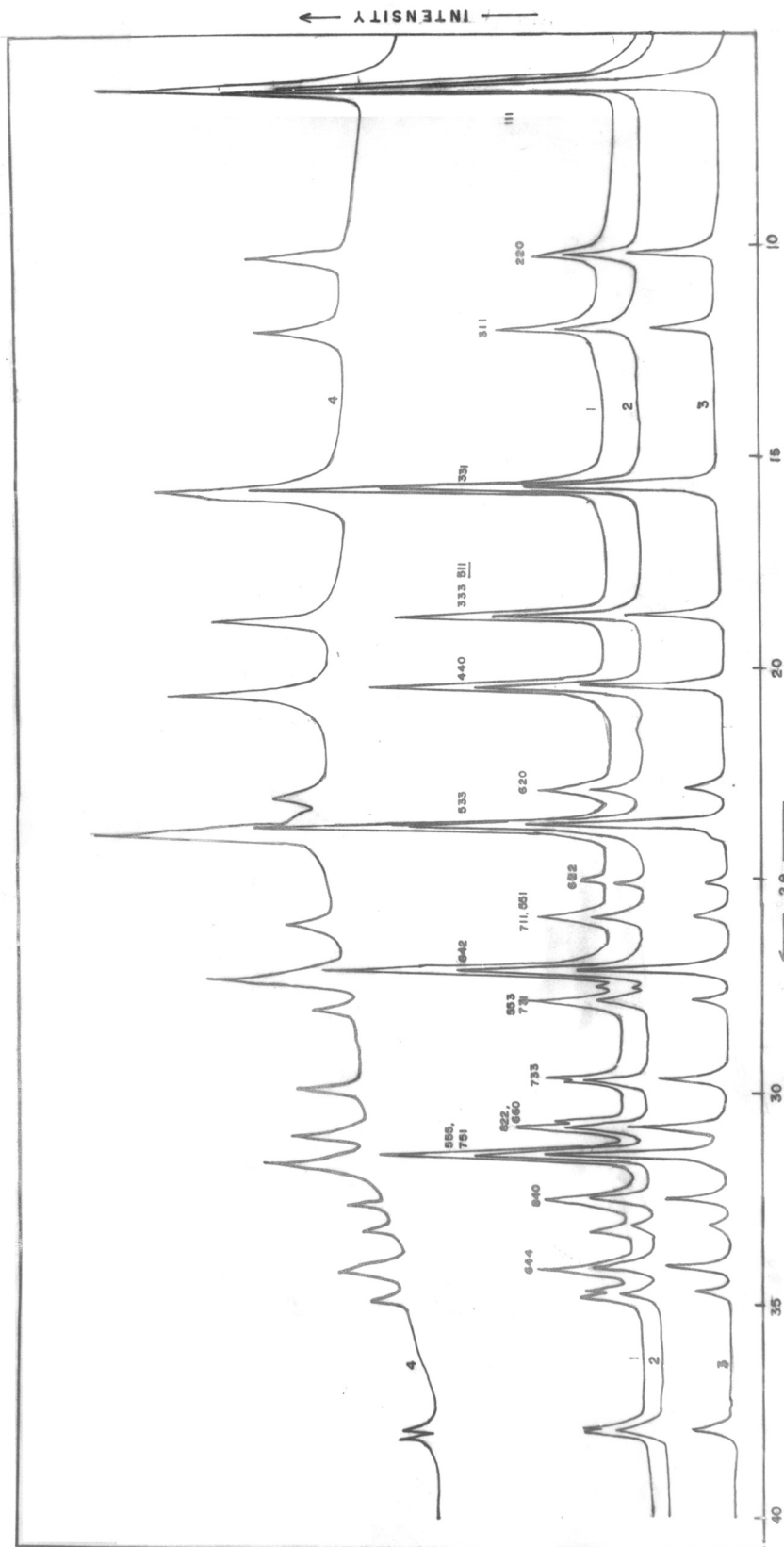


FIG. 3. TYPICAL X-RAY DIFFRACTOGRAMS OF ZEOLITES (1) NaY, (2) FeNaY (82), (3) FeNaY (82), (4) FeNaY (82, 500, 10)

Table-3 : X-ray intensities and
unit cell constants

	NaY	FeNaY(37)	FeNaY(44)	FeNaY(61)	FeNaY(75)	FeNaY(82)
$a \text{ \AA}$	24.601	24.586	24.617	24.594	24.573	24.614
hkl						
111	100.0	100.0	100.0	100.0	100.0	100.0
220	20.2	19.1	19.2	19.8	21.4	24.1
311	24.6	22.0	38.5	19.2	20.1	17.7
331	90.2	85.1	95.4	67.0	56.5	57.7
333 & 511	54.7	53.0	60.8	36.8	29.2	27.7
440	60.7	52.4	60.0	41.8	37.7	41.2
620	19.1	19.6	23.9	14.3	13.6	12.9
533	89.1	81.6	99.2	64.8	62.3	55.9
711 & 551	18.0	17.9	26.2	14.8	13.6	10.6
642	75.4	68.5	61.5	48.4	42.2	40.0
553 & 731	20.8	17.9	33.1	9.9	13.0	11.2
733	17.5	18.5	24.6	17.6	15.6	20.0
822 & 660	27.3	25.6	24.6	22.0	19.5	23.2
751 & 555	61.2	56.0	57.7	43.9	45.5	49.4
840	20.8	20.8	26.9	17.6	16.9	18.8
664	22.9	22.6	26.9	16.5	16.9	17.7

reference to NaY, at higher ferric exchanges, the distortion of framework due to Fe^{3+} ions may be possible explanation for the decrease in intensities.

2.3B Thermal analysis

Fig. 4 shows typical thermograms for NaY and FeNaY. In Table-4 peak temperatures for all the samples are presented.

The NaY zeolite shows a single endothermic peak corresponding to the dehydration of water at 80° - 320°C . The exothermic peak corresponding to the structure breakdown of the zeolite is at 842°C . On the other hand, the DTA curves for the iron exchanged zeolites show three endothermic peaks between 160° - 400°C and one exothermic peak at 840° - 870°C .

FeNaY(37), FeNaY(44), FeNaY(61) and FeNaY(75) (where the numerical figure in the parenthesis indicates % Fe^{3+} exchange) show the first endothermic peak maxima at 165, 170, 160 and 160°C respectively corresponding to the desorption of physically adsorbed and weakly chemisorbed water on to the framework oxygens through O---H linkages. In case of higher exchanged FeNaY(82), this peak shows further splitting with peak maxima at 110°C and 160°C . Second endothermic peak is at 290°C which is due to desorption

Table-4 : Composition of samples and peak temperatures in DTA

Zeolite	Unit cell composition	Endothermic peak °C			Exo-thermic peak °C
		First peak	Second peak	Third peak	
		°C	°C	°C	
NaY	$\text{Na}_{57}(\text{AlO}_2)_{57}(\text{SiO}_2)_{135} \cdot (268\text{H}_2\text{O})$	180	-	360	240
FeNaY(37)*	$\text{Fe}_7\text{Na}_{39}(\text{AlO}_2)_{57}(\text{SiO}_2)_{135} \cdot (269\text{H}_2\text{O})$	165	290	395	370
FeNaY(44)	$\text{Fe}_{8.4}\text{Na}_{29.6}(\text{AlO}_2)_{57}(\text{SiO}_2)_{135} \cdot (270\text{H}_2\text{O})$	170	290	400	370
FeNaY(61)	$\text{Fe}_{11.6}\text{Na}_{19}(\text{AlO}_2)_{57}(\text{SiO}_2)_{135} \cdot (250\text{H}_2\text{O})$	160	290	400	360
FeNaY(75)	$\text{Fe}_{13.5}\text{Na}_{12.7}(\text{AlO}_2)_{57}(\text{SiO}_2)_{135} \cdot (228\text{H}_2\text{O})$	160	290	400	350
FeNaY(82)	$\text{Fe}_{15.6}\text{Na}_{11.2}(\text{AlO}_2)_{57}(\text{SiO}_2)_{135} \cdot (252\text{H}_2\text{O})$	110 a 160	295	395	350

* The bracketed figure signifies the percent ferric exchange.

ΔT
 — EXO —
 — ENDO —

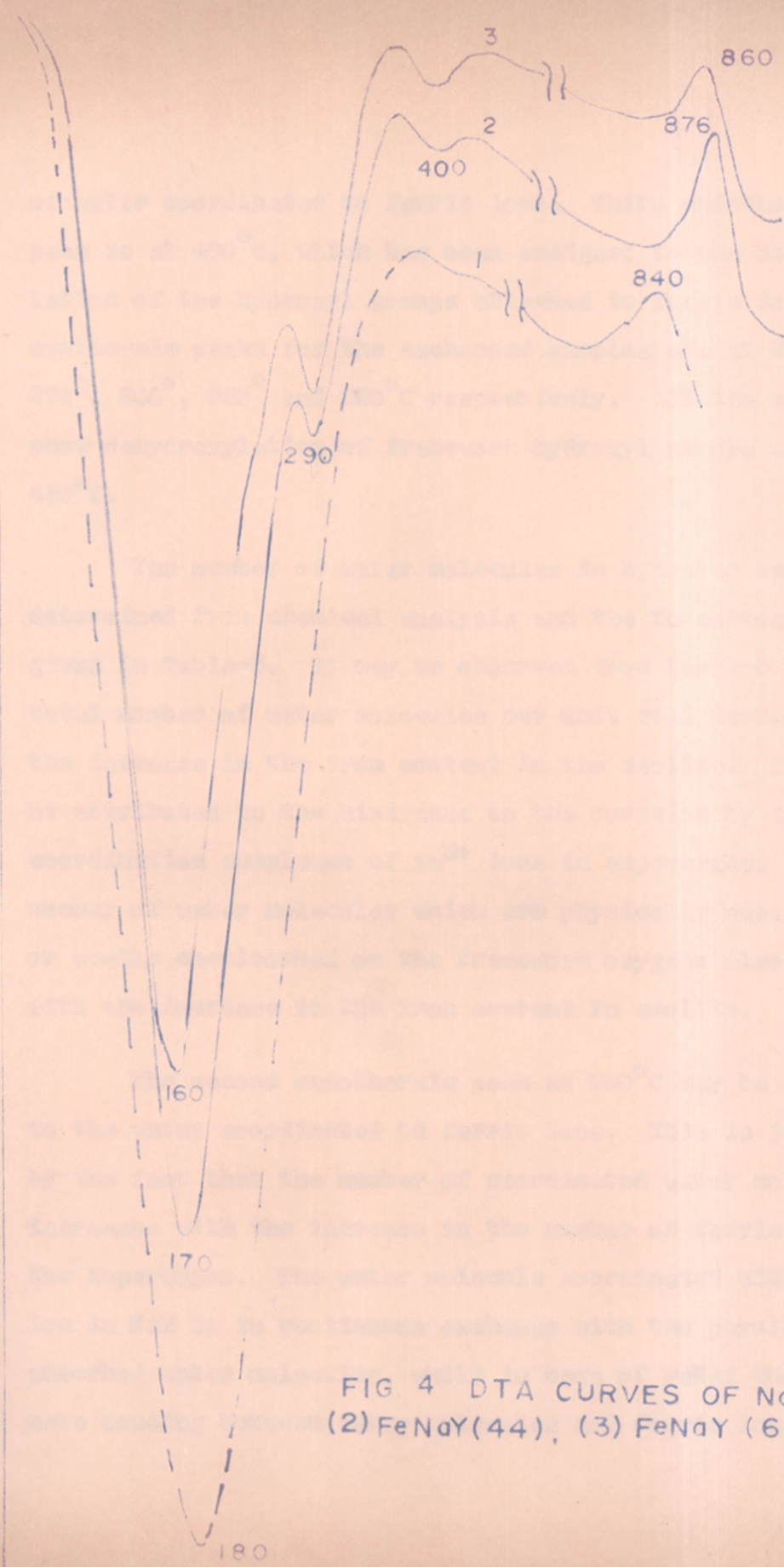


FIG 4 DTA CURVES OF NaY (dotted),
 (2) FeNaY(44), (3) FeNaY (61)

of water coordinated to ferric ions. Third endothermic peak is at 400°C , which has been assigned to the dehydroxylation of the hydroxyl groups attached to ferric ions. The exothermic peaks for the exchanged samples are at 370° , 370° , 360° , 350° and 350°C respectively. All the samples show dehydroxylation of framework hydroxyl groups after 450°C .

The number of water molecules in hydrated samples determined from chemical analysis and the TG curves are given in Table-5. It may be observed from Table-5 that total number of water molecules per unit cell decreases with the increase in the iron content in the zeolite. This may be attributed to the hindrance to the sorption by the coordination complexes of Fe^{3+} ions in supercages. The number of water molecules which are physically adsorbed or weakly chemisorbed on the framework oxygens also decreases with the increase in the iron content in zeolite.

The second endothermic peak at 290°C may be ascribed to the water coordinated to ferric ions. This is justified by the fact that the number of coordinated water molecules increases with the increase in the number of ferric ions in the supercages. The water molecule coordinated with Na^{+} ion in NaY is in continuous exchange with the physically adsorbed water molecules, while in case of FeNaY the coordinate bonding between water molecules and ferric ion is

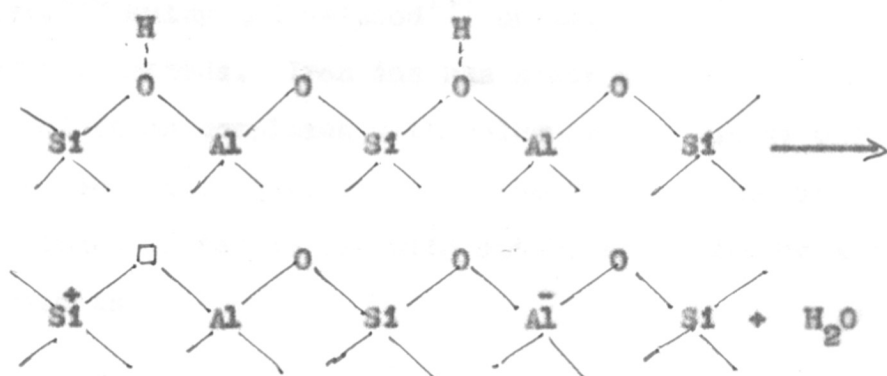
Table-5 : Per cent weight loss and number of water molecules desorbed per u.c.

Zeolite	Number of ferric ions per unit cell	Per cent weight loss				
		Total ignition method	Total TG method	First peak	Second peak	Third peak
						After 480°C
NaY	-	27.91	27.50 (263.00)*	26.00 (253.4)	-	1.50 (14.6)
FeNaY(37)	7.1	27.24	27.50 (269.5)	22.00 (215.7)	3.00 (29.4)	1.50 (14.7)
FeNaY(44)	8.4	27.40	27.00 (269.9)	21.66 (216.6)	3.00 (30.0)	1.54 (15.4)
FeNaY(61)	11.6	26.40	26.34 (251.0)	19.66 (187.3)	3.48 (33.2)	1.38 (17.9)
FeNaY(75)	12.7	24.90	25.20 (228.0)	18.40 (166.5)	3.60 (32.6)	1.34 (16.6)
FeNaY(82)	15.6	26.28	26.33 (251.5)	18.66 (178.2)	4.33 (41.4)	2.00 (19.1)

* The values given in the parentheses indicate the number of water molecules desorbed per unit cell.

sufficiently strong to make them thermally distinct as compared to other molecules. This is supported¹⁶⁵ by the values of water solvation energies of Fe^{3+} ion (1385 KJ/mole) which is very much larger as compared to that of Na^+ ion which is 403 KJ/mole.

The third endothermic peak at 400°C is due to the dehydroxylation of OH groups attached to ferric ions. The number of water molecules corresponding to this peak increases approximately in 1:1 ratio with the increase in the number of ferric ions. This observation is used to explain the process of dehydroxylation. The dehydroxylation after 450°C is due to the removal of framework oxygens and Bronsted acid centres, represented as



Aquocomplex of iron

The first endothermic peak with a maximum at about 170°C is a characteristic property of all the zeolites. The Fe^{3+} exchanged zeolites showed a second distinct peak at 290°C . Morice and Rees¹⁵⁶ and Garten et al.¹⁵² observed that on sorption of water there was a decrease in the quadrupole splitting in the Mossbauer spectra indicating an increase in symmetry around iron ion. This shows that the sorbate molecules are occupying vacant coordination positions around these ions. Mossbauer studies¹⁵² support solvated ferric ions having octahedral symmetry in hydrated state.

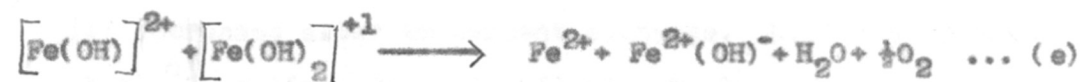
Aquocomplexes of iron ions in water were characterised by Sillen,¹⁶⁶ Mulay and Selwood¹⁶⁷ by magnetic susceptibility and spectral methods. Iron ion has a strong tendency to form coordination complexes with molecules or anions which can share lone pair of electrons. The dissociation of hexa-aquo complexes of ferric ion with octahedral symmetry may be represented as



This complex has an octahedral symmetry and can exist only in supercages.

Dehydroxylation

Third endothermic peak at 400°C may be attributed to the dehydroxylation of hydroxyl groups attached to ferric ions. Mossbauer studies¹⁵² also support the dehydroxylation process around 400°C. The simultaneous analysis of DTA and TG indicates that during dehydroxylation approximately one molecule of water is desorbed per ferric ion. The dehydroxylation of $[\text{Fe}(\text{OH})]^{2+}$ may be represented by the following processes:



Reactions (a) to (e) have been proposed and discussed by Garten et al.¹⁵² Based on the TG data, ^(Table-5) we propose reaction (f) for dehydroxylation process, along with reactions (a) and (b).

Reactions (c), (d) and (e) however do not explain the thermal data satisfactorily. The quantitative measurements of Bronsted acid centres before and after the dehydroxylation may give clue for the possibility of reaction (f).

Cation distribution

The cations can occupy different sites in zeolite cages. The cations occupying sites I' and II' in sodalite cages have tetrahedral symmetry. The aquocomplex $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ has octahedral symmetry, and considering the steric factor this complex should exist in the super-cages near site II.

In case of hydrated FeNaY(44), about 8 ferric ions are present per unit cell. Out of 8 ferric ions, 6 ions should be in the supercages which explains the liberation of 30 water molecules corresponding to second endothermic peak. ^(Table-5) The remaining two cations may occupy the site I' or II' in the sodalite cages. The occupancy of sites I, I' or II' increases after 44 percent exchange. During dehydration at 400°C, cations from site II migrate to site II' or possibly few may occupy site I in hexagonal prism. The migration of cations is supported by the adsorption studies of Coughlan and Kilmartin.¹⁶⁸ The cation distribution in hydrated state is summarised in Table-6.

Table-6 : Cation distribution (in hydrated state)

Zeolite	Ferric ions		Sodium ions	
	Site II*	Sites I, I' or II'	Site II	Sites I, I' or II'
NaY	-	-	32	26
FeNaY(37)	6, 29H ₂ O	1	14	23
FeNaY(44)	6, 30H ₂ O	2	14	18
FeNaY(61)	6.6, 33H ₂ O	5	12	8
FeNaY(75)	6.6, 33H ₂ O	7	12	5
FeNaY(82)	8.2, 41H ₂ O	7.4	7	4

It may therefore be concluded from the present studies that quantitative data on the coordination complexes of transition metal ions which exist in the supercages of zeolites can be evaluated from careful thermal analysis.

Kinetics of water desorption

A number of non-isothermal methods have been proposed and summarized in several review articles.^{169,170,171} The methods fall into two distinct approaches for the determination of kinetic parameters from thermogravimetric measurements. The two approaches are the differential and the integral methods. These methods use the general non-isothermal kinetic equation,

$$\frac{d\alpha}{dt} = \left(\frac{A}{a}\right) (\exp - E/RT) \cdot f(\alpha) \quad \dots (1)$$

where $a = (dT/dt) =$ linear heating rate ($^{\circ}\text{C}/\text{min.}$),

$A =$ Arrhenius pre-exponential factor,

$R =$ gas constant,

$(d\alpha/dt) =$ the rate of loss per degree,

$\alpha =$ fractional weight loss

$f(\alpha) =$ function of the weight loss.

Freeman and Carroll method :

Freeman and Carroll¹⁷² introduced a differential method based on equation (1) with the arbitrarily chosen

Table-7 : Kinetic parameters for dehydration
of zeolites

Zeolite	Order of reaction (n)			Energy of activation for first peak Kcals/mole	Rate constant K_1 (arbit.units)
	First peak	Second peak	Third peak		
NaY	1.23	-	-	5.58	0.97
FeNaY(37)	0.99	-	-	5.46	0.92
FeNaY(44)	1.18	1.13	1.40	5.98	1.68
FeNaY(61)	1.26	0.99	1.26	5.32	1.98
FeNaY(75)	1.17	1.26	1.61	5.86	1.97
FeNaY(82)	1.18	1.02	1.03	4.23	1.78

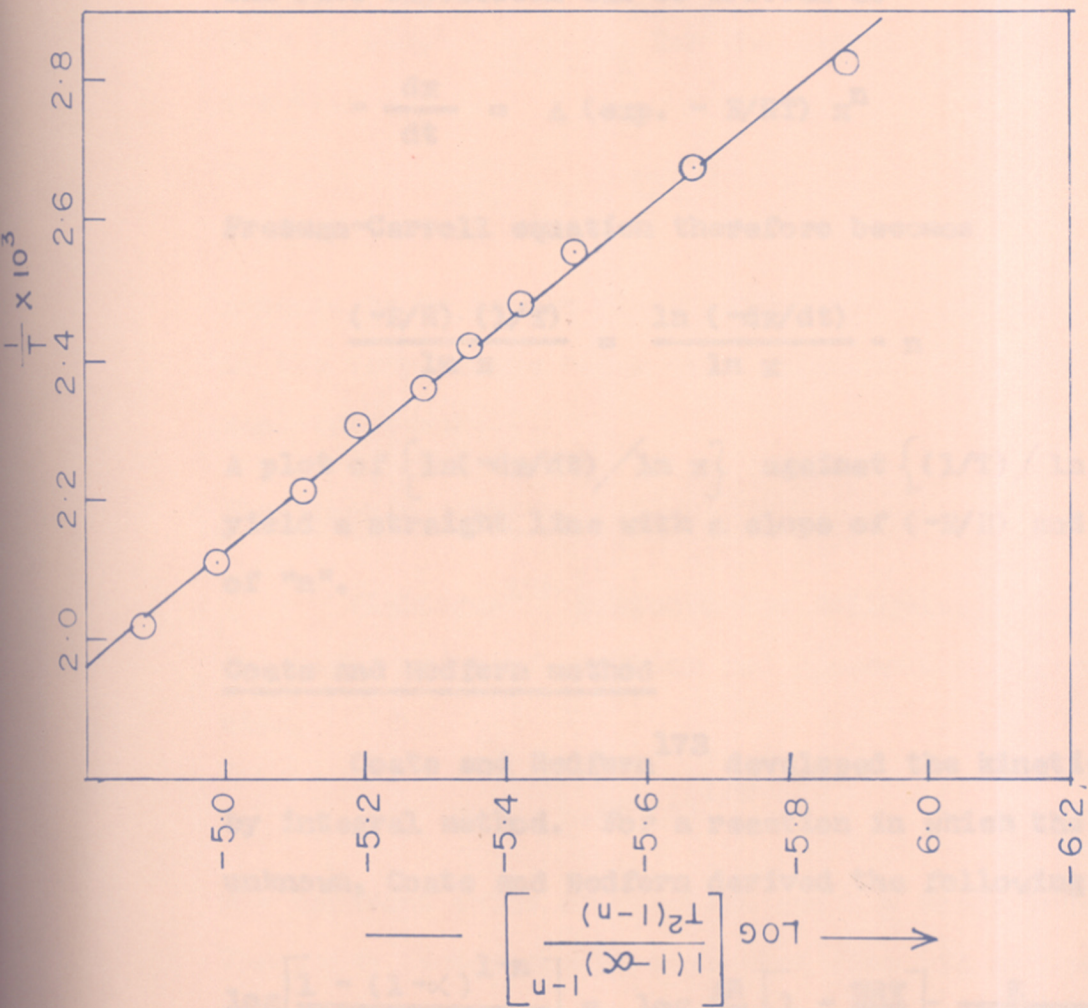


FIG - 5 COATS - REDFERN PLOT OF FeNaY(60)

$f(x) = x^n$, where x is the mole fraction of the reactant and n is apparent order of reaction. In analogy with homogeneous kinetics:



The rate expression can be written as

$$-\frac{dx}{dt} = A (\exp. - E/RT) x^n \quad \dots (2)$$

Freeman-Carroll equation therefore becomes

$$\frac{(-E/R) \cdot (1/T)}{\ln x} = \frac{\ln (-dx/dt)}{\ln x} - n \quad \dots (3)$$

A plot of $\{\ln(-dx/dt)/\ln x\}$ against $\{(1/T)/\ln x\}$ should yield a straight line with a slope of $(-E/R)$ and intercept of " n ".

Coats and Redfern method

Coats and Redfern¹⁷³ developed the kinetic equation by integral method. For a reaction in which the order is unknown, Coats and Redfern derived the following equation:

$$\log \left[\frac{1 - (1-x)^{1-n}}{T^2 (1-n)} \right] = \log \frac{AR}{aE} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.303 RT} \quad \dots (4)$$

where α is the fraction of the sample decomposed at time 't' and 'a' is the heating rate. A plot of either

$$\log \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2 (1 - n)} \right] \text{ against } (1/T) \text{ or where } n = 1,$$

$\log \left[\frac{-\ln (1 - \alpha)}{T^2} \right]$ against $(1/T)$ should result in a straight line of slope $-\frac{E}{2.303 R}$ for the correct value of n. The quantity

$$\frac{AR}{aE} \left[1 - \frac{2RT}{E} \right]$$

appears to be reasonably constant for most values of E and in the temperature range over which water desorption in zeolites occurs.

Kissinger's method

Kissinger¹⁷⁴ proposed the following equations to calculate order of reaction and apparent energy of activation,

$$n = 1.26 (S)^{1/2} \quad \dots (5)$$

n = apparent order of reaction and S = shape index factor. The index factor can be evaluated from DTA as described by Kissinger.

$$\frac{d \left(\ln \frac{a}{T_m^2} \right)}{d \left(\frac{1}{T_m} \right)} = - \frac{E}{R} \quad \text{..... (6)}$$

where T_m = peak temperature and a = heating rate. The plot of $\left(\ln \frac{a}{T_m^2} \right)$ against $(1/T_m)$ should be linear.

Piloyan and Novikova equation¹⁷⁵

$$\ln \Delta t = C - \frac{E}{RT} \quad \text{..... (7)}$$

The plot of $(\ln \Delta t)$ against $(1/T)$ should give a slope equal to $(-E/R)$.

Ozawa method

Ozawa¹⁷⁶ proposed the following equation:

$$\log a + 0.4567 \frac{E}{RT_m} = \text{constant} \quad \text{..... (8)}$$

The plot of $(\log a)$ against $(1/T)$ should give a slope equal to $(0.4567E/R)$. The equation takes into account of the effect of heating rate and the apparent energy of activation is reported to be independent of heating rate effects.

The apparent order of reaction for the desorption of water for NaY and ferric exchanged Y zeolites has been calculated from the DTA curves using Kissinger's equation:

$$n = 1.26 (S)^{1/2}$$

For the first two endothermic peaks the order of reaction is nearly equal to one. The dehydration process of the kind,



may therefore be considered as first order reaction. In case of third endothermic peak, the order of reaction is about 1.5 ± 0.2 . This signifies that the dehydroxylation process may be dependent on the activity of two "reactants" i.e. molecularity is two.

Using the values of order of reactions evaluated by Kissinger's method, we have calculated the energy of activation for the desorption of water corresponding to the first endotherm using Coats-Redfern equation. Coats-Redfern plots are reasonably linear. The values of the order of reaction and energy of reaction are given in Table-7. Typical Coats-Redfern plot is shown in Fig. 5. The apparent energy of activation for the water desorption is about 5.5 Kcals/mole.

Rate constant calculations

The rate of desorption is given by,

$$\frac{-d(N/N_0)}{dt} = -\frac{d\alpha}{dt} = \frac{\Delta T}{S} \quad \dots\dots (9)$$

where ΔT is the height of the peak in DTA, S is the total area under the curve.

$$\frac{d\alpha}{dt} = A(\exp - E/RT) \quad \dots (10)$$

$$k = A(\exp - E/RT) \quad \dots (11)$$

From (9), (10) and (11) we get

$$\frac{\Delta T}{S} = k(1 - \alpha)^n$$

$$k = \left(\frac{\Delta T}{S}\right)/(1 - \alpha)^n \quad \dots (12)$$

Using equation (12), rate constants of water desorption for NaY and ferric exchanged Y zeolites are calculated and given in Table-7.

The values of rate constant increases with the increase of ferric exchange. The presence of aquocomplexes of ferric ions in supercages hinders the physically adsorbed water molecules making them comparatively less stable in supercages thereby increasing the rate of desorption of physically adsorbed molecules with the increase in the number of aquocomplexes of iron.

Effect of heating rate

It has been observed that the shapes of TG and DTA curves vary with a number of experimental parameters, such

as heating rate, particle size, sample size (weight), furnace atmosphere, etc. The effects of these parameters have been discussed¹⁷¹ in detail.

The DTA curves for FeNaY(82) with different heating rates (Fig. 6) show that at lower heating rates (2.5° and 4.1°C/min.), the first dehydration peak splits into two at about 90° and 110°C with an additional peak at 280°C . The data on the effect of heating rate on various peak temperatures (maxima) are given in Table-8. For heating rates, 2.5° and 4.1°C/min. , the dehydroxylation peak at 400°C is absent. While at higher heating rates, 8° and 10°C/min. , the peak at $\sim 90^{\circ}\text{C}$ is not observed. With increase of heating rate the peak positions in DTA are shifted towards higher temperature. These changes may be due to incomplete isothermal equilibrium condition in non-isothermal dehydration of zeolites. Every peak indicates a definite species of water molecules and DTA data supports the multistep desorption of water which is a consequence of energetic heterogeneity of surface potential.

Attempts have been made to take into account the effect of heating rate on kinetic parameters. Table-9 shows the values of energy of activation for the dehydration corresponding to first DTA peak of FeNaY(82) calculated by

Table-2 : Effect of heating rate on DTA peak temperature FeNiY(82)

Heating rate °C/min.	Peak temperatures °C		
	First peak	Second peak	Third peak
1) 2.5	90 and 170	280	-
2) 4.1	98 and 190	285	-
3) 5.3	160	295	400
4) 8.0	165	300	410
5) 10.0	165	300	415

Table-9 : Activation energy for dehydration
of Fe₂SO₄(82)

Method	Energy of activation Kcals/mole (First peak)
1) Coats-Redfern	4.23
2) Kissinger	11.92
3) Ozawa	13.05
4) Piloyan-Novikova	Not applicable

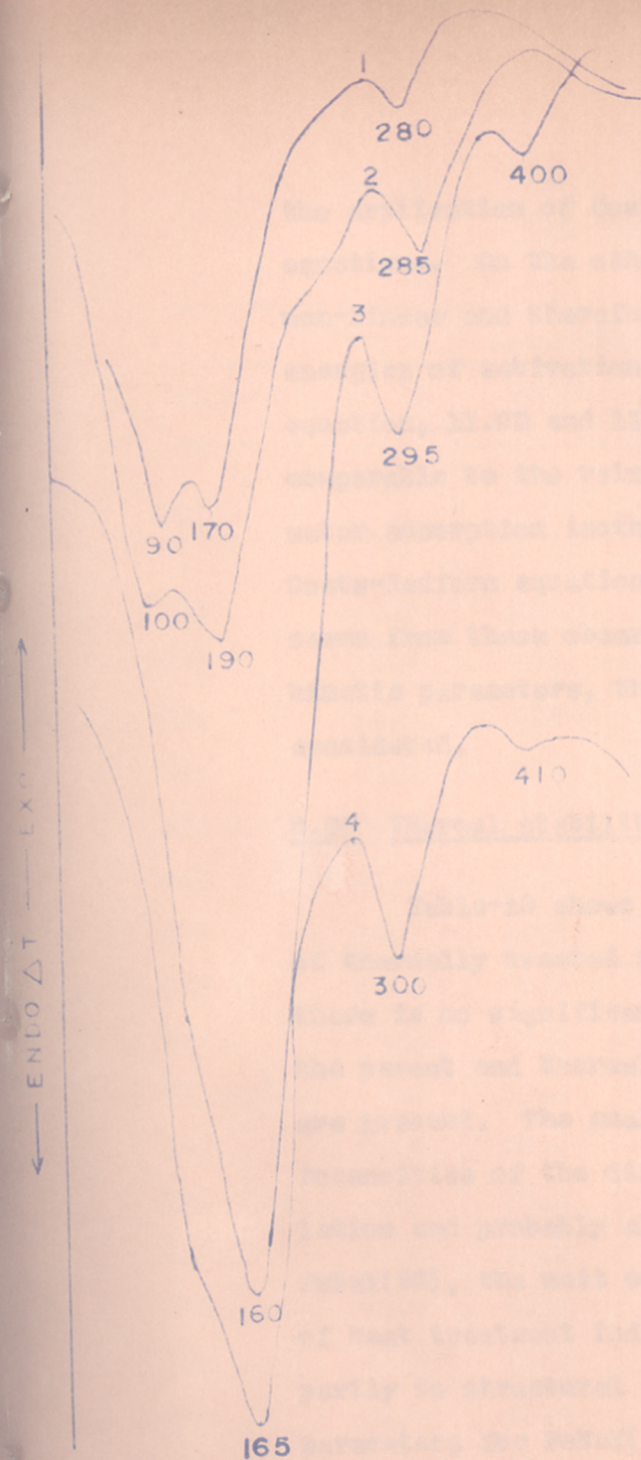


FIG 6. EFFECT OF HEATING RATES ON DTA CURVES OF FeNaY (82)

1) 2.5 °C/min, (2) 4.1 °C/min
(3) 5.3 °C/min, (4) 8.0 °C/min

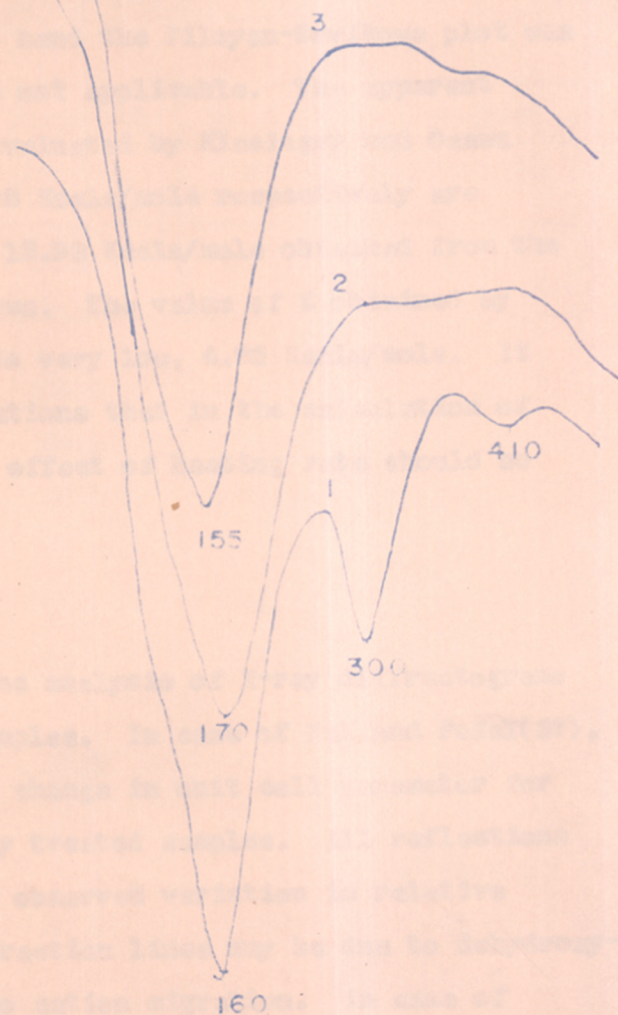


FIG. 7, EFFECT OF THERMAL TREATMENT. DTA CURVES OF
1) FeNaY (82), (2) FeNaY (82, 500, 2)
(3) FeNaY (82, 500, 10)

the application of Coats-Redfern, Kissinger and Ozawa equations. On the other hand the Piloyan-Novikova plot was non-linear and therefore not applicable. The apparent energies of activation evaluated by Kissinger and Ozawa equation, 11.92 and 13.05 Kcals/mole respectively are comparable to the value 12.93 Kcals/mole obtained from the water adsorption isotherms. The value of E obtained by Coats-Redfern equation is very low, 4.23 Kcals/mole. It seems from these observations that in the calculation of kinetic parameters, the effect of heating rate should be considered.

2.3C Thermal stability

Table-10 shows the analysis of X-ray diffractograms of thermally treated samples. In case of NaY and FeNaY(37), there is no significant change in unit cell parameter for the parent and thermally treated samples. All reflections are present. The small observed variation in relative intensities of the diffraction lines may be due to dehydroxylation and probably also cation migration. In case of FeNaY(82), the unit cell parameter a_0 decreases as a result of heat treatment indicating unit cell contraction or partly to structural collapse. The values of unit cell parameters for FeNaY(82), FeNaY(82,500,2) and FeNaY(82,500,10) decrease with heat treatment and are 24.614, 24.515 and 24.456 respectively.

Table-10 : X-ray intensities and unit cell constants after thermal treatment

	NaY	FeNaY(37)	FeNaY(82)	FeNaY(82)	FeNaY(82)
Treatment	500°C, 10 hrs.	500°C, 10 hrs.	500°C, 10 hrs.	500°C, 2 hrs.	Untreated
a Å	24.662	24.600	24.456	24.515	24.614
hkl					
111	100.0	100.0	100.0	100.0	100.0
220	22.8	24.0	44.9	26.6	24.1
311	19.2	18.6	30.0	25.4	17.7
331	63.0	67.2	67.7	69.2	57.7
333 & 511	27.4	35.8	44.1	48.5	27.7
440	43.3	53.9	58.3	41.4	41.2
620	13.7	18.1	-	-	12.9
533	64.8	78.9	81.9	71.6	55.9
622	6.8	8.8	-	-	-
711 & 551	9.6	12.3	-	-	10.6
642	50.2	56.4	52.0	42.0	40.00
731 & 553	9.1	16.2	-	-	11.2
733	20.6	19.6	21.3	16.6	20.0
822 & 660	24.7	27.0	21.3	23.7	28.2
751 & 555	55.7	61.3	37.0	38.5	49.4
840	23.7	20.6	-	-	18.8
664	16.9	19.6	-	-	17.7

Table-11 shows the effect of heat treatment on DTA peaks. In case of NaY, the dehydration peak is shifted towards lower temperature. The DTA of FeNaY(37) shows a shift of the exothermic peak towards higher temperature after heat treatment. A significant change in DTA curve for FeNaY(82) is observed on heat treatment. Fig. 7 shows the effect of thermal treatment on FeNaY(82).

The untreated FeNaY(82) sample shows three distinct endothermic peaks at 160, 290 and 400°C (Fig. 7). As discussed earlier the first peak is due to the dehydration of water, second is assigned to the dehydration of hexa-aquo complexes of Fe^{3+} in supercages. The third peak is assigned to the dehydroxylation of $(\text{OH})^-$ groups attached to Fe^{3+} ions. After the heat treatment and subsequent hydration the second and third peaks corresponding to the hexa-aquo complexes of iron i.e. $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ were absent. This shows an irreversible cation migration of Fe^{3+} ions from supercages into the hexagonal prisms.

Table-12 shows the effect of heat treatment on percent loss of water obtained from the TG. The water content in NaY decreases by about 1.5%. The heat treatment of zeolite FeNaY(37) shows a decrease in total water content. The percent weight loss corresponding to first peak of dehydration is increased by 1.5 - 2 %. Because of heat treatment,

Table-11 : Effect of heat treatment on DTA curves

Catalyst	Duration of heat- ing at 500°C in hours	First dehydra- tion peak °C	Comple- tion of dehydra- tion peak °C	Exothermic peak for structure breakdown °C
NaY	-	180	360	840
NaY(500, 2)	2	165	325	870
NaY(500, 5)	5	160	310	850
NaY(500, 10)	10	165	320	850
FeNaY(37)	-	165	380	870
FeNaY(37, 500, 2) *	2	165	330	900
FeNaY(37, 500, 5)	5	165	345	900
FeNaY(37, 500, 10)	10	155	330	900
FeNaY(82)	-	160	380	880
FeNaY(82, 500, 2)	2	170	375	875
FeNaY(82, 500, 5)	5	150	295	860
FeNaY(82, 500, 10)	10	155	315	870

* FeNaY(37, 500, 2) represents
37% Fe exchange, heated at 500°C
for 2 hours.

Table-12 : Effect of heat treatment on percent weight loss

Catalyst	Percent weight loss			
	Total	Region of first peak	Region of second peak	Region of dehydroxylation (third) peak
NaY	27.5	26.0	-	-
NaY(500, 2)	26.0	24.25	-	-
NaY(500, 5)	27.0	24.5	-	-
NaY(500, 10)	25.75	24.25	-	-
FeNaY(37)	27.5	22.0	3.0	1.0
FeNaY(37, 500, 2)	25.0	23.5	-	-
FeNaY(37, 500, 5)	25.25	23.5	-	-
FeNaY(37, 500, 10)	25.25	24.0	-	-
FeNaY(82)	26.5	19.5	4.0	1.25
FeNaY(82, 500, 2)	23.0	19.5	2.5*	1.0*
FeNaY(82, 500, 5)	21.75	18.5	2.75*	1.0*
FeNaY(82, 500, 10)	21.5	17.5	1.7*	1.0*

* No distinct peak was observed.

Fe^{3+} ions irreversibly migrate into sodalite cages or hexagonal prisms. Therefore, in heat treated samples, hexa-aquo complexes of iron do not exist. However, Fe^{3+} ions strongly interact with framework oxygens, in tetrahedral or octahedral symmetry. The existence of $[\text{Fe}(\text{OH}(\text{H}_2\text{O})_5)]^{2+}$ complexes in supercages hinders the incoming water molecules, thereby reducing the adsorption capacity.

2.3D Infrared spectra

Infrared spectroscopy is a tool used for the study of structures and to detect the presence of the polyhedral building units present in the zeolite frameworks. Flanigen et al.⁴⁷ have carried out an extensive infrared investigations on a large number of zeolites over the frequency range, 200-1300 cm^{-1} . These authors established an association between structural group frequencies of the zeolite and the infrared bands. The fundamental vibrations of $\text{T}(\text{Si}/\text{Al})-\text{O}_4$ tetrahedra of the zeolite framework are observed in the region 200-1300 cm^{-1} . Above 1300 cm^{-1} , bands corresponding to the adsorbate molecules and hydroxyl groups (of framework) are present. The region below 1300 cm^{-1} gives information regarding the structural aspects of the zeolite framework itself. While the region above 1300 cm^{-1} is useful in studying the adsorbate-adsorbent interaction and nature and variation in acidic properties of zeolites.

Below 1300 cm^{-1} , the spectra can be grouped into two classes, those due to internal vibrations of TO_4 consisting of asymmetric stretch ($1250\text{-}950\text{ cm}^{-1}$), symmetric stretch ($720\text{-}650\text{ cm}^{-1}$) and T-O bend ($500\text{-}420\text{ cm}^{-1}$) due to external vibrations of TO_4 consisting of asymmetric stretch bands which occur as a shoulder ($1250\text{-}1050\text{ cm}^{-1}$), symmetric stretch ($820\text{-}750\text{ cm}^{-1}$), double ring ($650\text{-}500\text{ cm}^{-1}$) and pore opening ($420\text{-}300\text{ cm}^{-1}$) bands.

Fig. 8 shows typical IR spectra of NaY and Fe^{3+} exchanged Y zeolites. The infra-red spectral data of NaY and Fe^{3+} exchanged zeolites are summarised in Table-13. The IR spectra of FeNaY zeolites have the general features of original NaY zeolite with some additional details of the characteristic bands showing the specific influence of the polyvalent counter cation. With the increase of Fe^{3+} exchange the peaks are broadened which may be attributed to the strong Fe^{3+} framework interaction. The spectra does not indicate any breakdown in the structure of the ferric exchanged zeolite samples. However, the band corresponding to double ring at $\sim 560\text{ cm}^{-1}$ is affected. In case of NaY, FeNaY(44), FeNaY(75) and FeNaY(82), the double ring bands are observed at 561.80 , 561.80 , 558.66 and 555.56 cm^{-1} respectively. At higher degree of ferric exchange, the Fe^{3+} ions occupy sites I or I', thereby interacting strongly with double ring. We can therefore conclude from IR data

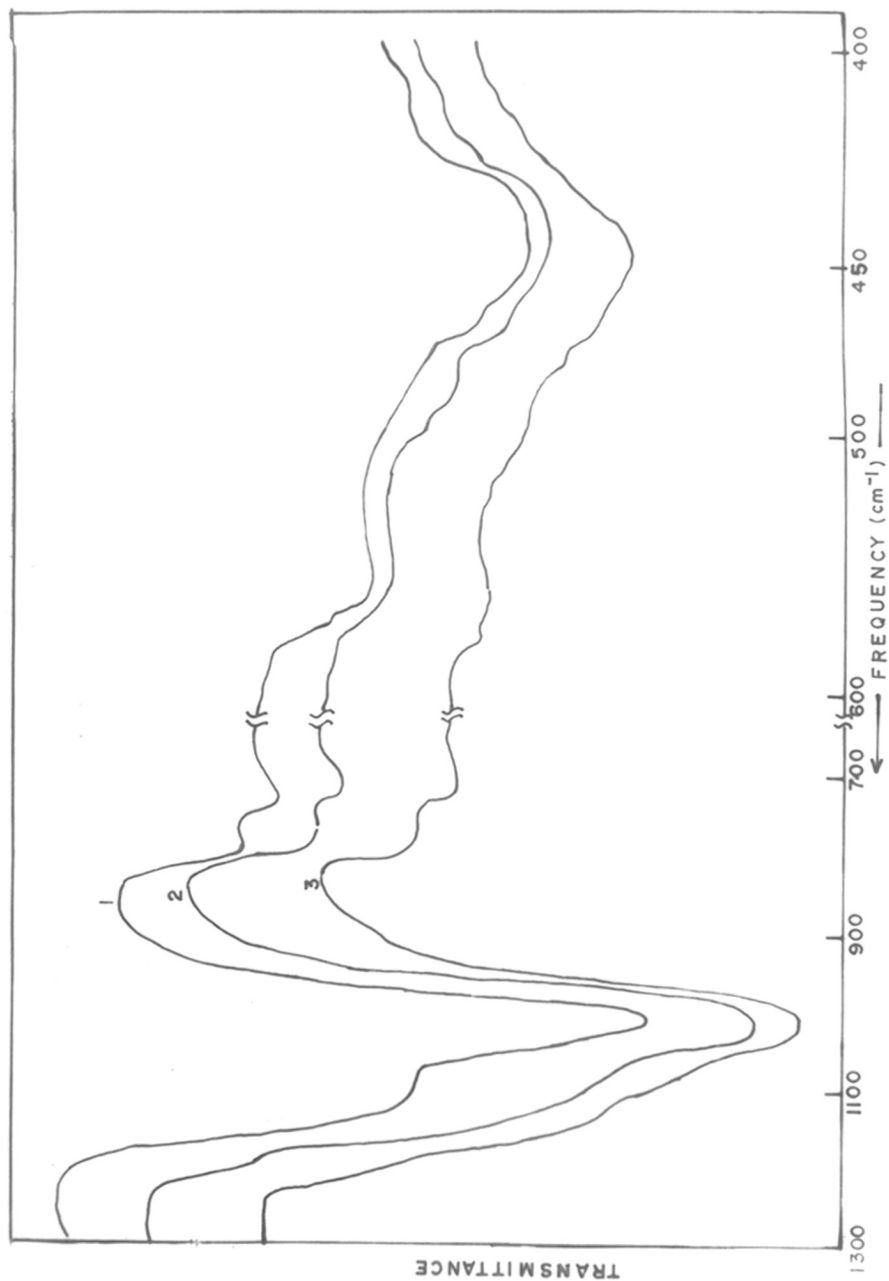


FIG 8. TYPICAL INFRA-RED SPECTRA OF (1) NdY, (2) FeNdY (44), (3) FeNdY (82)

Table-13 : Infra-red peak positions (cm^{-1})

	Asymmetric stretch	Symmetric stretch	Double ring	T-O bend
1. NaY	1150 (ms)	1010 (s)	770 (m)	710 (m)
2. FeNaY(37)	1130 (ms)	1010 (s)	775 (m)	705 (m)
3. FeNaY(44)	1140 (ms)	1010 (s)	760 (m)	710 (m)
4. FeNaY(61)	1140 (ms)	1000 (s)	775 (m)	710 (m)
5. FeNaY(75)	1140 (ms)	1010 (s)	780 (m)	710 (m)
6. FeNaY(82)	1160 (ms)	1010 (s)	770 (m)	710 (m)

s = strong
 m = medium
 ms = medium strong

that the basic Y zeolitic structure is preserved during ferric ion exchange.

2.3E Visible spectra

If the cations in zeolites are exchanged by transition metal ions, the zeolite may be coloured. This colour will vary with the degree of hydration and the nature and percent cation exchange. Some interesting examples of colour changes due to cation hydration (solvation) have been reported.^{25c} When the silver exchanged form of zeolite type A which is initially white is dehydrated, the colour changes to a deep yellow-red and ultimately to a bright yellow. Nickel exchanged A zeolite¹⁷⁷ changes in colour from green to pink upon dehydration. Cobalt cation form changes from pink to blue colour upon dehydration. The colour changes in zeolites have been used as an indication for the presence of water vapour.

Ferric exchanged Y zeolites are found to be yellowish in colour. With increase in iron content, the colour changes from yellow to yellowish-brown. All the FeNaY samples show a broad band at about 350 nm. The absorbance increases with the increase in iron content in the zeolite samples. Therefore, every iron ion is contributing to the absorbance at 350 nm. Only FeNaY(82) shows additional bands at 210 nm and 250 nm. The increase in absorbance with respect to percent ferric exchange is represented in Fig. 9.

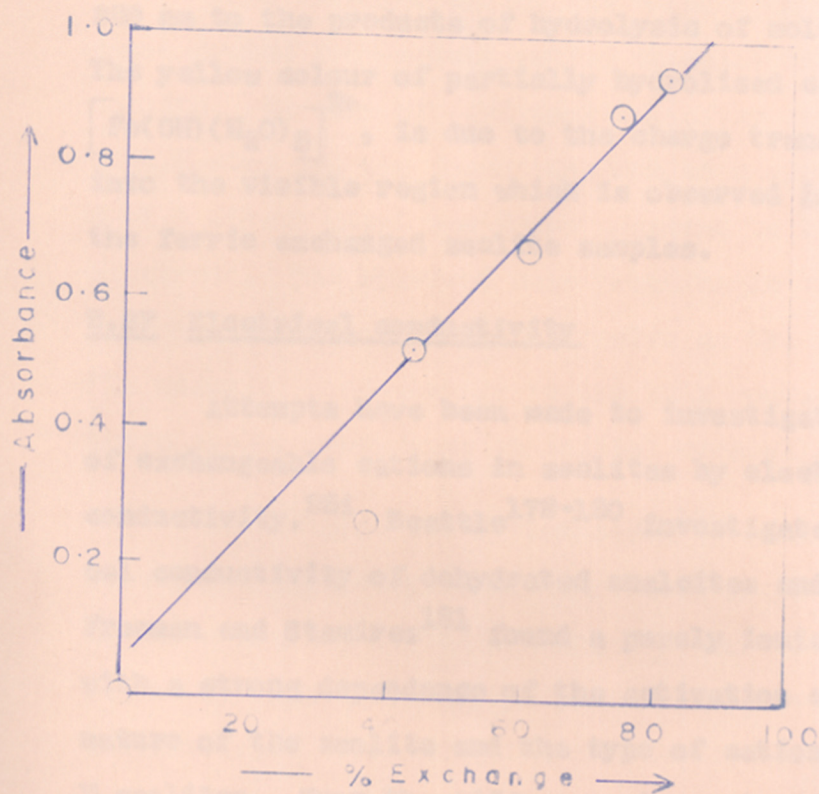


FIG 9: A PLOT OF ABSORBANCE AT 350 nm Vs. PERCENT FERRIC EXCHANGE

The nature of hydration of Fe^{3+} ions in aqueous solution is well established by magnetic susceptibility and spectral studies.^{166,167} The absorbance maximum at about 240 nm was ascribed to solvated Fe^{3+} ions and the band at 350 nm to the products of hydrolysis of solvated Fe^{3+} ions. The yellow colour of partially hydrolysed cation e.g. $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$, is due to the charge transfer tailing into the visible region which is observed in case of all the ferric exchanged zeolite samples.

2.3F Electrical conductivity

Attempts have been made to investigate the mobility of exchangeable cations in zeolites by electrical conductivity.²⁵¹ Beattie¹⁷⁸⁻¹⁸⁰ investigated the electrical conductivity of dehydrated analcites and chabazite. Freeman and Stamires¹⁸¹ found a purely ionic conduction with a strong dependence of the activation energies on the nature of the zeolite and the type of cation, in A, X and Y zeolites. From the difference in activation energy between X and Y, Freeman and Stamires¹⁸¹ concluded that at least two types of cation sites exist in lattice. In the X type, the lower activation energies were explained by the population of the less energetic sites. The decrease of the activation energy in X and Y zeolites with increasing

monovalent cationic radius was in contrast with the results found for analcite and indicated the openness of the zeolitic framework in X and Y zeolites.

Mass transfer during the conduction process was demonstrated from actual cation transfer in Ag exchanged X zeolite. In case of Ag-X zeolite, after 12 hours at 110 V dc, 1 wt. % zinc ion was found adjacent to a zinc electrode and 2 wt. % silver metal was found adjacent to the opposite gold electrode. The observed mass transfer in the conduction process eliminates cation vacancies as the charge carriers. The measured conductivity is the bulk conductivity because there was no dependence on initial crystallite size.

Schoonheydt and Uytterhoeven¹⁸² also attributed the electrical conductivity of dehydrated X and Y zeolites to the migration of the exchangeable cations in the supercages. A dipole absorption process was observed at low temperatures. Following the hypothesis advanced by Barrer and Saxon-Napier¹⁸³, this dipole absorption was ascribed to the migration of the cations. Jansen and Schoonheydt^{184,185} studied the effect of various adsorbed molecules on the electrical conductivity of X and Y zeolites. Morris¹⁸⁶ reported a dielectric study of 5A zeolite in the presence of various adsorbed molecules.

Fig. 10 shows the plots of specific conductivity against temperature for NaY and Fe³⁺ exchanged Y zeolites. The trend in conductivity values is NaY > FeNaY(37) > FeNaY(44) > FeNaY(82). At 25°C, conductivity values are 76×10^{-5} , 8.9×10^{-5} , 5.5×10^{-5} and $0.064 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ respectively. The conductivity decreases with the increase in percent ferric exchange but not linearly. It is established that the electrical conductivity in zeolites is due to the cations present in the supercages. Sodium ions form cationic aqueous solutions in supercages while ferric ions form hydrolysis products of hexa-aquo complexes. The mobility of Na⁺ ions is more than the bulky ferric complexes which supports the trend in specific conductivity of NaY and Fe³⁺ exchanged samples.

In case of NaY, conductivity decreases with increase of temperature and reaches a minimum value at about 250°C. It is found from the thermogravimetric analysis that upto 250°C, 22.7 % water is desorbed from the zeolite cavity. The hydration energy stabilises cations in supercages in preference to the cationic sites in sodalite and hexagonal prisms. As the water molecules surrounding the cations are removed, the cations tend to interact with the framework occupying electrostatically favourable sites. The increase in cation-framework interaction decreases the mobility of cations. Above 250°C, the conductivity of Na⁺ ions increases.

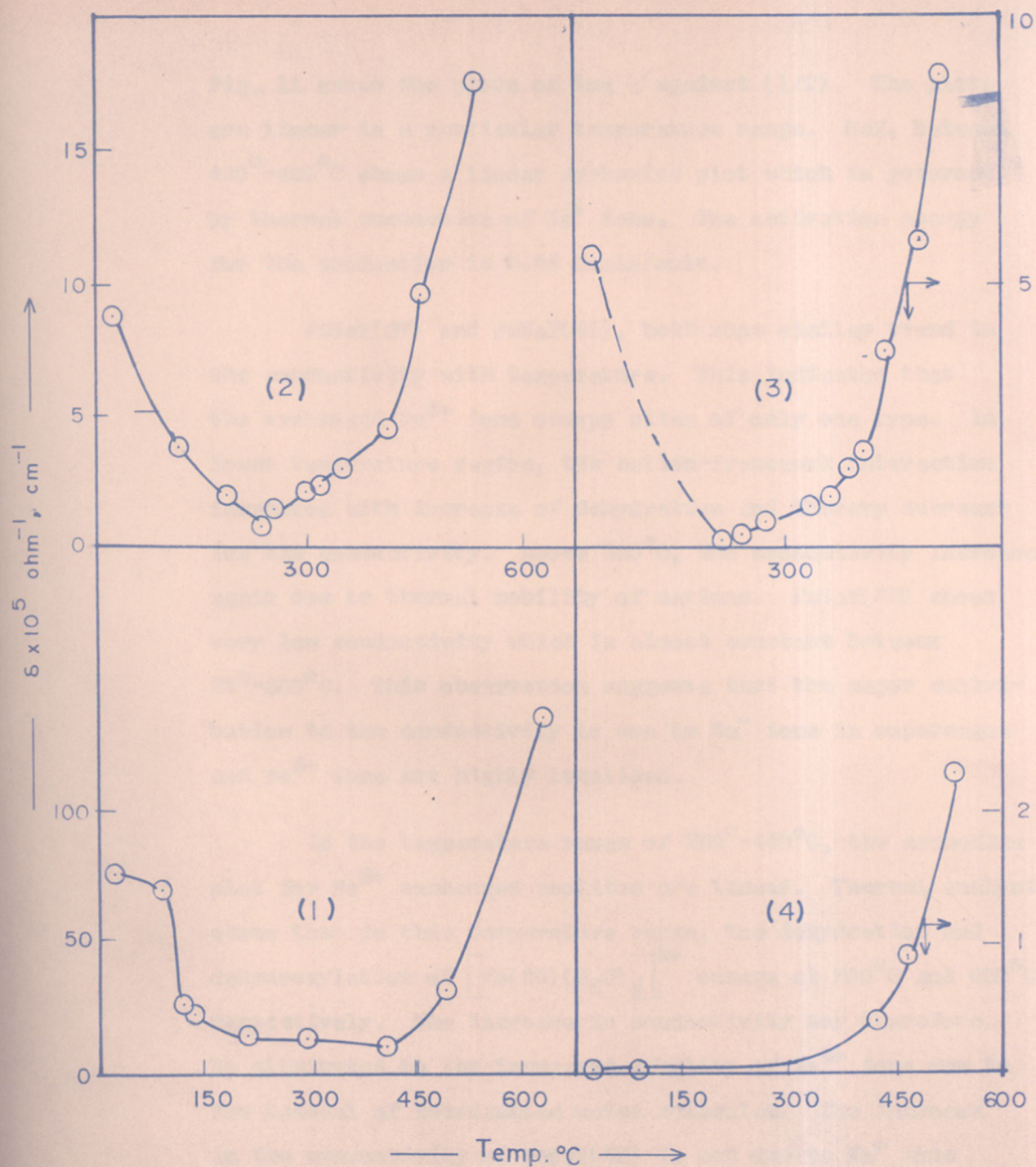


FIG. 10 : SPECIFIC CONDUCTIVITY AS A FUNCTION OF TEMPERATURE
 (1) NaY, (2) FeNaY (37), (3) FeNaY (44), (4) FeNaY (82).

Fig. 11 shows the plots of $\log \sigma$ against $(1/T)$. The plots are linear in a particular temperature range. NaY, between 400° - 600° C shows a linear Arrhenius plot which is governed by thermal conduction of Na^{+} ions. The activation energy for the conduction is 5.56 Kcals/mole.

FeNaY(37) and FeNaY(44), both show similar trend in the conductivity with temperature. This indicates that the exchanged Fe^{3+} ions occupy sites of only one type. In lower temperature region, the cation-framework interaction increases with increase of dehydration and thereby decreasing the conductivity. Above 250° C, the conductivity increases again due to thermal mobility of cations. FeNaY(82) shows very low conductivity which is almost constant between 25° - 300° C. This observation suggests that the major contribution to the conductivity is due to Na^{+} ions in supercages and Fe^{3+} ions are highly localised.

In the temperature range of 250° - 450° C, the Arrhenius plot for Fe^{3+} exchanged zeolites are linear. Thermal analysis shows that in this temperature range, the dehydration and dehydroxylation of $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ occurs at 290° C and 400° C respectively. The increase in conductivity may therefore be attributed to the increased mobility of Fe^{3+} ions due to the removal of coordinated water molecules. The increase in the conductivity of FeNaY(82) is not due to Na^{+} ions because in the same temperature range (250° - 400° C) the

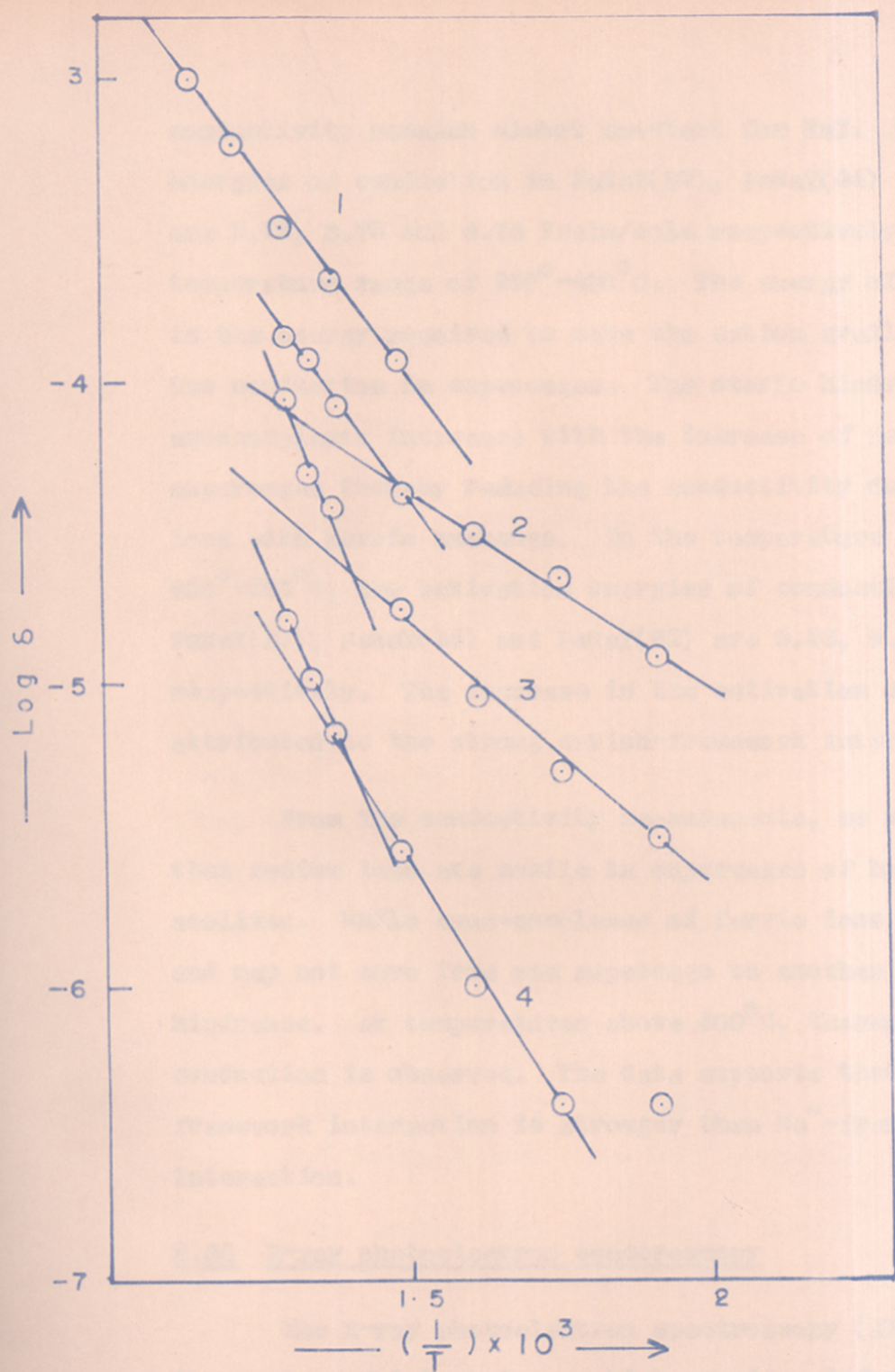


FIG. 11: PLOTS OF $\text{LOG } \sigma$ AGAINST $(\frac{1}{T})$

(1) NaY, (2) FeNaY (37), (3) FeNaY (44), (4) FeNaY (82)

conductivity remains almost constant for NaY. The activation energies of conduction in FeNaY(37), FeNaY(44) and FeNaY(82) are 2.78, 3.78 and 6.76 Kcals/mole respectively, in the temperature range of 250°-400°C. The energy of conduction is the energy required to make the cation available for the conduction in supercages. The steric hindrance due to aquocomplexes increases with the increase of Fe³⁺ ions in supercages thereby reducing the conductivity due to Fe³⁺ ions with ferric exchange. In the temperature range of 400°-525°C, the activation energies of conduction for FeNaY(37), FeNaY(44) and FeNaY(82) are 5.56, 9.54 and 9.54 respectively. The increase in the activation energy is attributed to the strong cation-framework interaction.

From the conductivity measurements, we may conclude that sodium ions are mobile in supercages of hydrated zeolites. While aquo-complexes of ferric ions are localised and may not move from one supercage to another due to steric hindrance. At temperatures above 400°C, thermal cationic conduction is observed. The data supports that the Fe³⁺-framework interaction is stronger than Na⁺-framework interaction.

2.36 X-ray photoelectron spectroscopy

The X-ray photoelectron spectroscopy (XPS) is one of the most useful techniques which provides information on the

chemical states of transition metal cations and is quantitative enough to compare the catalytic properties. The XPS studies¹⁸⁷⁻¹⁸⁹ have been shown to be very powerful aids to understand the oxidation processes, intrinsic surface states, formation of thin overlayers and chemisorption. The application of XPS has been extensively reviewed.¹⁹⁰⁻¹⁹⁴

Recently transition metal cation exchanged zeolites have been studied by XPS.¹⁹⁵ Formation of intermediate states of Ni and Cu by reduction with CO has been reported. Using XPS, Vedrine et al.¹⁹⁶ found Pd(I) formation in PdY zeolite reduced with H₂. Similarly the formation of Rh(I) species¹⁹⁷ in RhY zeolite as a stable intermediate during the reduction of Rh(III) to Rh metal by heat treatment in vacuum has been detected by XPS. XPS has been used to investigate¹⁹⁸⁻²⁰⁰ the external layers of some zeolite surfaces. It has been shown that Si/Al ratio of the external surface is roughly twice that of the bulk.

The typical X-ray photoelectron spectra for NaY and FeNaY zeolites are shown in Figs. 12-14.

The orbital binding energies for Na, Al, Si, Fe and oxygen are summarized in Tables-14 and 15. The

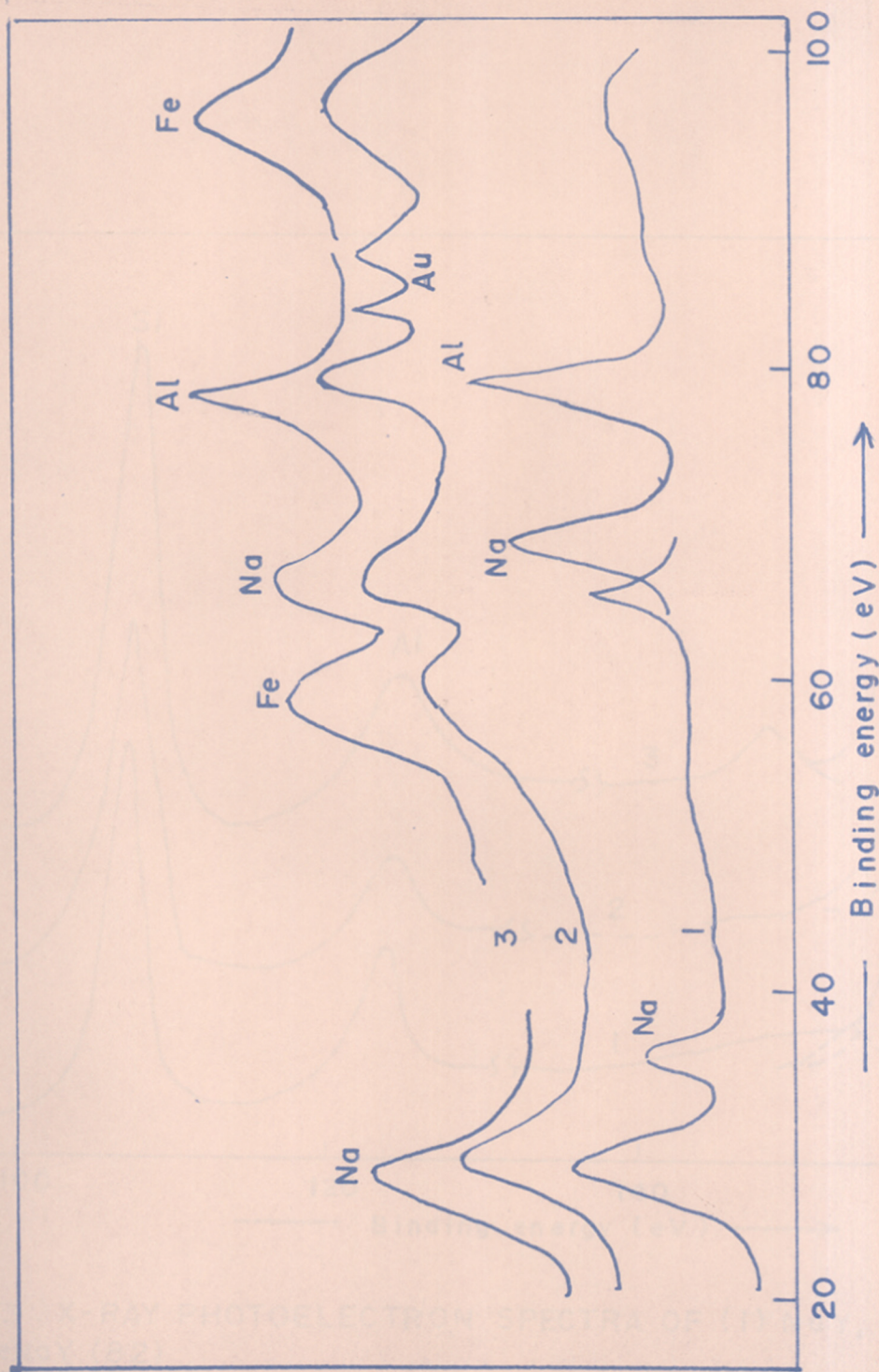


FIG.12: X-RAY PHOTOELECTRON SPECTRA OF (1) NaY, (2) FeNaY (82), FeNaY (82, 500.5).

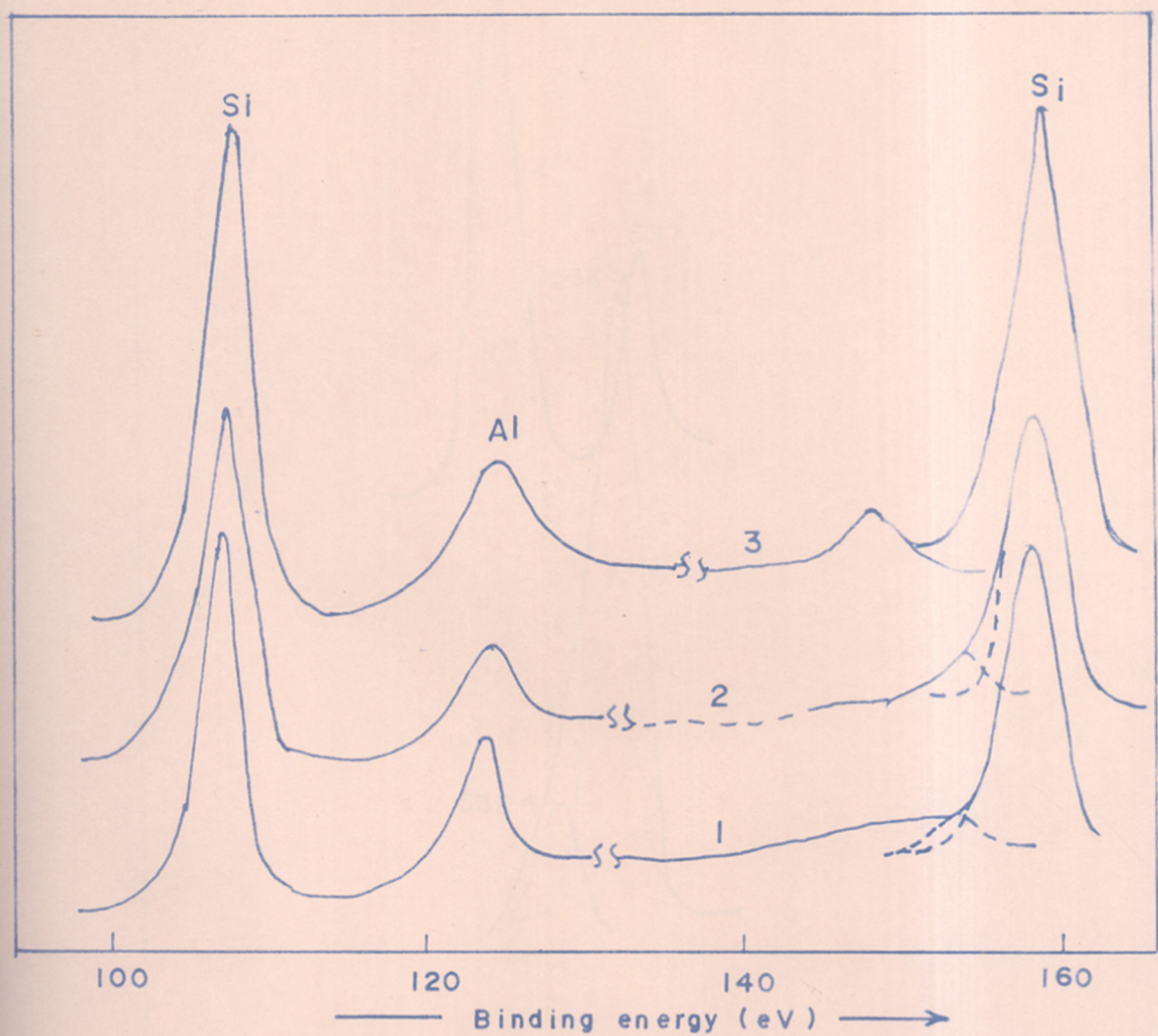


FIG.13: X-RAY PHOTOELECTRON SPECTRA OF (1) NaY, (2) FeNaY(46), (3) FeNaY(82).

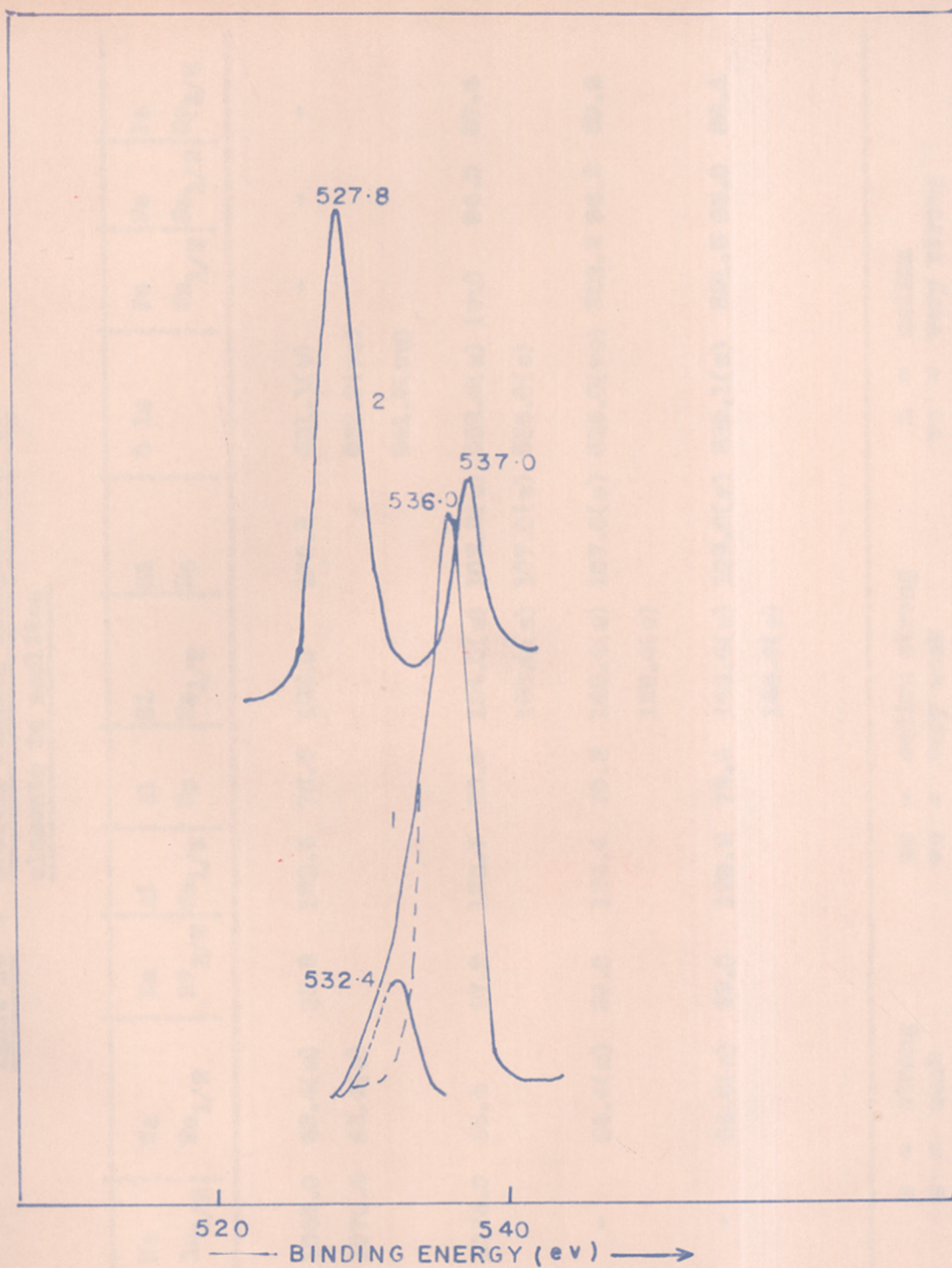


FIG.14: X-RAY PHOTOELECTRON SPECTRA OF O1S PEAK FOR
(1) FeNaY (46), (2) FeNaY (46, COKED).

Table-14 : Orbital binding energies (eV) of elements in zeolites

Catalyst	Na 1s _{1/2}	Na 2s _{1/2}	Na 2p _{3/2}	Al 2s _{1/2}	Al 2p	Si 2s _{1/2}	Si 2p	O 1s	Fe 2s _{1/2}	Fe 3s _{1/2}	Fe 3p _{3/2}
NaY	1068.0	65.4(m)	35.8	123.4	78.5	158.0	106.8	531.1(w)	-	-	-
	1076.4	68.4(s)						535.9(vs)			
								541.8(vw)			
FeNaY(46)	1076.0	66.4	27.9	123.7	78.9	154.0(v)	102.8(v)	532.4(w)	(vw)	96.0	57.6
						158.0(s)	107.0(s)	536.0(s)			
FeNaY(82)	-	66.4(m)	29.0	124.4	79.2	148.4(v)	107.0(s)	536.0(vs)	853.2	96.8	59.6
						158.4(s)					
FeNaY(82) heated at 500°C for 5 hours	-	66.4(m)	28.0	123.2	78.4	146.4(v)	105.0(s)	535.1(s)	851.5	96.0	58.4
						156.0(s)					

s = strong ms = medium strong m = medium
w = weak vw = very weak vs = very strong

Table-15 : Orbital binding energies (eV) of elements in zeolites

	Na	Na	Na	Al	Al	Si	Si	O	Fe	Fe	Fe
	1s _{1/2}	2s _{1/2}	2p	2s _{1/2}	2p	2s _{1/2}	2p	1s	2s _{1/2}	3s _{1/2}	3p _{1/2}
FeNaY(46) coked sample	-	65.2	31.4	119.8	74.8	154.3 (s)	103.1	527.8 (s)	-	-	-
						160.1 (m)		537.0 (ms)			
						165.7 (m)					
Na-Zeolon	1068.4	68.0	35.6	123.2	78.2	146.6 (w)	106.6	532.0 (w)	-	-	-
	1076.8		38.6			157.4 (s)		535.5 (vs)			
								541.0 (w)			
								543.5 (vw)			
FeNa-Zeolon (59)	1074.0	69.0	28.6	122.8	78.2	146.8 (w)	107.2	533.2 (s)	844.8	97.4	56.6
			39.0			157.0 (s)		541.8 (m)			

s = strong
w = weak

ms = medium strong
vw = very weak

m = medium
vs = very strong

parent NaY zeolite shows two Na 1s peaks at 1068 and 1076.4 eV and two Na 2s peaks at 65.4 and 68.4 eV. Since the difference between the peaks is 8.4 eV, the peaks cannot be attributed to tetrahedral and octahedral coordination of Na^+ in the zeolite. Moreover, the chemical analysis of the parent NaY sample showed 60 Na^+ (unwashed) and 57 Al^{3+} ions per unit cell while washing the sample with distilled water, Na^+ content reduced to 57 Na^+ /unit cell. Besides the water treatment of the zeolite reduced the pH from 10 to 8.5. It appears therefore that parent zeolite contains excess of Na^+ (trapped NaOH) and the second Na 1s peak is probably due to the trapped NaOH. This was further confirmed by the absence of second Na 1s peak in FeNaY(46) zeolite.

Effect of ion exchange

Ion exchange of NaY with ferric ions does not affect the binding energies evaluated from the XPS except for the decrease in the height of Na lines. The binding energies of Al 2s and Al 2p levels in NaY and FeNaY(82) zeolites are at 123.4, 124.4 eV and 78.5, 79.2 eV respectively, while that for O 1s peak the binding energy remains unaltered at 535.9 eV. Due to the introduction of Fe^{3+} , the binding energies shift to higher values. The unit cell composition of FeNaY(82) shows 1s ferric ions which occupy sites II, II', I and I'.

On account of strong electrostatic interaction of Fe^{3+} with the framework Al atoms, the electron density around Al is distorted towards Fe^{3+} , thereby reducing the electron-electron repulsion experienced by 2s and 2p electrons. The electrical conductivity measurements discussed in Chapter 2.3F also support a strong Fe^{3+} ----framework interaction.

Zeolite surface composition

During the process of ferric ion exchange, dealumination of the zeolite did not occur and the bulk silicon-aluminum ratio $(\text{Si}/\text{Al})_B$ for all the samples was 2.37. The silicon-aluminum composition of the external layers in the sodium and ferric exchanged Y zeolites can be calculated from the relative intensities of 2p peaks in the XPS using the following equation¹⁹⁸:

$$\frac{I_1}{I_2} = \frac{n_1}{n_2} \times \frac{\lambda_1}{\lambda_2} \times \frac{\sigma_1}{\sigma_2} \times \frac{S_1}{S_2} = \frac{n_1}{n_2} \cdot [T_{1,2}]$$

where I = area under the curve including satellites.

λ = mean free path of the photoelectrons of kinetic energy E_c .

S = transmission factor of the spectrometer for an energy factor E_c .

σ = effective ionization cross section.

n = atomic concentration of the elements studied.

For the given elements, the ratio in the square bracket is a constant which is called a "relative spectrometer intensity factor" and is designated as $I_{1,2}$.

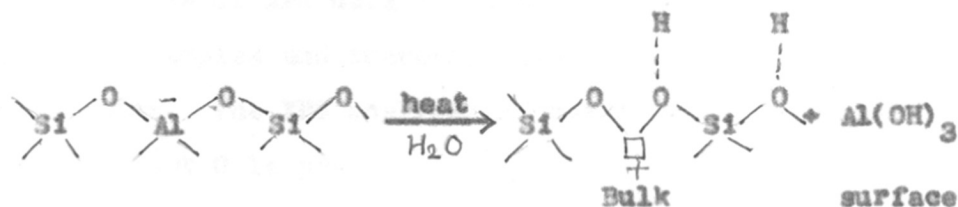
The (Si/Al) ratios for the zeolite samples investigated by XPS are given in Table-16. These ratios denoted by $(Si/Al)_B$ and $(Si/Al)_S$ refer to the bulk composition determined by chemical analysis and estimated by XPS respectively. The surface $(Si/Al)_S$ ratios are higher than $(Si/Al)_B$ bulk and show a small increase with percent ferric exchange. This indicates that the external zeolite surface is aluminum deficient. Tempere et al.¹⁹⁸ studied the (Si/Al) composition of zeolites with varying (Si/Al) ratio and showed a partial dealumination of the surface of the zeolites A, X and Y.

In order to examine the effect of thermal activation, FeNaY(82) zeolite was heated at 500°C for 5 hours before recording the X-ray photoelectron spectra. The surface $(Si/Al)_S$ ratio was found to decrease from 4.48 to 2.51 after thermal treatment. The heat treatment of FeNaY(82) may cause dehydroxylation of framework hydroxyl groups and during simultaneous dealumination, bulk aluminum may migrate to the surface thereby decreasing the surface (Si/Al) ratio. The Table-14 shows that the energies of 2p and 2s of Al and Si decrease by 0.8 eV and 1.6 eV respectively. The surface

Table-16 : Bulk and external surface (Si/Al)
composition of zeolites

Sample	(Si/Al) 2p XPS area ratio	(Si/Al) s gm. atom ratio	(Si/Al) B gm. atom ratio
NaY	4.94	3.89	2.37
FeNaY(46)	5.08	4.00	2.37
FeNaY(82)	5.69	4.43	2.37
FeNaY(82,500,5)	3.18	2.51	2.37
FeNaY(46, coked)	7.5	5.91	2.37
Na-Zeolon	6.70	5.27	5.2
FeNa Zeolon(59)	7.33	5.77	5.2

migration of aluminum on activation may be represented as



Kerr⁽²⁰¹⁾ has discussed the mechanism of dealumination of zeolites in detail.

Catalyst aging

In catalytic dehydrogenation of ethyl benzene to styrene, FeNaY(46) zeolite showed decrease in dealkylation activity after three hours due to coke formation. The examination of coked sample by XPS revealed that the binding energies of Al 2s, 2p decrease by about 3.2 eV. The Si 2s level showed three peaks at 154.3, 160.1 and 165.7, the difference between two successive ^{peaks} being 5.8 eV. On the other hand, the Si 2p level showed only one peak at 103.1 eV.

Two peaks are observed for O 1s and 527.8 and 537.0 eV (Fig. 14), one corresponding to the framework oxygen on which coke is deposited and the other free from coke. This may be due to the strong chemical interaction of coke with framework oxygens.

The above studies show that the XPS could be useful in the trapped and surface impurities present in the zeolites. The analysis of XPS data revealed aluminum deficient surface in fresh samples and increased aluminum content on thermal activation. The XPS analysis of coked catalyst revealed two distinct O 1s peaks, corresponding to two types of framework oxygens.

CHAPTER - III : ADSORPTION AND DIFFUSION STUDIES

3.1 INTRODUCTION

Acidic centres of zeolites are characterised by infrared spectroscopy, titration method using Hammett indicators or adsorption and desorption of basic molecules like ammonia, n-butylamine or pyridine. Ammonia molecules enter into sodalite and supercages, while n-butylamine and pyridine do not enter into sodalite cages. Attempts²⁰²⁻²⁰⁶ have been made to determine the number and strength of acidic centres through measurements of base adsorption. The adsorption of n-butylamine (NBA) is useful in determining the number and strength of acidic centres in supercages of zeolites where the catalytic reactions occur.

From the measurements of adsorption of CO_2 and NH_3 on various modified zeolites Coughlan and coworkers^{207,208} calculated the chemical potential, enthalpy and entropy and established the sequence in the strength of adsorbate-adsorbent interaction. Steinburg et al.²⁰⁹ measured integral heats of adsorption of some basic molecules on ion-exchanged zeolites by calorimetric method.

Mishin et al.²¹⁰ reported adsorption isotherms and heat of adsorption of NBA on dealuminized Y type zeolites. They concluded that the silanol groups formed during dealumination are not strong acid centres, and the number

of adsorption centres (cations and protonated centres) is reduced due to dealumination.

Adsorption isotherms

The investigation of adsorption isotherms is a valuable aid in obtaining information concerning the nature of the adsorption process. From the isotherm and its temperature dependence various thermodynamic parameters are evaluated. The comparison of experimental sorption isotherms and theoretical model, if valid, and the thermodynamic quantities like heat of adsorption help in the understanding the nature of adsorbate-adsorbent interaction and the nature of the catalyst.

Several attempts^{25j, 211-215} have been made to develop adsorption isotherm equations. Langmuir made the first attempt to develop adsorption isotherm equation. Langmuir equation is represented as follows:

$$\theta = \frac{x}{x_m} = \frac{BP}{1 + BP} \quad \dots (1)$$

where x = quantity adsorbed in the solid,

x_m = quantity adsorbed at the completion of monomolecular layer,

B = constant at constant temperature,

P = pressure of adsorbate.

Langmuir model assumes that, (1) the energy of adsorption is constant i.e. no energetic heterogeneity exists, (2) the adsorption is on localised sites, (3) the maximum adsorption capacity corresponds to complete monomolecular layer.

At very low pressures, the term "BP" may be neglected in comparison to unity and the equation simplifies to

$$x = x_m BP \quad \dots\dots (2)$$

This means that the adsorption is proportional to pressure which is Henry's law. At high pressures, the value of BP is very large relative to one and the equation reduces to $x = x_m$. The isotherm contour rises steeply and then becomes horizontal at high pressures.

The Langmuir equation (1) may be rewritten in the form :

$$\frac{P}{x} = \frac{1}{x_m BP} + \frac{P}{x_m} \quad \dots\dots (3)$$

The value of (P/x) plotted against P yields a straight line with a slope of $(1/x_m)$. Another method is to plot the Langmuir coefficient, B , against the adsorption expressed as θ .

$$B = \frac{\theta}{P(1 - \theta)} \quad \dots\dots (4)$$

If the Langmuir isotherm applies, the constant B does not vary with the level of coverage or adsorption.

The BET (Brunauer, Emmett and Teller) equation is expressed as

$$\frac{P}{V(P_s - P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \cdot \frac{P}{P_s} \quad \dots (5)$$

where P_s is the saturation vapour pressure, V_m is the volume adsorbed at the monomolecular layer and C is a constant.

The plot of $\left(\frac{P}{V(P_s - P)}\right)$ against $\left(\frac{P}{P_s}\right)$ gives a straight line if BET is applicable. The BET equation was developed for multilayer adsorption. It is the modification of Langmuir concepts of adsorption for multilayer formation and is not applicable to zeolites.

In the Polanyi theory, the characteristic curve is the relationship between the work of adsorption, A, and the filled volume of the adsorption space, w.

$$A = RT \ln \frac{P_s}{P} \quad \dots (6)$$

and $w = av^* \quad \dots (7)$

where a = the amount of adsorbate in millimoles per gm. at temperature T and equilibrium pressure P, v^* is the molar volume of the adsorbate and P_s is the saturation vapour pressure.

Polanyi theory was modified by Dubinin and Radushkevich²¹⁶ to apply to microporous adsorption and void filling. The equation takes the form of

$$w = w_0 \exp - \frac{KA^2}{\beta^2} \quad \dots (8)$$

where w_0 = constant and represents the volume of the adsorption space or pore volume,

β = affinity coefficient which is constant.

Substituting for A, work function, equation (8) can be rewritten as :

$$w = w_0 \exp - \frac{B}{\beta^2} \left(T \ln \frac{P_s}{P} \right)^2 = av^* \quad \dots (9)$$

The equation (9) can be expressed as,

$$\log w = \log w_0 - \frac{B}{2.303 \beta^2} \left(T \log \frac{P_s}{P} \right)^2 \quad \dots (10)$$

$$\text{or} \quad \log a = C - D \left(\log \frac{P_s}{P} \right)^2 \quad \dots (11)$$

where B = a constant which is independent of temperature and is characteristic of the adsorbent porous structure,

$$C = \log \frac{w_0}{v^*}$$

$$D = \frac{0.434 BT^2}{\beta^2}$$

A plot of $(\log a)$ versus $(\log \frac{P_2}{P})^2$ should be linear if the equation is applicable.

The constant β , the affinity coefficient, indicates the strength of adsorbate-adsorbent interaction; w gives the void volume. In the region of volume-filling, Dubinin equation is of great use in the understanding of adsorption process.

Heat of adsorption

All adsorption processes involving physical adsorption are exothermic. For the adsorption to take place the free energy change must be negative. From the thermodynamic relation,

$$\Delta G = \Delta H - T \Delta S$$

where ΔH = heat of adsorption,

ΔG = free energy change for adsorption,

ΔS = entropy change for adsorption.

The adsorbate molecules are arranged in ordered form in adsorbed state, so ΔS is expected to be negative. The heat of adsorption is the true measure of the strength of the adsorbate-adsorbent interaction, while ΔS suggests the trend in the localisation of adsorbed molecules.

There are three terms referring to the heat of adsorption. These are :

- (1) The isothermal integral heat of adsorption is the total heat involved in the adsorption process from zero adsorbate loading to some final adsorbate loading at a constant temperature.
- (2) The differential heat of adsorption ($\Delta \bar{H}$) is the change in integral heat of adsorption with a change in adsorbate loading. It may be defined by the following equation:

$$\Delta \bar{H} = (\bar{H} - H_g)$$

where H_g is the molar enthalpy of the adsorbate gas and $\bar{H}$ is the partial molar enthalpy of the adsorbate. The differential heat of adsorption is dependent upon pressure, temperature and adsorbate coverage or loading.

- (3) The isosteric heat of adsorption, ΔH , is derived from adsorption isosteres. It is obtained from a plot of the $\log P$ vs $(1/T)$, at constant adsorbate loading, using the Clausius-Clapeyron equation,

$$\log P = \frac{-\Delta H}{2.303 R} \left(\frac{1}{T} \right) + \text{constant}$$

From pairs of isotherms, ΔH may be calculated from

$$\Delta H = -q_{st} = R \left(\frac{T_1 T_2}{T_2 - T_1} \right) \ln \frac{P_2}{P_1}$$

The isosteric heat is related to the differential heat of adsorption by $-q_{st} = \Delta \bar{H}$. Isosteric adsorption heats which are obtained from a family of adsorption isosteres are plotted as a function of the adsorbate loading and by subsequent graphical integration the isothermal integral heat of adsorption is evaluated.

Entropy of adsorption

The differential entropy of adsorption is determined from the logarithmic plots since it is equal to the product of the absolute temperature and the isosteric heat of adsorption. The differential molar entropy is obtained as,

$$\bar{S} = S_g^0 + R \ln \frac{P^0}{P} + \frac{\Delta \bar{H}}{T}$$

where S_g^0 = molar entropy of the gas at standard pressure P^0 . The molar entropy varies with the amount sorbed.

Attempts have been made^{25k} to relate heat of adsorption, $\Delta \bar{H}$, to several component interaction energies. At 0°K, $\Delta \bar{H}$ is given by,

$$\Delta H = \phi_D + \phi_R + \phi_P + \phi_{F-Q}$$

$$\phi_D = \text{dispersion energy} = (-A/r^6)$$

$$\phi_R = \text{repulsion energy} = (B/r^{12})$$

$$\phi_P = \text{polarisation energy} = \frac{-\alpha C^2}{2r^4} - \frac{F^2}{2}$$

$$\phi_{F-Q} = \text{electrostatic quadrupole energy} = (CQ/2r^3)$$

where A, B and C are constants and r is the distance of separation. α is the polarizability, F is the field strength. Methods of estimating constants and energy terms have been given by Barrer and Gibbons.^{217,218}

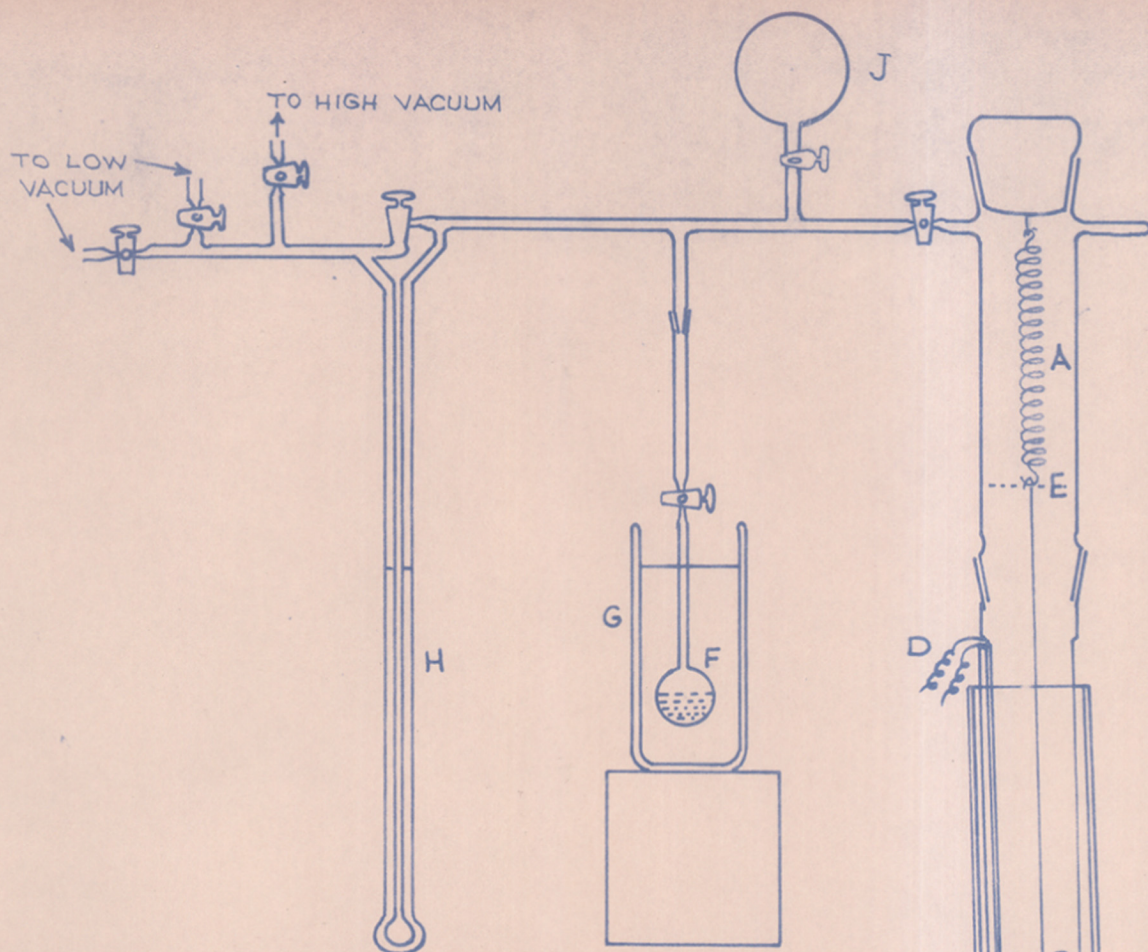
3.2 EXPERIMENTAL

The iron zeolites were prepared by treating Linde NaY zeolite (SK-40, Lot No. 96805000) supplied by Union Carbide, U.S.A., with aqueous solutions of ferric acetate-acetic acid at about 4.0 pH at 27°-30°C. After exchange all samples were washed with hot distilled water until the washings were free from acid, oven dried at 120°C overnight and stored in a constant humidity atmosphere over a saturated solution of ammonium chloride. The ferric exchanged samples are yellow in colour, with brownish tinge at higher exchanges. The X-ray diffraction patterns of all the samples showed crystalline nature of the Fd3m symmetry. The chemical compositions of the samples were determined by the conventional gravimetric analysis and sodium by flame photometric method.

Apparatus and procedure

Isotherms for the sorption of water and NBA on NaY and ferric exchanged samples were measured in the temperature range of 100° - 350° C by the gravimetric method using a calibrated silica spring balance. The sample bucket was suspended from the hook on the silica spring. The balance case was connected to high vacuum system consisting of rotary pump, mercury diffusion pump, cold traps and McLeod gauge for measuring the pressure. With this arrangement ultimate vacuum of about 10^{-6} torr was obtained. The adsorbate liquid was made free of air by freeze-thaw technique and was kept in a thermostat at constant temperature. Manometer was used for the measurement of the equilibrium pressure. The schematic diagram of the apparatus is shown in Fig. 15.

Approximately 100 milligrams of the zeolite powder was pressed into a pellet and weighed accurately in the aluminium bucket. The bucket was attached to the spring and the glass case was fixed to the assembly. The cathotometer was focussed on the reference point and the system was evacuated. The temperature of the sample was increased slowly and maintained at 350° C for four hours till a constant weight was obtained. The sample was brought to the desired



- A - SILICA SPRING
- B - ALUMINIUM BUCKET
- C - FURNACE OR THERMOSTAT
- D - THERMOCOUPLE
- E - REFERENCE POINT
- F - LIQUID BULB
- G - THERMOSTAT
- H - MANOMETER
- J - GAS RESERVIOR

FIG - 15 :

GRAVIMETRIC ADSORPTION UNIT

temperature and exposed to the adsorbate vapour at a desired pressure. The sorption readings were obtained from the change in weight of the sample after equilibrium was obtained. The adsorption isotherms were obtained by progressive increase of the vapour pressure and noting the adsorption. The reproducibility was checked in some experiments. For each temperature, after finishing adsorption isotherms, the amount of adsorbate irreversibly retained under high vacuum ($\sim 10^{-6}$ mm) was also noted.

3.3 RESULTS AND DISCUSSION

3.3A Sorption of n-butylamine on zeolites

Typical families of isotherms for NBA on a series of ferric exchanged Y zeolites are presented in Figures 16 and 17. At 350°C, the trend of the number of NBA molecules adsorbed per unit cell is



NBA molecules are chemisorbed on cations and acidic protons in supercages. Infra-red studies²¹⁹ showed that NBA molecules interact strongly with Na^+ ions in Y zeolite. X-ray diffractograms show the loss of crystallinity at higher percent ion-exchanges. FeNaY(61) and FeNaY(75) adsorbs less number of NBA molecules because of distortion of framework structure. Due to Na^+ -NBA interaction, NaY zeolite adsorbs larger amount of NBA.

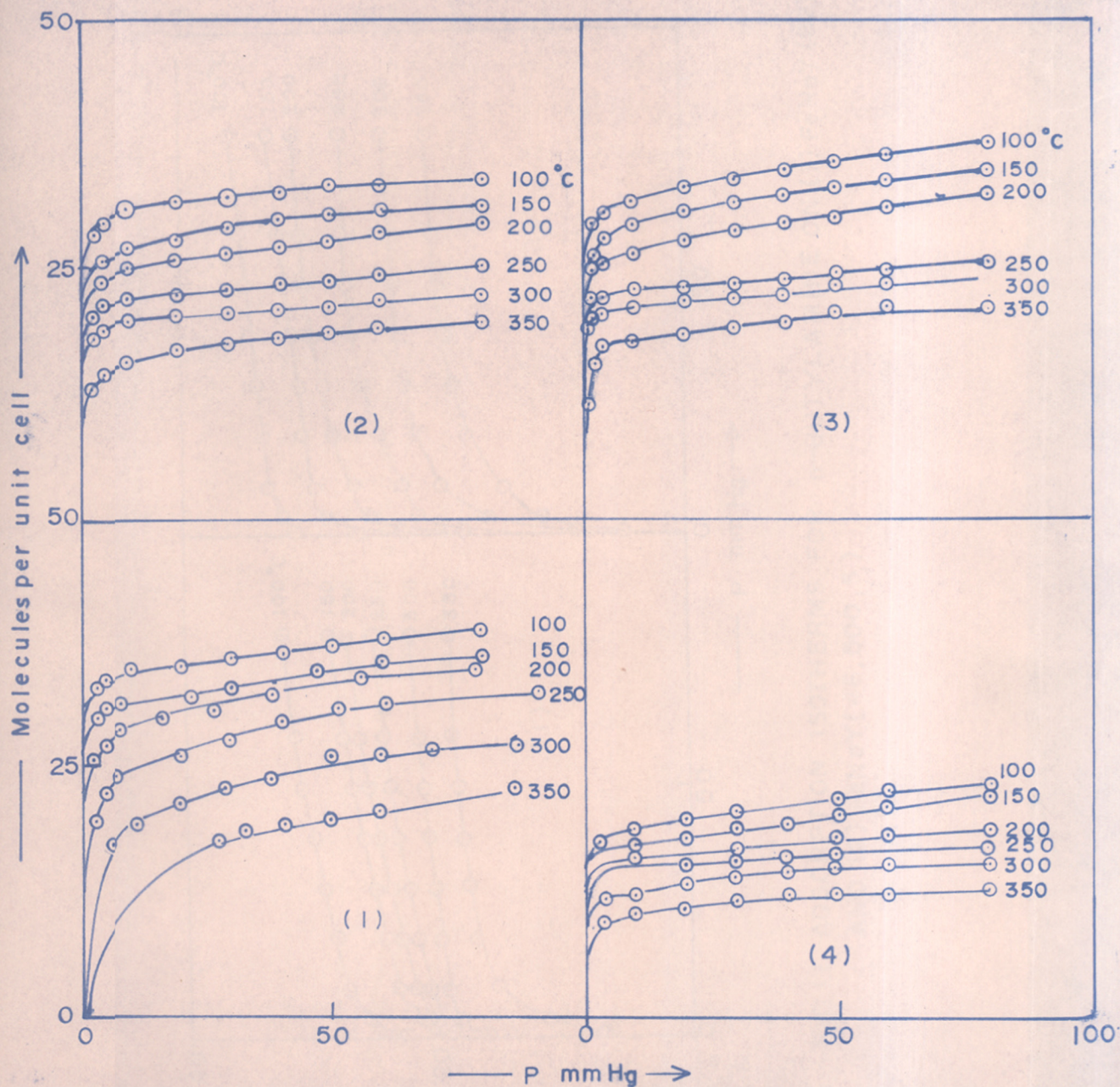


FIG.16: ADSORPTION ISOTHERMS FOR n BUTYLAMINE ON (1) NaY
(2) FeNaY(37), (3) FeNaY(46), (4) FeNaY(75)

Figs. 18 and 19 show irreversible adsorption of NBA (at 10^{-6} torr) as a function of temperature and ion-exchange. This data gives the trend in the strength of interaction with different samples at various temperatures. It may be concluded that above 200°C , the strength of acidic centres of catalysts follows the sequence



This indicates that the interaction of NBA is stronger with Fe^{3+} ions or H^{+} ions than with Na^{+} ions. The strongest acidic centres are present in FeNaY(46) and weakest acidic centres are in NaY among the six samples. Though The number of interacting centres are more in FeNaY(46) and NaY compare to other samples.

To observe the effect of heat treatment, FeNaY(46) was heated at 500°C for five hours in air. The rate of NBA adsorption and adsorption isotherms for thermally treated sample designated by FeNaY (46, 500, 5) were found to be similar to those for FeNaY(46) untreated. However, irreversible adsorption for FeNaY(46, 500, 5) showed that the interaction of NBA with catalyst was weaker than that for FeNaY(46). This is likely to be due to the loss of acidic protons during thermal treatment by dehydroxylation process and the migration of Fe^{3+} ions into sodalite cages occupying sites inaccessible to NBA molecules.

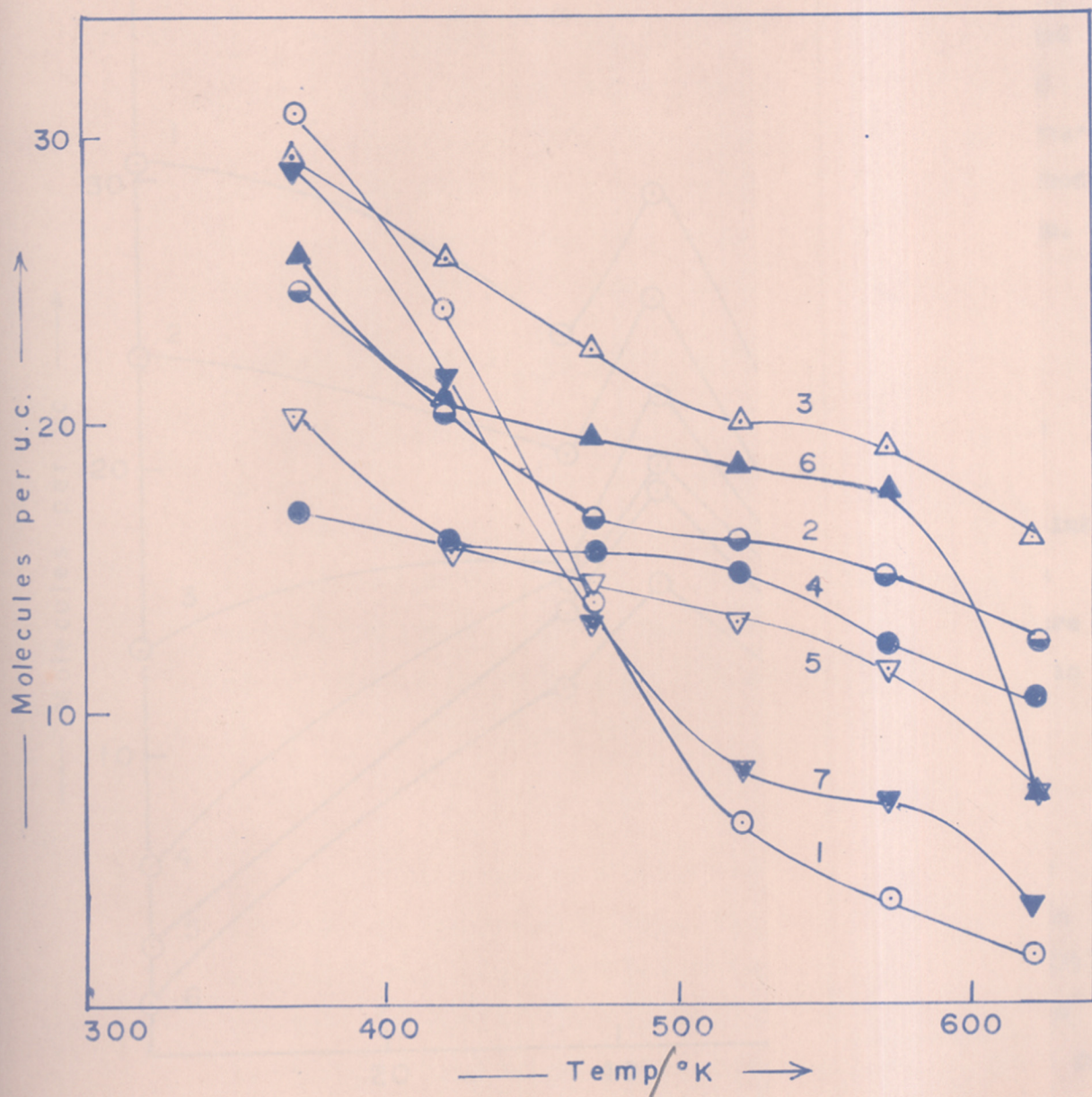


FIG.18: RETENTION OF ADSORBED *n*-BUTYLAMINE UNDER HIGH VACUUM ON (1) NaY, (2) FeNaY, (37); (3) FeNaY (46); (4) FeNaY (61); (5) FeNaY (75); (6) FeNaY (82); (7) FeNaY (46, 500, 5).

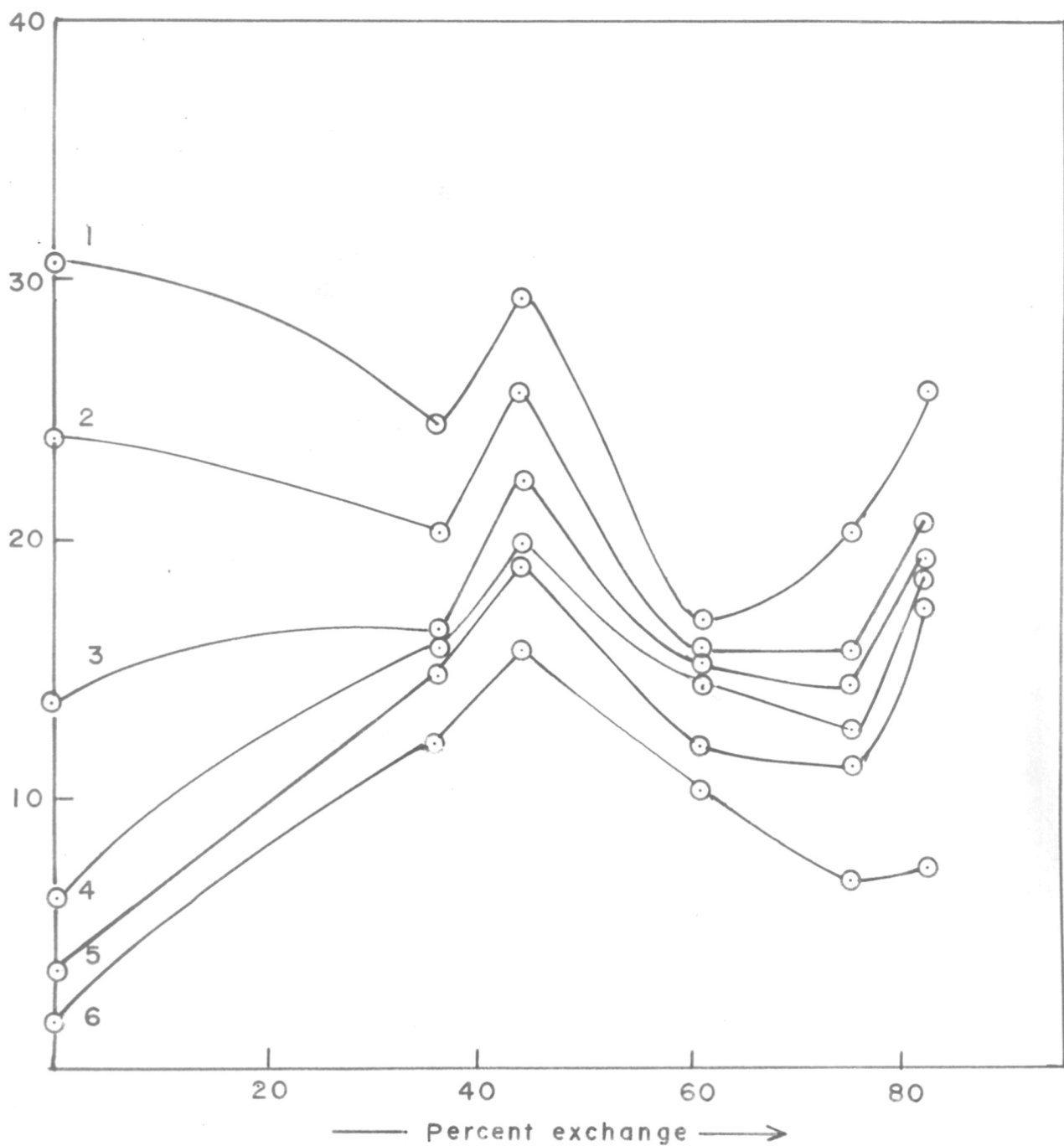


FIG.19: IRREVERSIBLE *n*-BUTYLAMINE ADSORPTION WITH RESPECT TO PERCENT FERRIC EXCHANGE AT TEMPERATURES (1) 100°C, (2) 150°C, (3) 200°C, (4) 250°C, (5) 300°C (6) 350°C.

Adsorption isotherms

The adsorption isotherms of NBA on ferric exchanged Y zeolites show typical Langmuir pattern. Plots of (P/a) vs P are linear (Fig. 20). The concept of monolayer formation is applicable because each NBA molecule is chemisorbed on one active centre only i.e. on cation or acidic proton. Fig. 20 shows a typical Langmuir plots for FeNaY(46).

Chemical affinity of the adsorbed phase

The chemical potential ($\Delta\mu$) decreases when a gas is transferred reversibly and isothermally from the gas phase at a standard pressure P_0 (taken as 760 mm of Hg) into an infinite amount of sorbate-sorbent mixture over which equilibrium pressure is P . The value of $-\Delta\mu$ is a measure of affinity of the sorbate for the sorbent. The change in chemical potential is given by,

$$G = \Delta\mu = RT \ln \frac{P}{P_0}$$

Fig. 21 shows the plot of $-\Delta\mu$ values against the molecules of NBA per unit cell. The affinity sequence in general is $\text{NaY} > \text{FeNaY}(46) > \text{FeNaY}(46, 500, 5) > \text{FeNaY}(37) > \text{FeNaY}(82) > \text{FeNaY}(61) > \text{FeNaY}(75)$. The affinity sequence is similar throughout the entire coverage range and that for equilibrium adsorption capacity of catalysts. This suggests

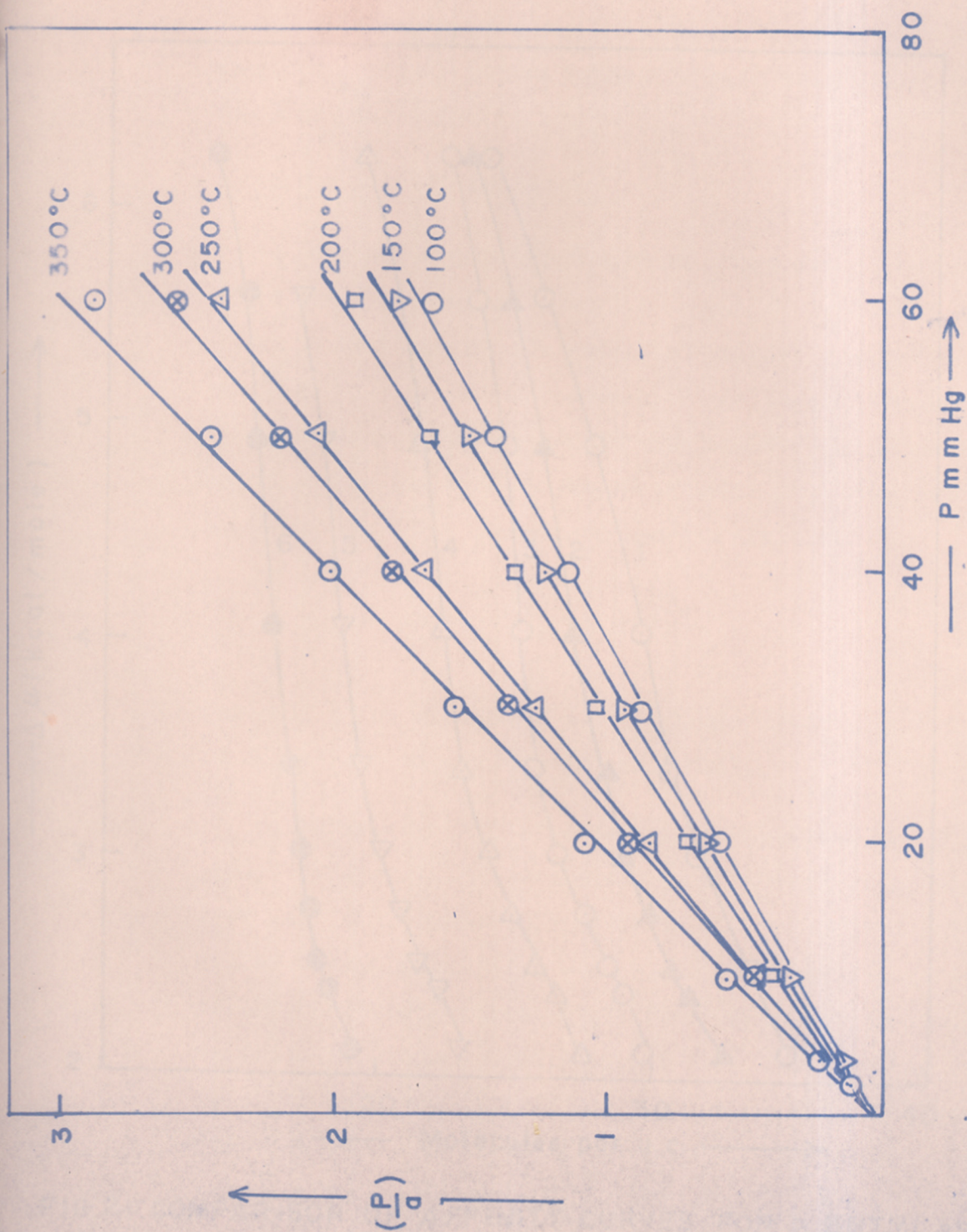


FIG.20: TYPICAL LANGMUIR PLOTS FOR $\text{FeNdY}(46)\text{-n BUTYLAMINE SYSTEM AT DIFFERENT TEMPERATURES}$

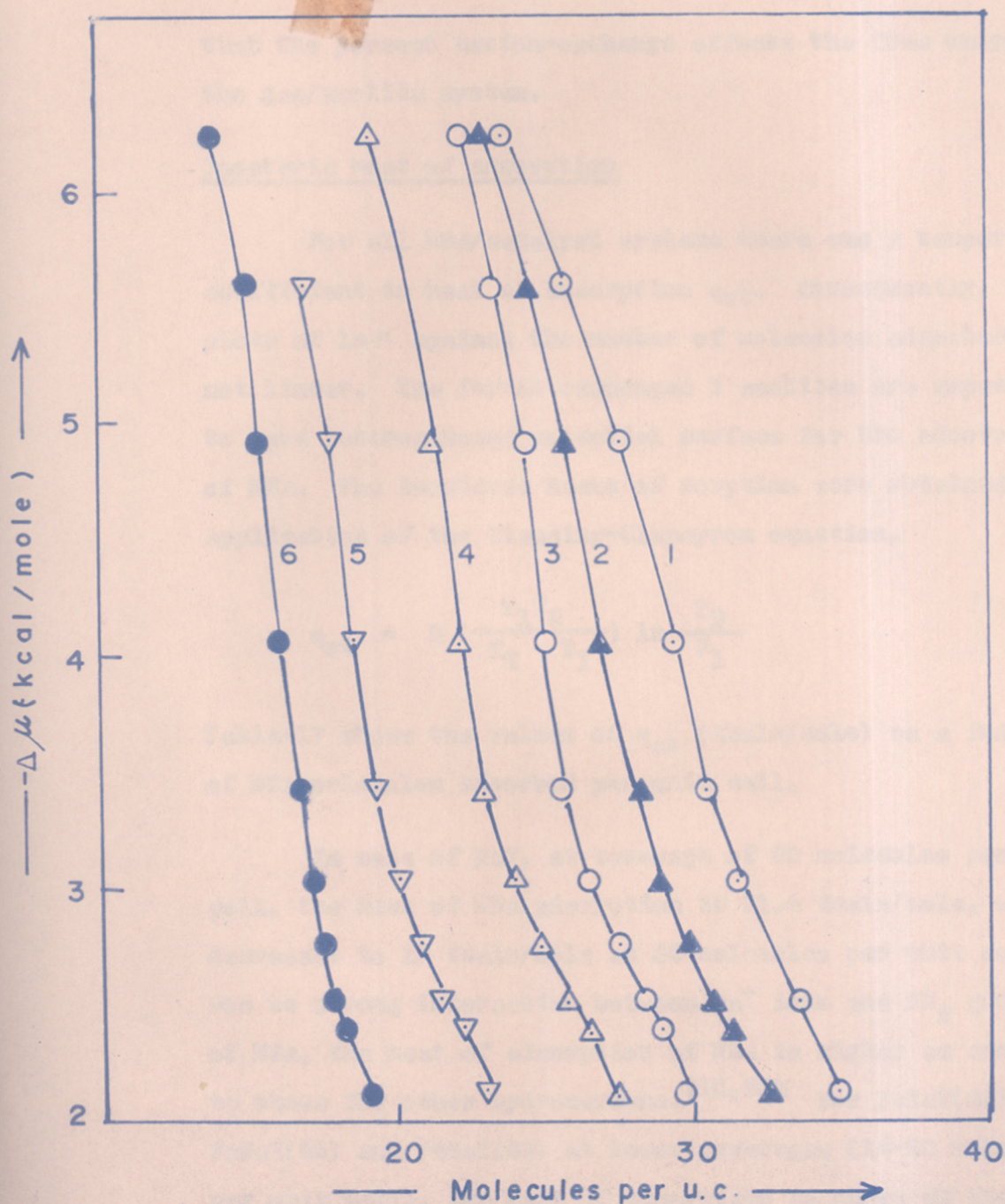


FIG. 21: COMPARISON OF AFFINITY CURVES FOR *n* BUTYLAMINE SORPTION ON 1) NaY (2) FeNaY (37), (3) FeNaY (46), (4) FeNaY (61), (5) FeNaY (75), (6) FeNaY (82)

that the percent cation-exchange affects the free energy of the gas/zeolite system.

Isosteric heat of adsorption

For all NBA/catalyst systems there was a temperature coefficient in heat of adsorption q_{st} . Consequently, the plots of $\ln P$ against the number of molecules adsorbed were not linear. The ferric exchanged Y zeolites are expected to have heterogeneous potential surface for the adsorption of NBA. The isosteric heats of sorption were obtained by application of the Clausius-Clapeyron equation,

$$q_{st} = R \left(\frac{T_1 T_2}{T_2 - T_1} \right) \ln \frac{P_2}{P_1}$$

Table-17 shows the values of q_{st} (Kcals/mole) as a function of NBA molecules adsorbed per unit cell.

In case of NaY, at coverage of 20 molecules per unit cell, the heat of NBA adsorption is 21.4 Kcals/mole, which decreases to 10 Kcals/mole at 35 molecules per unit cell. Due to strong interaction between Na^+ ions and NH_2 groups of NBA, the heat of adsorption of NBA is higher as compared to those for other hydrocarbons.^{210, 25k} For FeNaY(37), FeNaY(46) and FeNaY(82) at lower coverages (15-20 molecules per unit cell), the heat of adsorption is above 40 Kcals/mole,

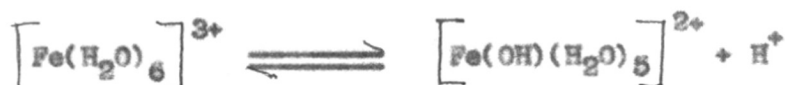
Table-17 : Isothermic heats of n-butylamine adsorption
(Kcals/mole)

Catalyst	Coverage molecules per unit cell					
	15	18	20	25	30	35
NaY	-	19.7	21.4	17.4	16.0	10.1
FeNaY(37)	37.5	42.5	22.3	20.1	14.5	-
FeNaY(46)	-	32.7	44.8	29.8	11.2	-
FeNaY(61)	-	14.4	5.0	-	-	-
FeNaY(75)	15.5	9.1	5.1	-	-	-
FeNaY(82)	41.0	34.9	19.8	13.6	-	-
FeNaY(46, 500, 5)	18.4	19.1	17.7	19.1	12.5	-

which is much higher than that for NaY. This indicates that the strength of NBA-cation interaction is higher in case of ferric exchanged Y zeolites. The adsorption data and low heat of adsorption values seem to indicate that in case of FeNaY(61) and FeNaY(75) the structure is distorted to a great extent and is also shown by X-ray diffraction. The heat of adsorption for FeNaY(46) at coverage of 20 molecules per unit cell reaches a maximum value of 44.8 Kcal/mole.

In case of thermally treated FeNaY (46, 500, 5) sample, the heat of adsorption is 18-20 Kcals/mole at 15-25 molecules per unit cell, which gradually reduces to 12.4 Kcals/mole at 30 molecules per unit cell. Due to thermal treatment, Bronsted acidic centres are destroyed and Fe^{3+} cations migrate into sodalite cages or hexagonal prisms, the sites which are inaccessible to NBA molecules. The heats of adsorption of NaY and FeNaY (46, 500, 5) are comparable because in both the cases NBA molecules are interacting only with Na^+ ions in supercages. Though adsorption isotherms and chemical potential values for FeNaY(46) and FeNaY (46, 500, 5) are approximately same; the q_{st} values and irreversible adsorption (Fig. 18) indicate that FeNaY(46) has stronger acidic centres. It is worth to note here that even after rehydration, FeNaY(46, 500, 5) showed lower acidity. The migration of Fe^{3+} ions to sodalite and hexagonal prism is

probably an irreversible process and $\text{Fe}^{3+}\text{-O-Fe}^{3+}$ may be existing in sodalite cages.



The dissociation of water may not take place in case of FeNaY(46, 500, 5) after thermal treatment. Some of the Bronsted acidic centres are destroyed during thermal treatment by dehydroxylation process as confirmed by the TG analysis of the samples. As a result (H^+ ions) Bronsted acidic centres are present in less number thereby reducing the acidity. DTA also does not give any support for the existence of aqua-complex of ferric-ion after thermal treatment. While DTA data helps in proposing the presence of $\left[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5\right]^{2+}$ in supercages in case of FeNaY(46) untreated. Thus, adsorption of n-butylamine, not only helps in understanding the comparative strength and number of acidic centres in the parent and thermally treated catalyst samples but also the cation site distribution.

Basic molecules like n-butylamine are adsorbed on cations (Fe^{3+} or Na^+ ions) and acidic protons in supercages of Y zeolites. The equilibrium sorption values and chemical affinity sequence show direct proportionality to number of

interacting centres including acidic protons, while irreversible adsorption and heats of adsorption indicate the trend in the strength of sorbate-sorbent interactions. Among the ferric exchanged Y zeolites, FeNaY(46) has maximum number of strong acidic centres and is thermally stable and is therefore a better catalyst. The irreversible adsorption and heats of sorption support the Fe^{3+} ion migration into sodalite cages and reduced acidity after heating FeNaY(46) sample at 500°C for 5 hours in air.

3.3B Sorption of water on zeolites

Fig. 23 shows adsorption isotherms of water vapour on NaY, FeNaY(46), FeNaY(61) and FeNaY(82) zeolites. The adsorption isotherms show two regions in which two different phenomena govern the adsorption, above 200°C the interaction of water with cations and zeolitic framework and below 200°C volume-filling phenomenon, dominate the adsorption pattern.

At 300°C and 20 mm vapour pressure, NaY and FeNaY(82) adsorb 13 and 18.3 molecules per unit cell respectively. FeNaY(82) adsorbs larger number of water molecules on account of stronger interaction of water with Fe^{3+} ions. At 60°C and 20 mm pressure, NaY, FeNaY(46), FeNaY(61) and FeNaY(82) adsorb 208, 166, 143 and 123 molecules of H_2O per unit cell. Fe^{3+} ions in supercages form hexa-aquo complexes of the type $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$. These iron complexes sterically hinder

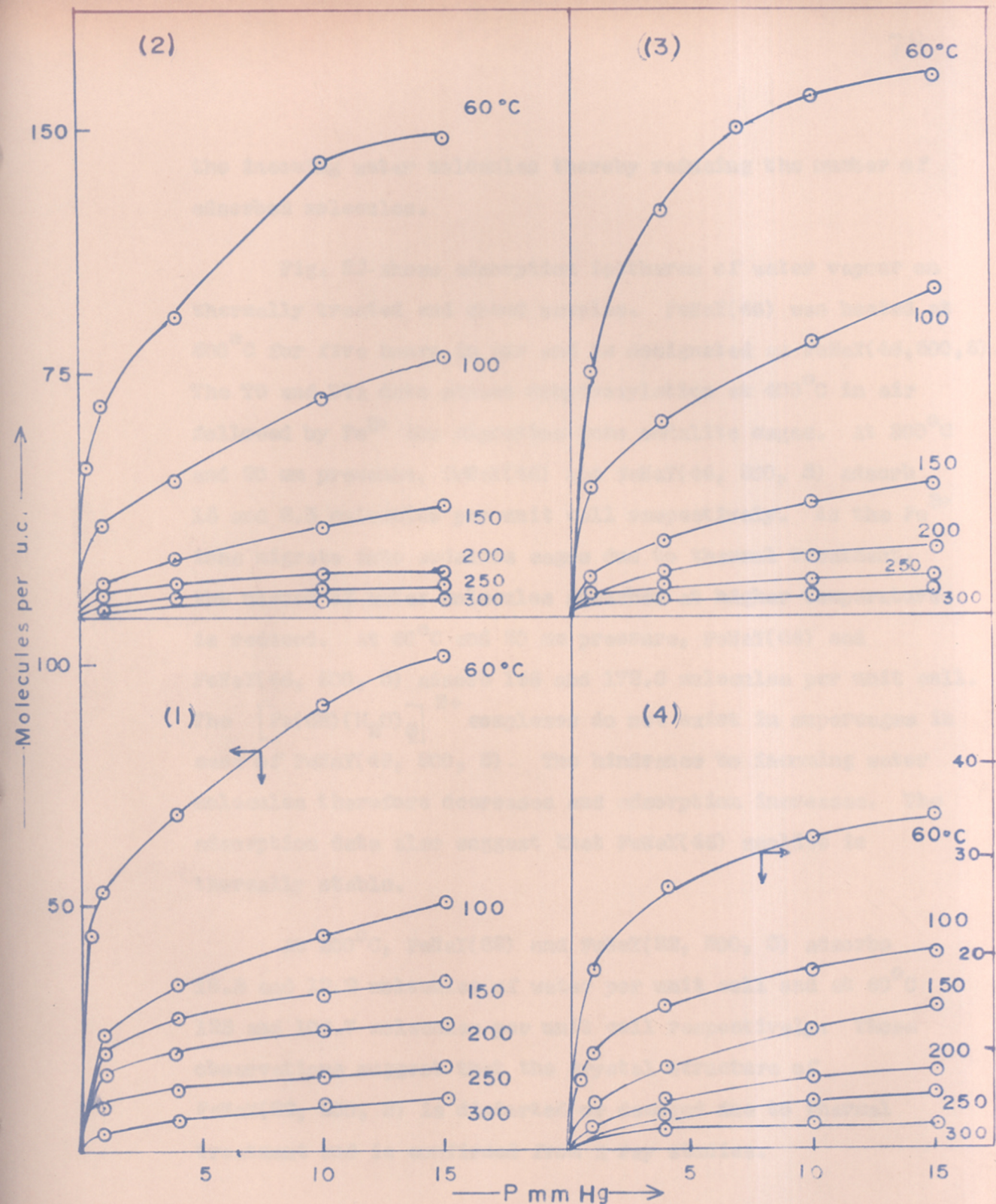


FIG. 22: ADSORPTION ISOTHERMS OF WATER ON:-(1) FeNaY (82,500,5) (2) FeNaY (46, RA), (3) FeNaY (46,500,5) AND (4) FeNaY (46, Coked)

the incoming water molecules thereby reducing the number of adsorbed molecules.

Fig. 22 shows adsorption isotherms of water vapour on thermally treated and coked samples. FeNaY(46) was heated at 500°C for five hours in air and is designated as FeNaY(46, 500, 5). The TG and DTA data showed dehydroxylation at 400°C in air followed by Fe³⁺ ion migration into sodalite cages. At 300°C and 20 mm pressure, FeNaY(46) and FeNaY(46, 500, 5) adsorb 15 and 8.5 molecules per unit cell respectively. As the Fe³⁺ ions migrate into sodalite cages due to thermal treatment, the number of water molecules adsorbed at higher temperatures is reduced. At 60°C and 20 mm pressure, FeNaY(46) and FeNaY(46, 500, 5) adsorb 166 and 172.5 molecules per unit cell. The $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ complexes do not exist in supercages in case of FeNaY(46, 500, 5). The hindrance to incoming water molecules therefore decreases and adsorption increases. The adsorption data also suggest that FeNaY(46) zeolite is thermally stable.

At 300°C, FeNaY(82) and FeNaY(82, 500, 5) adsorbs 18.3 and 12.2 molecules of water per unit cell and at 60°C 123 and 106.7 molecules per unit cell respectively. These observations suggest that the crystal structure of FeNaY(82, 500, 5) is distorted or damaged due to thermal treatment and is confirmed from X-ray studies.

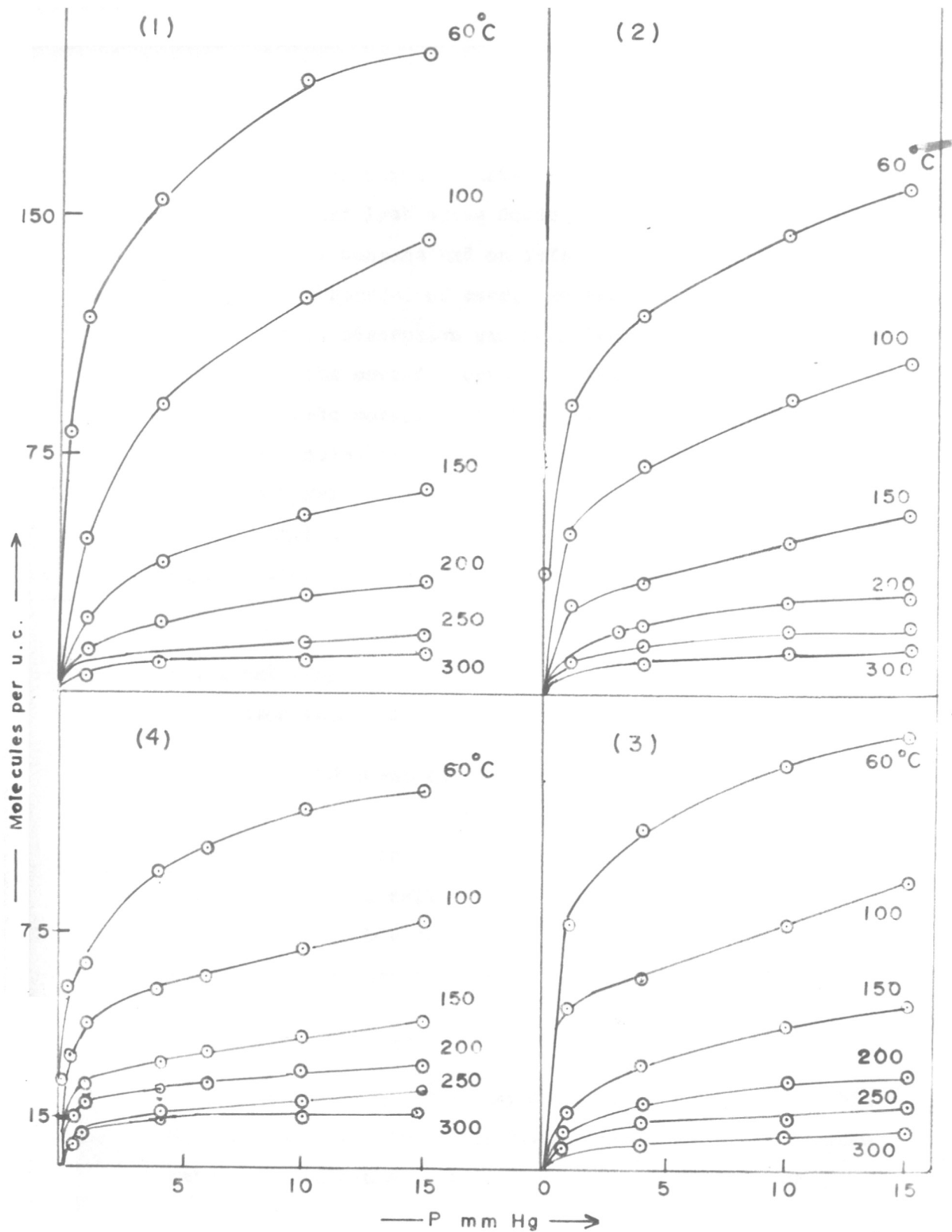


FIG.23: ADSORPTION ISOTHERMS OF WATER ON (1) NaY, (2) FeNaY(46) (3) FeNaY(61) AND (4) FeNaY(82).

The adsorption of water vapour on FeNaY(46, coked) which shows catalyst aging during the oxidative dehydrogenation of ethyl benzene and on FeNaY(46, RA), a catalyst sample after removal of coke, was carried out. In case of coked sample, adsorption was drastically reduced as large volumes of the cavities were occupied by (hydrogen deficient) polymeric coke material itself. Fig. 23 shows that FeNaY(46, RA) adsorb approximately the same number of water molecules as the parent FeNaY(46) zeolite. The adsorption studies thus confirm that after reactivation, FeNaY(46) retains its crystal structure and can be reused for the catalytic reaction.

Fig. 24 shows the adsorption of water vapour on different samples as a function of time. The trend in the saturation adsorption capacity supports the above predictions.

Fig. 25 shows the number of water molecules irreversibly adsorbed by zeolites under high vacuum ($\sim 10^{-6}$ torr) at different temperatures. The number of water molecules retained per unit cell follows the sequence FeNaY(82) > FeNaY(46) > NaY > FeNaY(46, RA) > FeNaY(46, coked). This trend indicates the strength of adsorbate-adsorbent interaction.

Adsorption isotherms

At 300°C, Langmuir equation is applicable but Dubinin equation is not. At higher temperatures, only chemisorbed water is retained on zeolites. Particularly cations

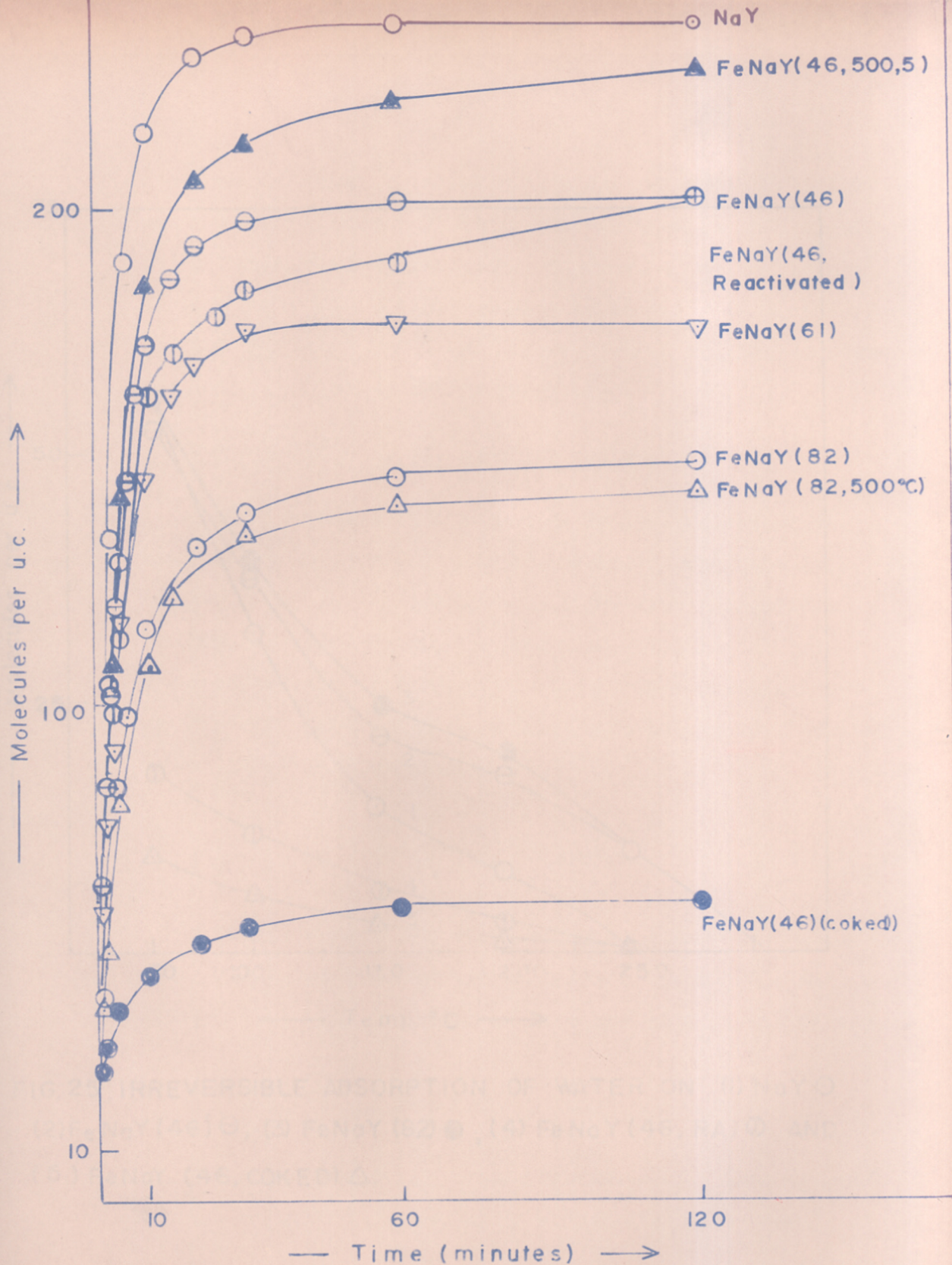


FIG. 24: RATE STUDIES OF WATER AT 24°C

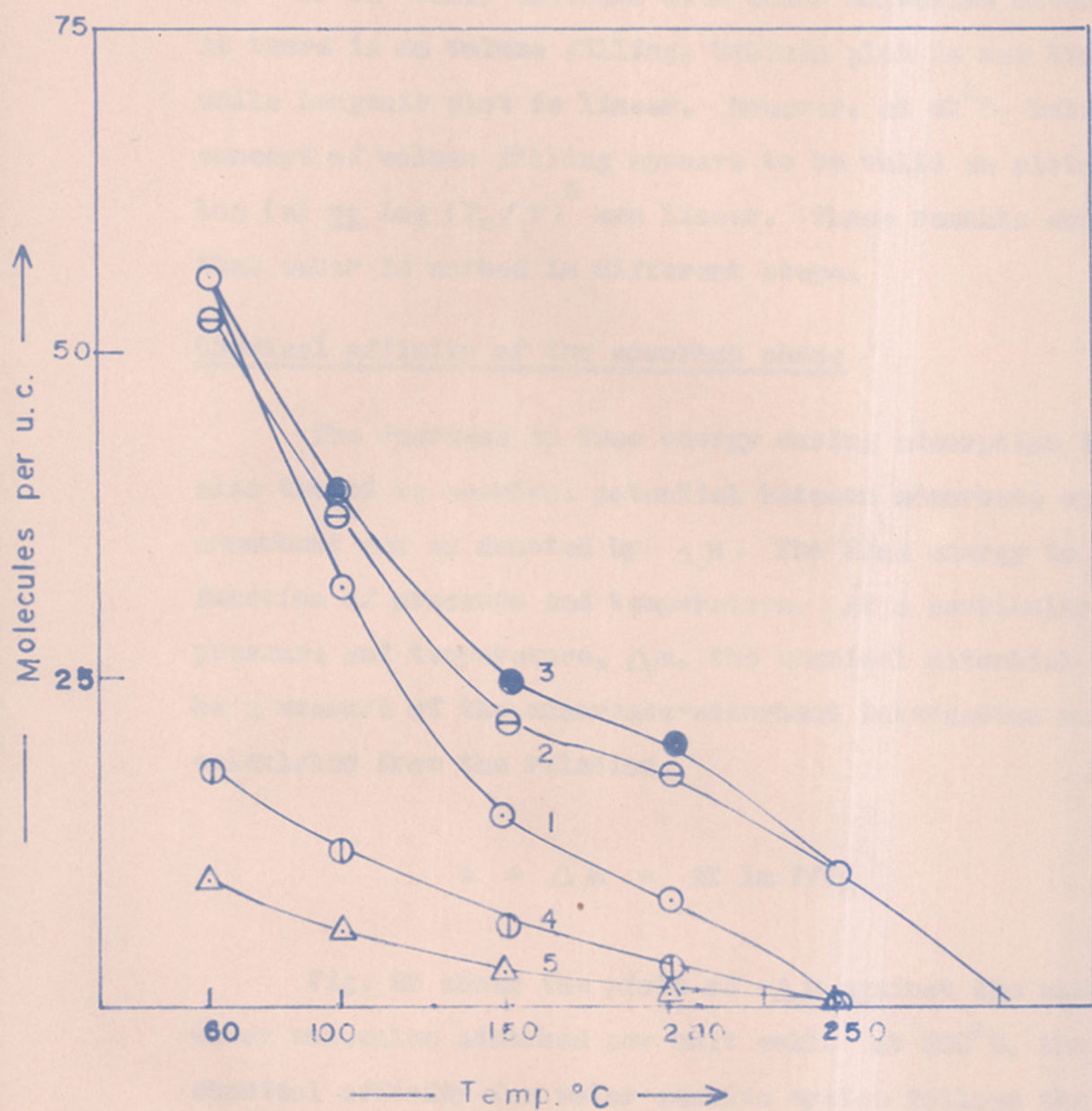


FIG. 25: IRREVERSIBLE ADSORPTION OF WATER ON (1) NaY ○, (2) FeNaY (46) ⊖, (3) FeNaY (82) ●, (4) FeNaY (46, RA) ⊕ AND (5) FeNaY (46, COKED) △.

(Fe^{3+} or Na^+ ions) interact with water molecules directly. As there is no volume filling, Dubinin plot is not linear, while Langmuir plot is linear. However, at 60°C , Dubinin concept of volume filling appears to be valid as plots of $\log(a)$ vs $\log(P_s/P)^2$ are linear. These results confirm that water is sorbed in different steps.

Chemical affinity of the adsorbed phase

The decrease in free energy during adsorption is also termed as chemical potential between adsorbate and adsorbent and is denoted by $\Delta\mu$. The free energy is a function of pressure and temperature. At a particular pressure and temperature, $\Delta\mu$, the chemical potential can be a measure of the adsorbate-adsorbent interaction and is calculated from the relation,

$$G = \Delta\mu = RT \ln P/P_0$$

Fig. 26 shows the plots of $-\Delta\mu$ against the number of water molecules adsorbed per unit cell. At 300°C , the chemical affinity for water-zeolite system follows the trend:



at a coverage of 12 molecules per unit cell. The strength of $\text{H}_2\text{O} \cdots \cdots \text{Fe}^{3+}$ interaction is higher than $\text{H}_2\text{O} \cdots \cdots \text{Na}^+$

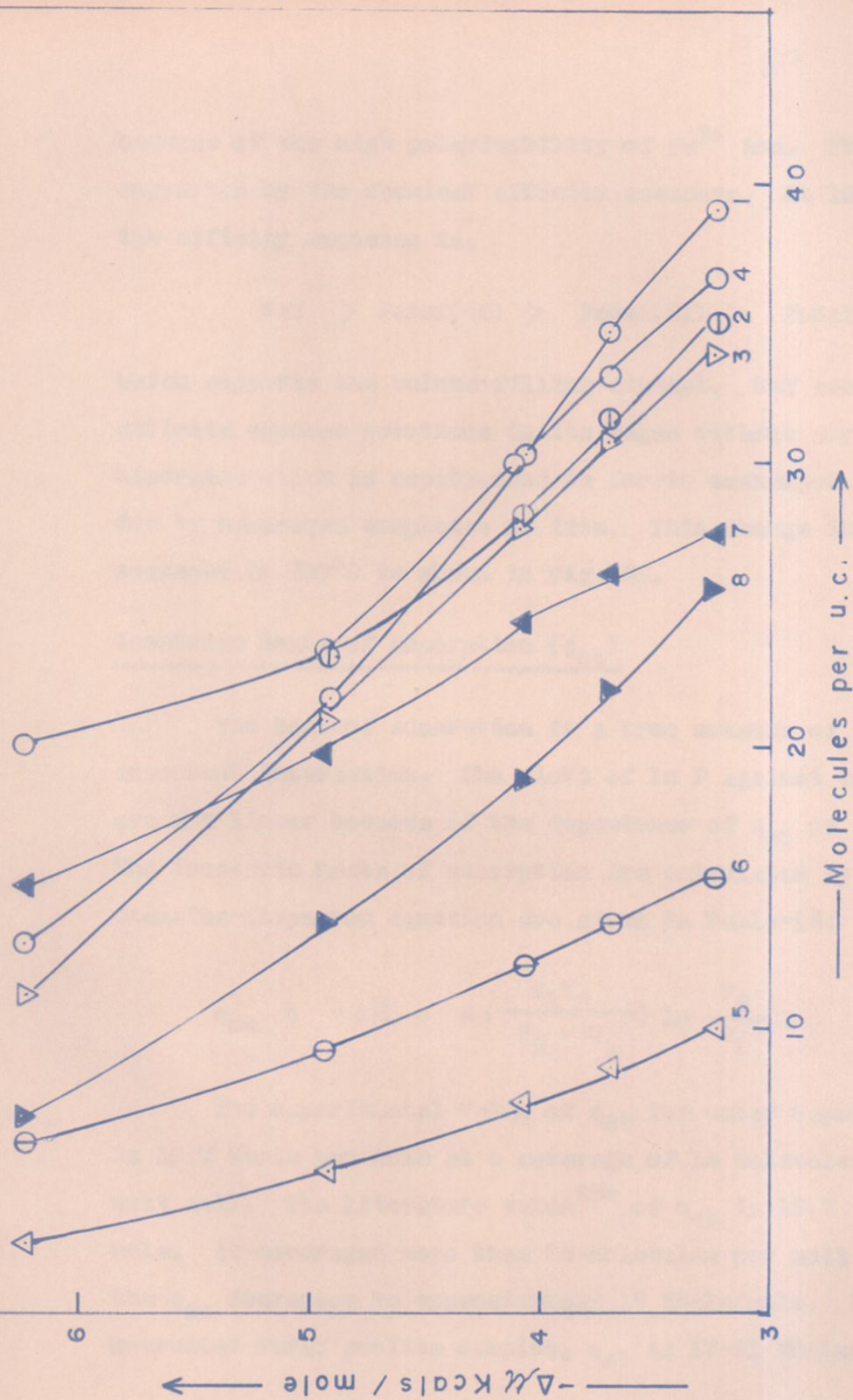


FIG. 26: CHEMICAL POTENTIAL AGAINST WATER COVERAGE AT 200°C. (1) NaY (○); (2) FeNaY (46) (⊖)
 (3) FeNaY (61) (▽); (4) FeNaY (82) (○); (5) FeNaY (46, Coked) (Δ); (6) FeNaY (46, RA) (⊖);
 (7) FeNaY (82, 500, 5) (▲); AND (8) FeNaY (46, 500, 5) (▼)

because of the high polarizability of Fe^{3+} ion. This is supported by the chemical affinity sequence. At 100°C , the affinity sequence is,



which supports the volume-filling concept. NaY zeolite forms cationic aqueous solutions in its cages without any steric hindrance which is experienced in ferric exchanged samples due to hexa-aqua complexes of iron. This change in affinity sequence at 200°C is shown in Fig. 26.

Isosteric heats of adsorption (q_{st})

The heat of adsorption is a true measure of adsorbate-adsorbent interaction. The plots of $\ln P$ against coverage are not linear because of the dependence of q_{st} on temperature. The isosteric heats of adsorption are calculated by using Clausius-Clapeyron equation are given in Table-18:

$$q_{st} = -\Delta\bar{H} = R \left(\frac{T_1 T_2}{T_2 - T_1} \right) \ln \frac{P_2}{P_1} .$$

The experimental value of q_{st} for water vapour on NaY is 19.7 Kcals per mole at a coverage of 15 molecules per unit cell. The literature value^{25k} of q_{st} is 19.7 Kcals per mole. At coverages more than 24 molecules per unit cell, the q_{st} decreases to approximately 12 Kcals/mole. For untreated FeNaY zeolite samples, q_{st} is 17-21 Kcals/mole at

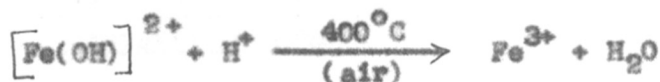
Table-18 : Isothermic heats of water adsorption
(Kcal/mole)

Catalyst	8	15	24	30	45	75
NaY	-	19.7	12.0	12.7	11.0	13.3
FeNaY(46)	-	16.5	13.5	14.7	15.1	12.6
FeNaY(61)	-	13.5	15.1	11.0	11.7	14.3
FeNaY(82)	-	17.0	11.6	13.6	15.4	12.9
FeNaY(46, 500, 5)	21.0	12.6	12.4	14.1	15.1	12.5
FeNaY(46, coked)	-	8.3	14.2	-	-	-
FeNaY(46, RA)	17.6	15.4	16.3	13.6	13.4	12.1
FeNaY(82, 500, 5)	-	22.7	11.6	6.3	18.7	-

coverage of 8 to 15 molecules per unit cell. Invariably, for FeNaY samples q_{st} is 15 Kcals/mole at coverage of 45 molecules per unit cell. For NaY, q_{st} is 11 Kcals/mole at the same coverage. In FeNaY zeolite surface potential is higher due to Fe^{3+} ion, even in sodalite cages, therefore q_{st} is higher than that for NaY. As expected, at low coverages there exists strong interaction between water molecules and the catalytic active centres particularly cations (Fe^{3+} , Na^+ , H^+ ions) and therefore q_{st} is higher ^{than} at higher coverages when volume-filling phenomenon dominates.

The process of water adsorption can be visualised as follows. At low coverages, adsorbed water molecules interact strongly with Fe^{3+} ions in supercages to form (hexa-) aqua complexes of iron as confirmed by thermal analysis studies. With the increase in uptake of water, some of water molecules enter into sodalite cavities at coverage of 45 molecules per unit cell and interact with ferric ions therein. In case of NaY, the interaction of water molecules at low coverage, 15 molecules per unit cell, is stronger while at a coverage of 24 molecules per unit cell onwards, q_{st} remains constant till about 75 molecules per unit cell, indicating not much of variation in surface potential.

In case of FeNaY samples, DTA studies support the dehydroxylation at $400^{\circ}C$,



In all experiments, the activation temperature was 350°C . We expect that $[\text{Fe}(\text{OH})]^{2+}$ may exist even after activation at 350°C . So the dissociation of water takes place to a lesser extent. The volume filling phenomenon dominates above the coverage of 75 molecules per unit cell. The adsorption studies support different mechanisms in the uptake of water in ferric exchanged Y zeolites indicating heterogeneity in surface potential.

We may conclude that the hexa-aqua complexes of iron decrease the total adsorption capacity. The chemical affinity sequence shows that $\text{Fe}^{3+} \cdots \text{H}_2\text{O}$ interaction is stronger than $\text{Na}^+ \cdots \text{H}_2\text{O}$ interaction. Below 200°C the volume-filling phenomenon dominates. Sodium ions form cationic aqueous solution in supercages while ferric ions form more localised hexa-aqua complexes. Therefore, zeolite NaY shows more affinity for water in volume-filling region. The analysis of isosteric heats of adsorption suggests that the water adsorption is a multistep process, due to heterogeneity in surface potential.

3.3C Rates of sorption studies of aromatic compounds

The rates of sorption were measured gravimetrically using the gravimetric unit as described in the Chapter 3.2. The solvent bulb was kept at 24°C. The vapour pressures of benzene, toluene, ethyl benzene and styrene were 85, 25, 8 and 6 mm of Hg respectively.

Diffusion studies

The rate of sorption of ethyl benzene (EB) of NaY and FeNaY(∞) zeolites are presented in Fig. 27. The sorption is initially fast and reaches equilibrium value within 5 to 10 minutes. The equilibrium sorption value for ethyl benzene is found to decrease with increasing ferric content in the zeolite, for instance the number of ethyl benzene molecules sorbed per unit cell decreases from 31 to 22 for NaY and FeNaY(32). The sorption on ferric ions in the supercages appears to be directional and localized. The irreversible adsorption of ethyl benzene on the zeolites at different temperatures presented in Fig. 29 shows that FeNaY(46) retains more ethyl benzene above 200°C than NaY zeolite. This result suggests a stronger interaction in the former sample. This observation is also valid for the ferric Y zeolite in the pelleted form.

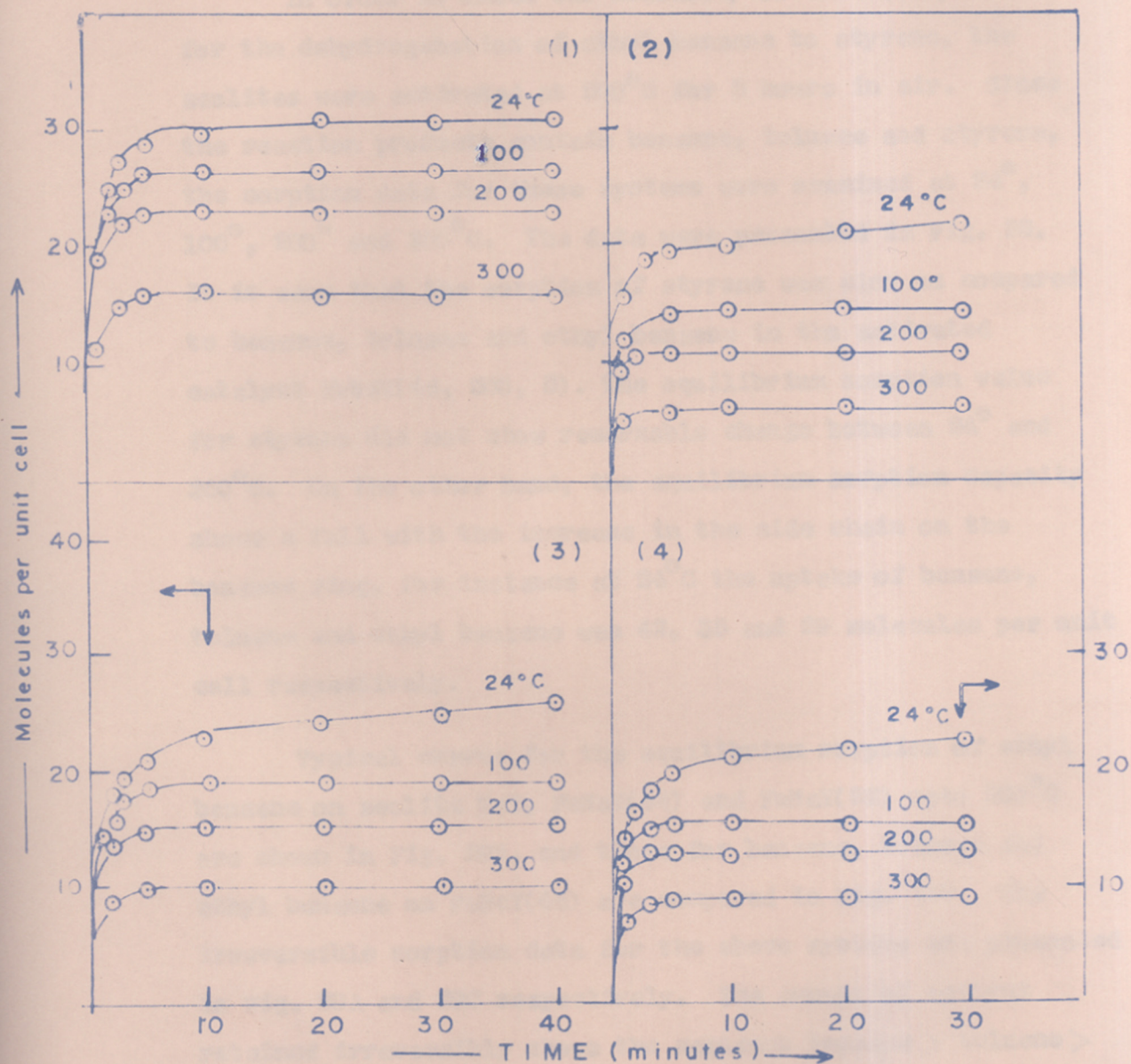


FIG.27: KINETICS OF SORPTION OF ETHYL BENZENE ($V_p = 8$ mm) ON
 (1) NaY, (2) FeNaY(82), (3) FeNaY(46), AND (4) FeNaY
 (46, PELLET)

In order to check the stability of the catalyst used for the dehydrogenation of ethyl benzene to styrene, the zeolites were activated at 500°C for 5 hours in air. Since the reaction products contain benzene, toluene and styrene, the sorption data for these systems were examined at 24° , 100° , 200° and 300°C . The data were presented in Fig. 28. It is seen that the sorption of styrene was slow as compared to benzene, toluene and ethyl benzene in the activated catalyst FeNaY(46, 500, 5). The equilibrium sorption value for styrene did not show remarkable change between 24° and 300°C . On the other hand, the equilibrium sorption capacity shows a fall with the increase in the side chain on the benzene ring, for instance at 24°C the uptake of benzene, toluene and ethyl benzene was 42, 35 and 29 molecules per unit cell respectively.

Typical curves for the equilibrium sorption of ethyl benzene on zeolite NaY, FeNaY(46) and FeNaY(82) upto 300°C are shown in Fig. 29B, and those for benzene, toluene and ethyl benzene on FeNaY(46) are compared in Fig. 29D. The irreversible sorption data for the above systems are presented in Fig. 29A and 29C respectively. The amount of sorbent retained irreversibly shows the sequence benzene > toluene > ethyl benzene at 24°C and above 200°C the trend is EB > T > B (Fig. 29). In contrast to the sorption of benzene, toluene and ethyl benzene, styrene shows entirely different behaviour.

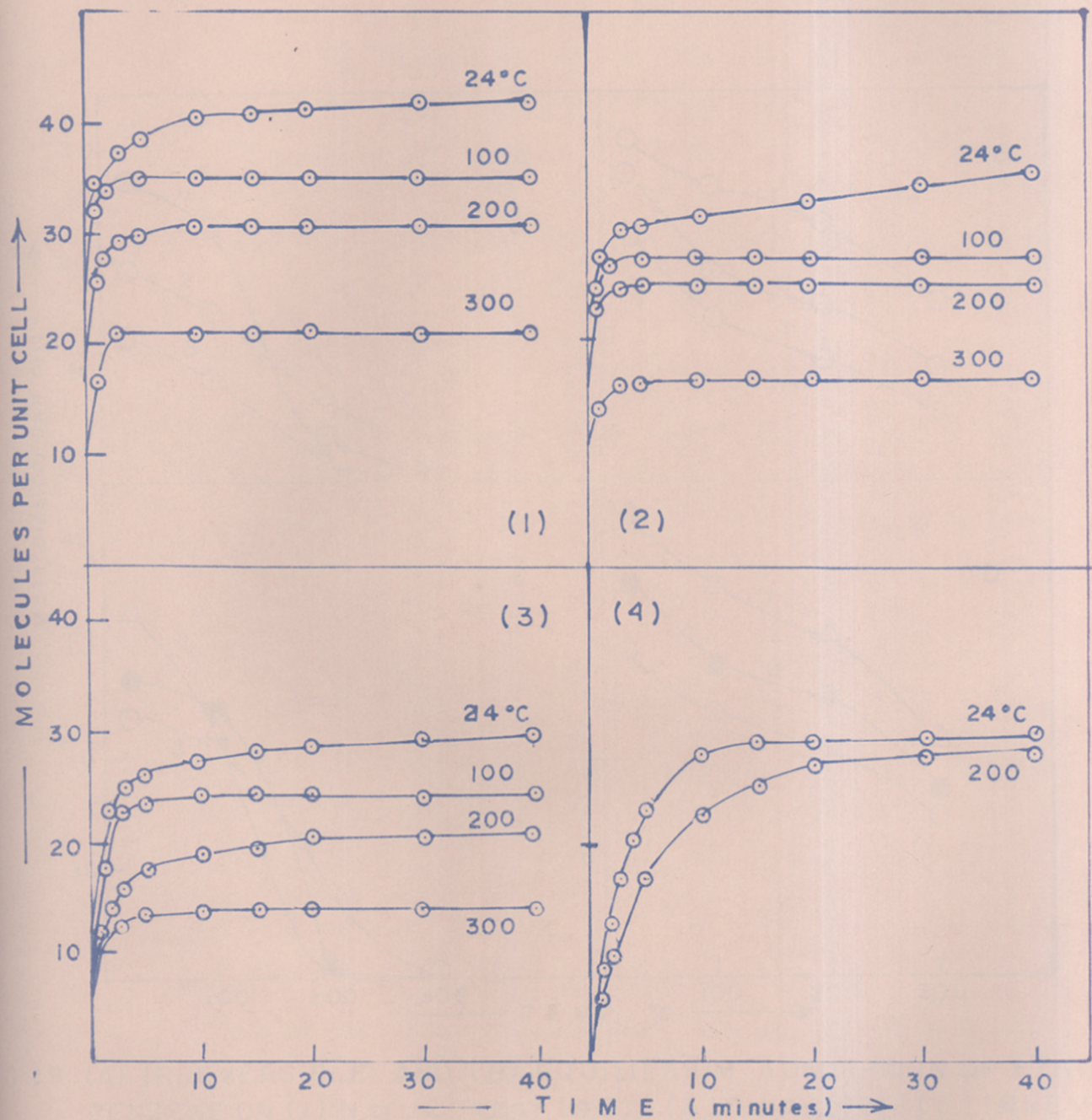


FIG.28: KINETICS OF SORPTION OF (1) BENZENE, (2) TOLUENE, (3) ETHYL BENZENE, (4) STYRENE, ON FeNaY (46, 500, 5).

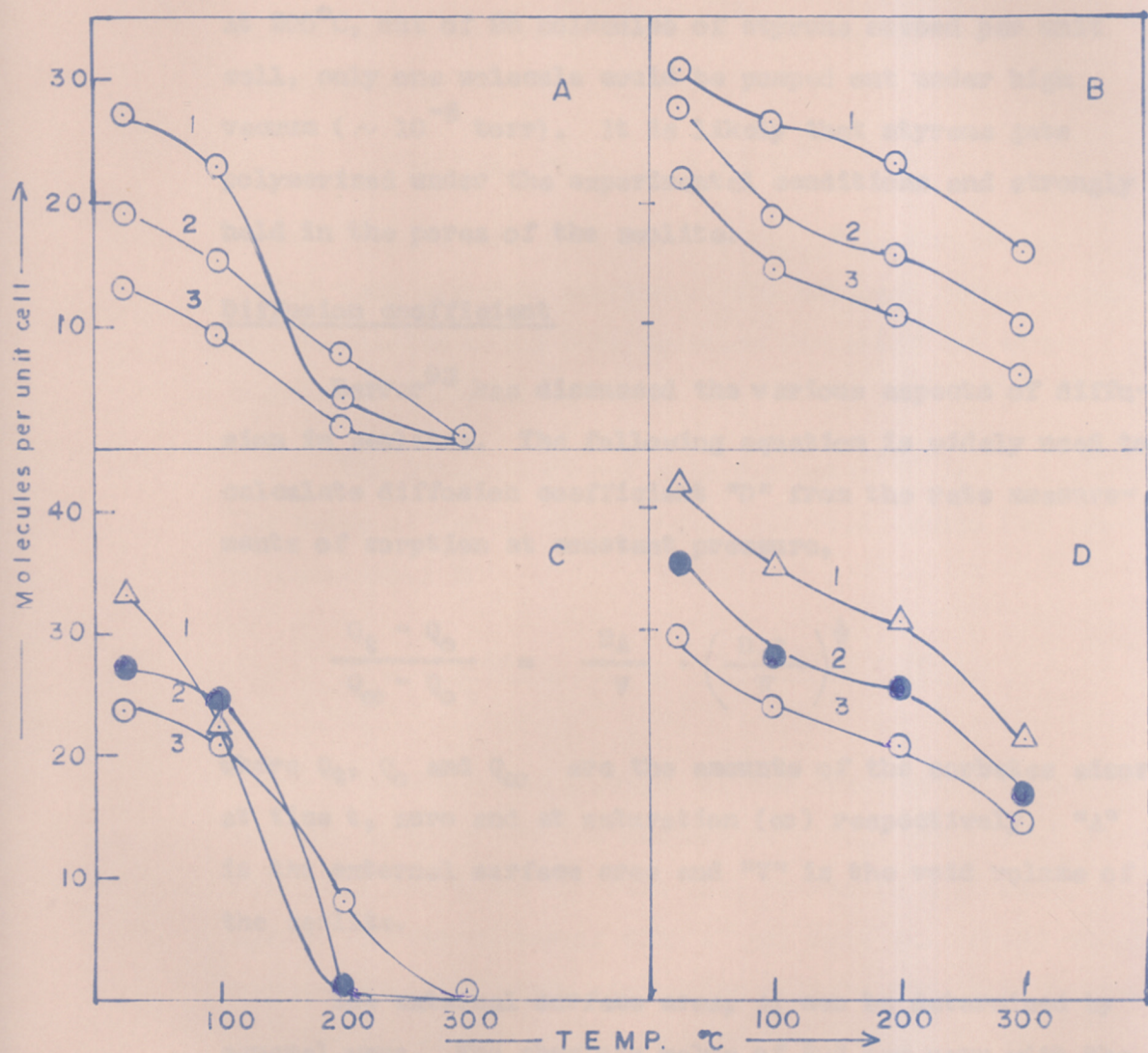


FIG 29: (A) IRREVERSIBLE AND (B) EQUILIBRIUM ADSORPTION OF ETHYL BENZENE ON (1) NaY, (2) FeNaY (46), (3) FeNaY (82) (C) IRREVERSIBLE AND (D) EQUILIBRIUM ADSORPTION OF (1) BENZENE, (2) TOLUENE AND (3) ETHYL BENZENE ON FeNaY (46,500,5)

Styrene is strongly and irreversibly held on the zeolite. At 200°C, out of 28 molecules of styrene sorbed per unit cell, only one molecule could be pumped out under high vacuum ($\sim 10^{-5}$ torr). It is likely that styrene gets polymerized under the experimental conditions and strongly held in the pores of the zeolite.

Diffusion coefficient

Barrer⁹³ has discussed the various aspects of diffusion in zeolites. The following equation is widely used to calculate diffusion coefficient "D" from the rate measurements of sorption at constant pressure,

$$\frac{Q_t - Q_0}{Q_\infty - Q_0} = \frac{2A}{V} \cdot \left(\frac{D \cdot t}{\pi} \right)^{\frac{1}{2}}$$

where Q_t , Q_0 and Q_∞ are the amounts of the sorbates adsorbed at time t , zero and at saturation (∞) respectively. "A" is the external surface area and "V" is the void volume of the zeolite.

The external surface area, A, can be determined by several ways. The absolute value of "D" may vary with the method of calculation of "A". "A" may be determined by the adsorption on water-filled crystals, so that N_2 or Kr sorption is limited to external areas. Barrer and Brook^{93b}

suggested a simple method to calculate "A". Even when "D" depends upon concentration, $a(t)^{\frac{1}{2}}$ law may be observed experimentally :

$$Q_t - Q_0 = Q_{\text{ext.}} + AK(t)^{\frac{1}{2}}$$

where "K" is a rate coefficient, " $Q_{\text{ext.}}$ " is the amount sorbed upon external surfaces. The external surface area was calculated using this equation for water and ethyl benzene as adsorbates.

The cross-sectional area for water²²⁰ is $10.6 \text{ \AA}^2$. The value of "A" is $25.3 \text{ m}^2/\text{gm}$. The void volume (V) can be determined by

$$d = \frac{1.66}{V} \cdot \frac{M}{1} = \frac{1.66 (59x + 60y)}{V^*}$$

where M is the formula weight of the framework of the zeolite, x and y are the numbers of (AlO_2) and (SiO_2) per unit cell and V^* is the unit cell volume in $\text{\AA}^3$. Here, we have used void volume of $6700 \text{ \AA}^3$ per unit cell (0.32 cc/gm) corresponding to argon adsorption (eliminating void volume of sodalite cages), which is effective volume in the sorption of aromatic molecules. While the total void volume corresponds to the adsorption of water and is equal to $7908 \text{ \AA}^3$ (0.38 cc/gm).

The diffusion coefficient is determined from the plot of $\left(\frac{Q_t - Q_0}{Q_{\infty} - Q_0}\right)$ against $(t)^{\frac{1}{2}}$. The slope of the straight line 'S' is $\left[\frac{2A}{V} \cdot \left(\frac{D}{\pi}\right)^{\frac{1}{2}}\right]$. By knowing A and V, the value of "D" is calculated using the relation

$$D = \frac{S^2 V^2 \pi}{4A^2}$$

The energy of activation for diffusion was calculated using the equation,

$$D = D_0 \exp. - E/RT.$$

The values of diffusion coefficients in the temperature range of 24^o-300^oC, the temperature-independent diffusion coefficients, D_0 , and energies of activation of diffusion for benzene, toluene, ethyl benzene and styrene on FeNaY(46, 500, 5) are tabulated in Table-19. The diffusion coefficients decreased with the increase of temperature. The D_0 values for benzene, toluene, ethyl benzene and styrene are 7.3×10^{-13} , 6.4×10^{-13} , 3.2×10^{-13} and 1.2×10^{-13} cm² sec⁻¹ respectively. The energies of activation for the diffusion are 320, 366, 732 and 1236 cal. per mole. The experimental data suggest that the mass transport of benzene and toluene is much faster and may not be rate-governing step in the reactions on this catalyst. While styrene which is strongly adsorbed in the supercages shows comparatively higher energy of activation for diffusion, the desorption of styrene may be rate-controlling step.

Table-19 : Diffusion coefficients and activation energy
of diffusion

Adsorbate	Diffusion coefficient, (D), (cm ² sec ⁻¹) x 10 ¹³				D ₀ (cm ² sec ⁻¹) x 10 ¹³	Activation energy of diffusion (cals./mole)
	300°C	200°C	100°C	24°C		
Benzene	4.9	7.8	9.7	10.5	7.3	320
Toluene	4.9	8.0	8.7	9.8	6.4	366
Ethyl benzene	4.2	4.9	6.7	7.7	3.2	732
Styrene	4.0	2.4	3.7	5.4	1.2	1235

CHAPTER - IV : DEHYDROGENATION OF ETHYL BENZENE

4.1 INTRODUCTION

The reactions catalysed by acidic centres have been extensively studied¹⁰⁹⁻¹¹¹ using zeolites. However, the activity of zeolites, having basically oxide structure, has not been explored in depth for oxidative dehydrogenation reactions even in case of industrially important reactions.

The oxidation of hexane and cyclohexane is catalysed by zeolites.²²¹ The complete oxidation of the lower C_2-C_3 hydrocarbons to CO , CO_2 and H_2O is also promoted on these catalysts.²²²⁻²²⁴ Benzene was obtained as one of the products in the oxidation of cyclohexane.²²¹ Acrolein was obtained from the partial oxidation of propylene on Cu-containing Y zeolites in presence of water vapour.²²² However, the activity of ferric exchanged zeolite for oxidative dehydrogenation of ethylbenzene to styrene has not been reported.

The industrial catalysts used for the dehydrogenation of ethyl benzene to styrene contain iron oxide along with Co/Mo oxides and a promoter like K_2O . Russo and coworkers²²⁵⁻²²⁹ studied the activity of γ -alumina, molybdena-alumina and various transition metal oxides supported on γ -alumina as catalysts for the oxidative dehydrogenation of ethyl benzene. They

reported the conversion from 23% to 45% and selectivity to styrene from 60% to 87%. Minachev and coworkers^{230,231} investigated the activity of sodium form of faujasite, chabazite, erionite and mordenite in dehydrogenation^{of} ethyl benzene.

Iron with redox behaviour and oxygen-carrier properties may be considered for this reaction as the first choice among the transition metals. Boudart and coworkers¹⁵² proposed the existence of $\text{Fe}^{3+} \text{---} \text{O}^{2-} \text{---} \text{Fe}^{3+}$ linkages in Y zeolites by infra-red and Mossbauer spectroscopy, while our results²³² helped in characterising the hydration properties and site occupancy of ferric ions with respect to temperature in Y zeolite. In this chapter, we report the catalytic activity of ferric exchanged Y zeolite in dehydrogenation of ethyl benzene.

4.2 EXPERIMENTAL

Catalyst

The unit cell composition of the exchanged zeolite used for catalytic activity is $\text{Fe}_9\text{Na}_{29}(\text{AlO}_2)_{57} \cdot (\text{SiO}_2)_{135} \cdot (270\text{H}_2\text{O})$, and (the zeolite) is designated as FeNaY(46). The X-ray diffraction pattern confirmed the crystallinity of the catalyst. For catalytic studies, the zeolite was mixed with 16% ferric exchanged bentonite, on hydrous basis, and extruded in (1/16") dia pellet form.

Apparatus and procedure

The experiments were carried out in a down flow tubular reactor at atmospheric pressure. The reactor consisted of a fused silica tube, 2 cms. in diameter and 30 cms. in length. The reactor was heated by a well-insulated metal block furnace. The top section of the reactor which functioned as a vapourizer and preheater was packed with inert porcelaine beads. The schematic diagram of the apparatus is shown in Fig. 30.

Reagent grade ethyl benzene was fed by a calibrated syringe pump at a constant feed rate, vapourized and passed through the catalyst zone. Oxygen or air was used as a carrier gas. The flow of oxygen/air was controlled by a needle valve and measured by a calibrated flow-meter. The reaction products were condensed and samples collected every hour were analysed by gas chromatography using SE-30 column.

The weighed amount of catalyst was charged in the reactor column. The temperature was slowly raised to 500°C or 550°C within a period of two hours and the catalyst was further activated for three hours at the desired temperature in the presence of oxygen or air. The activity of the catalyst was tested for two activation temperatures, 500°C and 550°C, and at five reaction temperatures varying from 300° to 550°C.

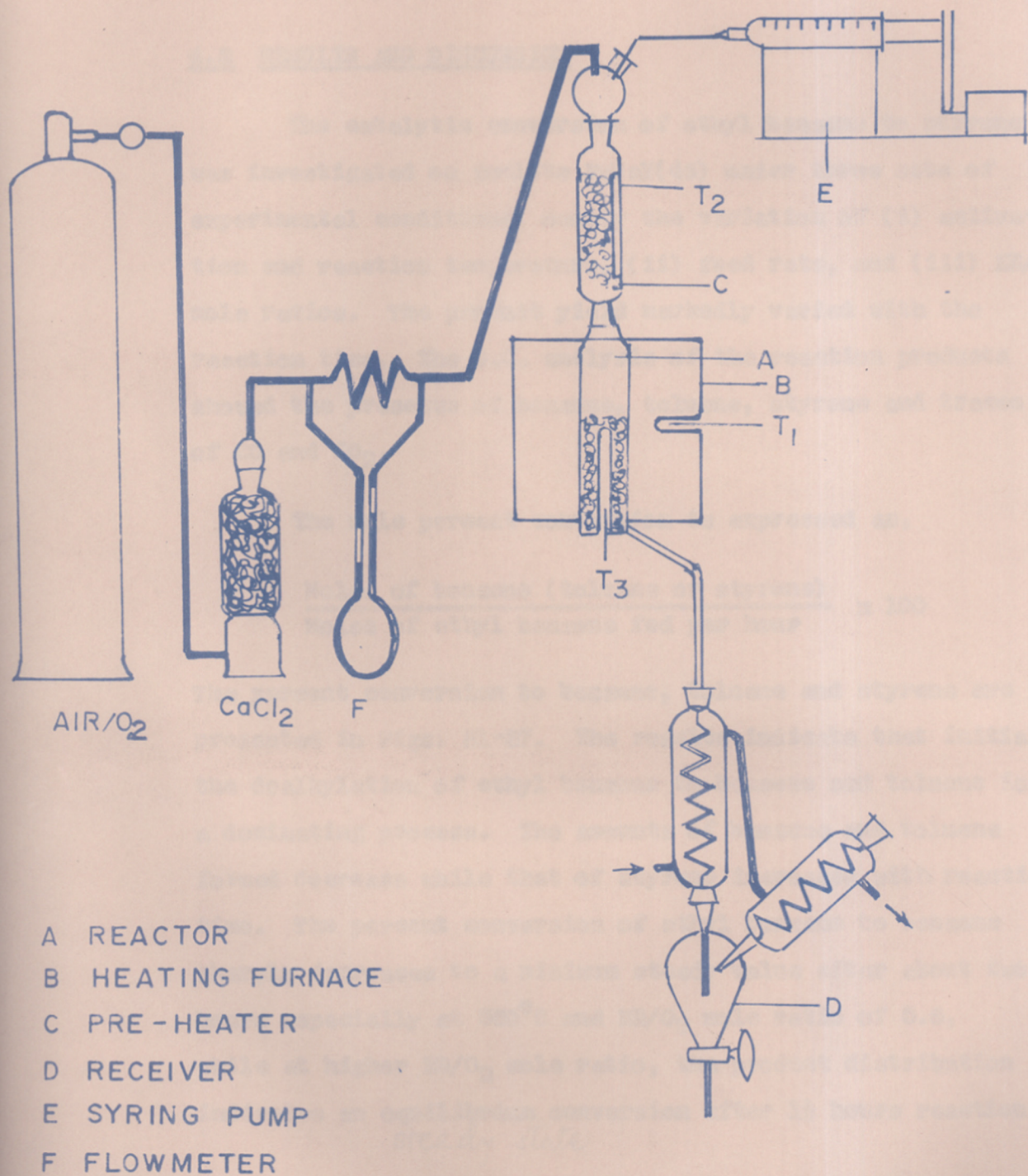


FIG. 30: SCHEMATIC DIAGRAM OF REACTOR SYSTEM

4.3 RESULTS AND DISCUSSION

The catalytic conversion of ethyl benzene to styrene was investigated on zeolite FeNaY(46) under three sets of experimental conditions, namely the variation of (i) activation and reaction temperature, (ii) feed rate, and (iii) EB/O₂ mole ratios. The product yield markedly varied with the reaction time. The G.C. analysis of the reaction products showed the presence of benzene, toluene, styrene and traces of CO and CO₂.

The mole percent conversion is expressed as,

$$\frac{\text{Moles of benzene (toluene or styrene)}}{\text{Moles of ethyl benzene fed per hour}} \times 100$$

The percent conversion to benzene, toluene and styrene are presented in Figs. 31-37. The results indicate that initially the dealkylation of ethyl benzene to benzene and toluene is a dominating process. The amounts of benzene and toluene formed decrease while that of styrene increases with reaction time. The percent conversion of ethyl benzene to benzene sharply decreases to a minimum steady value after about two hours especially at 550°C and EB/O₂ mole ratio of 5.6, while at higher EB/O₂ mole ratio, the product distribution indicates an equilibrium conversion after 1½ hours reaction.

steady state

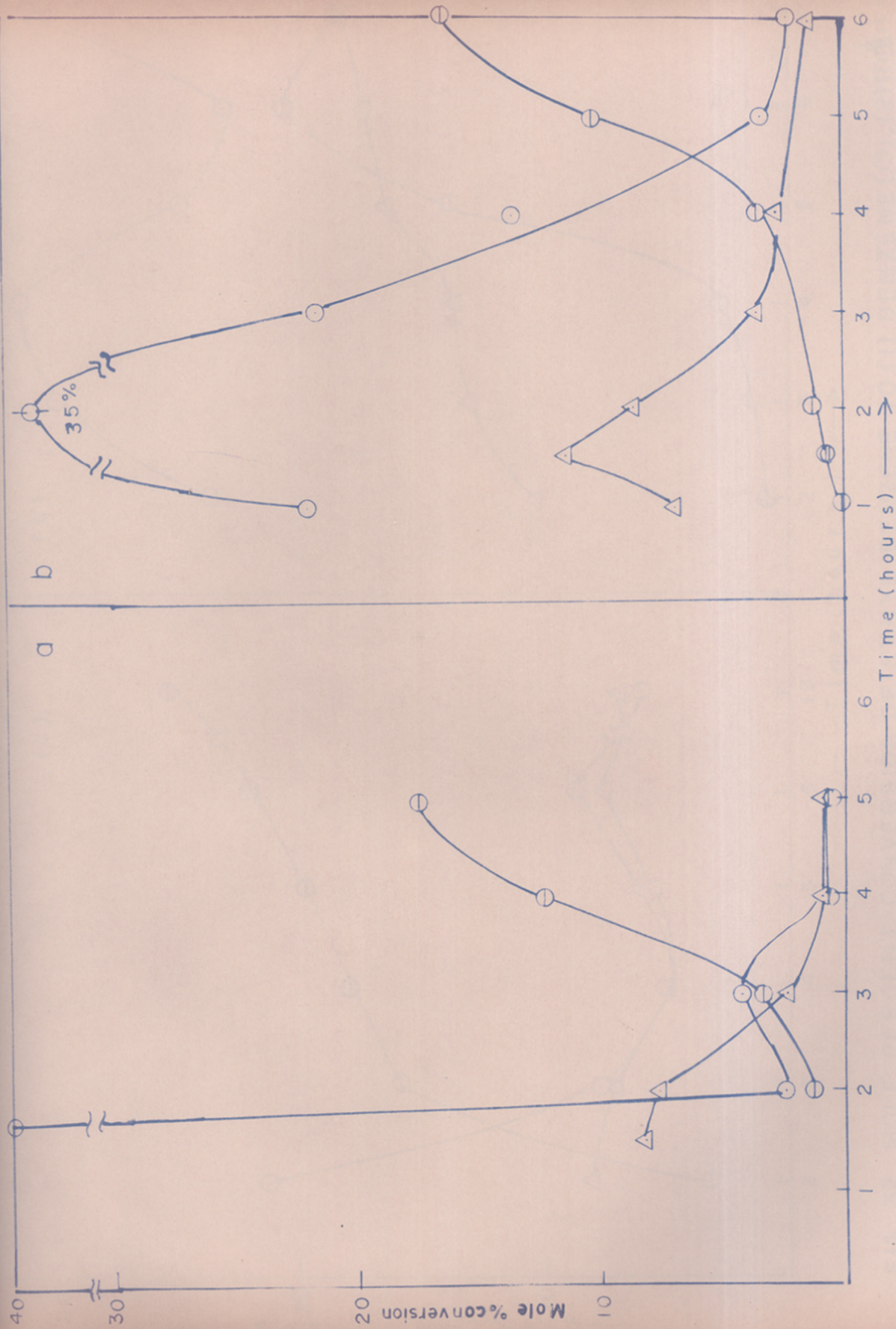


FIG. 31: MOLE PERCENT CONVERSION OF ETHYL BENZENE TO (1) BENZENE (○), (2) TOLUENE (△), AND (3) STYRENE (⊙), FOR ACTIVATION. TEMP. 500°C AND (EB/O₂) = 1:1. (a) REACTION TEMP. = 500°C, (b) REACTION TEMP. = 450°C

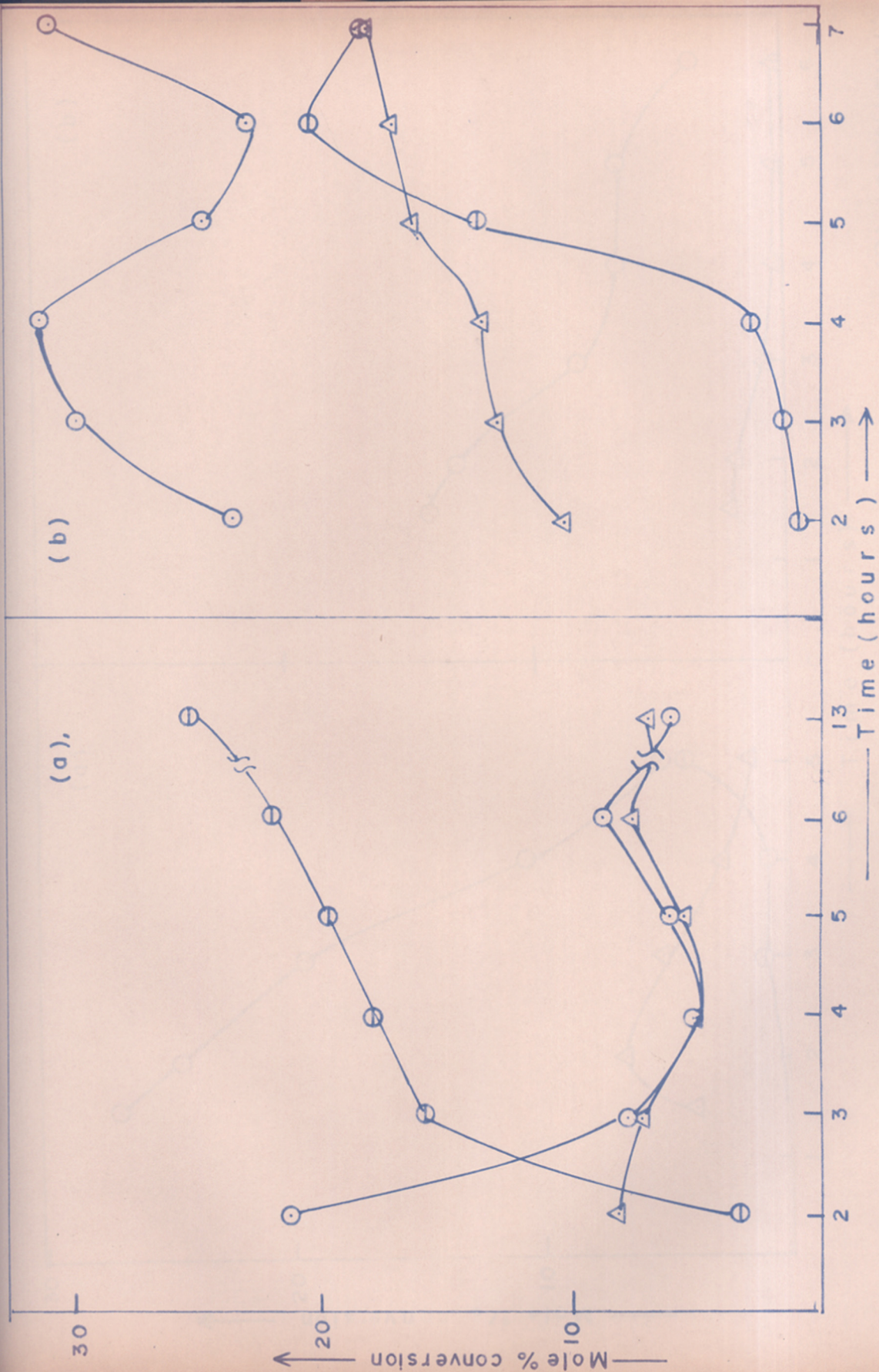


FIG. 32: MOLE PERCENT CONVERSION OF ETHYL BENZENE TO (1) BENZENE (○), (2) TOLUENE (Δ), AND (3) STYRENE (Θ), FOR (EB/O₂) = 1.1, 1) ACTIVATION TEMP. = REACT TEMP. = 500° (a) CAT (WT./BED VOL.) = 0.19, AND (b) 0.47 gm / C.6; (without binder)

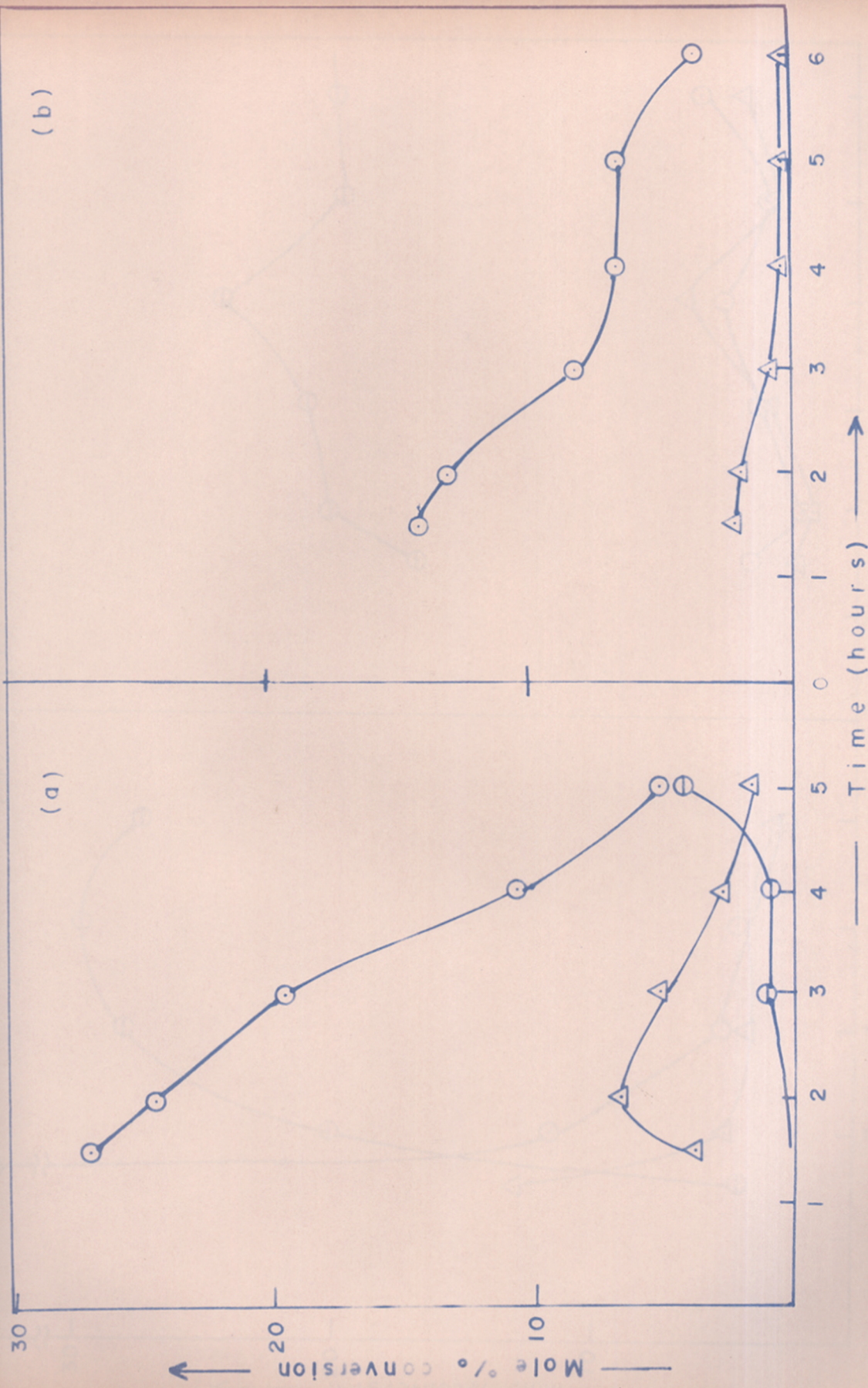


FIG. 33: MOLE PERCENT CONVERSION OF ETHYL BENZENE (1) BENZENE (○), (2) TOLUENE (△) (3) STYRENE (△) FOR ACTIVATION TEMP. = 500°C AND (EB/O₂) = 1:1, (a) REACT. TEMP. = 400°C (b) REACT. TEMP. = 350°C

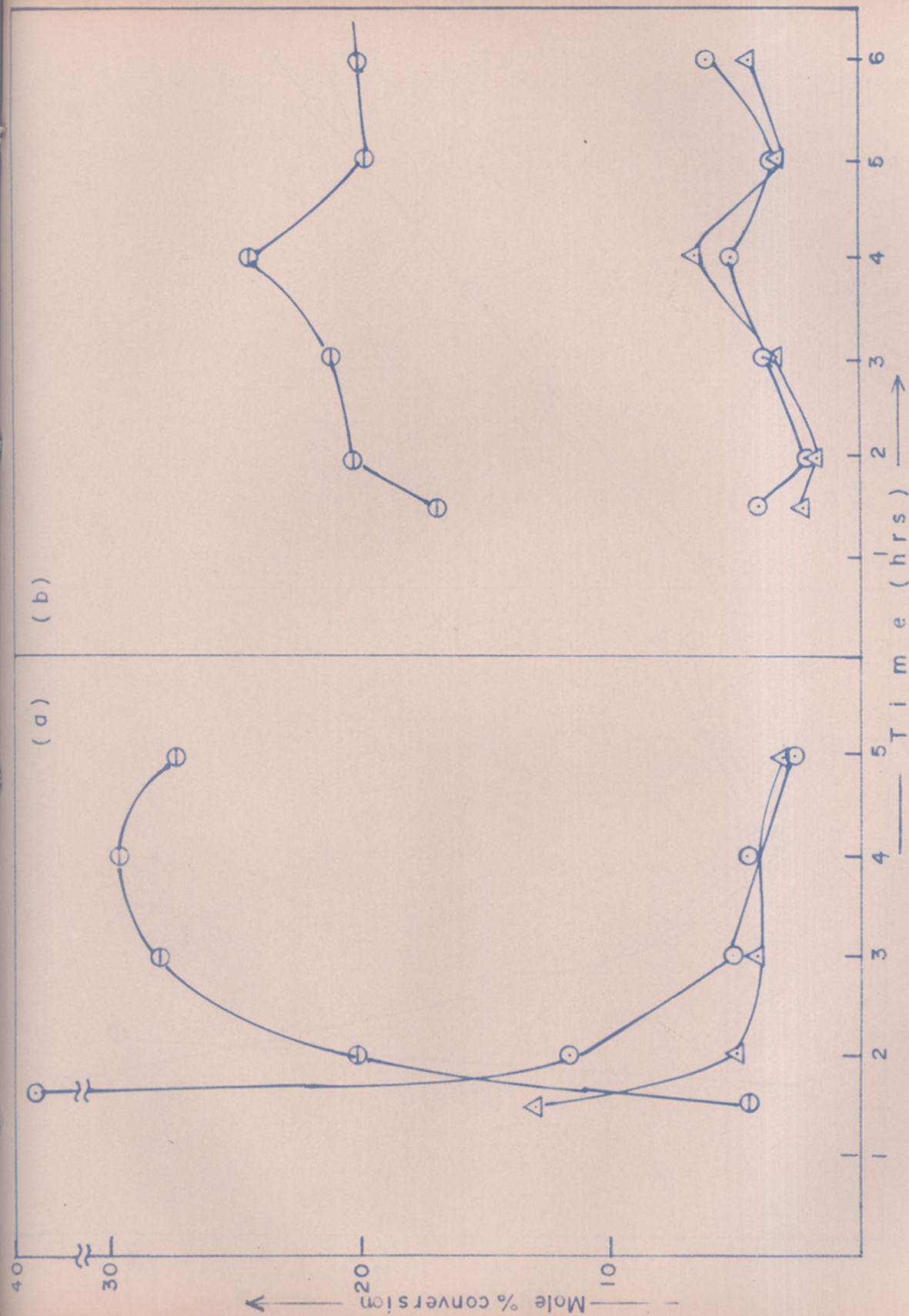
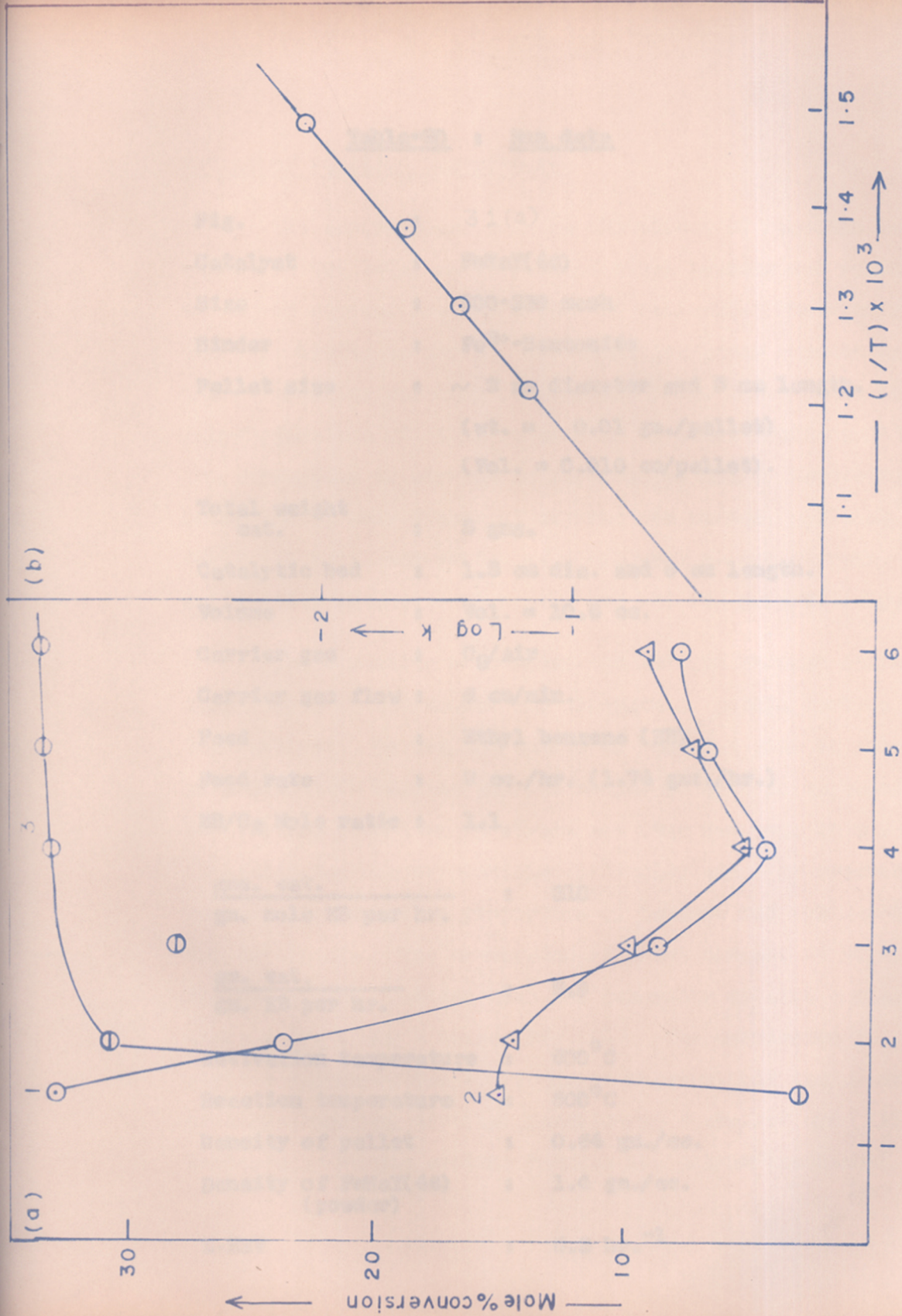


FIG 34: MOLE PERCENT CONVERSION OF ETHYL BENZENE TO (1) BENZENE (○), (2) STYRENE (Θ), (3) TOLUENE (Δ) FOR ACTIVATION TEMP. = 550°C AND REACT. TEMP. = 550°C ($\alpha \text{ XEB/O}_2$) = 5.6, (b) $\text{EB/O}_2 = 11.6$.



Time (hours) →

FIG 35: (a) MOLE PERCENT CONVERSION OF: E. B. TO (1) BENZENE (○), (2) TOLUENE (△), AND STYRENE (⊖) FOR (EB/O₂) = 1:1 ACTIVATION TEMP. = 550°C (b) ARRHENIUS PLOT FOR STYRENE

Table-20 : Run data

Fig.	:	31(a)
Catalyst	:	FeNaY(46)
Size	:	200-330 mesh
Binder	:	Fe ³⁺ -Bentonite
Pellet size	:	~ 2 mm diameter and 5 mm length. (wt. = 0.01 gm./pellet) (Vol. = 0.016 cc/pellet).
Total weight cat.	:	5 gms.
Catalytic bed	:	1.5 cm dia. and 6 cm length.
Volume	:	Vol. = 10.6 cc.
Carrier gas	:	O ₂ /Air
Carrier gas flow	:	6 cc/min.
Feed	:	Ethyl benzene (EB)
Feed rate	:	2 cc./hr. (1.74 gms./hr.)
EB/O ₂ Mole ratio	:	1.1
<u>gms. cat.</u> gm. mole EB per hr.	:	310
<u>gm. cat.</u> gm. EB per hr.	:	2.9
Activation temperature	:	500°C
Reaction temperature	:	500°C
Density of pellet	:	0.64 gm./cc.
Density of FeNaY(46) (powder)	:	1.4 gm./cc.
LHSV	:	5.3 hr. ⁻¹

Effect of reaction temperature

The experimental data on the effect of reaction temperature on the total conversion of ethyl benzene and selectivities to styrene are summarized in Table-21. The conversion and selectivity to styrene formation increases exponentially with increasing reaction temperature (Fig. 36). Since the dehydrogenation of ethyl benzene is an endothermic reaction, the conversion to styrene is favoured at higher temperatures. Below 350°C , only traces of styrene are formed, while at 550°C the total conversion of ethyl benzene and styrene selectivity increase to nearly 53% and 63% respectively.

The formation of benzene and toluene through dealkylation depend on the number and strength of acidic centres on the catalyst. During the course of reaction, coke is formed on the zeolite surface and the amount of coke is expected to increase with time on stream and thus decrease in number of acidic centres responsible for dealkylation or cracking, reducing the relative proportion of benzene and toluene in the catalysate. The conversion of ethyl benzene to styrene increases with reaction time and generally attains a steady state value after 3 hours (Fig. 31). The conversion to styrene increases due to two major reasons, (i) the cracking of ethyl benzene, parallel reaction is decreased and (ii) the decrease in acidic centres reduces the polymerisation of

Table-21 : Effect of reaction temperature

	T _A °C Activation temperature	Reaction temperature T _R °C	Total % conver- sion	% conversion to styrene	% selectivity to styrene	Mole styrene per mole EB/hr/gm. cat.
1	500	500	52.66	17.45	33.14	0.035
2	500	450	47.51	10.50	22.10	0.021
3	500	400	18.64	4.20	22.53	0.0024
4	500	350	-	-	-	in trace
5	550	550	52.93	33.4	63.10	0.0668

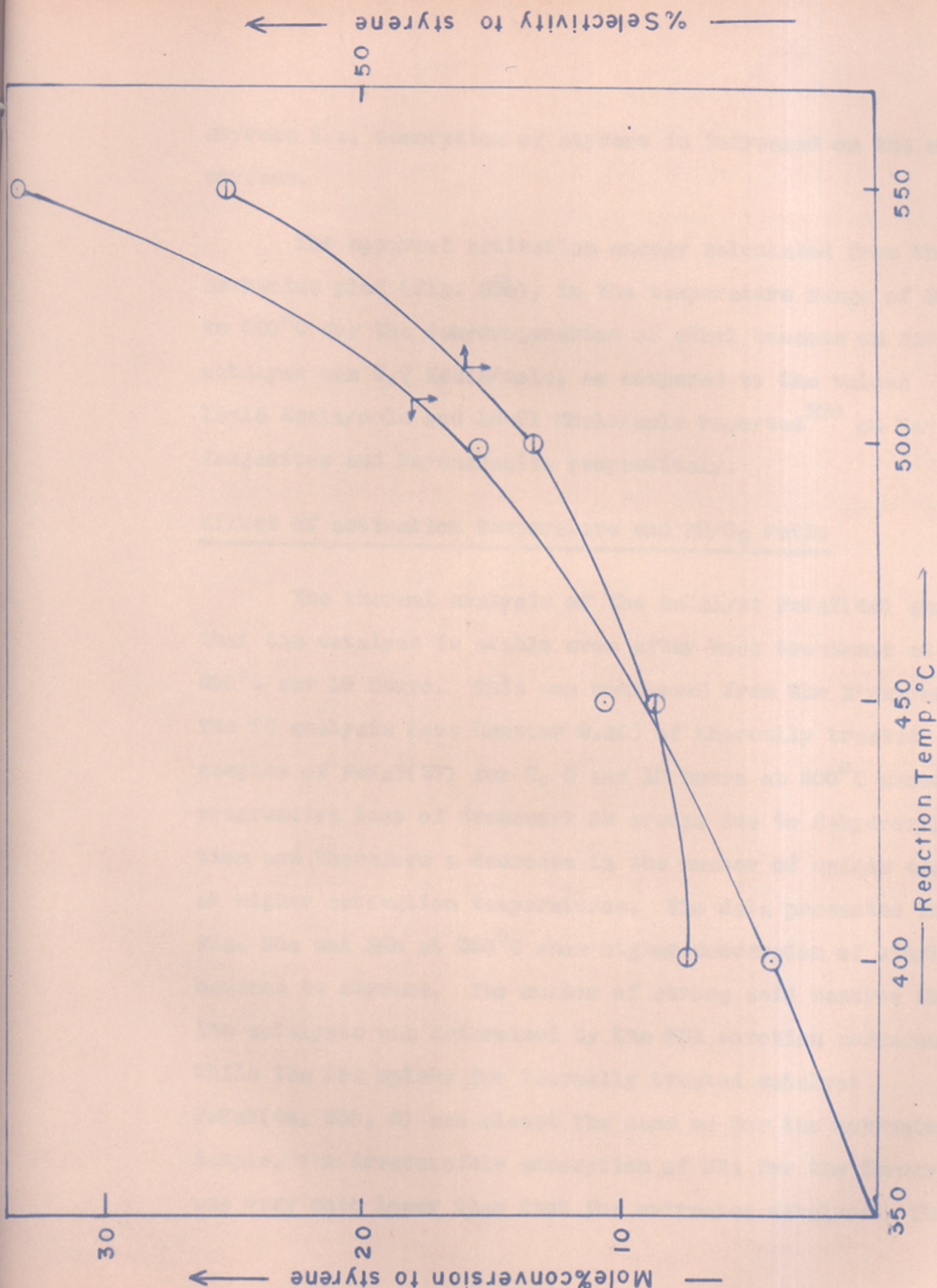


FIG. 36: THE EFFECT OF REACTION TEMP. ON MOLE % CONVERSION (O) , AND % SELECTIVITY (Θ) TO STYRENE

styrene i.e. desorption of styrene is increased on the coked surface.

The apparent activation energy calculated from the Arrhenius plot (Fig. 37b), in the temperature range of 350°C to 550°C for the dehydrogenation of ethyl benzene on FeNaY(46) catalyst was 2.7 Kcals/mole, as compared to the values 13-16 Kcals/mole and 18-21 Kcals/mole reported²³⁰ on Na-faujasites and Na-chabazite respectively.

Effect of activation temperature and EB/O₂ ratio

The thermal analysis of the catalyst FeNaY(46) showed that the catalyst is stable even after heat treatment at 500°C for 10 hours. This was confirmed from the X-ray analysis. The TG analysis (see Chapter 2.3C) of thermally treated samples of FeNaY(37) for 2, 5 and 10 hours at 500°C showed progressive loss of framework OH groups due to dehydroxylation and therefore a decrease in the number of acidic centres at higher activation temperatures. The data presented in Fig. 34a and 34b at 550°C show higher conversion of ethyl benzene to styrene. The number of strong acid centres in the catalysts was determined by the NBA sorption measurements. While the NBA uptake for thermally treated catalyst FeNaY(46, 500, 5) was almost the same as for the untreated sample, the irreversible adsorption of NBA for the former was very much lower than that for untreated catalyst. The

heats of adsorption of NBA on the two catalysts at a coverage of 18 molecules per unit cell were 19 Kcals/mole and 32 Kcals/mole indicating the stronger interaction of NBA with the latter. The NBA sorption studies therefore confirm that the thermal treatment of FeNaY(46) zeolite destroys strong acidic centres which are in turn responsible for dealkylation of ethylbenzene.

The effect of the variation of EB/O₂ molar ratio is indicated in Fig. 37. By increasing the ethyl benzene feed the catalyst coking rate increased and therefore the benzene and toluene content in the product decreased and consequently styrene yield increased. At 550°C, the conversion of ethyl benzene to styrene was higher for EB/O₂ = 1.1 than for 5.6, while the selectivity values for styrene was 78 % and 61 % respectively (Fig. 37). The increased selectivity to styrene with increase of ethyl benzene concentration in the feed (EB/O₂ molar ratio = 5.6) may probably be due to the increase in the number of collisions between ethyl benzene molecules and the active centres responsible for the dehydrogenation reaction. Fig. 38 shows the increase in percent conversion and selectivity to styrene with the increase in contact time.

The following scheme for the dealkylation and dehydrogenation of ethyl benzene is proposed on the basis of experimental observations :

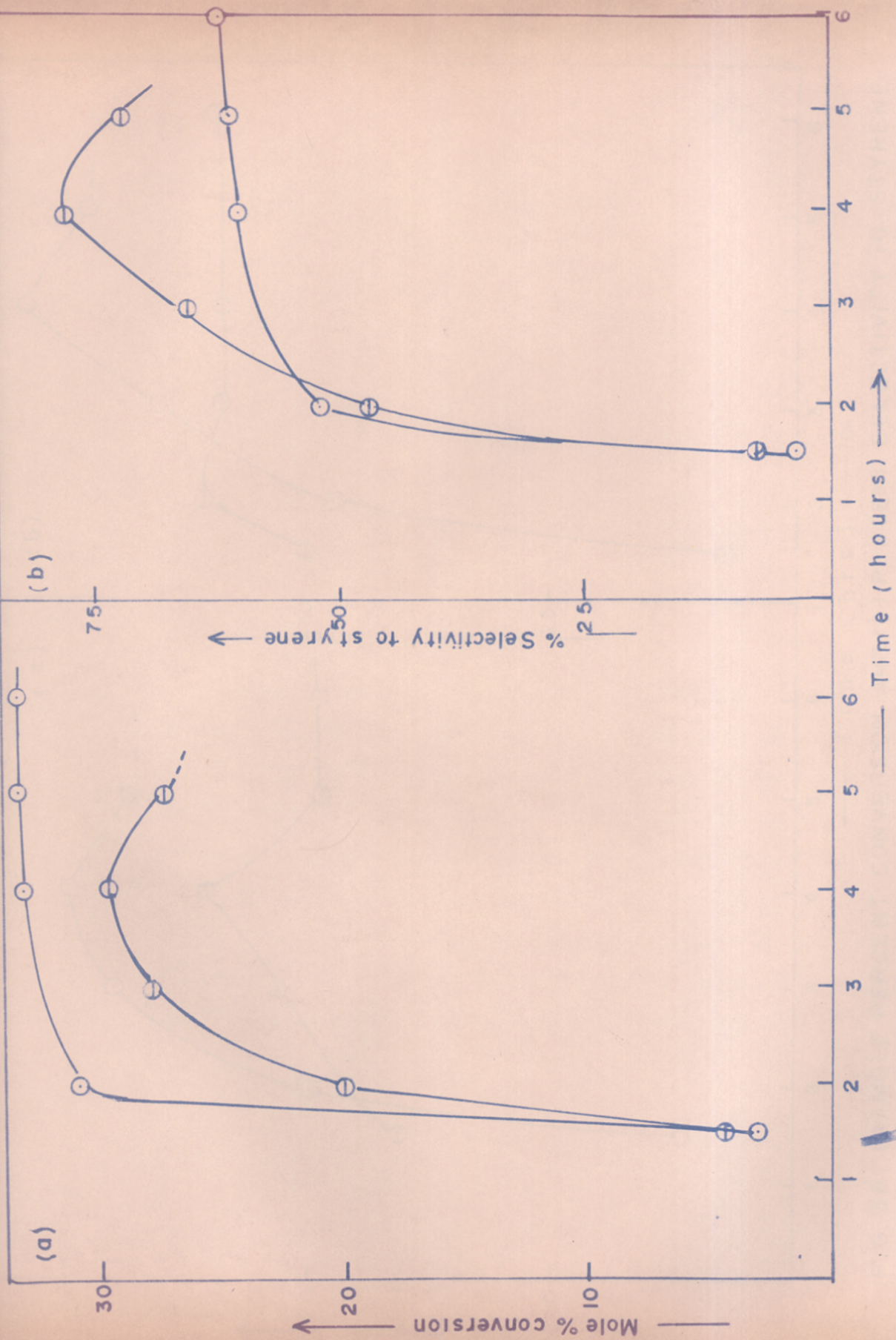


FIG.37: (a) MOLE PERCENT CONVERSION AND (b) PERCENT SELECTIVITY TO STYRENE FOR $(EB/O_2) = 1.1$ (O), AND 5.6 (⊗)

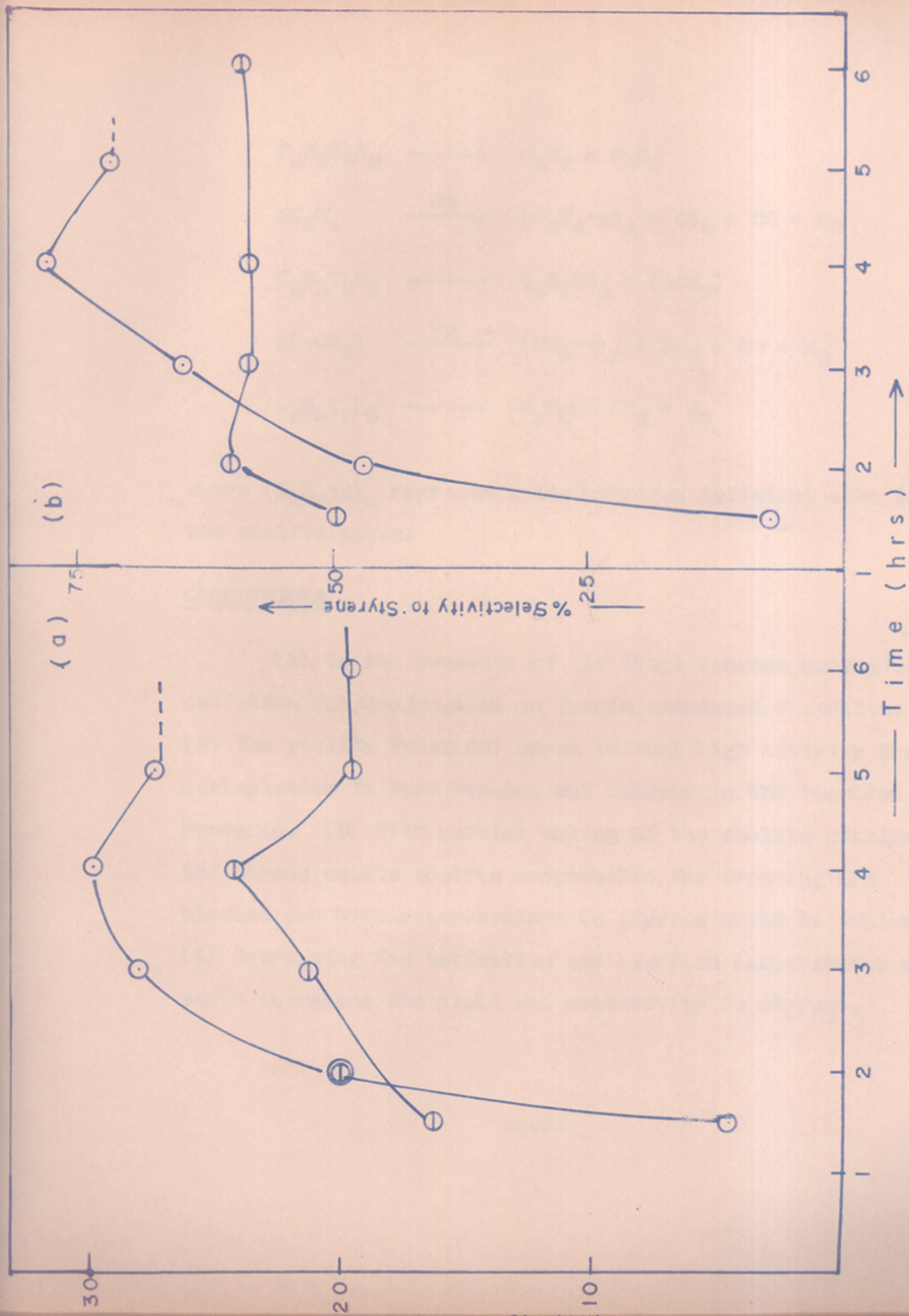
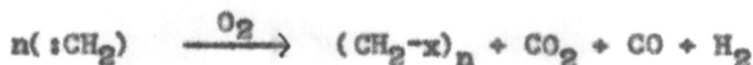
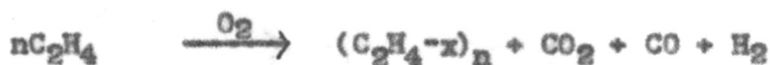


FIG. 38: (a) MOLE PERCENT CONVERSION AND (b) PERCENT SELECTIVITY TO STYRENE FOR CONTACT TIMES (1) $\tau_1 = 310$ (O) AND $\tau_2 = 155$ (Θ)



where $(\text{C}_2\text{H}_4-x)_n$ represents the hydrogen deficient coke in the zeolite pores.

CONCLUSIONS

- (1) In the presence of air ethyl benzene undergoes oxidation dehydrogenation on ferric exchanged Y zeolite.
- (2) The zeolite FeNaY(46) shows initial high activity for dealkylation to form benzene and toluene in the reaction products.
- (3) With partial coking of the zeolite catalyst the strong acidic centres responsible for cracking are blocked and higher conversions to styrene could be achieved.
- (4) Increasing the activation and reaction temperatures upto 550°C increases the yield and selectivity to styrene.

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no supplies were found.

SUMMARY

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S U M M A R Y

We have reported a systematic study of a series of ferric exchanged Y zeolites, their physico-chemical properties including adsorption and catalytic activity for oxidative dehydrogenation of ethyl benzene to styrene.

The ferric exchanged Y zeolites are characterised by X-ray diffraction, thermal analysis, infrared, visible spectroscopy, electrical conductivity measurements and X-ray photoelectron spectroscopy. The X-ray diffraction patterns of all the samples showed Fd3m group. Considering 533 plane, which is intense and least affected by ion-exchange, the decrease in the intensity in the X-ray patterns with ion-exchange is attributed to the distortion of the framework due to the presence of highly polarizable ferric ions and the loss of crystallinity. The lattice cell parameters, a_0 , of all the samples are about 24.60 Å.

On the basis of thermal analysis, the presence of $\text{Fe} \left[(\text{OH}) (\text{H}_2\text{O})_5 \right]^{2+}$ in supercages for fresh samples is proposed. The DTA curves for the ferric exchanged zeolites show three endothermic peaks between 150°C-450°C and exothermic peak at 840°C-870°C. The first endothermic peak with a maximum at about 170°C corresponding to the desorption of

water is a characteristic property of all the zeolites. The second distinct peak at 290°C is attributed to the desorption of water molecules associated with the ferric ions. While the third endotherm at 400°C is attributed to the dehydroxylation of hydroxyl groups attached to ferric ions. From TG data, the number of hexa-aquo complexes in supercages is determined and cations are distributed (at different sites) accordingly. The order of dehydration is found to be one. The values of apparent energy of activation for the dehydration of FeNaY(82) are 4.2, 11.9 and 13.1 Kcal/mole calculated respectively by Coats-Redfern, Kissinger and Ozawa methods. The thermal stability of FeNaY samples activated at 500°C for 2, 5 and 10 hours is studied by X-ray diffraction and thermal analysis. FeNaY(37) shows almost no loss of crystallinity while FeNaY(82) shows distortion of framework and loss of crystallinity. After the heat treatment and subsequent hydration second and third endothermic peaks in DTA corresponding to hexa-aquo complexes of iron were absent. These observations confirm the cation migration from supercage to the sodalite cage or hexagonal prisms.

Infra-red analysis showed that the basic Y zeolitic structure is preserved during ferric ion exchange. All the FeNaY samples show a broad band at about 350 nm. The

absorbance increases linearly with the increase in iron content in the zeolite samples. The band at 350 nm is ascribed to the products of hydrolysis of solvated ferric ions. The yellow colour of partially hydrolysed cation i.e. $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ is due to the charge transfer tailing into the visible region.

The specific conductivity decreases with the increase in the percent ferric exchange but not linearly. The mobility of sodium ions is more than the bulky ferric complexes in supercages which supports the trend in specific conductivity of the samples. Below 400°C, the conductivity is due to the cations in supercages and is affected by the degree of dehydration and the extent of cation-framework interaction. Above 400°C, thermal cationic conduction is observed. The activation energy of conduction increases with the increase of iron content. At higher percent exchange, the cationic sites in sodalite cage and hexagonal prism are occupied. The data indicate that the ferric-framework interaction is stronger than sodium-framework interaction.

The X-ray photoelectron spectroscopic studies revealed the presence of impurities like NaOH in the zeolite NaY. We have also reported XPS data with respect to ferric exchange,

activation, Si/Al ratio and coke-formation. The surface Si/Al ratios calculated from XPS indicate that the external zeolite surface is aluminum deficient. After thermal treatment of FeNaY(82) at 500°C for 5 hours, the surface (Si/Al)_s ratio is found to decrease from 4.48 to 2.51 which may be attributed to the dealumination followed by aluminum migration to the surface during heat treatment.

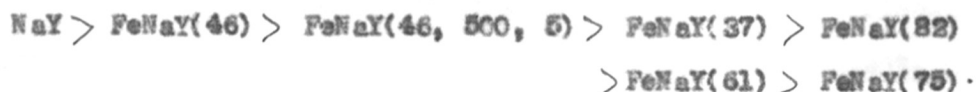
The examination of coked FeNaY(46) sample by XPS showed two distinct O 1s peaks, corresponding to the framework oxygens on which coke is deposited and the others free from coke.

The adsorption studies of n-butylamine (NBA) on NaY and ferric exchanged zeolites in 100°-350°C temperature range are discussed. The trend in the number of NBA molecules adsorbed at equilibrium per unit cell is NaY > FeNaY(46) > FeNaY(37) > FeNaY(82) > FeNaY(61) > FeNaY(75). NBA molecules are chemisorbed on cations and acidic protons in supercages. The irreversible adsorption of NBA (at 10⁻⁶ torr) as a function of temperature and ferric-exchange gives the trend in the strength of interaction. Above 200°C, the strength of acidic centres of catalysts follows the sequence:

FeNaY(46) > FeNaY(82) > FeNaY(37) > FeNaY(61) > FeNaY(75) > NaY.

The strongest acidic centres are present in FeNaY(46) and weakest in NaY, among the six samples. The NBA adsorption isotherms for thermally treated sample, FeNaY(46, 500, 5) were found to be similar to those for untreated FeNaY(46). However, irreversible adsorption for FeNaY(46, 500, 5) showed that the interaction of NBA with catalyst was weaker than that for FeNaY(46). This is due to the loss of acidic protons during thermal treatment by dehydroxylation process and the migration of ferric ions into sodalite cages occupying sites inaccessible to NBA molecules. The Langmuir plots for all the samples are linear which suggest that each NBA molecule is chemisorbed on one active centre only i.e. on cation or acidic proton.

The affinity for the sorption of NBA follows the sequence :



In case of NaY, at coverage of 20 molecules per unit cell, the isosteric heat of NBA adsorption (q_{st}) is 21.4 molecules per unit cell. For FeNaY(37) and FeNaY(82), at low coverages (15-20 molecules per unit cell), q_{st} is about 40 Kcals per mole and reaches a maximum value of 44.8 Kcals per mole for FeNaY(46). This supports that the strength of NBA-cation

interaction is higher in case of ferric exchanged Y zeolites. In case of thermally treated FeNaY(46, 500, 5) sample, the heat of adsorption is 18-20 Kcals per mole at a coverage of 15-25 molecules per unit cell which gradually decreases to ~ 12.4 Kcals per mole at $\theta = 30$ molecules per unit cell. The data on the irreversible adsorption and heats of sorption support the ferric ion migration into sodalite cages and reduced acidity due to dehydroxylation after thermal treatment. FeNaY(46) has maximum number of strong acidic centres and is thermally stable and therefore a better catalyst.

The water adsorption studies show two regions in which two different phenomena govern the adsorption. Above 200°C , the interaction of water with cations and zeolitic framework and below 200°C , volume-filling phenomenon dominate the adsorption pattern. The number of sorbed water molecules below 200°C , decreases with the increase of iron content. This is due to the hexa-aquo complexes of iron which hinder the incoming water molecules.

The equilibrium sorption of water shows that the FeNaY(46, 500, 5) is thermally stable while the structure of FeNaY(82, 500, 5) is damaged due to heat treatment. In case of FeNaY(46) coked sample, the water adsorption is

drastically reduced and FeNaY(46, RA) reactivated sample, adsorb approximately the same amount of water as the parent FeNaY(46) sample. At higher temperatures (at 300°C) Langmuir equation is applicable and at lower temperatures (60°C) Dubinin equation is applicable. At 300°C, the affinity sequence for water sorption is, $\text{FeNaY(82)} > \text{FeNaY(46)} > \text{FeNaY(61)} > \text{NaY}$. At 100°C, the affinity sequence is, $\text{NaY} > \text{FeNaY(46)} > \text{FeNaY(61)} > \text{FeNaY(82)}$, supporting volume-filling concept. The analysis of isosteric heats of adsorption suggests that the water adsorption is a multistep process due to heterogeneity in surface potential.

The rates of sorption of benzene, toluene, ethyl benzene and styrene on ferric exchanged Y zeolites are studied. The equilibrium sorption value for ethyl benzene is found to decrease with increasing ferric content in the zeolite. The amount of irreversible adsorption of ethyl benzene on FeNaY(46) is larger than that on NaY zeolite.

The amount of sorbent retained irreversibly on FeNaY(46, 500, 5) shows the sequence, ethyl benzene > toluene > benzene at 200°C. The apparent energies of activation for the diffusion of benzene, toluene, ethyl benzene and styrene are 320, 366, 732 and 1236 cal. per mole. The experimental data suggest that the mass transport of benzene and toluene

is much faster and may not be rate governing step in the reactions on this catalyst. While styrene which is adsorbed irreversibly in the supercages shows higher energy of activation for diffusion, the desorption of styrene may be rate-controlling step.

The study of the oxidative dehydrogenation of ethyl benzene to styrene is reported. We have carried out the reaction using FeNaY(46) zeolite as the catalyst with and without binder (bentonite). FeNaY(46) shows strong acidic centres as determined by n-butylamine sorption studies. These acidic centres are responsible for dealkylation and coke formation. In order to destroy these strong acidic centres higher activation temperature is favoured. The reaction being endothermic, conversion and selectivity to styrene increases with increase in the reaction temperature. The optimum temperature for the activation and reaction was found to be 550°C.

The selectivity to styrene was found to increase as ethyl benzene to oxygen ratio was increased, however the conversion decreased. The conversion to benzene and toluene decreased with reaction time and attained approximately constant value after about three hours. The dealkylation, deep oxidation and oxidative dehydrogenation reactions occur simultaneously on the catalyst. Since these are parallel

reactions, the product distribution changes with the decrease in acidic centres as a result of catalyst coking. The conversion to styrene increased with decrease in dealkylation products and remained constant for at least twelve hours after steady state was achieved. We may, therefore, conclude that FeNaY can be used as an active catalyst for cracking, alkylation reactions in the temperature range of 200-400°C. Above 400°C, it can be used for oxidation and oxidative dehydrogenation reactions, FeNaY(~ 46) being the best choice.
