TRANSFORMATIONS OF HYDROCARBONS OVER SHAPE SELECTIVE ZEOLITES

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CERTIFIED that the work incorporated in the thesis "Transformations of hydrocarbons over shape selective zeolites" submitted by Shri. Kondam Madhusudan Reddy was carried out by the candidate under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

(S. SIVASANKER)
Supervisor

CHAPTER I

REVIEW OF LITERATURE AND SCOPE OF THE THESIS

I.1. INTRODUCTION

The introduction of acid faujasites into industrial catalysts for fluid catalytic cracking in 1962 is a landmark in zeolite catalysis.[1-3] Since then, zeolite catalysts have been introduced in a number of industrial processes, especially in petroleum refining and the manufacture of organic commodity chemicals.[4-8] The advent of shape selective zeolites, especially ZSM-5, has enabled completely new selectivities in a large variety of catalytic reactions, both in academic research and in commercial applications,[9-11] like hydrocracking, hydrodewaxing, fluid catalytic cracking and xylene isomerization.

I.2. ZEOLITES

Zeolites[12,13] are crystalline aluminosilicates with uniform porous structures in which silica and alumina tetrahedra are linked through oxygens to form a rigid three dimensional framework. The alumina tetrahedra in the structure determine the framework charge. This is balanced by cations that occupy nonframework positions. A representative empirical formula for a zeolite is written as

$$M_{2/n}O \ . \ Al_2O_3 \ . \ xSiO_2 \ . \ yH_2O$$

where M represents the exchangable cations, generally from the group I and II, although other metal, nonmetal, and organic cations may also be used to balance the framework charge, and 'n' represents the cation valance. The value of 'x' is equal to or greater than 2 because Al^{3+} does not occupy adjacent tetrahedral sites.[14] According to Loewenstein, whenever two tetrahedra are linked by one oxygen bridge, the center of only one of them can be occupied by aluminum; the other center must be occupied by silicon or by another small ion of electrovalence 4 or more, such as phosphorous. Whenever two aluminum ions are the neighbours to the same oxygen anion, at least one of them must have a coordination number larger than 4, that is, 5 to 6 toward oxygen.

Since 1950, approximately 150 synthetic zeolites[15] have been made though only about 37 natural zeolites are known. It is estimated by crystallographers[16] that the zeolite structures known till today represent less than 10% of all possible zeolite structure types that could be formed. Typical examples of some synthetic zeolites and their characteristics are reported in table I.1

Zeolites are formed by crystallization under hydrothermal conditions from solutions containing species such as aluminates, silicates, sodium hydroxide, water molecules and organic templates. The product (zeolite) obtained is determined by the composition of the precursors and synthesis conditions like temperature, pH and duration of crystallization. Some recent reviews illustrate the various methods for synthesis.[17-23]

Zeolites are classified according to morphological characteristics,[17,18,24] effective pore diameter,[17,25] chemical composition,[27] and natural occurrence. Zeolites are characterized using techniques like X-Ray diffraction,[28] infra red spectroscopy,[15,29] nuclear magnetic resonance spectroscopy,[30-32]

TABLE I.1. [26]

Characteristic properties of some synthetic zeolites

Zeolite Type	SiO_2/Al_2O_3 ratio	Cation (in as synthesized material)	Pore diameter (Å)	Crystal structure	Adsorption capacities for H_2O (Wt%)
X	2.5-3	Na^+, Ca^{2+}	8-10	Body centered cubic	36.0
Y	3-6	Na^+	10	-do-	35.0
L	5-7	$K^+(Na)^+$	7.1-7.8	Hexagonal	12.0
ZSM-5	10-infinity	Na^+TPA	5.1 X 5.6	Ortho - rhombic	10.0
ZSM-11	- do -	Na^+TBA	5.1 X 5.5	Tetragonal	10.0
ZSM-12	100-600	Na^+TEA	5.6 X 6.1	Monoclinic	9.0
ZSM-34	22-40	Na^+TMA	6.4	Hexagonal	22.0
Silicalite (Aluminium free)		TBA	5.1 X5.6	Ortho-rhombic	2.4

TMA, TEA, TPA, TBA are tetra-methyl, tetra-ethyl, tetra-propyl, and, tetra-butyl ammonium hydroxide respectively.

temperature programmed desorption,[33,34] thermogravimetry, differential thermal analysis,[35,36] and sorption.[37-39]

I.3. CHARACTERISTIC PROPERTIES OF ZEOLITES

Zeolites are extremely useful due to their valuable properties.[40] Most notable of the physical and chemical properties are their ion exchange, adsorption abilities, acidic nature, shape selectivity, high thermal stability, and in some cases their resistance to coke deposition.

I.3.A. ION EXCHANGE

Ion exchange in a zeolite is a function of the amount of aluminum present in the framework. Each aluminum being trivalent and bonded to four oxygen atoms requires neutralization of the net negative charge on the tetrahedra. This is usually accomplished by the use of cations of alkali or alkali earth metals in the synthesis formulation. These cations, present in their hydrated form, are loosely bonded to the framework aluminium resulting in a high degree of mobility. They can be partially or completely replaced by other univalent, divalent or multivalent ions by percolation, hydrothermal fusion or vapour phase treatment.[41] Barrer,[42,43] Rees,[44] Sherry,[45,46] and others have studied in detail the ion exchange equilibria in X and Y zeolites. A comprehensive review on ion exchange phenomena has been published.[47]

I.3.B. ACIDITY

Zeolites possess both Brönsted and Lewis types of acid sites.[13,34] The isomorphous substitution of trivalent aluminum for the tetravalent silicon in the lattice as explained earlier creates a net negative charge on the alumina tetrahedra. This negative charge can be neutralized by extra framework ions or protons; if it is a proton it leads to a Brönsted acid site. In the absence of a compensating cation, the Al atom tends to acquire a pair of electrons to fill its p orbitals, such a structure leading to the formation of a Lewis acid site. Ward[48] has reviewed the creation of acid sites in zeolites. Both types of acid functions play an important role in the various catalytic reactions,[34,49] such as cracking, isomerization, alkylation, hydrogenation and dehydrogenation. The relative proportion of the two types of sites has been shown to be dependent on the dehydration temperature of the zeolite.

I.3.C. ADSORPTION

As early as 1846, D'Amour[50] demonstrated that water could be reversibly removed from a zeolite without altering its crystalline framework, resulting in a large intra crystalline surface area (> 97% of the total surface area).[51] The corresponding void volume of zeolites is also large, and, when this is coupled with electrostatic fields created in zeolites due to charge delocalization associated with framework aluminum, the adsorption capacity is tremendous.

Adsorbed molecules are retained within the intracrystalline channels. Access, however, is limited to the molecules having effective diameters small enough to permit entry through the pores of the zeolites. As a result, separation of mixtures of molecules based on molecular sieving property of zeolites[1] becomes possible.

I.3.D. DIFFUSION

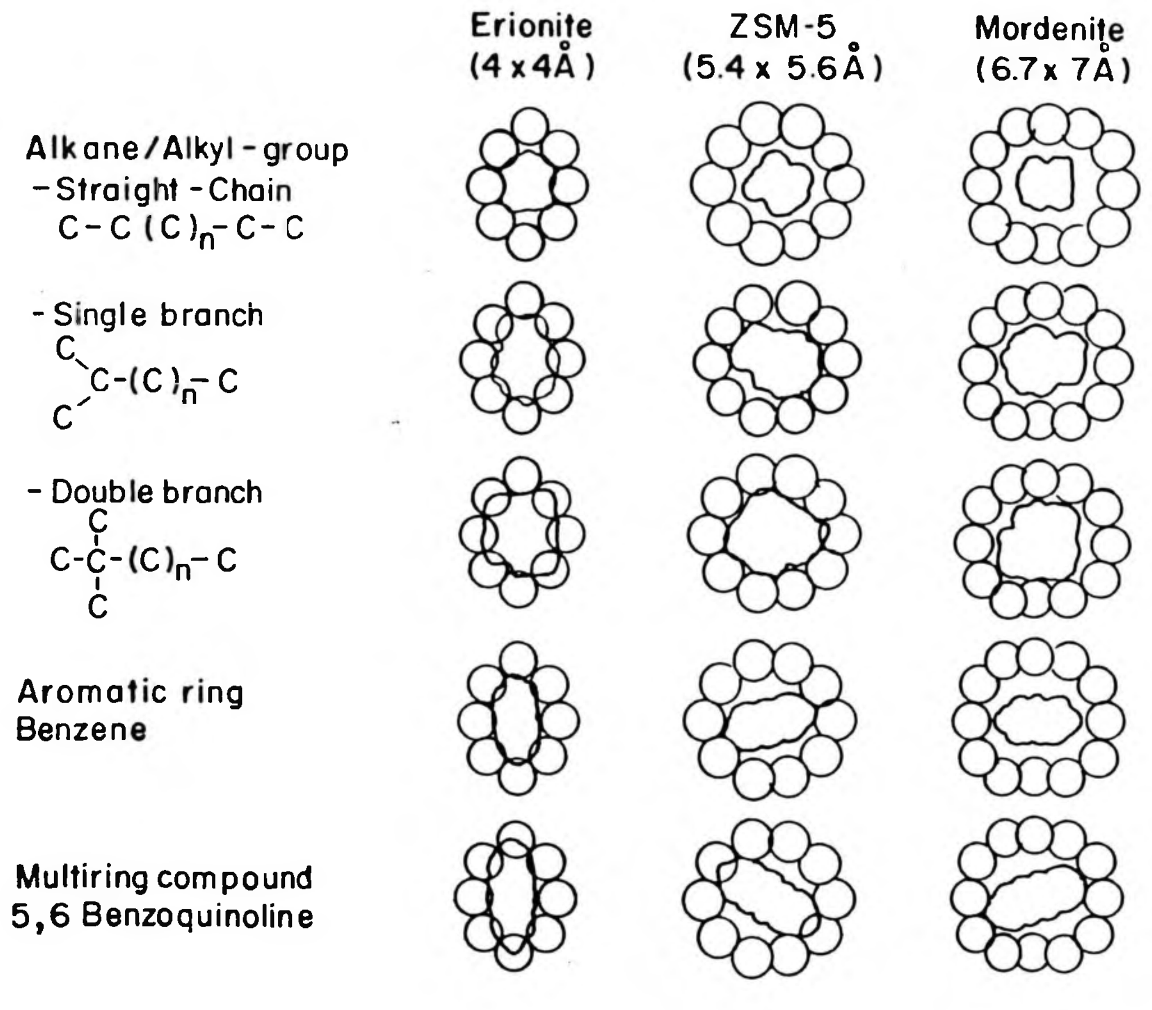
The classical theory of diffusion considers two regimes: the normal diffusion regime in which the pore size of the host material is greater than the mean free path of the diffusing molecules and the Knudsen regime for which the diffusivity decreases with pore dimension. Weisz has proposed a new diffusion regime called configurational diffusion[52] in zeolites. It implies that molecular migration within the zeolite framework necessitates the matching of size, shape and configuration of the diffusing species to the corresponding parameters of the zeolite as shown in figure I.1.

Barrer[53] reviewed the major features of diffusion in zeolites. Some of these were also discussed by Derouane.[54] Weisz and Prater[55] demonstrated that the observed rate of catalytic reactions in zeolites is moderated by an effectiveness parameter η,

$$k_{obs} = \eta k,$$

where k_{obs} is an observed rate constant, and k the intrinsic rate constant. Comprehensive reviews of diffusion processes in

Fig.I.1 MOLECULAR SIZE AND SHAPE MATCHING OF HYDROCARBONS WITH THE PORE DIMENSIONS OF SOME ZEOLITES (FROM REF.164)



zeolites have been presented by Barrer,[53] Timofeev[56] and Ruthven.[57] Diffusion coefficients depend mainly on the type and ionic form of the zeolite and the nature of adsorbate molecules.[58] The magnitude of diffusion coefficient decreases with increasing kinetic diameter of diffusing adsorbate.[13]

Diffusion plays an important role in molecular shape selective catalysis and the rates of diffusion processes can have a profound effect upon the apparent activity and selectivity of zeolite catalysts.[9,59,60] Diffusion and sorption properties of ZSM-5 have been evaluated systematically by many workers. Mobil researchers[61,62] have quantitatively reported the relative intracrystalline mobility of hydrocarbons in the ZSM-5 channel system and have made the following generalizations.

1. Linear aliphatics diffuse rather freely in HZSM-5 framework and can be adsorbed in both the channel systems.
2. Isoaliphatics experience steric hindrance effects which may restrict their diffusion in the sinusoidal channel system.
3. Aromatic compounds and methyl substituted aliphatics have strong preference for diffusion or adsorption in the linear and elliptical channels.

I.3.E. COKE FORMATION

Coking is an obstacle in the application of catalysts.[63] Hence, recently some selected problems of coke deposition like the role of zeolite pore structure in determining the chemical composition of the coke,[64,65] the interdependence of coking and deactivation rates and poisoning of acid sites by coke,[66] the influence of crystal size and morphology[67] on the coking behavior of HZSM-5 have been resolved.

The deposition of carbonaceous residues usually occurs during catalytic reaction and conversion of alkyl aromatics (by cyclization, dehydrogenation and alkylation) eventually leading to polyalkyl aromatics, the coke precursors. Coke deposition lowers the activity of a catalyst by site coverage and/or by pore blocking which prevent the access of the reactant to the active sites.[68] Walsh and Rollman had demonstrated[69] that the intracrystalline coking of zeolites is a shape selective process. The zeolites which provide enough space for the synthesis of poly alkyl aromatics inside the pores would therefore deactivate fast. Guisnet *et al*[70] identified the location of coke in three zeolites, namely, mordenite, Y, and HZSM-5 which differ in the channel system. The acidity measurements were performed by ammonia adsorption on fresh and deactivated catalysts. In contrast with the rapid ageing of either mordenite or offretite, the range of acid strength in HZSM-5 remained unchanged. This was attributed to the deposition of coke on the external surface in the case of HZSM-5 which does not inhibit the ammonia adsorption. This point was also proved by Walsh and Rollman[69] and they suggested that due to the restriction of the transition state, polyalkylaromatics were not formed in the channels.

Bülow *et al*[71] studied the coking of HZSM-5 samples of polycrystalline, spherical and polyhedral morphology during n-hexane and mesitylene cracking and distinguished between intracrystalline and surface coke and demonstrated the influence of intracrystalline and surface coke on the diffusion behavior of guest molecules. It is observed that the partially deactivated surface of ZSM-5 showed reduction in the pore apertures and channel dimensions, favoring p-xylene formation.[72] Ione et al[73] have reported the effect of aluminum content of ZSM-5 zeolite on catalyst stability in methanol reaction and have identified the coke synthesizing centres.

I.3.F. THERMAL STABILITY

Zeolites, in general, possess high thermal stability compared to other conventional sorbents and catalysts. Breck[13] has summarized the thermal properties of various zeolites and reported that the thermal stability of zeolite structures increases with Si/Al ratio. Upon calcination the structural stability depends on the method of heat treatment and Si/Al ratio[74].

Zeolites such as ZSM-5, mordenite and USY possess high thermal (upto 1283 K) and steam stabilities and are also stable to mineral acids (except HF) compared to other catalytically important zeolites.[37,75] These properties permit reactions to be carried out in the presence of water vapour and the regeneration of the deactivated catalyst at relatively high temperatures.

I.4.ISOMORPHOUS SUBSTITUTION IN ZEOLITES

Isomorphous replacement of lattice Al and Si by other ions is usually effected by synthesis from appropriate mixtures of the ions in the synthesis gel. Using Pauling criterion (ρ) [76], the probability of isomorphous substitution :

$Si^{4+} \Leftarrow\!\Rightarrow Me^{n+}$ and the stability of Me^{n+} position in tetrahedral oxygen surrounding can be predicted (where Me^{n+} is a non-aluminium cation and n is other than 4).

$$\rho = \frac{r_c}{r_o}$$

where r_c = cation radius, and r_o = oxygen ion radius

The tetrahedral surrounding should be stable for cations at $0.414 > \rho > 0.225$. This group of cations includes Al^{3+}, Mn^{4+}, Ge^{4+}, V^{4+}, Cr^{6+}, Si^{4+}, P^{5+}, Se^{6+} , and Be^{2+} .

Isomorphous substitution of elements like B, Be, Ga, Cr, Fe, V, Ti, Ce, Zr and P, for silicon and aluminium in zeolitic frameworks has been studied [17,77-83]. At present only the B and Fe-isomorphs seem to have industrial applications for pentasil type zeolite materials.

I.5. PENTASIL ZEOLITES

I.5.A. ZSM-5

ZSM-5 is a member of the pentasil zeolite group. The generic name " Pentasil Zeolite" was proposed by Kokotailo and Meier [84] to designate the group of structures having 5-1 secondary building units (Fig.I.2 (a)). The building units are linked through edges to form chains and these chains are connected to form sheets. Then, these sheets link to form a three dimensional framework. The silica and alumina tetrahedra which make up the framework of ZSM-5 consist of eight 5-membered rings. The elliptical 10-membered ring apertures are entrances to straight channels parallel to the crystallographic directions. The nearly circular 10-membered ring apertures are the entrances to the sinusoidal channels. They extend parallel to the crystallographic directions. The channel system of ZSM-5 consists of both sinusoidal and straight channels and has orthorhombic symmetry.

The composition of the unit cell of Na-ZSM-5 is :

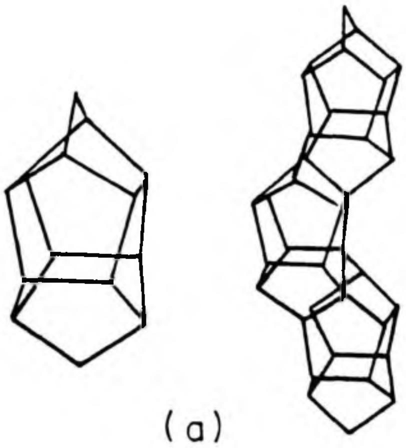
$$Na_n\ Al_n\ Si_{96-n}\ O_{196}\ \sim\ 16\ H_2O$$

where n is less than 27 and typically equal to 3.

The channel size of pentasil material is intermediate between those of the small pore (e.g. erionite, A : 4.0 Å) and large pore (e.g. Y : 8.0 Å) zeolites. The straight channels have diameter of about 5.4 X 5.6 Å and the sinusoidal (zig-zag) channels have about 5.1 X 5.5 Å free diameter (figure I.2(b)).

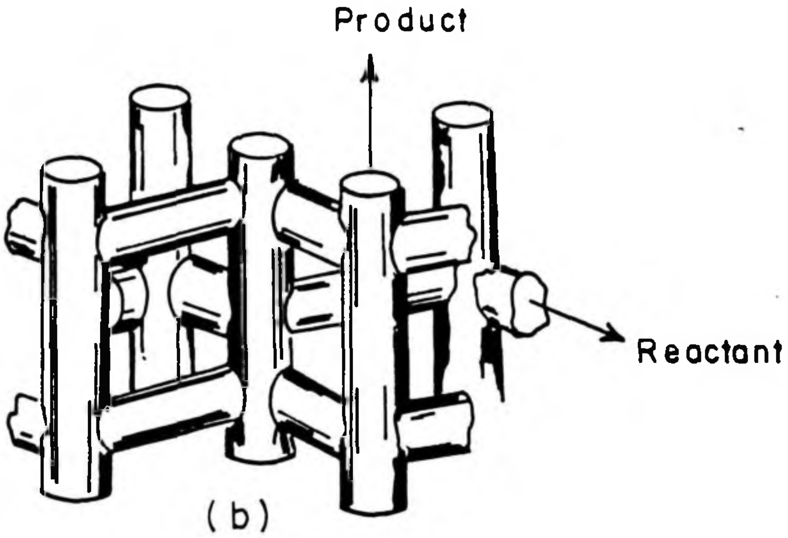
I.5.B. (B)-ZSM-5

ZSM-5 prepared in presence of B_2O_3[85] produces boralite which contains boron in isomorphous lattice positions.Due to its small size and its chemical features boron occupies a tetrahedral site but may undergo a trigonal environment in the absence of adsorbates.



(a)

Structural repeating units in the ZSM-5 frame work.



(b)

Schematic drawing of the channel system of ZSM-5

FIG. 1.2 : PORE STRUCTURE IN ZSM-5

In the pentasil type zeolites, Al content does not modify the unit cell appreciably in the Al content range, while boron causes an appreciable unit cell shrinkage [12].

Acidic and porous properties of zeolites may be changed by incorporation of elements of different sizes and chemical features. Acidity induced by lattice boron was shown to be much weaker than that due to lattice aluminium on the basis of temperature programmed desorption of ammonia (TPD)[86] and proton NMR[87]. Negligible activity of pure boron pentasil sample for acidic type reactions was reported[88].

I.5.C. (Fe)-ZSM-5

ZSM-5, when prepared from solutions containing mixed alkyl ammonium ions in the presence of Fe salts, contains Fe,isomorphously substituting Si atoms[89,12].

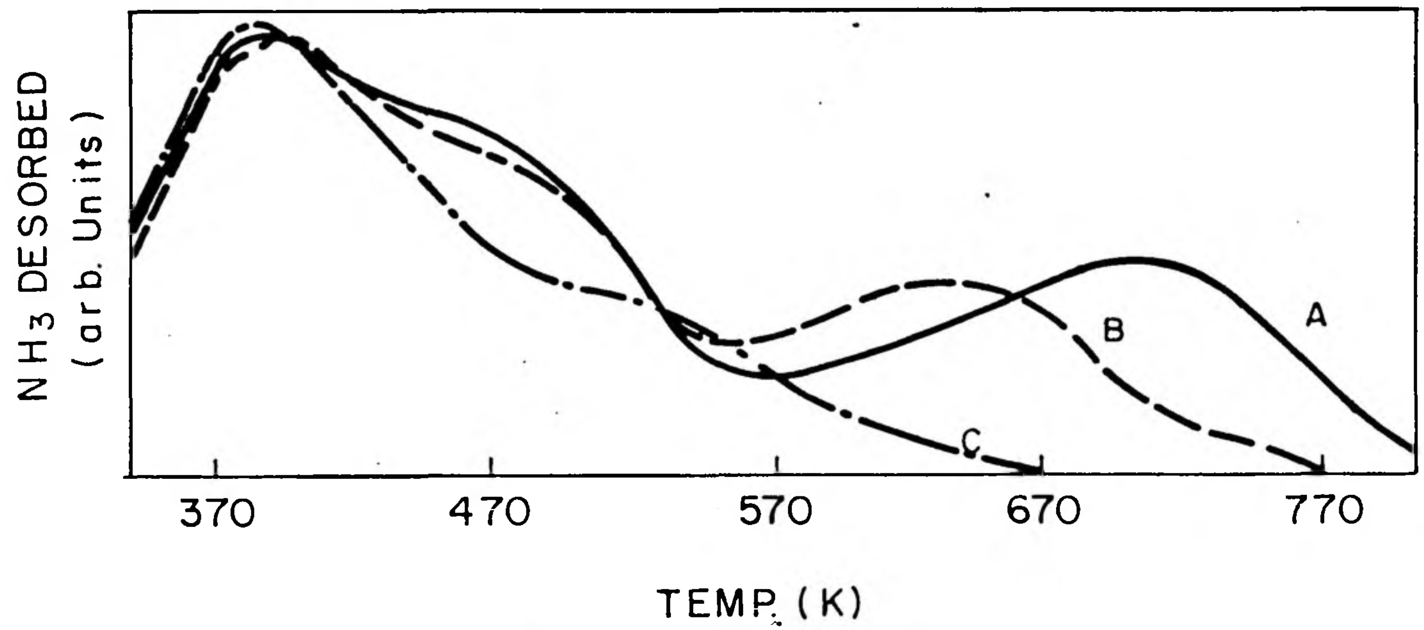
The confirmation of isomorphous substitution of Al^{3+}or Si^{4+} **by** Fe^{3+} in the pentasil lattice has been obtained by four different techniques, viz., 1) Mössbauer spectroscopy, 2) ESR spectroscopy, 3) vibrational spectroscopy of -OH groups (IR and FTIR), and, 4) ^{29}Si NMR spectroscopy.

The isomorphous substution of Al^{3+} by Fe^{3+} and B^{3+} reduces the acidity of ZSM-5[86]. The surface acidity profiles obtained from TPD of ammonia from ZSM-5, (Fe)-ZSM-5 and (B)-ZSM-5 are shown in figure I.3.

Three peaks are seen in the TPD profiles. The high temperature peak which quantifies the amount and strength of

Fig.1.3 **TEMPERATURE** PROGRAMMED DESORPTION PROFILES OF AMMONIA **FROM** ZSM-5 AND ITS ISOMORPHS (FROM REFERENCE 86)

(A: (Al)-ZSM-5; B: (Fe)-ZSM-5; C: (B)-ZSM-5)



strong acid centres occurs at 720 K, 640 K and 530 K for ZSM-5, (Fe)-ZSM-5 and (B)-ZSM-5, indicating that the acidity of the three isomorphs decreases in the order ZSM-5 > (Fe)-ZSM-5 > (B)-ZSM-5. The strength of the acid centres in (B)-ZSM-5 is very low, and has been found to exhibit negligible actvity for cracking and other acid catalysed reactions[88]. However, (Fe)-ZSM-5 is acidic enough to catalyse most acid catalyzed reactions which take place on ZSM-5[12].

I.6. CATALYSIS BY ZEOLITES

I.6.A. GENERAL CATALYSIS

During the past decade synthetic zeolites have been extensively used in petrochemical processes and they share the following six properties that make them attractive as heterogeneous catalysts[90].

1. Well defined crystalline structure.
2. High internal surface area (> 600 m^2/gm)
3. Uniform pores with one or more discrete sizes.
4. Good thermal stability.
5. Ability to sorb and concentrate hydrocarbons.
6. Highly acidic sites when ion exchanged with protons.

The most important advance in zeolite catalysis has been the ability to synthesize a large variety of crystal structures. Besides the synthesis of a large variety of basic structural types[90A], it has also been possible to a) alter and control the morphology and the size of the crystals b) to adjust the concentration gradient of active sites within each crystal and c) more recently, to isomorphously substitute other atoms in the place of silicon and aluminum, thereby changing their crystal stability and catalytic activity.

Zeolites ion exchanged with multivalent cations, are extensively used in petroleum and petrochemical processes for cracking, isomerization, alkylation, dealkylation[49,91], dehydrogenation, hydroisomerization, hydrocracking and related processes. Transition metal zeolites are active in polymerization of olefins[92], and isomerization and disproportionation of toluene.[93] Copper exchanged zeolite Y acts as a catalyst for oxidation reactions[94].

I.6.B. SHAPE SELECTIVE CATALYSIS

Shape selectivity is one of the unique properties possessed by zeolites which have pores of dimensions similar to the kinetic diameters of simple organic molecules. The principles of shape selective catalysis on zeolites have been discussed in a number of comprehensive reviews.[9,52,54,95-104,143] Recently, Chen and Garwood[101,143] have summarized the impact of shape selective catalysis on the petroleum and the petrochemical industries, with special emphasis on medium pore zeolites.

Molecular shape selectivities are distinguished or classified into four main types - reactant selectivity, product selectivity, restricted transition state selectivity and molecular traffic control.[98] The different types of shape selectivities are depicted in figure I.4 (a to c) and figure I.2.b.), and discussed below.

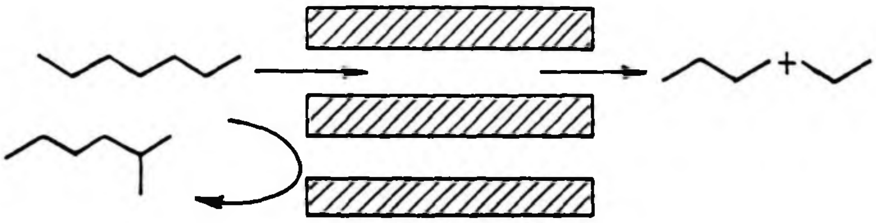
I.6.B.1 Reactant Shape Selectivity

This is expected to occur when only part of the reactant molecules are small enough to penetrate the zeolite pores and also when the reactant molecules differ widely in their configurational diffusion in the zeolites (figure I.4 a). Reactant selectivity may also arise from zeolite coulombic field (or polarity) effects.[101]

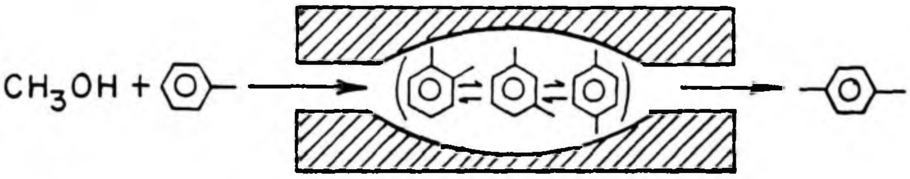
The reactants which cannot enter the zeolite channels and also those which possess lower diffusivity have a zero or small local concentration inside the zeolite channels and, therefore, will not be converted to any reasonable extent in comparison to the others. In catalytic processes which involve a number of consecutive and secondary hydrocarbon conversion reactions leading to the formation of a very large number of products, differing widely in their diffusivity, the reactant selectivity is expected to play a very significant role in deciding the observed product distribution, because of the fact that the products of the primary reactions become the reactants for the subsequent reactions and so on.

I.6.B.2. Product Shape Selectivity

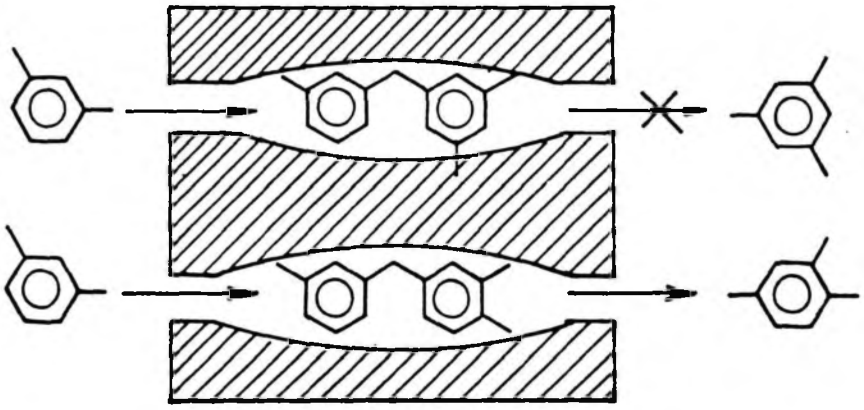
In catalysis over zeolites, product selectivity is observed when some of the products formed in the zeolite channels are too



REACTANT SELECTIVITY
(a)



PRODUCT SELECTIVITY
(b)



RESTRICTED TRANSITION STATE SELECTIVITY
(c)

FIG. 1.4: SHAPE SELECTIVITY IN ZEOLITES.

bulky to diffuse out and also when the products differ widely in their configurational diffusivity in the zeolite channels (figure I.4 b). The bulky products possessing lower diffusivity are converted either to less bulky/ faster diffusing products by equilibrium or by secondary reactions, or to bulkier products, which will eventually deactivate the zeolite by blocking its channels. Thus, the formation of high diffusivity products by diffusion reaction-interactions[97] is thereby favored.

I.6.B.3. Restricted Transition State Shape Selectivity

Restricted transition state selectivity (figure I.4 c) is observed in zeolites containing low volume cavities in which the active centres are located. Because of the local configurational constraints imposed on the molecular dimensions of the transition state complex by the size of the zeolite cavities, certain reactions requiring larger transition state complexes, the formation of which are not favored in the zeolite, are inhibited or the probability of their occurrence is greatly reduced. The reactions requiring smaller transition states proceed unhindered, by contrast.

This type of shape selectivity was first proposed by Csicsery[105] in order to explain the absence of symmetrical trialkylbenzenes in the product from the disporportionation of dialkyl benzenes over H-mordenite.

I.6.B.4. Molecular Traffic Control

A new type of shape selectivity in zeolites, containing intersecting channels of different diameters has been proposed and termed as molecular traffic control effect by Derouane and Gabelica.[106]

According to this concept, in the case of zeolites with more than one type of intersecting channels, the reactants enter preferentially through one type of channels, whereas products diffuse out by the other, thus minimizing counter diffusion. Derouane and Gabelica proposed that the traffic control in the conversion of methanol over ZSM-5 occurs as follows : The smaller reactant molecules enter the sinusoidal circular channels, whereas, the larger product molecules exit from the straight elliptiical channels (figure I.2 b). However, the existence of the molecular traffic control is not yet supported by experimental findings.

I.6.C.QUANTITATIVE MEASUREMENT OF SHAPE SELECTIVITY

I.6.C.1. Constraint Index

For many years, researchers in Mobil Research and Development Corporation, USA, have been making use of a "constraint index"[107] in their patent specifications for newly developed zeolites. The ***constraint index*** of a particular zeolite is determined[107] by carrying out cracking of an equimolar mixture of n-hexane and 3-methyl pentane under prescribed conditions and comparing the cracking rates of the two hydrocarbons as follows:

$$\text{Constraint Index} = [\log(1-X)_{\text{n-hexane}}] / [\log(1-X)_{\text{3-Me.pentane}}]$$

where, X is the fractional conversion.

The constraint index approximates to the ratio of the first order rate constants for the two cracking reactions. Since, the relative rates of cracking of n-hexane and 3-methylpentane, which differ markedly in their molecular size, are expected to be dependent on their relative diffusivities in the zeolite channels, the constraint index essentially measures the reactant selectivity of zeolites.

I.6.C.2 Refined contraint index

Martens et al[108] have shown that isomerization and hydrocracking of n-decane over Pt-H-zeolites, can be used to identify the structure and dimensions of void space of unknown zeolites. The ***refined constraint index*** (CI^*), defined as,

$$CI^* = 2\ Me\text{-}C_9/5\ Me\text{-}C_9$$

where 2 Me- C_9 = 2 methyl nonane,

5 Me- C_9 = 5 methyl nonane.

discriminates between various families of porous crystalline materials at lower conversions. Also, since the selectivity in the bifunctional methyl branching of n-decane is probably transition state controlled[109], the CI^* is expected to reflect the differences in size and geometry of the transition state or in the diffusion of mono branched olefins from acid site to metal cluster but will not reflect differences in diffusion of the ingoing feed molecules.

I.6.C.3. Spaciousness Index

Hydrocracking of C_{10}-naphthenes over bifunctional catalysts in the absence of shape selectivity is extraordinarily selective. Methyl cyclopentane and isobutane are by far the predominating products.[110] It can be shown that the favored pathways leading to isobutane and methylcyclopentane require bulky intermediates.[110] Based on mechanistic considerations, it has been predicted that, as the pores of the catalyst become narrower, hydrocracking of C_{10}-naphthenes proceeds less selectively and a larger number of cracked products are formed[111]. It is found that the molar ratio of isobutane and n-butane in the hydrocracked products is a valuable indicator for the effective pore width of bifunctional zeolite catalysts. Since this ratio increases with increasing pore width of the zeolite, it was named the ***spaciousness index*** (SI).[112,110] Ernst et al [113] investigated the influence of the yield of cracked products on the spaciousness index and found that SI is independent of the yield of cracked products and, hence, of reaction temperature.

I.6.C.4. O/P index in m-xylene isomeriztion

Xylene Isomerization involves parallel reactions leading to the formation of p- and o-xylenes. The relative rates of formation of the two products reflect their diffusionally limited transport and, consequently, reflect on the shape selectivity (mostly product selectivity) of the zeolite.[114] The ratio of observed rate constants for the formation of o- and p-xylenes

($R = k_{2\ obs}/k_{1\ obs}$), which is directly proportional to the square root of the ratio of the intracrystalline diffusivities of o- and p- xylenes ($R \propto \sqrt{D_{ortho}/D_{para}}$) can, therefore, form the basis of numerical values characteristic of specific pore structures in medium pore zeolites. These values are independent of crystal size and morphology.[114]

I.7. CRACKING OF ALKANES

The first catalytic use of zeolites was in cracking of heavy petroleum oils. Next came hydrocracking processes. Both the processes were based on faujasites. In the course of the commercial growth of the above processes, fundamental studies on the cracking of various model hydrocarbons have been simultaneously in progress. Since late 70's when shape selective refining processes like selectoforming, M-forming and dewaxing were introduced, fundamental studies on cracking and hydrocracking of model hydrocarbons over shape selective catalysts like erionite and pentasil zeolites have also been taken up in a number of laboratories[166,167]. A number of reviews on the cracking of model hydrocarbons over zeolites are now available[168,169].

In the cracking of alkanes, crackability increases with increasing chain length[169,170]. The ratio of initial cracking rates of nonane and hexane over Pt/Ca-Y is about 8.5[169]. It is however much less on ZSM-5, the ratio being only 3.2 [170]. However, as the carbon numbers increase further, rates of cracking increase much more rapidly on ZSM-5 till diffusion effects become prominent. For example the ratio of cracking rates between n-C_{12} and n-C_6 is 15.9 (extrapolated data of reference 169) for Pt-Ca-Y and is 22.9 for ZSM-5[170]. Similar differences have also been observed by other workers[171], when comparing the cracking rates of amorphous silica-alumina and ZSM-5. The ratios between n-C_{12} and n-C_6 cracking are 9 and 22 for amorphous silica-alumina and ZSM-5, respectively. ZSM-5 is a medium pore zeolite with pore dimensions of 5.4 x 5.6 Å, while Y has pores ~8 Å in diameter. Also Y has large supercages (13 Å diameter) which are interconnected by the pores. Thus, while cracking over ZSM-5 becomes diffusion limited in the case of bulkier branched paraffins, dimethyl (gem or vicinal) paraffins, it is still under reaction control in the case of Y.

Cracking is believed to go through carbenium ions produced by the protonation of olefins or by the abstraction of hydride ions. In the case of Y and silica-alumina, mechanisms involving beta scissions have been proposed[169]. Based on the studies of the cracking of normal and branched alkanes and alkenes over ZSM-5 of different crystallite sizes, Haag *et al*[170] have proposed mechanisms involving bulky transitions states. With the help of these mechanisms, they have been able to explain the relative rates of cracking of normal and substituted alkanes.

Most workers[170] have found cracking of alkanes to be a first order reaction. The rates decrease with increasing branching in the case of ZSM-5, attributed to diffusion constraints. For example, the diffusivity in ZSM-5 is 3 x 10^{-4} cm^2/sec for n-hexane while it is 4 x 10^{-3} cm^2/sec. for 2 methyl pentane and 7 x 10^{-8} for dimethyl butane at 811 K. They found the cracking of 2-methyl pentane to be diffusion controlled even when even slightly large crystallites of ZSM-5 (1.35 μm radius) were used[170]. However, they did not find any diffusion effects while using 0.025 μ m crystallites. These studies show the importance of diffusion effects in cracking hydrocarbons over ZSM-5. Activation energies between 63 and 126 KJ $mole^{-1}$ have been observed for the cracking of n-hexane over a number of zeolites.

An interesting situation occurs in the cracking of long chain alkanes over erionite, a high silica zeolite with pore dimensions around 4 x 4 Å. The reaction rate varies cyclically with increasing chain length with two maxima at C_6 and C_{10}-C_{12}, respectively[166]. This has been suggested to be due to the influence of the cage structure in the zeolite. Further, though the reaction is diffusion free upto n-C_{11}, it becomes constrained by diffusion effects beyond n-C_{12}[170-173].

An elegant comparison of the activities of a number of small, medium and large pore zeolites in the cracking of n-pentane has been made available by Derouane[174]. He has found that the specific cracking rates (cracking activity for Al^{3+} ion) is highest for the pentasil type medium pore zeolites. Even erionite has larger cracking activity than Y. The reasons could be (1) the operation of "nest effect" attributed to large field gradients and (2) the larger strength of the acid centres in small pore and medium pore zeolites with higher silica/alumina ratios.

I.8. COMMERCIAL SHAPE SELECTIVE CATALYTIC PROCESSES USING ZEOLITES

Over the past 30 years, many new synthetic zeolites, have been discovered and have found their way into commercial catalytic processes[115]. In recent years, the application of zeolites in shape selective catalysis has expanded rapidly[104,116-123]. Presently, a substantial amount of effort by petroleum and chemical companies is directed toward the discovery and use of unique zeolites in the following areas[90,124].

Petroleum refining.

Synfuels production.

Petrochemical manufacture.

NO_x abatement.

A list of commercial processes utilizing shape selective catalysis is given in table I.2.

I.8.A.GASOLINE UPGRADING

A number of petroleum companies have investigated shape selective zeolite catalytic processes for improving the octane quality of reformate and gasoline streams.[125-128]

Many Zeolite based reforming catalysts have been reported and patented[129-136]. A number of processes, like, a) Selectoforming[135], b) M-Forming [136], c) M-2 Forming [137], d) Cyclar[138], and, e) Aromaxsm [139], have been developed and

TABLE I.2 [143]

Name of the process		Purpose
Selectoforming	:	Octane boosting
M-Forming	:	- do -
Catalytic cracking	:	- do -
MDDW	:	Distillate dewaxing
MLDW	:	Lube dewaxing
M_2-Forming,Cyclar	:	Gas to aromatics
MOGD	:	Light olefins to gasoline and distillate.
MTG	:	Methanol to gasoline
MTO	:	Methanol to light olefins.
MVPI, MLPI, MHTI	:	Xylene isomerisation
MTDP	:	Toluene disproportionation
MEB	:	Ethyl bezene synthesis
Para selective reactions	:	p-xylene synthesis
	:	p-ethyl toluene synthesis

commercialized by a number of licensors. The catalysts used in these processes include shape selective zeolites such as Erionite and ZSM-5, and an alkaline wide pore zeolite, L. Some of these processes are described below in detail.

I.8.A.1. Selectoforming

In Selectoforming[135] octane improvement is achieved by cracking of n-alkanes. Erionite containing a small amount of non-precious metal hydrogenation component, such as Ni, is used as the catalyst. The catalyst selectivily hydrocracks the n-alkanes out of a naphtha reformate due to its small pores which permit the entry of only normal hydrocarbons[118,140,141]. The main by-product is LPG, principally propane.

The catalyst stability in this process is maintained by nickel which saturates olefins and prevents coke formation without hydrogenating the aromatics present in the feed[117,142].

I.8.A.2. M-Forming and M-2 Forming

The Selectoforming process was later superseded by the M-Forming process. In this process erionite is replaced by a medium pore zeolite, ZSM-5[136,137]

The catalyst performs two major functions, such as selective cracking of low octane alkanes and utilising the olefinic fragments to alkylate the benzene and toluene present in the reformate, and hence, boosting octane by aromatics alkylation.Due to reduction in the gaseous cracked products, there is an increase in liquid yield.

The major reactions involved in this process are[142]: 1) Selective cracking of normal and singly branched alkane molecules, 2) Formation of alkyl aromatics by the alkylation of benzene and toluene with olefinic cracked fragments, 3) Aromatics formation via cyclization and hydrogen transfer, and, 4) Redistribution of alkyl aromatics to produce a spectrum of aromatic products.

The latest in the line is the M-2 Forming process developed by Chen and Yan in 1986[137]. M-2 Forming produces additional aromatics by oligomerization of light olefins. This aromatization of light hydrocarbons, other than methane and ethane, is carried out over acidic forms of ZSM-5[104,145]. Even ethane can be aromatized very slowly[146]. Generally, C_3 to C_5 streams produced in catalytic crackers, cokers, steam naphtha cracker, as well as from LPG, are used in this process to obtain aromatic concentrates.

The activity and selectivity for the aromatization of hydrocarbons, including those in the C_3-C_{12} range[147] and ethane[148,149] are increased by introducing Gallium in high silica zeolites. This also enhances the activity for aromatization of olefins but does not affect the cracking ability of the zeolite[150].

I.8.A.3. Cyclar Process

This process incorporates a continuous catalyst regeneration technology (CCR) and is designed for producing aromatics from light (C_3-C_6) hydrocarbons. The Cyclar process is the joint development of UOP and British Petroleum (BP), announced in 1984 for the conversion of LPG to aromatic components suitable for gasoline blending[138]. The Cyclar processing of LPG can produce aromatic concentrates of exceptionally high octane ratings (RON= 111, and MON= 100)[139]. The yield of hydrogen from this process is claimed to exceed that obtained from catalytic reforming.

I.8.A.4. AROMAXsm Process :

A new reforming process AROMAXsm[139] is for selectively converting C_6 -C_7 alkanes to high octane aromatics.This process employs a catalyst comprising platinum on L-zeolite. It has no acid isomerization function. The entire catalytic function is supplied by the noble metal. The exceptional selectivity of Pt/L -type zeolite catalyst for aromatizing light alkanes has already been reported by Bernard[132]. In contrast to the behaviour of conventional bifunctional catalysts, AROMAXsm catalyst is more stable at low pressures.

I.8.B. CATALYTIC DEWAXING

Catalytic dewaxing is probably the first industrial application of shape selective zeolite catalysis. This process is based on the same principle as gasoline selectoforming, whereby n-paraffin (wax) molecules are selectively hydrocracked to lighter components, thereby improving the cold flow properties (e.g. pour point) of the lubricating oil. The catalyst used is a bifunctional one containing both hydrogenation and acidic components. Several companies, Mobil[151], British Petroleum[152-154] and Chevron[155] have developed dewaxing processes. Mobil's dewaxing catalysts are based on ZSM-5[156-159] while that of British Petroleum are based on erionite and mordenite[145,160]. The critical zeolite properties that are important for dewaxing are reactant and transition state selectivity. Reactant selectivity is essential to convert selectively the high pour normal alkane component of the oil, while the latter selectivity is necessary to prevent the deposition of coke within the pores. By restricting the size of transition state complexes that can be formed within the pores of the zeolite, bulky coke precursors like fused ring aromatics can be prevented from forming. This reduces the coking tendency of the zeolite improving its life.

The size of some typical hydrocarbons relative to the pore aperture of erionite, ZSM-5 and mordenite are depicted in figure I.1. Erionite (small pore zeolite, 4 x 4 Å pore diameter) permits the entry of only straight chain compounds, excluding even slightly branched molecules. Due to the small pore dimensions of erionite, the cracking of alkanes larger than C_{12} is diffusion limited. Therefore, erionite cannot be used to dewax oils heavier than atmospheric fractions.

On the other hand, the larger pore opening of ZSM-5 (medium pore zeolite, 5.4 x 5.6 Å, pore diameter) permits its use as a dewaxing catalyst for heavier fractions, like lubricating oils (lubes). It allows the entry of both normal and slightly branched alkanes but still excludes other large molecular weight lube range molecules. In the case of mordenite (large pore zeolite, 6.7 x 7 Å, pore diameter) it is less shape selective than ZSM-5. ZSM-5 will tend to dewax by preferentially converting the higher pour point normal and slightly methyl branched carbon chains, while mordenite will be less selective, and crack away the more desirable lube components. Bendoraitis *et al*[161] have reported larger lube oil yields from ZSM-5 than from mordenite.

The viscosity index of the ZSM-5 product is also significantly higher than that for mordenite. A further advantage of ZSM-5 over mordenite for dewaxing heavy petroleum fractions which have high coking tendencies is the operation of restricted transition state selectivity[105,162] in ZSM-5. ZSM-5 has a coking tendency atleast one order of magnitude less than mordenite[163]. As a result of mordenite's higher coking tendency, mordenite based dewaxing catalysts require the incorporation of a noble metal component (Pt or Pd) and also operation at high hydrogen pressures[164]. Also the processing of very heavy oils like bright stock may not be possible.

Heavy petroleum oils contain considerable amounts of nitrogen compounds which are catalytic poisons. These are usually large aromatics. These compounds will be excluded by ZSM-5 and not by mordenite. Hence, ZSM-5 will be less susceptible to nitrogen poisoning than mordenite. Figure I.1 depicts a similar situation. ZSM-5 does not permit the entry of 5,6 benzoquinoline into its pores, but mordenite does.

Mobil has commercialized two dewaxing processes called Mobil Distillate Dewaxing (MDDW) and Mobil lube oil dewaxing (MLDW).

I.8.C.1. Mobil Lube Oil Dewaxing (MLDW) Technology

In this process [159,165] two catalysts are used, one for pour point reduction and other for imparting oxidation stability to the MLDW product. The zeolite catalyst (ZSM-5) selectively cracks waxy molecules such as normal and slightly branched alkanes to lower boiling ranges, but does not convert any significant number of the lube oil molecules. As a result of the cracking reactions, some olefins are formed in the lube boiling range.The non-zeolite catalyst is an amorphous type which is used to saturate the small amount of alkenes that are created in the lube oil by the dewaxing catalyst. Thus it improves the stability, colour and demulsibility of the base oil.

The lube yields produced by this process are about 72% for the Light Neutral and about 90% for the Bright Stock. The Light Neutral can have a very low pour point, viz., 222 K, and is controlled by adjusting the furnace outlet temperature. The Bright Stock yield is about 10 - 15 % higher than in the solvent dewaxing process.

I.9. SCOPE OF THE THESIS

In the foregoing pages, the properties of zeolites, with special reference to their shape-selective characteristics and their applications in industrial catalytic processes were reviewed. It was noted that ZSM-5 based catalysts have many advantages over others due to their high activities, resistance to coking and nitrogen poisoning and shape selectivity. In fact, entirely new processes for petroleum refining and petrochemicals production have become possible due to the above properties. These processes have been the outcome of a large amount of research carried out on the physicochemical and catalytic properties of pentasil zeolites. Many of these have been examined in the foregoing review.

ZSM-5 exhibits unique behavior in the cracking of hydrocarbons. By virtue of the large field gradients existing inside its pores, the cracking activities and product selectivities differ from those of the commercially important large pore faujasites. **In this thesis** the cracking of a series of n-alkanes (hexane, heptane, octane and hexadecane) over ZSM-5 will be studied. Further, the influence of poisons like n-butyl amine and quinoline on the cracking of the above alkanes will be examined. Most commercial hydrocracking catalysts contain, in addition to the acid component (silica/alumina or Y-zeolite), small amounts of metals also. These metals enhance the activity of the acidic function by supplying olefins which crack easily on the acid centres. They also reduce the coking tendency of the catalyst. Therefore, the influence of various metal components like Ni, Pd, Zn and Zn/Pd on the cracking activity of ZSM-5 will be examined. In addition, the influence of the presence of sulfur in the feed will also be studied. The product selectivities obtained over the various metals will be analysed. For comparison purposes, the cracking of hexadecane on the large pore zeolites Y and Beta will also be studied.

Pyrolysis gasoline (PG) is a byproduct of the steam cracking of naphtha to obtain olefinic gases. It is rich in aromatics and is an important source of BTX and gasoline blending components. At present the processing of PG to BTX involves five steps involving fractionation, hydrogenation and solvent extraction.

These steps have been necessary because of the high olefinic content of the material. **In this thesis,** an attempt will be made to crack and reform pyrolysis gasoline over ZSM-5 containing catalysts inorder to eliminate the undesirable unsaturates and to enhance aromatics content. The studies will cover the optimization of zeolite content in the catalyst, the influence of process parameters, feedstock characteristics and poisons.

At present, catalytic dewaxing processes are available commercially for dewaxing lube oils and middle distillates. The principle behind dewaxing is shape selective cracking. Usually shape selective zeolites like ZSM-5 and erionite are used in commercial dewaxing catalysts. Sofar, not much fundamental information on the influence of zeolite properties, feed characteristics, poisons and process parameters on catalytic dewaxing is available. Studies will be carried out to gather the above information. Six different feedstocks containing different wax contents obtained from refineries will be used in these studies. They will be dewaxed on ZSM-5 with different physico chemical characteristics. Also the activity and benefits of Fe and B isomorphs of ZSM-5 will be studied.

The thesis will consist of five further sections viz.,

1. The experimental section describing the experimental methods and procedures adopted (chapter II).
2. The study of the cracking of model alkanes like hexane, heptane , octane and hexadecane (chapter III).

3. The study of zeolite containing reforming catalysts on the reforming/cracking of pyrolysis gasoline (chapter IV).

4. The investigations of dewaxing of lube raffinates over ZSM-5 (chapter V) and

5. The summary of the thesis.

CHAPTER II

EXPERIMENTAL

II.1. MATERIALS

II.1.A. ZEOLITES

II.1.A.1. ZSM-5

ZSM-5 of different silica/alumina ratios and crystallite sizes were synthesized by hydrothermal procedures similar to those described in the literature.[175,176] Sodium silicate, aluminium sulfate and tetrapropyl ammonium bromide (TPABr) were used in the synthesis. Zeolites with various silica/alumina ratios were prepared by changing the composition of the synthesis gel.[177] Variations in crystallite size were effected by varying the time and temperature of crystallization and nucleation.[177-179] The zeolites synthesized and their properties are shown in table I.1.

As a typical example, the synthesis of ZSM-5 with a silica/alumina ratio of 84 and an average crystallite size of about 2 μm is described below.

Aluminium sulfate (6.3 g) and sulfuric acid (18.37 g) were dissolved in water (230 ml) to yield solution A. TPABr (23.3 g) was added to a solution of sodium silicate (193.45 g + 233 ml water) to yield solution B. The two solutions A and B were then mixed in a stainless steel (SS 316) reactor vessel (500 ml capacity) with continuous stirring to form a free flowing gel, which had a composition of 4.38 $(TPA)_2O$. 27.0 Na_2O . Al_2O_3 . 87.7 SiO_2 . 3262 H_2O. The reactor was then closed and kept in an oven at 453 K for 24 hours. The reactor was cooled and the contents were filtered and washed with water till the filterate

TABLE II.1

Composition and properties of ZSM-5 zeolites

S.No.	SiO_2/Al_2O_3	Crystallite* Size (µm)	Cyclohexane** adsorption	Formula (dry basis)
1	58	0.1	7.5	$1.2Na_2O.1.6Al_2)_3.91.0SiO_2$
2	84	2.0	7.8	$0.8Na_2O.1.1Al_2O_3.92.4SiO_2$
3	186	5.0-6.0	8.0	$0.4Na_2O.0.5Al_2O_3.99.0SiO_2$
4	84	0.2	7.2	$0.8Na_2O.1.1Al_2O_3.92.4SiO_2$
5	84	0.1	6.9	$0.8Na_2O.1.1Al_2O_3.92.4SiO_2$

* Average crystallite size obtained from Scanning Electron Microscope pictures.

** Adsorption at $p/p_o = 0.5$ and temperature 298 K.

was free of anions. The residue was dried in an oven at 393 K for 12 hours. A part of the sample was used to determine the crystallinity by XRD. The remaining sample was spread into a thin bed in a petri dish and slowly heated in a furnace to 823 K and held at this temperature for 8 hours in a flow of dry air to decompose the intracrystalline organic base. Samples were analysed by conventional wet chemical analysis. XRD and IR spectroscopic measurements confirmed the identity of the sample as NaZSM-5.

II.1.A.2. (Fe)-ZSM-5

Synthesis of (Fe)ZSM-5 was done according to the procedure described in the literature.[177,178] Synthesis was carried out in a stainless steel autoclave (500 ml capacity) under autogeneous pressure. The reactant materials used were sodium silicate, ferric sulfate hexahydrate, sulfuric acid and TPABr. TPABr (23.1 g) was added to a solution of sodium silicate (188.61 g + 230 ml water) in the autoclave yielding a viscous TPA-silicate solution. Ferric sulfate (5.08 g) dissolved in water (236 ml) at 333 K was addedd to the TPA-silicate solution dropwise, with constant stirring. Sulfuric acid (17.92 g) was added to the above solution to maintain the pH at 10.2. A thick gel of composition $4.4\ (TPA)_2O\ .\ 25.5\ Na_2O\ .\ Fe_2O_3\ .\ 85.5\ SiO_2\ .\ 3292\ H_2O$ was formed. The gel was stirred well and the autoclave closed and heated under autogeneous pressure in an oven to a temperature of 443 K. It was held at this temperature for 24 hours and then quenched to stop the crystallization process. The solid product was separated by filteration, washed with distilled water and dried in an oven at 393 K for 8 hours. The samples synthesized as above were calcined in a flow of dry air in a furnace at 753 K for 8 hours to decompose the organic cation.

The zeolite samples synthesized were characterized by XRD, IR and thermal analysis. In addition to these techniques, ESR studies were also carried out to confirm the state of the ferric ion incorporated in the zeolite[177]. The ESR spectra showed peaks at $g = 2.0$, 4.3 and 5.3. The peak at $g = 2.0$ can be ascribed to the Fe^{3+} hexacoordinated complex located at cationic sites of the hydrated zeolites. The peak at $g = 4.3$ and 5.3 are ascribed to tetrahedrally coordinated Fe^{3+} in the framework.[177,179]

II.1.A.3. (B)-ZSM-5

This isomorph was supplied in the hydrogen form by Dr.S.G.Hegde of the National Chemical Laboratory, Pune, India. Its SiO_2/B_2O_3 ratio was 174.

II.1.A.4. Na-Y

The Na-Y sample (Linde LZ Y52 powder) used in these studies was obtained from Alfa products, Ma, U.S.A. The sample had an average crystallite size of 1.5 μm with the following composition in weight percent on dry basis:

63.56 SiO_2, 23.32 Al_2O_3, 9.20 Na_2O.

II.1.A.5. ZEOLITE BETA

The sample of zeolite Beta used in this study was provided by Dr.Rajiv Kumar (National Chemical Laboratory, Pune, India). The H-form of the sample was prepared by repeatedly exchanging the Na-form with NH_4NO_3 solution (2N, 20 ml/g, 6h) at 353 K, washing the exchanged zeolite with de-ionized water, and drying in air at 383 K.

II.1.B. SURFACE PASSIVATED ZEOLITES

H-ZSM-5 (sample A) with a small crystallite size (0.2 μm average size) and silica/alumina ratio of 84 was surface passivated. Sample H-(Si)ZSM-5 was prepared from sample A by passivating its external surface with silica. The passivation was done by adding 50 g of sample A to a solution of di-trimethyl silylamine (20.87 g) in n-hexane (100 ml), distilling off the n-hexane, and decomposing the silicon compound at 773 K in air for 6 hours to deposit the silica (15 wt%) on the external surface. The preferential deposition of the SiO_2 on the surface was ascertained by XPS measurements. Further, adsorption experiments gave similar values for adsorption of n-hexane on both the samples (11.3 wt% and 10.9 wt% for H-ZSM-5 and H-(Si)ZSM-5 at p/p_0 = 0.5 at 298 K) confirming that silica was not deposited inside the pores of the zeolites.

II.1.C. CATALYSTS

II.1.C.1. ALKANE CRACKING AND HYDRODEWAXING CATALYSTS

(i) Preparation of Extrudates

Catalyst extrudates were prepared with the different zeolites by incorporating alumina as described below.

The required amount of a commercial alumina mono hydrate (Catapal B, supplied by Vista Chemical Co., USA) and the zeolite were blended thoroughly and then kneaded by adding a 4 wt% solution of acetic acid such that the total amount of acid in the mixture was 2 wt%. Extra water (deionised) was added, if necessary, to give the consistency of a very stiff dough. This material was next extruded using a hand press (similar to a sodium press). The extrudates were dried first at room temperature, then at 383 K for 12 hours and calcined at 773 K for 6 hours. In the case of catalysts containing (Fe)ZSM-5, the calcination temperature was 753 K. The diameter of the extrudates was 1.5 mm after calcination. The extrudates were broken into 4-6 mm pieces and stored.

Metals were loaded on the extrudates by impregnation, while they were incorporated into the zeolites by ion-exchange procedures. Table II. 2 lists the metal-loading procedure adopted and the metal salt used in the preparation of the different catalysts. The typical impregnation and ion exchange precedures are described below:

(i) Impregnation Procedure

The extrudates were taken in a beaker and a solution of the required metal salt containing enough metal to give the required metal content on the catalyst on dry basis was added to it. The volume of the salt solution was such as to cover the extrudates completely with an aqueous layer. The mixture was gently heated on a water bath (333 K) with gentle stirring to evaporate all the water. The extrudates were then dried at 383 K for 12 hours and later calcined at 773 K for 6 hours (753 K for (Fe)ZSM-5).

(ii) Ion exchange Procedure

Ion exchange was carried out over the NH_4^+ form of the zeolite. The Na-form of the zeolite was exchanged with 2N $NH_4(NO_3)$ solution for 6 h periods at 353 K atleast four times to convert the zeolite into the NH_4^+ form. The volume of the solution used each time was 20 times the weight of the zeolite being exchanged. In between the exchanges, the zeolite was separated by decantation or centrifuging. After the fourth exchange, the zeolite was washed and dried at 383 K for 12 hours. This NH_4^+ form of the zeolite was used for further ion exchanging with the metal salts. The required amount of the NH_4^+ form of the zeolite was taken in a round bottom flask and about 10 volumes of the metal salt solution containing the required amount of the metal was added. The mixture was stirred and kept under reflux at 363 K for 12 hours. The zeolite was separated by centrifuging and washed with water two times (20 ml/g). The zeolite was dried at 383 K for 12 hours, calcined at 773 K for 6 hours and used for making the final catalysts. The zeolite was analysed for metal content. The catalysts prepared and used in the cracking of alkanes and for dewaxing of petroleum oils are listed in tables II.2(a) and II.2(b).

II.1.C.2. ZEOLITE CONTAINING REFORMING CATALYSTS

The reforming catalysts were prepared by physically blending the required quantities of the H form of the zeolite with powdered alumina hydrate (Boehmite) as per following procedure.

Alumina hydrate, (Catapal B obtained from M/s Vista Chemicals Co.), 105 g and the zeolite, 4.2 g were mixed throughly in powder forms (200 - 400 mesh) in one litre beaker. The mixture was then transferred to a mortar. A dough was then made by adding 25 ml of dilute HNO_3 (0.497 N) and kneading. Extrudates were prepared from the dough using a hand extruder. These extrudates were dried in air for 8 h at room temperature and then transferred to an oven to dry at 383 K for 12 h. Finally these extrudates were calcined at 823 K for 5 h. The extrudates were 1.5 mm in diameter.

(i). Chlorine loading

The extrudates were next loaded with chlorine (1% wt.) prior to platinum incorporation. The presence of chlorine in the extrudates leads to uniform impregnation of H_2PtCl_6. The following procedure was adopted for loading chloride ions on the

TABLE II.2 (a)

Catalysts used in hydrodewaxing

S.No.	Catalyst	Metal content (as metal, wt%)	SiO_2/ M_2O_3	Crystallite Size (μm)[1]	Zeolite/ Binder(wt%)	Metal Compound	metal loading procedure
1.	Ni-ZSM-5	2.0	84	0.2	65/35	$Ni(NO_3)_2.6H_2O$	Impregnation
2.	Ni-ZSM-5	2.0	84	2.0	65/35	$Ni(NO_3)_2.6H_2O$	Impregnation
3.	Ni-(Si)ZSM-5⁺	2.0/(15.0)	84	0.2	65/35	$Ni(NO_3)_2.6H_2O$	Impregnation
4.	Ni-ZSM-5	2.0	58	0.1	65/35	$Ni(NO_3)_2.6H_2O$	Impregnation
5.	Ni-ZSM-5	2.0	94	0.1	65/35	$Ni(NO_3)_2.6H_2O$	Impregnation
6.	Pt-ZSM-5	0.3	186	0.1	65/35	$(NH_3)_4Pt(NO_3)_2$	Impregnation
7.	Pt-(Fe)ZSM-5	0.3	182	0.1	65/35	$(NH_3)_4Pt(NO_3)_2$	Impregnation
8.	Pt-(B)ZSM-5	0.3	174	0.1	65/35	$Ni(NO_3)_2.6H_2O$	Impregnation

1. Average crystallite size values obtained from SEM pictures of 'as synthesized' zeolites.

+. SiO_2 deposited on surface of zeolite crystallites: amount deposited in wt% mentioned in brackets (surface passivation, cf. p.46)

TABLE II.2 (b)

Catalysts used in cracking of n-alkanes

S.No.	Catalyst	Metal content (as metal,wt%)	SiO_2/M_2O_3	Crystallite Size (μm)[1]	Zeolite/ Binder(wt%)	Metal Compound	metal loading procedure[3]
1.	H-ZSM-5	0.0	84	0.1	65/35	------	------
2.	Ni-ZSM-5	2.0	84	0.1	65/35	$Ni(NO_3)_2.6H_2O$	Impregnation
3.	Zn-ZSM-5	2.5	84	0.1	65/35	$Zn(NO_3)_2.6H_2O$	Impregnation
4.	Pd-ZSM-5	0.2	84	0.1	65/35	$(NH_3)_4Pd(NO_3)_2$	Impregnation
5.	Pd/Zn-ZSM-5[2]	0.3/1.0	84	0.1	65/35	$(NH_3)_4Pd(NO_3)2$/	Impregnation
6.	H-ZSM-5	0.0	84	0.1	100/0	------	-------
7.	H-Y	0.0	5.2*	1.5	100/0	------	-------
8.	Pd-Y	0.3	5.2*	1.5	100/0	$(NH_3)_4Pd(NO_3)_2$	Ion Exchange
9.	Pd-ZSM-5	0.3	84	0.1	100/0	$(NH_3)_4Pd(NO_3)_2$	Ion Exchange
10.	Pt-Beta	0.3	90	0.5	100/0	$(NH_3)_4Pt(NO_3)_2$	Ion Exchange
11.	Pt-(Fe)ZSM-5	0.3	88	0.5	100/0	$(NH_3)_4Pt(NO_3)_2$	Ion Exchange

1. Average crystallite size values obtained from SEM pictures of 'as synthesized' zeolites.
2. Order of incorporation of metal : Zn first, Pd next. Calcination of the sample was done after the first impregnation before the loading the second metal.
3. Impregnation was done on extrudates and ion exchange was done on zeolite powder.

* The parent Na-Y (Linde LZ Y52) had an average crystallite size of 1.5 μm.

catalyst.

29.0 ml of HCl (1.13 N) were diluted with 1000 ml of distilled water in a two litre beaker. The catalyst (71 g) was added to the dilute HCl and kept for 2 h. The catalyst was then removed from the solution and dried in an oven at 473 K for 6 h. The chloride picked up by the catalyst was estimated by standard procedures. The chloride content was 0.95 wt.% in the extrudates.

(ii). Platinum loading

50.00 g of the chlorided extrudates were added with stirring to a solution of 0.8 g of H_2PtCl_6 in 1400 ml of distilled water. Intermittant stirring of the mixture was carried out for 24 h. The extrudates were then removed from the solution and dried at 493 K for 6 h and then calcined at 823 K for 8 h. The estimation of the platinum loaded on the catalyst was carried out by atomic absorption spectroscopic methods. The platinum loaded was 0.6 % wt. The catalyst contained 5 wt% zeolite. Other catalysts were prepared by varying the metal and zeolite contents.

II.1.D. FEED MATERIALS

Pure hydrocarbons, pyrolysis gasoline and petroleum fractions were used in the studies.

II.1.D.1. PURE HYDROCARBONS

n-Hexane and n-heptane were obtained from British Drug House, Bombay, India. n-Octane was obtained from Alfa products, Ma., USA. n-Hexadecane was obtained from S.D. fine chemicals Pvt. Ltd, Boisar, India. All the hydrocarbons were distilled and stored over 4A molecular sieve. Gas chromatographic analysis showed that the distilled hydrocarbons had purities greater than 99.5 wt%.

II.1.D.2. PYROLYSIS GASOLINE

Pyrolysis gasoline was obtained from two different sources, viz. National Organic Chemical Industries Limited, Thane, India and a European company. Usually small amounts (5 l) of the samples were collected at a time. As the samples were unstable, they were stabilized by the addition of 100 ppm of ditertiary butyl phenol after fractional distillation to obtain the desired cut. The distilled samples were stored at 270 K.

II.1.D.3. PETROLEUM OILS

(i) Atmospheric Gas oil (AGO)

This was supplied by Bharat Petroleum Corporation Ltd., Bombay, India. Its source was Bombay High crude.

(ii) Spindle (SN), Light neutral (LN), Inter neutral (IN), Heavy neutral (HN) raffinates

These were supplied by Madras Refineries Ltd., Madras, India. The source of these oils was a Persian crude. These oils were raffinates, obtained after the removal of the aromatic fraction by furfural extraction.

TABLE II.3

Feeds used for Hydrodewaxing

Feed name	Source	Pour point (K)	Density (g/cc,298 K)	Sulfur (wt%)	Nitrogen (ppm)	paraffins (wt%)
Atmospheric Gas oil (AGO)	Bombay High	313	0.86	0.17	150	30
Spindle oil Raffinate (SN)	Persian	290	0.84	0.22	---	16
Light neutral Raffinate (LN)	Persian	309	0.86	0.50	---	12
Inter neutral Raffinate (IN)	Persian	321	0.87	0.81	48	8
Heavy neutal Raffinate (HN)	Parsian	331	0.88	1.10	234	4
Bright stock Raffinate (BS)	Middle East	333	0.93	2.45	103	--

TABLE II.4

Distillation characteristics of the feedstocks

(True Boiling Point Distillation by Gas Chromatography - ASTM D2887)

% off (wt)	At Temperature, K					
	AGO	SN	LN	IN	HN	BS
5	571	571	640	681	737	744
10	595	588	653	697	750	771
20	619	606	669	716	767	794
40	661	631	690	741	787	829
50	663	642	699	752	795	843
60	673	651	708	762	803	857
80	696	672	730	788	823	893
90	712	687	747	807	839	941
95	734	699	763	823	852	993

(iii) Bright stock raffinate

This was obtained from Indian Oil Corporation, Haldia, West Bengal, India. The oil was obtained from the vacuum residue of a middle east crude by propane deasphalting and dearomatized.

The properties and distillation characteristics of all the oils are presented in tables II.3 and 4. The "simulated distillation" gas chromatograms of some of the oils (ASTM D 2887)[180] are presented in figure II.1.

II.1.E. GASES

Nitrogen, hydrogen, helium and oxygen were high purity gases, IOLAR grade, supplied by Indian Oxygen Limited, Bombay, India. Before using, all these were passed over activated molecular sieves (4 A) to remove traces of moisture.

Compressed air was obtained from oil free compressers (Babicon,Hitachi,Japan) in the laboratory and dried over 4 A molecular sieves before use.

II.2. APPARATUS

II.2.A. ATOMOSPHERIC PRESSURE REACTOR

A microreactor was used to carry out reactions at atmospheric pressure. The reactor consisted of a fused silica tube, 1.5 cm i.d., and 35 cm long, with a B-14 ground silica socket and a side limb (5 cm long) with a stopcock attached to it at the top. The feed was injected through B-14 socket by a hypodermic needle (size 16) inserted into a teflon plug fitting

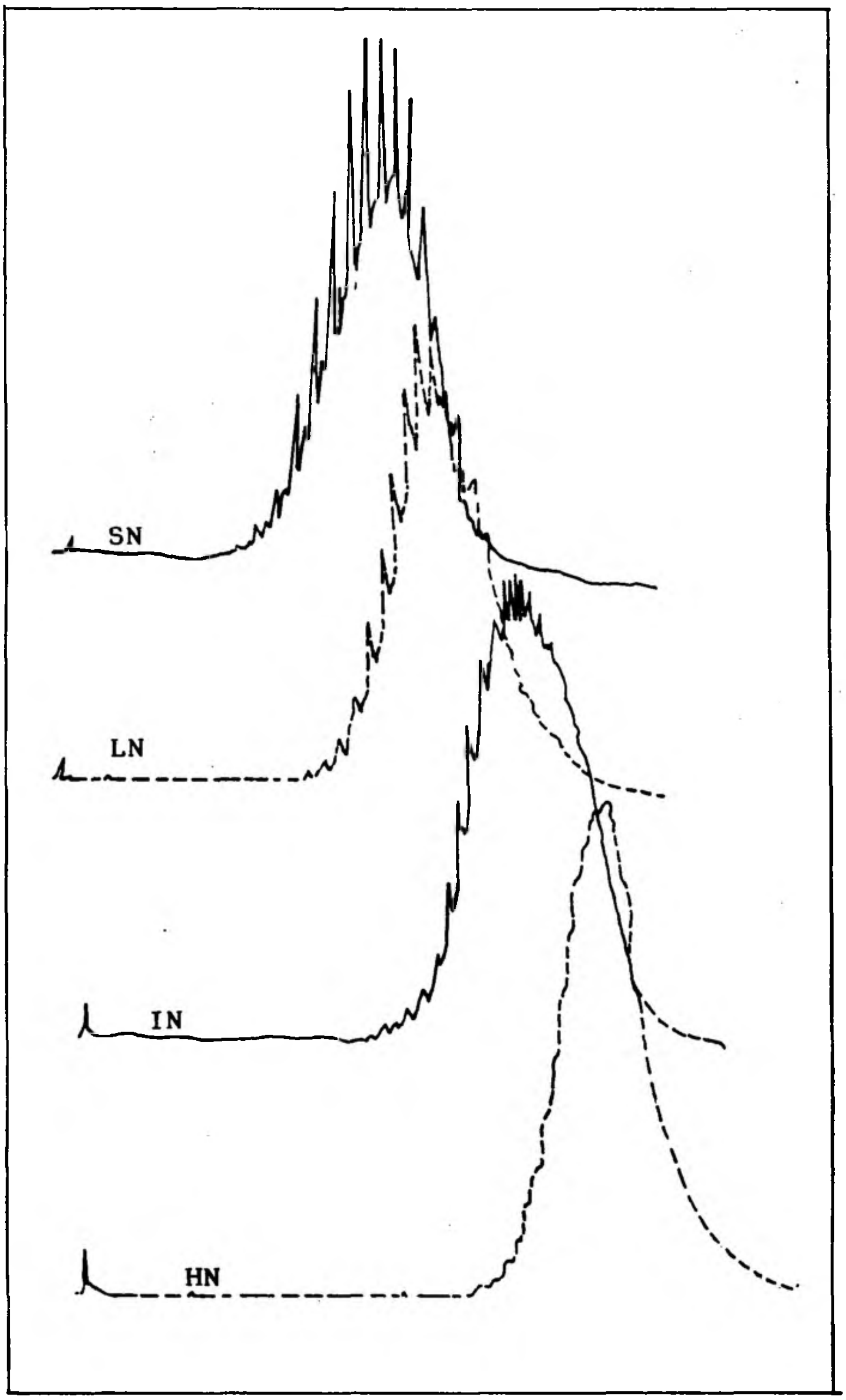


Fig II.1 GAS CHROMATOGRAMS OF FEEDS

into a socket. An infusion pump (supplied by M/s B.Braun Melsunger A.G., FRG) was used to pump the reactants through the needle. The side limb was used to pass the required gases (nitrogn, air or hydrogen). The reactor had a thermowell (5 mm o.d.) to measure the temperature of the catalyst bed. The reactor ended in long stem at the bottom with a B-12 cone attached to it. A water cooled (water temperature around 278 K) condenser (20 cm long) was attached to the bottom end of the reactor and the products collected in a reciever consisting of a small round bottomed flask (50 ml capacity) with a side limb as an outlet for product gases. The reactor was inserted into a furnace whose temperature could be controlled ± 1 K with temperature controllers. A calibrated U-tube capillary manometer coupled with a needle valve was used to meter the amount of gas being fed to the reactor. A sketch of the reactor system is shown in figure II.2.

II.2.B.HIGH PRESSURE REACTOR

A high pressure reactor (model BL-2) supplied by M/s Geomecanique, Paris, France was used in these studies. A simplified diagram of the reactor unit is shown in figure II.3. The reactor (volume = 220 ml) was made of SS 316 and was 88.5 cm long and had an i.d. of 19 mm. It had a thermowell running all along the length of the reactor (o.d. = 6 mm). Four thermocouples could be inserted through the thermowell to measure the reactor temperature at four different points. The furnace was made up of 5

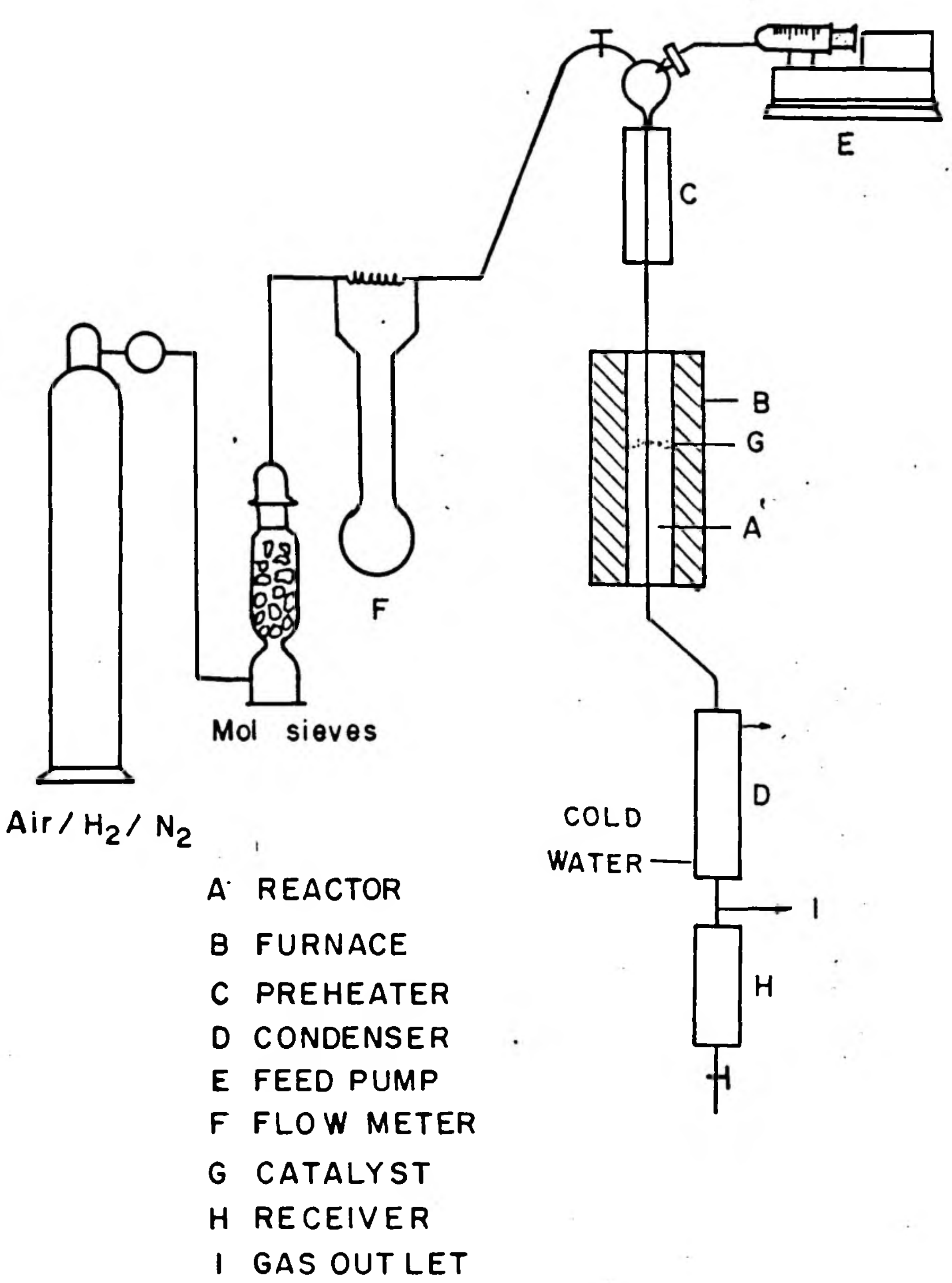
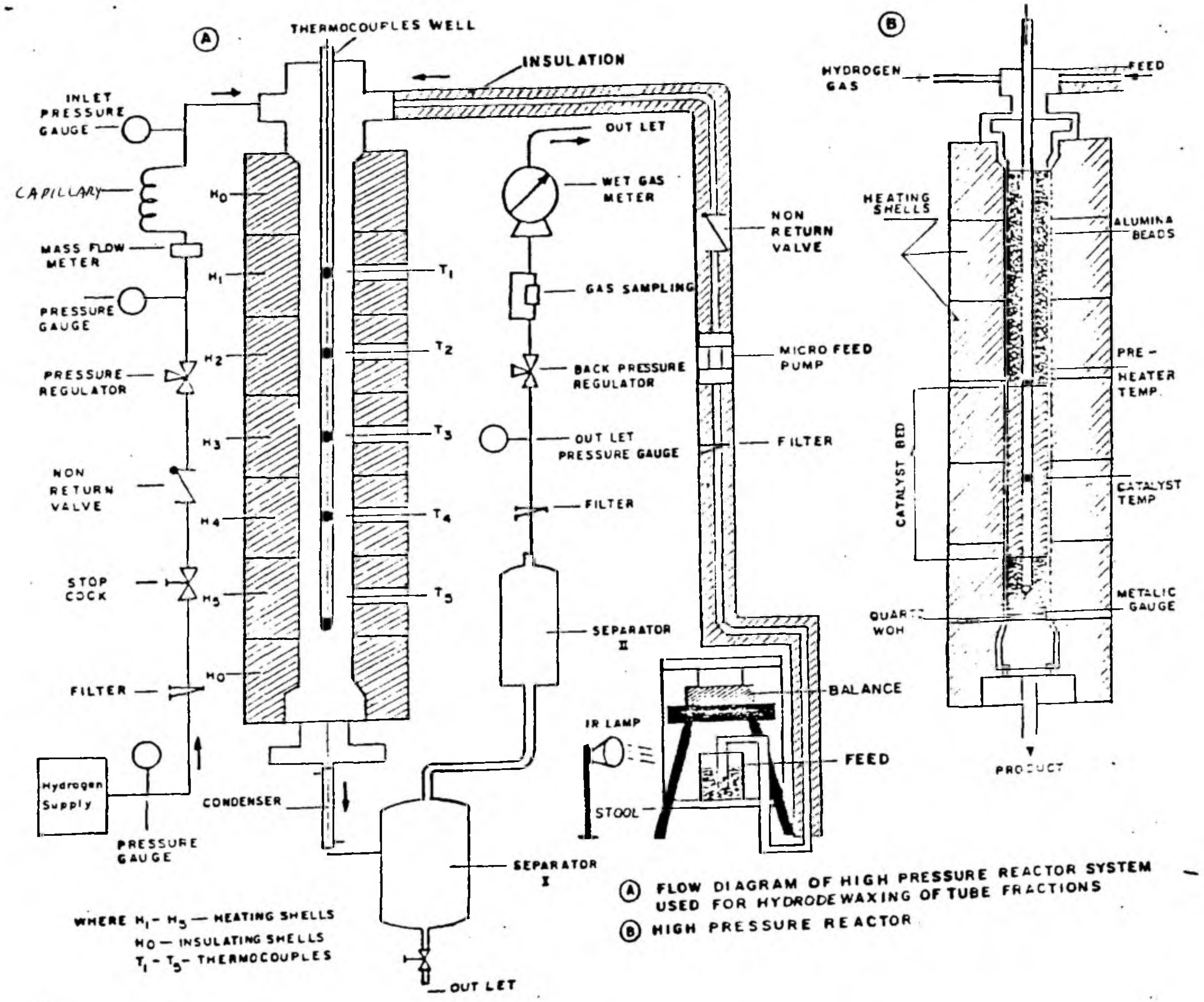


FIG. II.2. REACTOR USED FOR CATALYTIC REACTIONS



Ⓐ FLOW DIAGRAM OF HIGH PRESSURE REACTOR SYSTEM USED FOR HYDRODEWAXING OF TUBE FRACTIONS

Ⓑ HIGH PRESSURE REACTOR

Fig II. 3 HIGH PRESSURE REACTOR USED IN STUDIES shells (zones) whose temperatures could be independently controlled with 5 temperature controllers. Gases were introduced via mass flow controllers, while the outgoing gases were measured by a wet gas flowmeter.

II.3. EXPERIMENTAL PROCEDURE

II.3.A. CATALYTIC REACTIONS

Usually 1-3 g of catalyst crushed into small pieces (10-14 mesh) were used in the studies in the case of atmospheric reactions. About 60-80 g catalyst (1.5 mm x 3 mm) was used in the case of high pressure reactions. The general procedures adopted are described below.

I.3.A.1. ATMOSPHERIC PRESSURE REACTIONS

(i) Reaction

1. Load catalyst (10-14 mesh).
2. Dry by passing air (4 h, 773 K, 50 ml/min).
3. Purge with nitrogen, cool to 373 K or less.
4. Introduce hydrogen (50 ml/min) and raise temperature to 723 K. Hold temperature for 2 h.
5. Adjust temperature to operating temperature, adjust gas flow rate to required value and inject feed.
6. Collect liquid product and analyze periodically. Also analyse gas samples simultaneously.

(ii) Regeneration

1. Flush the catalyst with nitrogen at 523 K.
2. Introduce a mixture of nitrogen and air (90 vol% nitrogen and 10 vol% oxygen). Hold at 523 K for 1 h.
3. Raise temperature slowly in steps of 50 K till 723 K is reached. Hold for 2 h.
4. Raise temperature to 773 K. Hold for 4 h.
5. Flush in nitrogen and cool to room temperature. If reaction is carried out immediately, the drying step described above under "reaction" (step 2) is avoided.

II.3.A.2. HIGH PRESSURE REACTIONS

(i) Dewaxing reactions

1. Load catalyst after breaking to 1.5 x 3 mm size.
2. Dry by passing air (100 ml/min, 773 K, 4 h).
3. Purge with nitrogen, cool to 373 K or less.
4. Introduce hydrogen (200 ml/min) and raise temperature to 723 K. Hold temperature for 4 h.
5. Pressurize to required pressure. Adjust hydrogen flow rate.
6. Inject heavy naphtha (WHSV = 1 h^{-1}) and raise temperature to 523 K.
7. Inject feed at desired rate and simultaneously raise temperature to desired value.
8. Collect product periodically and analyze both the liquid and gas fractions.

(ii) Hydrofinishing reactions

1. Carryout steps 1 to 3 described above. However, cool to room temperature.
2. Pressurize with hydrogen to 3.5 M Pa. Adjust hydrogen flow rate.
3. Inject heavy naphtha (383-413 K) containing 1.0 wt% carbon disulfide at WHSV = 2 h^{-1} and H_2/oil = 300 v/v.
4. Raise temperature to 523 K slowly after the catalyst is "wetted" by the liquid. Hold at 523 K for 1 h.
5. Raise temperature to 623 K. Hold till H_2S break through occurs. Hold for 1 h. Stop the sulfur feed.
6. Adjust pressure and temperature to required value and inject the oil to be hydrotreated.

(iii) Reforming reactions (Pyrolysis gasoline)

1. Load catalyst after breaking to 1.5 x 3 mm size.
2. Dry by passing air (100 ml/min, 773 K, 4 h).
3. Purge with nitrogen, cool to 373 K or less.
4. Introduce hydrogen (200 ml/min) and raise temperature to 723 K. Hold temperature for 4 h.
5. Pressurize to required pressure. Adjust hydrogen flow rate.
6. Cool to 523 K. Inject sufiding feed (200 ppm dimethyl disulphide in n-hexane) at WHSV = 2 h^{-1} and hydrogen/oil (mole) = 6 till 0.03 g per 100 g of sulfur has been injected.
7. Inject feed at desired rate and simultaneously raise temperature to desired value.

8. Collect product periodically and analyze both the liquid and gas fractions.

(iv) Regeneration of catalyst

1. Flush the catalyst with nitrogen (250 ml/min) at 523 K for 2 h.
2. Cool to 423 K. Introduce regeneration gas (95 vol% nitrogen and 5 vol% air) at a rate of 1 l/min. Hold for 1 h.
3. Slowly raise temperature to 523 K (1 K/min). Hold for 2 h.
4. Slowly raise temperature to 723 K in steps of 50 K. Hold for half an hour at each step and hold for 3 h at 723 K. Raise to 753 K and hold for 6 h.
5. Introduce a gas with higher oxygen content (5 vol% oxygen) and hold for 6 h.
6. Introduce air (20 vol% oxygen) and hold for 2 h. Raise temperature to 773 K . Hold for 6 h.
7. Flush in nitrogen and cool.

<u>Note</u>:

1. At no time the catalyst bed temperature is allowed to go up by 10 K more than the set value. If there is a larger temperature rise, the regeneration is stopped and continued again after cooling.

2. If the reaction is carried out immediately after the regeneration, the drying step in the reaction sequence is avoided.

(v) Shutting down the reactor after reaction

This is done by shutting off all heaters (both line and furnace) and injecting heavy naphtha instead of feed till clean naphtha comes out and the reactor has cooled to 473 K. The naphtha is cut off and only hydrogen is passed till the temperature falls to less than 323 K. The unit is sealed in hydrogen under pressure.

II.4. ANALYSIS AND CALCULATIONS

II.4.A. COMPOSITION

Both the product gases and liquids were analyzed. The gases (C_1-C_5) were analyzed using a gas chromatographic refinery gas analyzer (model 5880 A, supplied by Hewlett Packard Asia Ltd., Hongkong, China). When heavier components (C_5^+) were present in the gas, a capillary column (Crosslinked Methyl silicon, used in PONA analysis) (50 m x 0.2 mm, 0.5 μm thickness film, fitted in a HP 5880 A gas chromatograph was used for the separation. The same column was used for analysis of light petroleum fractions and reactants and products with final boiling points not exceeding 473 K. A simulated distillation analyzer (model 5880 A supplied by Hewlett packard, Hongkong) was used for the analysis of the heavier petroleum fractions to obtain distillation data for dewaxed oils and products. The detector for both capillary and simulated distillation analysis was a flame ionization detector.

The gas chromatographic conditions were varied depending on the analysis and these are not reported in the thesis.

II.4.B. POUR POINT MEASUREMENT

Pour points of the oils were measured as described by ASTM method D-97.[181] Multi refrigerated baths supplied by Stanhopa-Seta Limited, England were used for the measurements.

II.4.C. VISCOSITY AND VISCOSITY INDICES

The viscosity of the oils were measured using calibrated Ostwald's viscometers (ASTM method D-2162)[182] as described by ASTM method D 445[183]. Viscosity Indices were calculated from the viscosity values of the oils obtained at 313 K and 373 K as described by ASTM method D 2270[184]. A mineral oil bath with accurate temperature control (± 0.01 K) was used in the measurement.

II.4.D. MASS-BALANCE CALCULATIONS

II.4.D.1. CRACKING OF NORMAL ALKANES

In the case of n-hexane and n-heptane the products and uncoverted reactants were totally in the gaseous state. Hence, gas analysis was enough to obtain the conversion levels and products yield distributions. In the case of n-octane, some liquid product was also obtained. So, both gas and liquid product analysis were carried out to obtain conversion and yields. Generally the product liquid was collected for a given period of time and weighed. Knowing the weight of liquid product and the weight of the gaseous fraction (from weight of feed input - weight of liquid product), and the analysis of the gas and liquid products, conversion and product break up could be calculated.

II.4.D.2. REFORMING OF PYROLYSIS GASOLINE

These reactions were carried out at both atmospheric and higher pressures (0.1 MPa to 1.0 MPa). The mass balance calculations were done in a manner similar to that for the n-octane cracking experiments.

II.4.D.3. HYDRODEWAXING OF PETROLEUM OILS

In the case of long duration experiments, mass balances were obtained every 8 hours. During a period of 2 to 4 hours (duration of mass balance), the total feed and hydrogen injected were determined. The gas at outlet was analysed at least four times during this period in a gas chromatograph, and the gas composition averaged out. Further, the total gas flowing out during the above period was also found out with a calibrated wet gas meter. At the end of the period (2 to 4 hours), the liquid product was collected and analysed. Also the liquid product was weighed. From the weight of the total feed injected and the weight of the liquid product, the weight of gaseous fraction was estimated.

Due to the high pressure of the reaction (3.0 to 6.0 MPa) a large quantity of gases (C_3 and C_4 fraction) gets dissolved in the product. These gases escape (at the time of collecting the product). For accurate mass balance, these gases have to be estimated. Therefore, these gases were collected by using a special reciever and gas measuring burette. Knowing the input and output of hydrogen, the amount of hydrogen produced in the reaction is determined. A complete mass balance is then worked out. Usually the mass balance were accurate to ± 2 wt%. Also product distribution was found out by knowing the liquid yield, the C_5- in the liquid, the gas yield and the C_5+ in the gas, and integrating the two sets of analytical results after multiplying them by the respective weight factors.

An example of a complete mass balance calculation is reported below:

Details of mass balance calculations

Feed : Bright stock
Duration of run : 110 minutes.
Temperature : 693 K
WHSV : 0.88 h^{-1}
Pressure : 4.5 MPa
hydrogen/oil : 556 v/v
DWO pour point : 260 K
Catalyst : Ni-ZSM-5

(i) Explanatory note for mass balance calculations

Mass balance is carried out over a certain period (say 1-2 hours). In this case 110 minutes, the weight of feed injected is found out from the balance.

The total volume of hydrogen passed is calculated from mass flow meter.

The volume of hydrogen and cracked gases (outlet gas) during this period is obtained from wet gas meter.

The hydrogen purity of the outlet gases is found by gas chromatography analysis.

Hydrogen consumed by the reaction in 110 min. = (inlet hydrogen - outlet gas) X (hydrogen purity) 1.

The product was collected in a reciever at the end of the run. The dissolved gas liberated from the product was measured using a special reciever and collected in a calibrated gas burette.

The outlet and dissolved gases are analysed by gas chromatography. The average molecular weights of the gases (excluding hydrogen) are calculated. Knowing the volume of the gases and the average molecular weights, the weight of C_1-C_4 fraction and the C_5+ fraction are calculated.

Knowing the weight of total amount of products (liquid + C_1-C_5+ gases) and the individual C_1 to C_4 break up, the yields of C_1-C_4 gases were calculated.

A weighed quantity of the liquid product is distilled in vacuum using nitrogen trap to collect the volatiles. The percentage distilling below IBP is found out. The yield of DWO is calculated.

The total weight of C_5+ -IBP = (weight of material distilling below IBP) + (weight of C_5+ from gas fraction). The yield of C_5+ to IBP fraction is calculated.

(ii) Calculations

1. Weight of feed passed : 97.89 g
2. Weight of liquid product collected : 87.98 g
3. Volume of dissolved gases (C_1-C_5) : 0.81 l (NTP)
4. Average molecular weight by G.C. : 55.93 g/mole
5. Volume of hydrogen passed : 59.8 l (NTP)
6. Volume of outlet gases : 57.8 l (NTP)
7. Purity of hydrogen : 92.85 vol %
8. Volume of C_1-C_5+ in outlet gases : $\frac{57.8 \times (100-92.85)}{100}$

   : 4.13 l
9. Average molecular wight of outlet gas (C_1-C_5+) by g.c. : 49.26 g/mole
10. Volume of hydrogen consumed : $\frac{(59.8 - 57.8)}{100} \times 92.85$

    : 6.13 l (NTP)
11. Weight of hydrogen consumed : 0.55 g
12. Weight of C_1-C_5+ in outlet gases : $\frac{\text{Av.mol.Wt.} \times \text{vol.}}{22.414}$ g

    : 9.08 g
13. Weight of C_1-C_5+ in dissolved gases : " : 2.01 g

Section A

Gas Analysis

Gas (hydrocarbon composition)	wt% (excluding hydrogen) Outlet gas	 Dissolved gas
C_1	1.04	0.08
C_2	5.33	1.63
C_3	44.97	31.45
i-C_4	21.46	20.25
n-C_4	13.72	18.20
C_5	10.94	22.35
C_6+	2.54	5.94
Average molecular weight	49.26 g/mole	55.93 g/mole
Volume of gas	4.13 l	0.81 l
Weight of C_1-C_5+ gas	9.08 g	2.01 g
Weight of C_1-C_4	7.86 g	1.44 g
Weight of C_5+ in gas	1.22 g	0.57 g

Total C_1-C_4 9.30 g

Total C_5+ in gas 1.79 g

Section B

Liquid Analysis (By distillation)

Weight of liquid product : 87.98 g

Weight of DWO collected : 80.12 g

Weight of C_5+ -IBP : 7.86 g

Total C_5+ -IBP (including C_5 +
component in gas)(9.86 + 1.79) : 9.65 g

Section C

Mass-Balance

Input

Feed	: 97.89 g
Hydrogen	: 0.55 g
Total	: 98.44 g

Output(based on distillation and gas yield break up)

Products:

DWO	: 80.08 g
C_5+ -DWO	: 9.64 g
C_1-C_4	: 9.30 g
Total	: 99.02 g

Error in mass balance = 0.55 wt%.

Based on the above gas analysis and liquid break up, the yield of individual components are worked to be:

Product yields from dewaxing

C_1	C_2	C_3	i-C_4	n-C_4	C_5+ -IBP	DWO(IBP-FBP)
0.09	0.50	4.70	2.36	1.61	9.68	81.06

CHAPTER III

HYDROCRACKING OF n-ALKANES

III.1 INTRODUCTION

Since 1960 catalytic cracking has received considerable importance in petroleum refining where it is used mainly for the production of gasoline, jet fuels, middle distillates and lubricants. In these processes, heavy hydrocarbon fractions are cracked into lower molecular weight fractions, such as gasoline, increasing thereby, the yield of motor fuels. Zeolite cracking catalysts have many advantages over conventional silica-alumina amorphous catalysts.

Subsequently, high pressure hydrocracking processes based on zeolite (X and Y) catalysts were introduced in commercial practice. These processes have gained wide acceptance in the petroleum refining industry.

The outstanding advantages of zeolite based hydrocracking are flexibility as well as high quality of the products with good catalyst stability and resistance towards poisons. In the course of its commercial growth, the chemistry of hydrocracking over various types of bifunctional catalysts has been scrutinized with model hydrocarbons, most commonly with alkanes. Several reviews on this subject are now available[168,169], showing that the product distributions are markedly influenced by relative strength of hydrogenation activity versus acidity of the catalyst.

On bifunctional metal-acid catalysts, alkane transformations are believed to occur through the following steps:

(a) dehydrogenation of the alkanes on the metal;

(b) transport of olefins to the acid sites from the metal sites;

(c) isomerization or cracking of olefins on the acid sites through carbenium ion intermediates;

(d) transport of the olefins from the acid to metallic sites;

(e) and hydrogenation of these olefins over the metallic sites.

Even though, hydrocarbon cracking takes place on the acid centres, the over all reaction is bifunctional.

Steps **a** and **e** are very rapid, and when the two types of active centres are in close proximity, steps **b** and **d** may not be rate limiting. Thus, the reaction rate depends on step **c**, the number and strength of acid centres affecting the cracking reaction. The presence of a metallic compound assists the cracking reaction by ensuring a supply of olefins to the acid centres of the zeolite. Olefins are easily converted into carbenium ions which transform into other products. Further, the metallic component can also hydrogenate the unsaturated cracked products and assist their desorption, thereby minimizing secondary cracking of the products. Though, in the absence of sulfur, hydrogenolysis of the paraffins on some metals is possible, this is not significant when sulfur is present in the feed.

A large amount of data on the hydrocracking of many normal paraffins over medium pore ZSM-5 is available in the literature[166,167]. However, a systematic study of the role of supported metals in the cracking of different hydrocarbons over ZSM-5 is not available, especially in the presence of sulfur and nitrogen compounds. Hydrocracking of paraffins on ZSM-5 is interesting due to its shape-selectivity characteristics, discovered by Weisz and Frilette[185].

In this chapter the studies of the cracking of n-hexane, n-heptane, n-octane and n-hexadecane in the presence of hydrogen on different metal loaded ZSM-5 are being reported. The hydrocracking activity of large pore Y and Beta are also reported for comparison purposes. The activities of the different metal loaded zeolite catalysts were evaluated at different temperatures and their product selectivities are examined. The influence of sulfur and nitrogen in the feed was also investigated.

The experiments were carried out in a small down flow type fixed bed reactor which has been described in the chapter II along with the methods used for analysis of the products. Pure (>99.5%) hydrocarbons were used in these studies. Sulfur containing feeds were prepared by spiking the hydrocarbons with 0.2 % sulfur as dimethyl disulfide, and nitrogen containing feeds were prepared by adding different amounts (ppm levels) of n-butyl amine and quinoline to the pure hydrocarbons. Procedures adopted in the preparation of the catalysts have already been described in chapter II. All the catalysts used are listed in table II.2(a). Before each run the catalyst was activated by flowing air for 2 h at 773 K. The metal loaded catalysts were reduced with flowing hydrogen for 4 h at 533 K prior to cracking experiments.Detailed procedures have been reported in chapter II.

III.2 HYDROCRACKING OF n-HEXANE, n-HEPTANE AND n-OCTANE

Studies on the cracking n-hexane, n-heptane and n-octane were carried out over H-ZSM-5 at different temperatures and times on stream. The influence of nitrogen containing poisons in the feed on the activity and product selectivity was also investigated. Studies on the cracking of n-hexane were also carried out over Ni-ZSM-5 both in the presence and absence of sulfur. Influence of sulfur on the reaction rate was examined.

Figure III.1 presents the results of the cracking of n-hexane over H-ZSM-5 at 533 K, 563 K and 593 K at different times on stream both in the presence and absence of nitrogen poison. It is noticed that the catalyst deactivates at all temperatures, the deactivation being more pronounced at the higher temperatures. The activity, however, tends to stabilize (with mild deactivation) after 4 hours on stream. The activation energy calculated for the cracking reaction at times on stream between 1 to 3 hours is 60 ± 4 K J mole^{-1}. Applying Voorhies equation,[186]

$$a = A\ t^{-n} ,$$

where a is conversion at time t, we can calculate the values of n, the deactivation coefficient (for the loss of cracking activity) at different temperatures. These are presented in table III.1. The deactivation coefficient increases, as expected, with increasing temperature (0.178 at 533 K and 0.396 at 593 K).

The influence of adding two different levels of nitrogen (as n-butylamine) in the feed was examined. Increasing amounts of n-butylamine in the feed increase the deactivation of the

Fig III.1 nC_6 CRACKING OVER ZSM-5

(Pressure: 0.1 MPa; WHSV: 3.0 h^{-1}; nC_6 partial pressure: 0.0340 MPa; H_2 partial pressure: 0.0659 MPa)

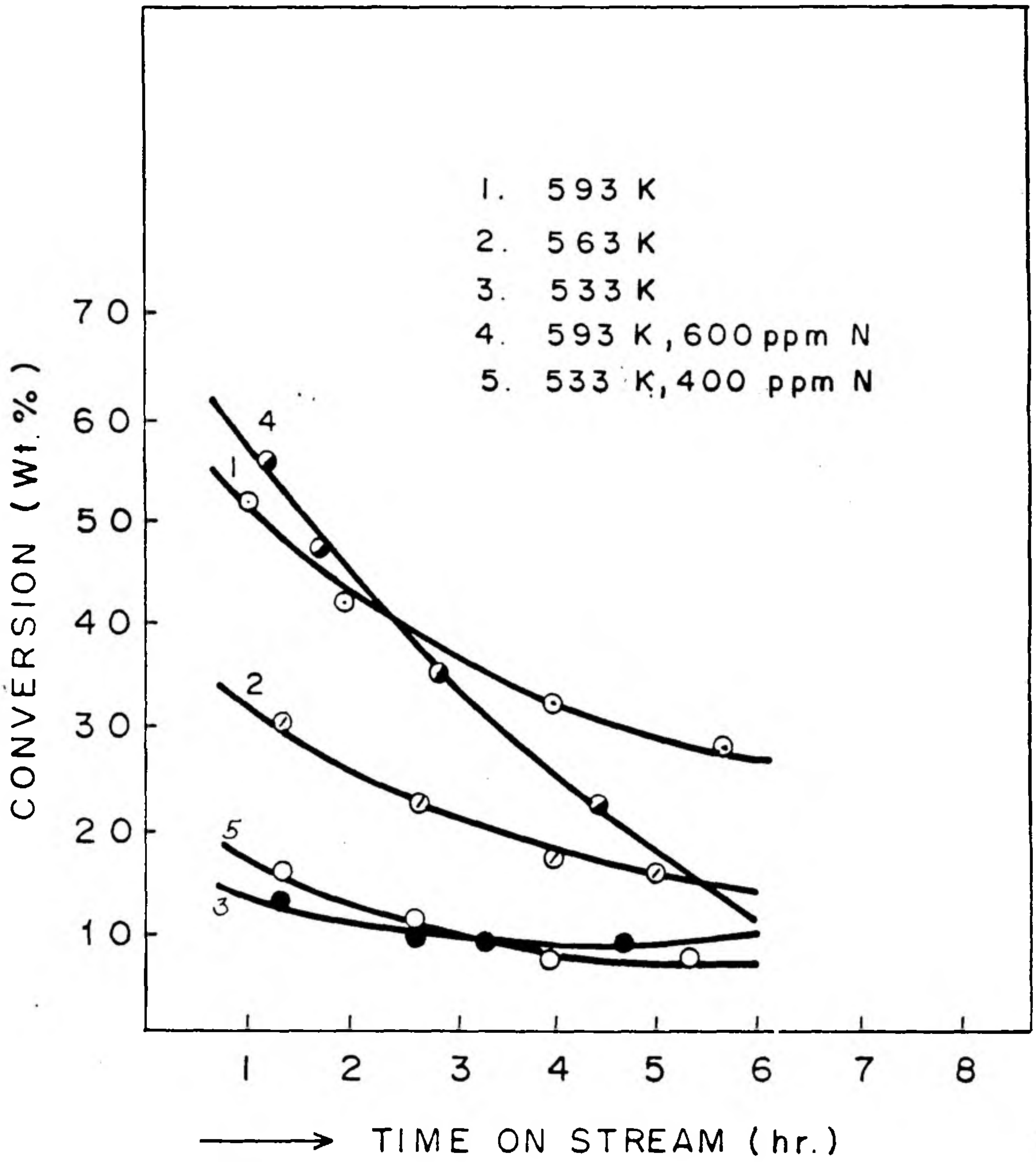


Table III.1

Hydrocracking of n-C_6, n-C_7 and n-C_8

(Zeolite : ZSM-5; Silica/Alumina = 84; 0.1μm crystallites)

Reaction conditions : **n-Hexane:**
WHSV : 3.0 h^{-1}
partial press. : 0.0340 MPa
H_2 partial press. : 0.0659 MPa

Feed rate : 3.67 $\times 10^{-2}$ moles g^{-1} h^{-1}
n-Heptane:
WHSV : 3.0 h^{-1}
partial press. : 0.0310 MPa
H_2 partial press. : 0.0690 MPa

Feed rate : 3.16 $\times 10^{-2}$ moles g^{-1} h^{-1}
n-Octane:
WHSV : 3.0 h^{-1}
Partial press. : 0.0280 MPa
H_2 partial press. : 0.0720 MPa

Feed rate : 2.85 $\times 10^{-2}$ moles g^{-1} h^{-1}

Feed	Poison (ppm)	Catalyst	Temp. (K)	Activity at time 1 hour (mole g^{-1} hr^{-1}) (x 10^3)	Deactivation coefficient (n)#
n-Hexane	---	HZSM-5	533	4.59	0.178
n-Hexane	---	HZSM-5	593	18.72	0.396
n-Hexane	600 N*	HZSM-5	593	20.80	1.216
n-Hexane	400 N*	HZSM-5	533	6.12	0.673
n-Hexane	---	Ni-ZSM-5	593	20.55	0.084
n-Hexane	400 N*	Ni-ZSM-5	593	17.25	0.102
n-Hexane	2000 S+	Ni-ZSM-5	593	20.92	---
n-Hexane	400 N* +2000 S+	Ni-ZSM-5	593	21.65	0.128
n-Heptane	---	HZSM-5	593	22.59	0.111
n-Heptane**	---	HZSM-5	593	33.39	0.046
n-Heptane	600 N*	HZSM-5	593	21.16	0.400
n-Heptane	400 N#	HZSM-5	593	18.88	0.120
n-Heptane	400 N*	HZSM-5	593	21.16	0.319
n-Octane	---	HZSM-5	593	20.08	0.058
n-Octane	600 N*	HZSM-5	593	20.58	0.052

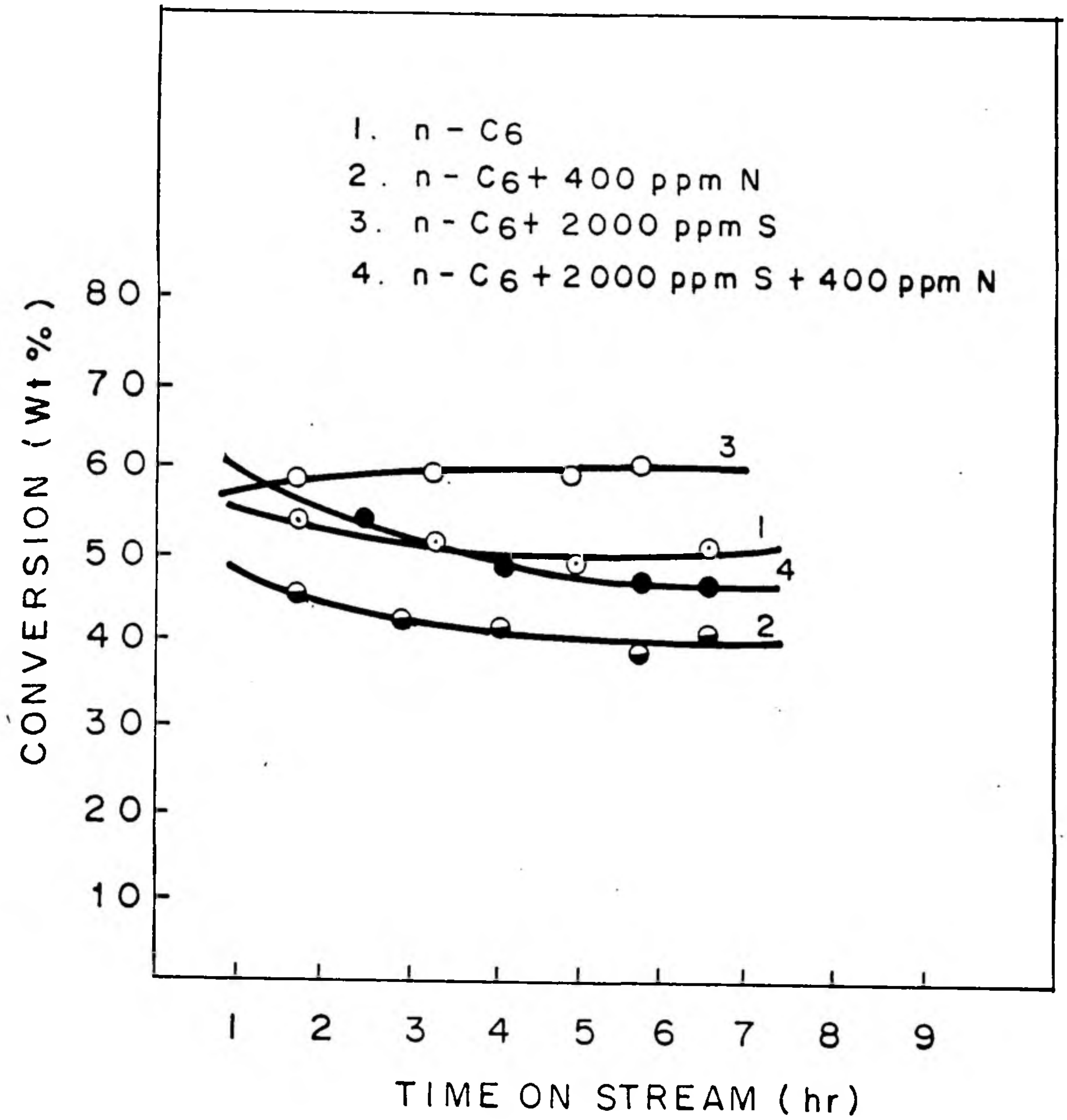
*n-Butylamine, + as Dimethyl disulphide, #Quinoline and
** WHSV: 7.5 h^{-1} : Feed rate : 7.5 x 10^{-2} moles h^{-1} g^{-1}
# n is deactivation coefficient (Voorhies eqation)[186].

catalyst. The deactivation coefficients in the presence of n-butylamine in the feed are also presented in table III.1. These values increase with increasing nitrogen content. (0.673 at 400 ppm 1.216 at 600 ppm). However, it should be noted that the two different levels of nitrogen have been tried out at two different temperatures, viz 533 and 593 K. The increased activity observed in the presence of the nitrogen poison both at 593 K and 533 K at a time on stream of one hour (table III.1) is **probably** due to lower deactivation by coke in the presence of nitrogen, especially of the active centres on the external surface of the crystallites. The external surface contribution in the zeolite crystallites used in these studies is expected to be around 2 % of the total area, though the contribution of these sites to activity may be more. Coke poisoning being irreversible would deactivate the external surface within the first few minutes. The presence of a reversible poison like nitrogen on the surface may delay the deactivation for some time by blocking the sites responsible for coking. However, it should be noted that the first experimentally measured point was at 1 hour, and at zero hour (intial) the activities would have been the same irrespective of whether nitrogen was in the feed or not.

The results of cracking of n-hexane on a 2 % Ni loaded HZSM-5 are presented in figure III.2. The catalyst was prepared by an ion-exchange-cum-impregnation procedure as described in chapter II. Given that the silica/alumina ratio of ZSM-5 was around 80, it could have exchanged only 0.01 wt % of Ni. The rest of the Ni

Fig.III 2 CRACKING OF n-HEXANE OVER Ni-ZSM-5

(Pressure: 0.1 MPa; nC_6 partial pressure: 0.034 MPa; H_2 partial pressure: 0.0659 MPa; WHSV: 3.0 h^{-1}; Temperature: 593 K)



must have deposited over the external surface of the crystallites and on the binder alumina which constituted 35 wt % of the catalyst.

The influence of binder alumina itself on the reaction was very small as ascertained by blank experiments carried out at 593 K using 100 % alumina extrudates. At the above temperature the intital cracking activity was less than 0.4 wt % but it deactivated at the end of 2 hours to less than 0.1 wt %. However isohexanes were produced to the extent of 2.2 wt % at 2 hours on stream. In the case of a 2 % Ni/alumina catalyst, the activities were slightly higher, the cracking (hydrogenolysis) and isomerization activities being about 0.3 wt % and 3.6 wt % at 2 hours on stream.

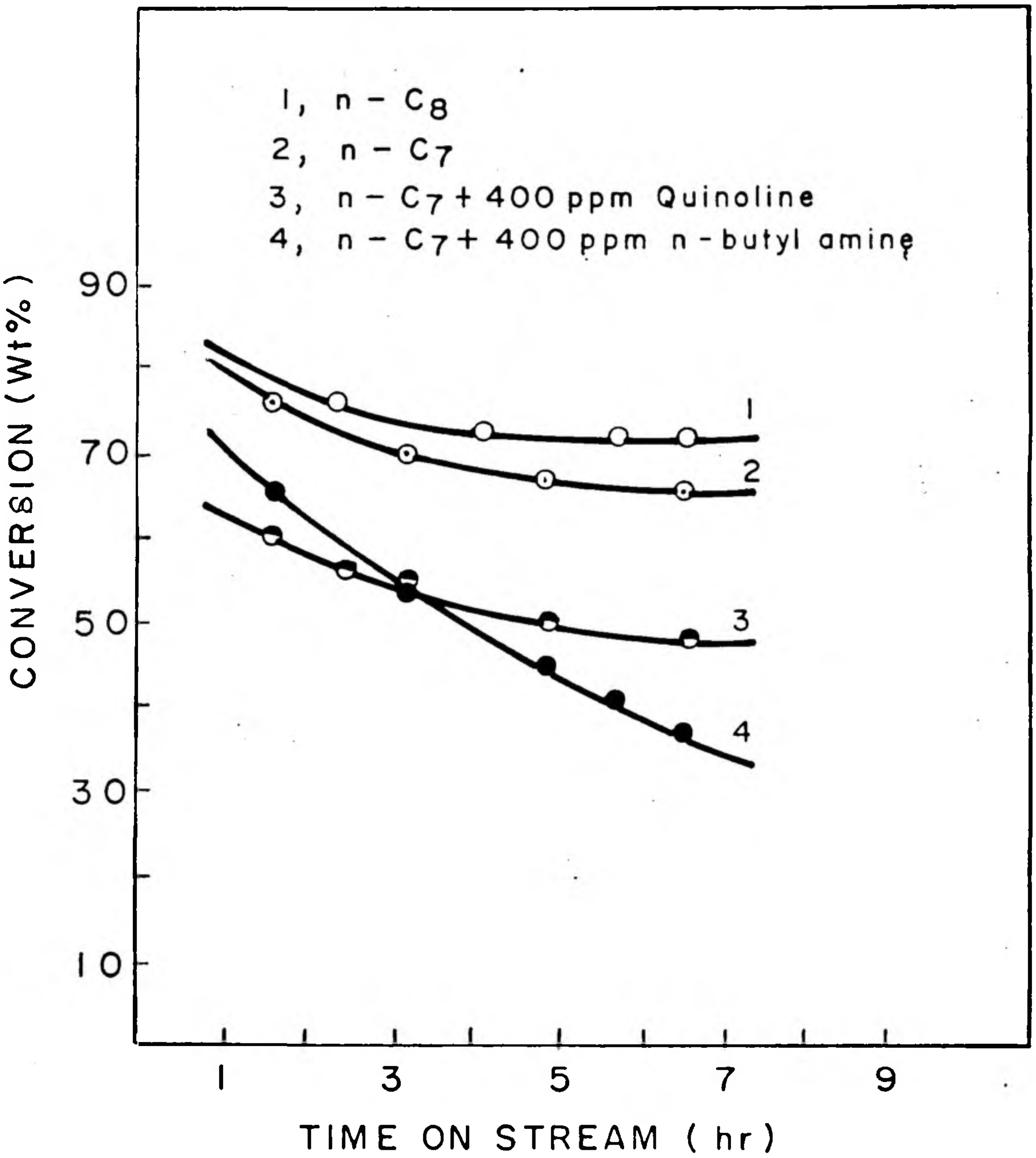
It is observed (figure III.2 and table III.1) that the activity of the catalyst increases on loading Ni. Also the deactivation of the catalyst is also less when compared to H-ZSM-5 as seen from the lower value for the deactivation coefficient. (0.084 for Ni-ZSM-5 and 0.396 for H-ZSM-5) at 593 K. When 600 ppm of nitrogen (n-butylamine) is introduced, the deactivation rate increases, the deactivation rate being again smaller than in the case of H-ZSM-5 (0.102 for Ni-ZSM-5 at 593 K and 0.673 for H-ZSM-5 at 533 K). When 0.2 wt % sulfur (as dimethyl disulfide) is added to the feed, the deactivation decreases still and in fact no deactivation was observed till 6 hours on stream. Further, the activity itself increases. The increased activity observed for Ni-ZSM-5 could be due to the cooperative action of Ni metal in the cracking reaction, the reaction being a bifunctional one. In the presence of sulfur, the deactivation of the Ni by coke deposition decreases and this prevents deactivation of the catalyst. The coke precusors formed are likely to be hydrogenated by the metallic (and sulfide) components in the catalyst. However, as the studies were carried out only upto about 7 hours, any deactivation occurring beyond this time is not known. When sulfur (0.2 wt %) and nitrogen (400 ppm) are present together in the feed, deactivation is observed, the rate being about the same as that in the absence of sulfur (table III.1).

The results of the studies carried out on the cracking of n-heptane and n-octane are presented in figure III.3. These studies were carried out at 593 K. It is observed that the deactivation coefficient becomes lower as the carbon number increases (cf. Table III.1). It is 0.396, 0.111 and 0.058 for n-hexane, n-heptane and n-octane, respectively at 593 K. Further, increasing the feed rate also decreases the deactivation coefficient. It is 0.111 at a n-heptane feed rate of 3.16 X 10^{-2} moles g^{-1} h^{-1},while it is only 0.046 at a feed rate of 7.5 X 10^{-2} moles g^{-1} h^{-1} (Table III.1).

Again, the influence of nitrogen poison is less with the larger hydrocarbons. For example when 600 ppm nitrogen is present in the feed, at a temperature of 593 K, the deactivation coefficient is 1.22 for n-hexane, while it is 0.4 for n-heptane and 0.08 for n-octane. The possible explanations are (1) n-hexane cracking needs stronger acid centres which are easily

Fig.III 3 CRACKING OF nC_7 AND nC_8 OVER ZSM-5

(Pressure : 0.1 MPa; Partial pressures of hydrocarbons and hydrogen: See table III.1; WHSV: 3.0 h^{-1}; Temperature: 593 K)



poisoned by nitrogen. (2) At 600 ppm the partial pressure of nitrogen is very low compared to the hydrocarbon feedstock (2.7×10^{-5} MPa for n-butylamine and ~ 0.03 MPa for the hydrocarbons), and under these conditions, the n-butylamine molecules have to counter diffuse into the pores displacing the hydrocarbon molecules. When the molecules are larger, the counter diffusion of the smaller n-butylamine molecule becomes less favourable. When we examine the case of quinoline, we find that its poisoning activity is less than that of n-butyl amine due to its bulkier nature and slower diffusivity.

The kinetics of cracking on H-ZSM-5 has been found to be first order for n-hexane and n-octane by Haag *et al*[170]. Our studies also have suggested a first order kinetics for the cracking of n-hexane, n-heptane and n-octane. This conclusion was reached based on the linear plot obtained when conversion was plotted against contact time. Such a plot for n-heptane is presented in figure III.4. For a first order reaction, the rate constant (k) can be calculated from the equation[187]:

$$k = (1/\tau) \ln [1/(1-\epsilon)]$$

Where $\tau = V/F$, V = Volume of catalyst, F = Feed rate per second and ϵ = fractional conversion.

The rate constants calculated for the different hydrocarbons are 0.611 $\sec^{-1}$ for n-hexane, 1.418 $\sec^{-1}$ for n-heptane and 1.501 $\sec^{-1}$ for for n-octane. Thus, the crackability of n-octane at 533 K is about 2.5 times that of n-hexane.

Haag *et al*[170] have reported a value of 1.9 for the ratio of

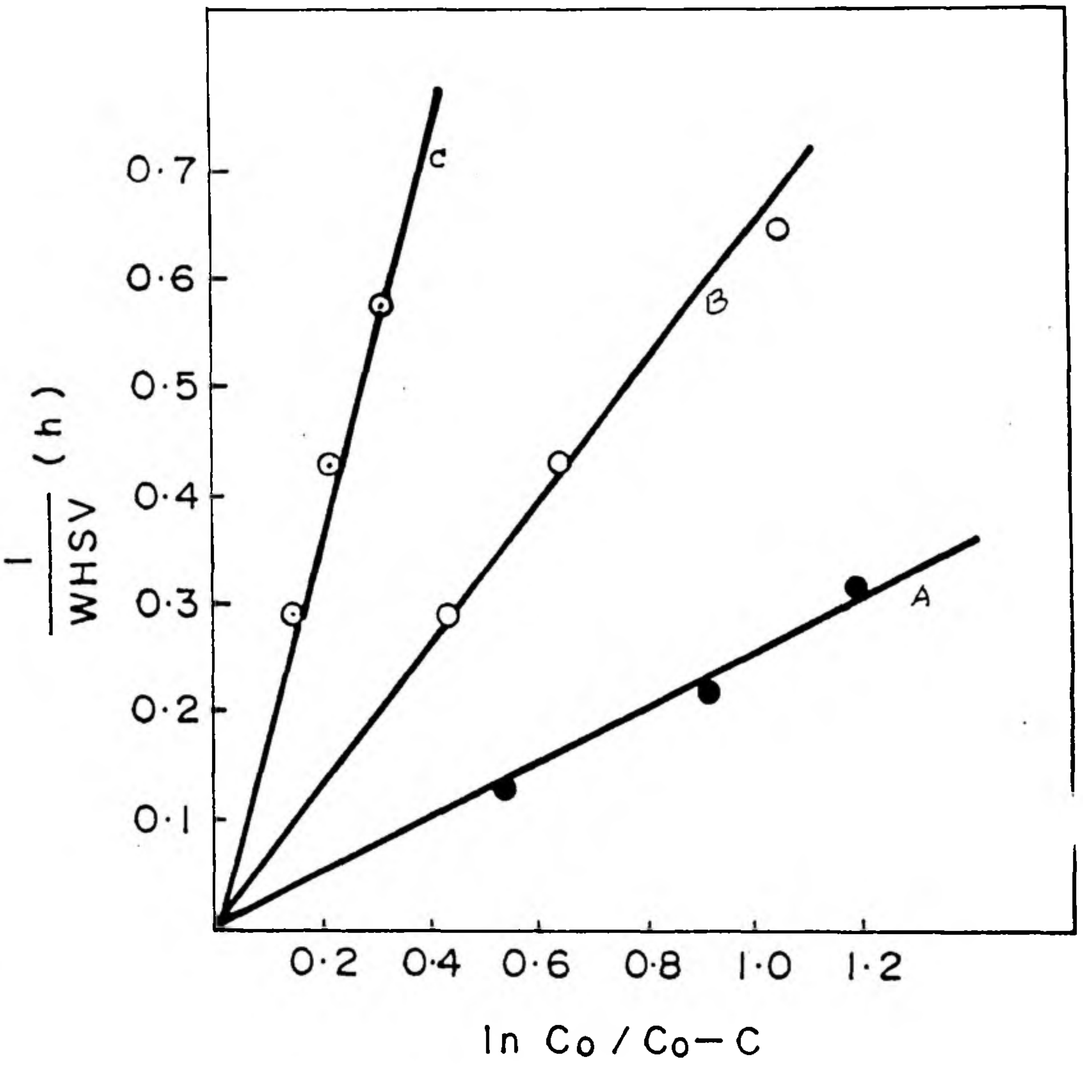


Fig. III 4 FIRST ORDER PLOTS FOR n-ALKENE CRACKING

(Pressure: 0.1 MPa; For other variables see relevant places in text; A: nC_7 on HZSM-5; B: nC_{16} on Pt-Beta; C: nC_{16} on Pt-Y) the cracking rates for n-hexane and n-octane at 811 K. It is generally believed that strong diffusion inhibition occurs when $k'(R^2/D) > 2$, where k' is the observed rate constant and R is the average radius of the crystallites.

For $R = 5 \times 10^{-6}$ cm, and knowing k' and D we can check whether diffusion effects are present. The diffusion coefficient (D) for n-hexane has been reported[170] to be 3×10^{-4} cm^2/sec at 811 K. Assuming a reasonable E_a of 20 KJ $mole^{-1}$ (~5 Kcal $mole^{-1}$), the D at 533 K is 6×10^{-5} cm^2/sec. In the case of n-C_6,

$$0.611(2.5X10^{-13}/6.0X10^{-5}) << 2.$$

Thus, it is appears that diffusion effects are absent in the cracking of n-C_6. Similarly, in the case of n-heptane and n-octane also the diffusion effects are likely to be absent as the values of D are expected to be only marginally larger than that for n-hexane. In fact Haag *et al*[170]. did not observe any diffusion effect even for nonane on much larger crystallites (1.35×10^{-4} cm radius).

Typical product distributions obtained from the cracking of n-hexane and n-heptane are presented in table III.2.

The interesting aspects of the product distribution are the very low amounts of the iso products. The iso/normal ratios are smaller than thermodynamic equilibrium values, and those normally obtained on amorphous silica/alumina and faujasites. This can be attributed to steric restrictions imposed on the transition state during the formation of isoparaffins and product shape selectivity effects.

Table III.2

n-Hexane and n-Heptane hydrocracking over H-ZSM-5

Conditions:

Temperature : 593 K
Pressure : 0.1 MPa
WHSV : 3 h^{-1}
Time on stream : 2 hours
n-Hexane:
partial press. : 0.0340 MPa
H_2 partial press. : 0.0659 MPa
n-Heptane:
partial press. : 0.0310 MPa
H_2 partial press. : 0.0690 MPa

component	Product distribution (wt%)	
	n-Hexane	n-Heptane
C_1	0.008	0.011
C_2 =	0.153	0.360
C_2	0.060	0.086
C_3 =	0.699	2.126
C_3	2.938	8.593
C_4 =	2.204	5.655
i-C_4	0.693	2.134
n-C_4	2.938	6.281
C_5 =	0.419	0.860
i-C_5	1.086	2.707
n-C_5	1.191	2.670
C_6 =	0.477	1.287
i-C_6	1.048	1.001
n-C_6	85.710	0.863
C_7 =		0.590
i-C_7		0.482
n-C_7		62.046
Others	0.477	2.247

III.3 HYDROCRACKING OF n-HEXADECANE

III.3. A. STUDIES ON H-ZSM-5

The results of cracking n-hexadecane at 533 K are presented in fig III.5 and table III.3. The influence of nitrogen in the feed has been investigated at different levels. The value of the deactivation coefficient increases with increasing nitrogen content of the feed. When the feed nitrogen content is 2000 ppm, total deactivation of the catalyst occurs at about 140 minutes i.e., after 1.2×10^{21} molecules of n-butylamine have been passed. The total number of acid centers (zeolitic, calculated from Al^{3+} content) is 3.2×10^{20} molecules. In other words, the number of molecules of the nitrogen base required for neutralization of all the acid centres is about four times the number of the acid centres. A similar result has been reported by Namba *et al*[188]. They found that activity for the conversion of p-xylene by H-ZSM-5 could be totally suppressed by quinoline molecules only when about 3 times the number of Al^{3+} atoms present in the zeolite were passed. This suggests that at the low concentration of the poison used (2.7×10^{-5} MPa) every molecule of the poison is not able to counterdiffuse into the pores and reach the acid centres. Hence, a larger number of the base molecules are required to poison the active sites.

An interesting observation (Table III.3) is that the deactivation coefficient (n) is directly related to the nitrogen content of the feed. A plot of n versus the concentration of nitrogen (ppm) gives a near straight line (Figure III.6) the

Fig. III 5 CRACKING OF nC_{16} ON ZSM-5: INFLUENCE OF NITROGEN PIOSON

(Pressure: 0.1 MPa; Temperature : 513K; WHSV: 3.0 h^{-1}; nC_{16} partial pressure: 0.016 MPa; H_2 partial pressure :0.084 MPa)

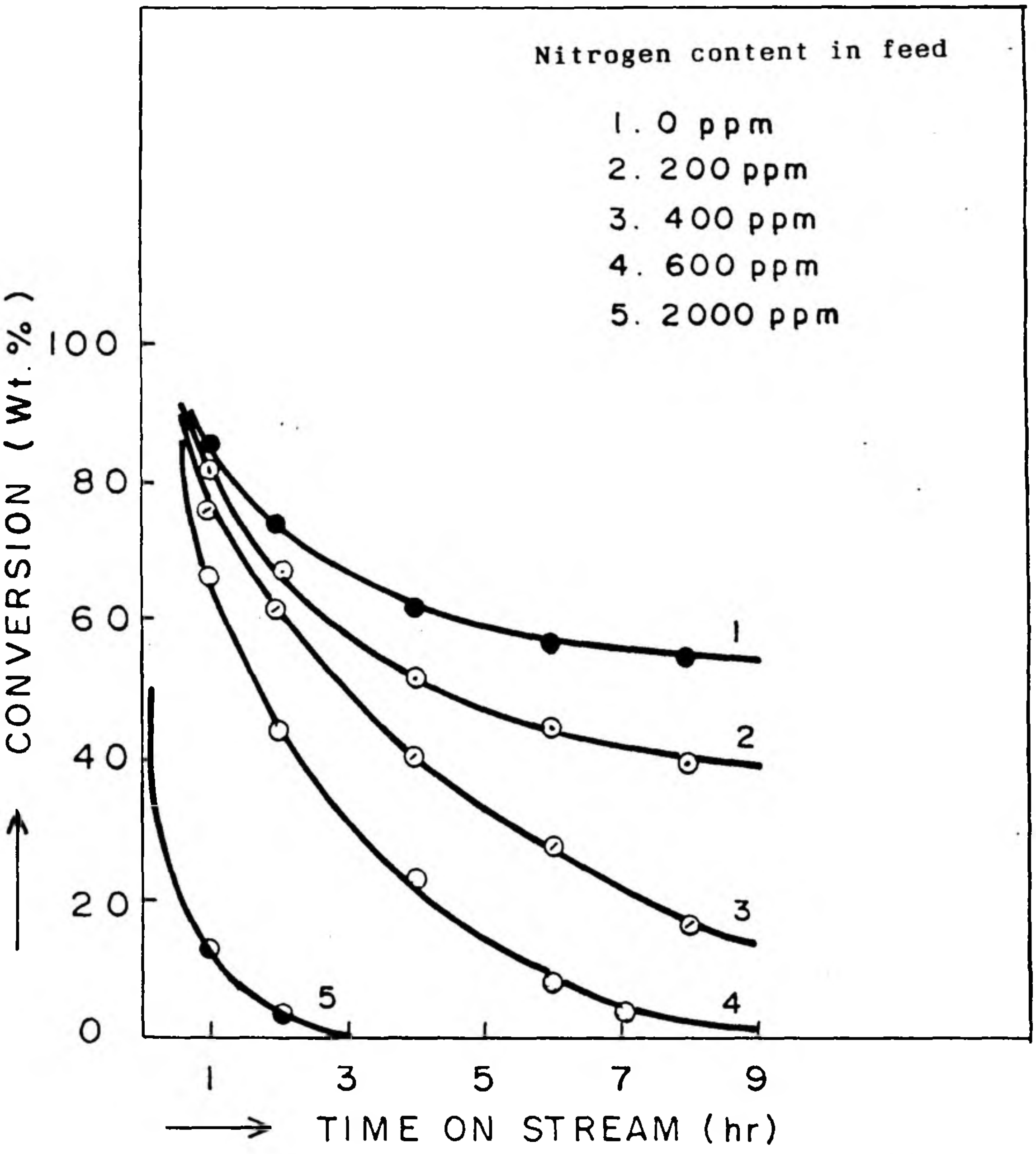


Table III.3

Hydrocracking of n-Hexadecane over H-ZSM-5

Reaction Conditions: T = 513 K
P = 0.1 MPa
WHSV = 3 hr^{-1}.
partial press. =0.016 MPa
H_2 partial press.=0.084 MPa

nitrogen as n-butylamine (ppm)	Activity at time 1 hour (mole g^{-1} hr^{-1}) (x 10^2)	Deactivation coefficient (n)#
0	2.24	0.169
200	1.95	0.245
400	1.89	0.334
600	1.63	0.535
2000	0.26	0.855

in equation $k = A\ t^{-n}$ (Vordhies equation)[186]

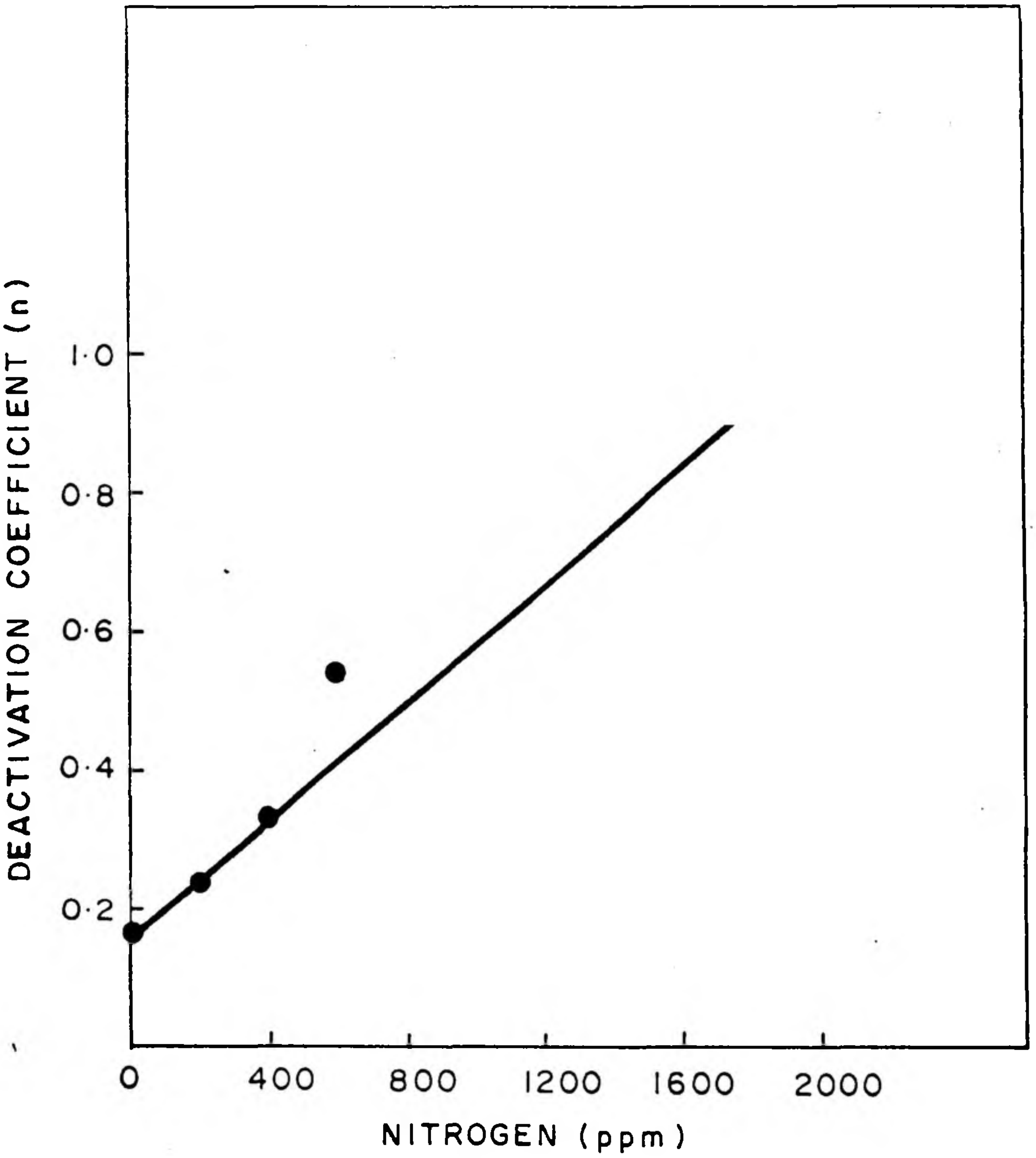


FIG.III.5

RELATIONSHIP BETWEEN DEACTIVATION COEFFICIENT (n) AND NITROGEN CONTENT

(See text for details of experimental conditions) intercept being the deactivation coefficient in the case of the pure feed. This suggests that, **in the case of** $n\text{-}C_{16}$, the two deactivation mechanisms (coking and nitrogen-poisoning) are independent of one another and take place simultaneously.

The diffusion coeffiecient (D) for the diffusion of $n\text{-}C_{16}$ in ZSM-5 pores is not readily available from the literature. However, the diffusion of many n-paraffins in zeolite A has been reported by many workers[189]. For example Ruthven and Eic[189] have reported values of 2.13×10^{-9} and 4.14×10^{-10} cm^2/sec, for the diffusion coefficient (D) of $n\text{-}C_7$ and $n\text{-}C_{16}$ in zeolite A at 533 K[189]. Zeolite A has a smaller pore dimension than ZSM-5 (4.1 Å vs. 5.5 Å). Hence it is likely that the lower limit value of D for $n\text{-}C_{16}$ cannot be less than 1×10^{-10} cm^2/sec. Infact, it is likely to be an order (or two) larger than this value. Using this value for D, we can check for diffusion inhibition during $n\text{-}C_{16}$ cracking also. From the experimental studies at 533 K, the value of k, the first order rate constant is 0.648 sec^{-1}.

Applying the test equation for diffusion inhibition[187] $k'(R^2/D) > 2$, where R = radius of the crystallite,

$$0.648(2.5 \times 10^{-13} / 1 \times 10^{-10}) = 1.62 \times 10^{-3} \ll 2$$

This shows that diffusion effects are absent under the condition of our cracking tests.

Another method of checking for the presence of diffusion control is to examine the energy of activation (E_a) for the reaction. In the case of diffusion controlled reactions over conventional oxide catalysts, E_a values are low because of the relatively small dependence of bulk and Knudsen diffusion coefficients with temperature. For bulk diffusion of substance A into B,

$$D_{AB} = \frac{1.00 \times 10^{-3} T^{1.75} (1/M_A+1/M_B)^{1/2}}{P[(\Sigma AV_i)^{1/3} + (\Sigma BV_i)^{1/3}]^2}$$

where, T is temperature (K), M_A and M_B are the molecular weights, P is pressure in atm., and ΣAV_i and ΣB_{Vi} are the diffusion volumes for molecules A and B. Here, the dependence of diffusivity[190] upon temperature is $T^{1.75}$. In the case of Knudsen diffusion, $D_K = 9700\ r\ \sqrt{T/M}$, where r = radius of the pore and M = molecular wieght of the diffusing species, and the temperature dependence of diffusion is $T^{1/2}$. However, in the case of zeolites the diffusion phenomenon is different from the bulk or Knudsen diffusion and is called configurational diffusion. The diffusivity of molecules inside the pores of the zeolites has an exponential dependence with temperature (just like a chemical reaction),

$D_o = D\ e^{-E/RT}$, and activation energies of 8.0 to 84.0 KJ $mole^{-1}$ have been reported[190].

Hence, in the case of zeolites, one has to be careful while interpreting E_a measurements obtained from temperature dependence of rate studies.

In the case of n-C_{16} cracking over ZSM-5, E_a is found to be 74 KJ $mole^{-1}$. This is larger than the E_a value of 55 KJ $mole^{-1}$ reported by Ruthven and Eic[189] for n-C_{16} diffusion in the hydrophillic zeolite A. Due to the larger pore dimensions and hydrophobicity of ZSM-5, the E_a value for diffusion of n-hexadecane into its pores is expected to be much smaller than the value reported for zeolite A. Therefore, the large E_a (74 KJ mole^{-1}) obtained in these studies confirm that the n-hexadecane cracking is in the domain of chemical reaction control under the conditions of these studies.

III.3.B. INFLUENCE OF METAL LOADING

The hydrocracking of n-hexadecane has also been studied over ZSM-5 loaded with different metals. The list of the catalysts used in these studies has already been reported in table II.2(b) in chapter II. The procedure adopted in their preparation have also been reported in chapter II.

Table III.4 reports the conversion and Arrhenius parameters over the different catalysts. It also describes the catalysts. In table III.5 the product distribution obtained over the catalysts are presented. For the sake of convenience the product distribution is being reported only for blocks of compounds, C_1+C_2, C_3+C_4 and C_5-C_{15}. While, C_1+C_2 is mostly produced by the hydrogenolysis over metals, C_3 and C_4 are produced mostly by hydrocracking over the acid centres. The other products C_5-C_{15} are the outcome of both hydrogenolysis and cracking reactions. The ratio of hydrogenation and hydrocracking activities of the catalysts is approximated by the ratios of the products C_1+C_2/C_3+C_4. The ratio of propane : propylene in the products

Table III.4

Influence of the metallic function on the hydrocracking of n-hexadecane

Conditions:
WHSV = 3.0 h^{-1}
Temp.= 593 K
Press. = 0.1 MPa
partial press. = 0.016 MPa
H_2 partial press. =0.084 MPa

Catalyst	Metal content (wt%)	Feed	Conversion (wt%) at 513 K	Ea KJ $mole^{-1}$	A (relative)
H-ZSM-5	0.0	n-C_{16}	33.5	74.1	1.22×10^{7}
Pd-ZSM-5	0.2	n-C_{16}	99.0	76.6	6.96×10^{7}
Zn-ZSM-5	2.5	n-C_{16}	33.3	74.1	1.22×10^{7}
Zn/Pd-ZSM-5	1.0/0.3	n-C_{16}	60.2	77.1	4.84×10^{-7}
Ni-ZSM-5	2.0	n-C_{16}	46.4	56.5	2.75×10^{-5}
H-ZSM-5	0.0	n-C_{16}^{*}	54.0	35.6	2.86×10^{-7}
Pd-ZSM-5	0.2	n-C_{16}^{*}	52.5	37.3	2.75×10^{-3}
Zn-ZSM-5	2.5	n-C_{16}^{*}	60.6	36.4	2.53×10^{-3}
Zn/Pd-ZSM-5	1.0/0.3	n-C_{16}^{*}	39.2	32.2	1.22×10^{-3}
Ni-ZSM-5	2.0	n-C_{16}^{*}	53.5	42.3	1.65×10^{-4}

* Feed was doped with 0.2 wt% sulfur as dimethyl disulphide.

Table III.5

Influence of the metallic function on the hydrocracking of n-hexadecane

(Zeolite : ZSM-5; Silica/Alumina = 84; Crystallite size = 0.1 μm)
Reaction conditions : T = 513 K; P = 0.1 MPa; partial press. =0.016 MPa; WHSV = 3 hr^{-1}
H_2 partial press. =0.084 MPa (nC_{16})

Catalyst	Conversion (wt%)	Production distribution			propane : propene ratio	$\frac{C_1+C_2}{C_3+C_4}$ x 100
		C_1-C_2	C_3-C_4	C_5-C_{15}		
H-ZSM-5	33	0.70	27.40	71.88	1.20	2.6
Ni-ZSM-5	46	0.54	34.50	65.70	2.20	1.6
Pd-ZSM-5	99	3.89	40.05	55.56	**very large**	10.5
Zn-ZSM-5	33	0.63	32.59	66.77	1.20	2.0
Pd/Zn-ZSM-5	60	0.62	29.80	69.56	4.10	2.1
H-ZSM-5*	54	2.72	24.42	72.86	1.30	12.7
Ni-ZSM-5*	54	0.64	19.47	79.88	1.60	3.4
Pd-ZSM-5*	53	0.59	27.83	71.57	1.50	2.2
Zn-ZSM-5*	61	1.11	21.95	76.93	1.00	5.2
Pd/Zn-ZSM-5*	54	0.70	38.43	60.87	1.30	1.8

***** n-hexadecane spiked with 0.2 wt % sulfur as dimethyl disulphide.

measures the hydrogenation capability of the metallic function and also the hydrogen transfer ability of the catalyst[192]. These ratios are also reported in table III.5.

Examining table III.4, we find that the activation energies are higher when pure n-hexadecane is used than when sulfur is present in the feed (56.5 to 77.4 KJ mole^{-1} vs. 32.2 to 42.3 KJ mole^{-1}). The reasons for the lower values of activation energy observed in the presence of sulfur are not clear. Apart from decrease in E_a values, values of A (in Arrhenius equation, rate = A $e^{-E\ /RT}$) also are lower in the presence of sulfur. The decrease in A could be due to decrease in the number of active sites taking part in the reaction. However, due to the lower activation energy (E_a), the observed conversions are not very different from those observed in the case of the pure feed. In fact H-ZSM-5, Ni-ZSM-5 and Zn-ZSM-5 have higher activities in the presence of sulfur. The reasons, again, are not clear.

An interesting consequence of the simultaneous decrease in E_a and A leads to a compensation effect[191]. Figure III.7 shows a plot of E_a against log A. A staight line is observed indicating a compensation effect.

Examining table III.5, we observe that in the absence of sulfur, the conversion increases when metal component (except Zn) is incorporated. The activities of the samples increase in the order H-ZSM--5 = Zn-ZSM-5 < Ni-ZSM-5 < Pd/Zn-ZSM-5 < Pd-ZSM-5. If we look at the propane : propylene ratios we notice that they increase in the order H-ZSM-5 = Zn-ZSM-5 < Ni-ZSM-5 < Pd/Zn-ZSM-5

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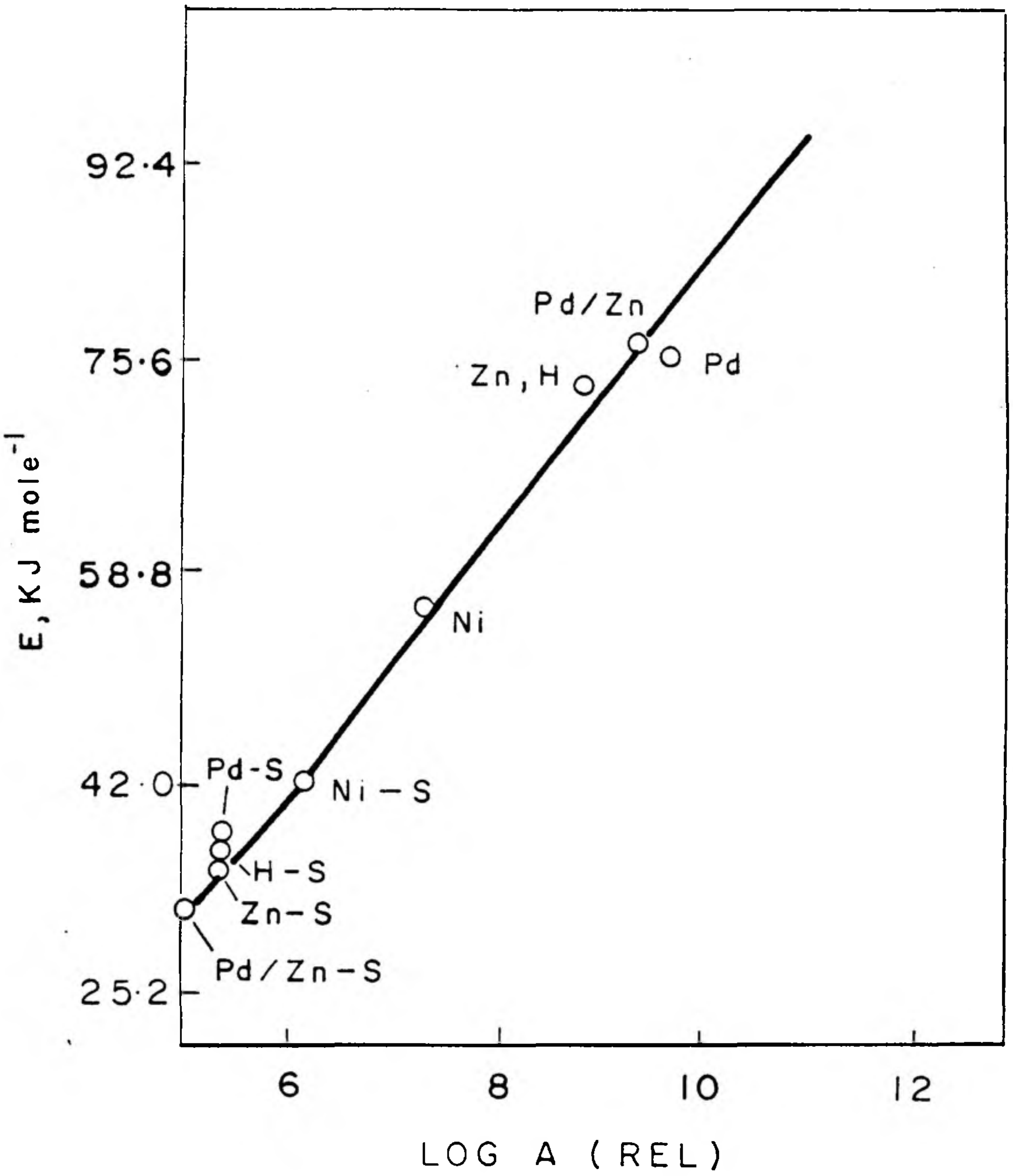


Fig. III 7 COMPENSATION EFFECT IN THE CRACKING OF nC_{16} OVER METAL LOADED ZSM-5

(See text for experimental details)

< Pd-ZSM-5 which is identical to the order of activities. This order is also the same as what one expects for the hydrogenation capabilities of the above metallic functions; Zn will be expected to be least active, while Pd will be the most active, with Ni and Pd-Zn holding intermediate positions. Thus we find that the increase in activities is a direct consequence of the metallic component, the greater the hydrogenation /dehydrogenation ability of the metal, the greater the activity of the catalyst. The increaed activities due to metal incorporation could come from either the assistance offered by the metal to the cracking process (dualfunctional cracking) or from the hydrogenolysis activity of the metal itself. Examing the C_1+C_2 : C_3+C_4 ratios in the last column of table III.5, we notice that except in the case of Pd, the other metal functions have not significantly increased the hydrogenolysis activity of H-ZSM-5. This suggests that the enhancement of activity by the metals (in the absence of sulfur) is more due to their assistance to cracking than to their hydrogenolysis activities (except in the case of Pd).

In the presence of sulfur, however, the metals do not appear to have much influence on the activity of the H-ZSM-5. Surprisingly, sulfur increses the activity of the H-ZSM-5 itself. The reason for the increased activity of H-ZSM-5 in the presence of sulfur is not clear; it could be due to the creation of more acidic -SH groups on the zeolite´s surface. The propane : propylene ratios are nearly the same for all samples, suggesting total suppression of the metallic (hydrogenation) function by sulfur. Similarly, except for H-ZSM-5 and Zn-ZSM-5, the C_1+C_2 : C_3+C_4 are nearly the same. The reasons for the increased activities and hydrogenolysis characteristics of Zn and H forms in the presence of sulfur is not again clear.

Another observation from table III.5 is the increase in the yield of the gaseous fraction on addition of the metallic component especially in the absence of sulfur. In Figure III.8. the selectivities of the various metals for the gas and liquid products in the presence and absence of sulfur are presented as a function of conversion. The figure shows clearly that the metallic function is responsible for larger gas yields and that sulfur suppresses the gas yields. Ideally the best metallic components for maximizing liquid yields are Pd-Zn-S, Ni-S and Pd-S.

III.3.C. n-HEXADECANE HYDROCRACKING OVER LARGE PORE ZEOLITES

Table III.6 compares the hydrocrcking activities of different metal loaded zeolites. The zeolites used are ZSM-5, its isomorph, (Fe)-ZSM-5 in which Fe^{3+} atoms are occupying the lattice positions of Al^{3+}, Y and Beta. ZSM-5 and its isomorph are medium pore zeolites (pore diameter ~5.5 Å) with high silica/alumina ratio, Y is a large pore zeolite (pore diameter 7 Å) with low silica/alumina ratio and Beta is a large pore (pore diameter 7 Å) zeolite with high silica/alumina ratio. The silica/alumina ratios of the zeolites are presented in table II.2(b). All the zeolites were used as granules (14-18 mesh)

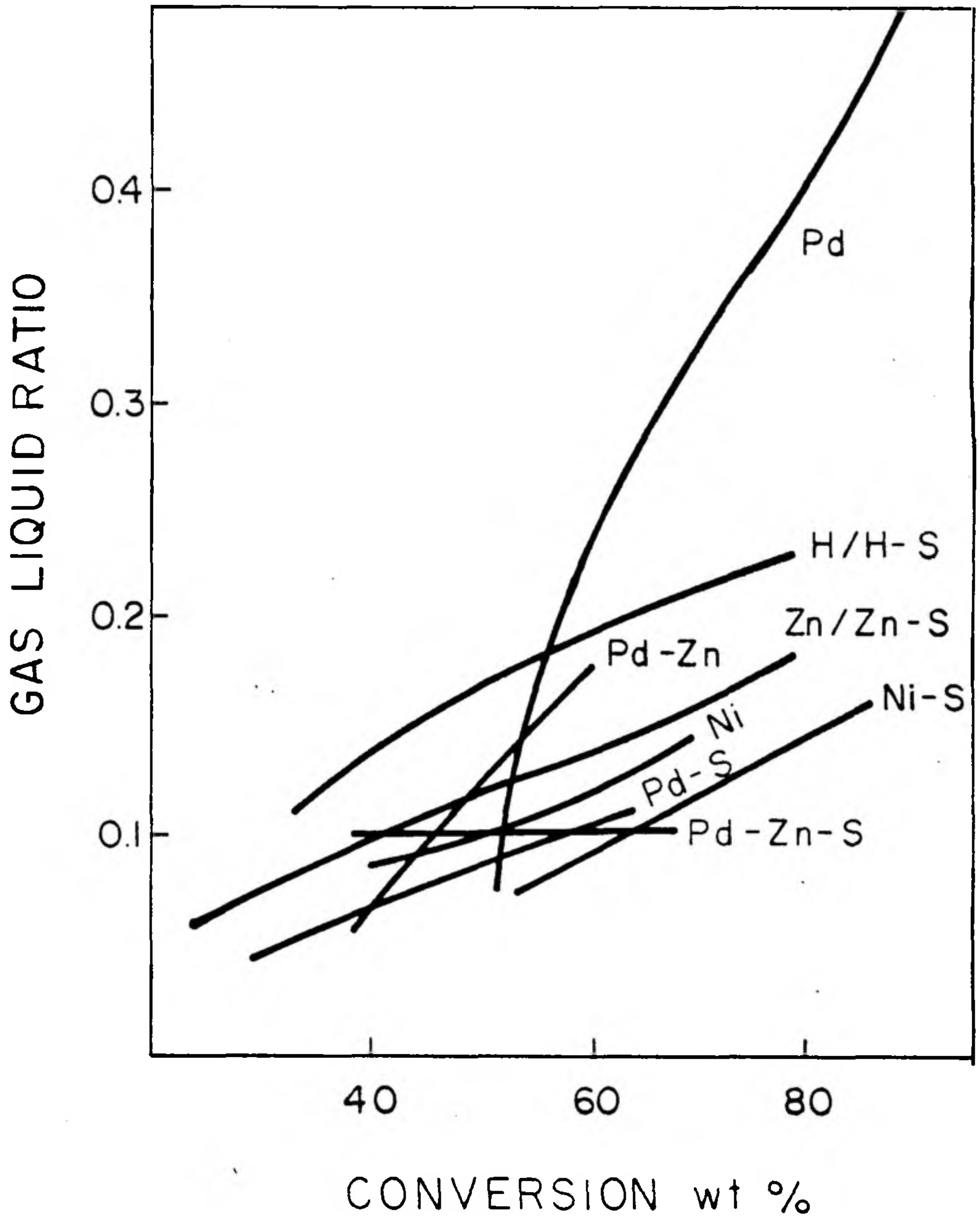


Fig.III 8 INFLUENCE OF THE METALLIC COMPONENT ON GAS: LIQUID RATIOS IN THE CRACKING OF nC_{16} OVER ZSM-5 (See text for details)

Table III.6

Hydrocracking activities of different metal loaded zeolites

Feed : n-hexadecane

conditions:

WHSV = 3.0 h^{-1}
Temp. = 513 K
Press.= 0.1 MPa
partial press. = 0.016 MPa
H_2 partial press. = 0.084 MPa

Catalysts	metal content (wt%)	SiO_2/Al_2O_3 ratio of zeolite	cracking rate at 613 K (g hr^{-1} g^{-1})	deactivation coefficient $(n)^+$
HZSM-5	0.0	84.0	30.8	0.17
Pd-ZSM-5	0.3	84.0	100.2	0.09
HY	0.0	5.7	3.3	0.88
Pd-Y	0.3	5.7	6.9	0.44
Pt-Beta	0.3	90.0	8.1	0.23
Pt(Fe)ZSM-5*	0.3	88.0	65.6	0.12

* Fe^{3+} isomorph of ZSM-5.

\+ from $k = A\ t^{-n}$ (Voorhies equation[186]) obtained at conversion levels between 40-60 wt%.

prepared by crushing pellets of 100% zeolite. The Pt and Pd were loaded by an ion-exchange procedure outlined in chapter II. The deactivation coefficients (n) for the samples are also presented in table III.6. The cracking activities have been expressed as the number of grams of feed cracked per hour per gram of the zeolite. It is noticed that both the ZSM-5 and (Fe)-ZSM-5 have much higher cracking activities than Y inspite of their smaller pore dimesnions and lower number of acid centres in them (lower Al^{3+} content). Zeolite Beta has a higher silica/alumina ratio of 90, but its activity is slightly larger than that of Y.

The substitution of Al^{3+} by Fe^{3+} in ZSM-5 has been shown to reduce the strength of its acid sites[86]. The greater cracking activity of ZSM-5, and more so that of (Fe)-ZSM-5, when compared to Y inspite of their smaller pore dimensions can be explained by the operation of wall effects termed "Nest effect" by Derouane[191] or greater field gradients[193]. In any case, earlier discussions had discounted the possibility of diffusion inhibition in the cracking of n-hexadecane over ZSM-5. In fact, in the cracking of n-pentane, even the small pore zeolite, erionite (pore diameter ~4.1 Å) was found to have specific activities larger (by an order of magnitude) than large pore Y.

The kinetics of cracking n-hexadecane over both medium pore and large pore zeolites follows a first order reaction with respect to the hydrocarbon. This conclusion was reached from plots of concentration versus contact time. The plots for the cracking of n-hexadecane over Y and beta are presented in figure III.4.

Examining the deactivation coefficients for the different catalysts, we notice that the medium pore zeolites ZSM-5 and (Fe)-ZSM-5 have much lower values than the large pore zeolites Y and Beta. The reason for this is that deactivation is caused by coke deposition, especially inside the zeolites pores, and this phenomenon is not possible in the case of the medium pore zeolites due to the lack of sufficient space inside the pores to accomodate the large polynuclear molecules constituting coke. The resistance of ZSM-5 to coke deposition is considered to be a classic case of restricted transition state selectivity[105]. In the case of the large pore zeolites coke depostion occurs easily inside the pores and rapid deactivation takes place.

Another observation is that the presence of a hydrogenating component like Pt or Pd reduces the deactivation rate. For example, in the case of Y, the incorporation of 0.3 wt % Pd decreases the deactivation coefficient from 0.88 to 0.44. Similarly the already low deactivation coefficient of 0.12 on HZSM-5 is further reduced to 0.09 when Pd is incorporated.

III.4.CONCLUSIONS

The studies carried out on the hydrocracking of n-hexane over H-ZSM-5 have shown that deactivation increases with increasing temperatures and increasing nitrogen content. The cracking activity increases with chain length, but surprisingly the deactivation coefficient also decreases. Further, the influence of deactivation by nitrogen also becomes less when chain length is increased. This assumes significance in that many of the applications of ZSM-5 involve shape selective cracking of large hydrocarbon molecules.

The studies carried out on the cracking of hexadecane over H-ZSM-5 and various metal loaded ZSM-5 have revealed a compensation effect. Though the origin of the compensation effect is not clear, the results are interesting.

Hydrocracking activities and product selectivities of the catalysts are affected by the metal components and the presence of sulfur in the feed.

ZSM-5 and its Fe isomorph, (Fe)-ZSM-5, posses much higher cracking activities than large pore Y and Beta. The former zeolites also deactivate less rapidly than the large pore zeolites.

CHAPTER IV

HYDROCRACKING AND REFORMING OF PYROLYSIS GASOLINE

IV.1. INTRODUCTION

The important characteristics of ZSM-5 are shape selectivity and resistance to poisoning by coke. The former property has found numerous commercial applications. Two of these are selectoforming and dewaxing. In selectoforming[135] octane improvement of gasoline (or reformates) is achieved by the selective cracking of n-alkanes. In dewaxing[151,156] pour point of petroleum oils is decreased by the selective cracking of n-alkanes. The combination of high acid strength and medium pore size leads to a yet another property viz. oligomerization. This property of ZSM-5 (and derived materials) is used in commercial processes like "Cyclar"[138] AND "M-forming"[144] in which low molecular weight hydrocarbons are oligomerized primarily into gasoline range aromatics.

Yet another application of ZSM-5 lies in its ability to resist poisoning by coke deposition. ZSM-5 should be a suitable cracking catalyst for highly olefinic hydrocarbons which tend to deactivate (by coking) most acid catalysts. In this chapter, the results of the investigations on the cracking of olefins in pyrolysis gasoline by ZSM-5 and (Fe)-ZSM-5 containing catalysts will be reported.

Pyrolysis gasoline is a by-product (C_5 to 473 K + fraction) obtained during the manufacture of olefins by steam cracking of naphtha and other hydrocarbon material. The yield of pyrolysis gasoline is about 15-25 wt % of the weight of the naphtha feed. Thus, very large quantities of this material are available in the industry. Pyrolysis gasoline is rich in aromatics (>60 wt%) and olefins and diolefins (bromine number= 60-90). This makes it a good source of aromatics. However, the extraction of aromatics by solvents is made difficult by the presence of olefins which get into the aromatic fraction and also damage the solvent. Further, the diolefins polymerize rapidly and make the handling and storage of pyrolysis gasoline difficult and dangerous. The present scheme for pyrolysis gasoline utilization generally consists of five distinct steps[194] viz.,

1. selective hydrogenation of diolefins on Ni or Pd-alumina catalysts.
2. fractionation to separate the heavy ends.
3. saturation of olefins using Co-Mo catalysts,
4. separation of aromatics from the saturates by solvent extraction and
5. fractionation of BTX (Benzene, Toluene and Xylenes) from the heavier aromatics.

The above scheme for extracting BTX from pyrolysis gasoline, apart from being expensive, often results in the loss of 1-5 wt% aromatics during the extraction process.

The typical composition of pyrolysis gasoline from two commercial sources are reported in table IV.1.

It is apparent from the above table that both the feeds contain enough alphatics in the C_6-C_8 range (mostly olefins) which could be transformed into aromatics by reforming. Such an operation will not only increase the aromatics content of

Table IV.1

Composition of the feedstocks (pyrolysis gasoline) used

Component	PG 1*	PG 2*
C_5-C_6	11.00	25.60
Aliphatics in BTX range	8.18	3.67
Benzene	73.78	37.59
Toluene	7.02	15.20
Xylenes	0.02	3.38
Styrene	--	5.61
Ethyl benzene	--	1.45
Dicyclopentadiene	--	7.48
Bromine number	20.50	79.00

* Source : PG 1; National Organic chemical Industries Limited, Thane, India.
PG 2; European plant.

Feed : PG 2

P	5.0
O	25.0
N	5.0
A	65.0

pyrolysis gasoline, but also make it (reformate) suitable for aromatics extraction by solvents.However, conventional reforming catalysts cannot do this job because of (1) very rapid deactivation due to polymerization of olelfins and diolefins and (2) thermodynamic limitation on the aromatic content of the product at the high pressures of reforming necessary to reduce catalyst deactivation. Actually aromatic loss could occur due to high pressure reforming.

An alternative option, namely that of cracking the aliphatics on ZSM-5, which does not accumulate much carbon, thereby producing a product containing primarily aromatics is being examined in this section. Two types of zeolites were used in these studies. These were ZSM-5 and its Fe isomorph (Fe)-ZSM-5. Both ZSM-5 and (Fe)-ZSM-5 were incorporated in a matrix of γ-alumina containing Pt and chlorine. Different levels of zeolite were used in the studies. The preparation of these catalysts has been described in chapter II. The experimental procedures adopted for catalytic activity testing and analysis of products and reactants have also been described in chapter II. The experiments were carried out at atmospheric pressure (0.1 MPa) and at higher pressures (0.5 to 2.0 MPa) in stainless steel reactors. The gas and product analysis were made using a capillary column (PONA analyser supplied by Hewlett Packard, USA).

IV.2. HYDROCRACKING/REFORMING OF PYROLYSIS GASOLINE

In table IV.2 the results of cracking a pyrolysis gasoline fraction on ZSM-5 catalyst are reported. The catalyst used contained 50 wt% ZSM-5 (0.1 μ m diameter crystallites and silica/alumina ratio 84) and 50 wt% γ-alumina. The experiments were carried out at atmospheric pressure (0.1 MPa) in the absence of any gas at 723 K. The product was collected and analyzed over a period 66 hours. Both the feed and the product compositions are presented in the table. It is noticed that aromatics are produced by the catalyst. The increase in aromatics content in the product is about 8 wt% at a time on stream of 6 h (80.85 wt% in product after 6 hours on stream and 72.6 wt% in feed). This much aromatics could not have come from dehydrocylization of the C_6-C_8 paraffin/olefin fraction as there is no reforming component (Pt-alumina-Cl) in the catalyst. Oligomerization of the cracked hydrocarbon fragments is probably the major source of aromatics. Examining the aromatics fraction, there is a loss of benzene and C_9 + aromatics, and a gain of C_7 and C_8 aromatics, the C_8 gain being quite large. Apparently, benzene udergoes transalkylation with a part of the C_9 + fraction, while another part of the C_9 + fraction undergoes partial dealkylation to C_7 and C_8 aromatics. When a mixture of C_6 to C_9 + aromatics is passed over ZSM-5, a very large number of reactions including alkylation, dealkylation, disproportionation and translkylation take place and it is difficult to explain the aromatic distribution obtained in the product. The aromatics gain observed is a consequence, as

Table IV.2

Cracking of pyrolysis gasoline over ZSM-5 catalyst

Catalyst : ZSM-5 (0.1μm, SiO_2/Al_2O_3 = 84), 50 wt%; Al_2O_3, 50 wt%

Conditions:

Temperature : 723 K

WHSV : 1.2 h^{-1}

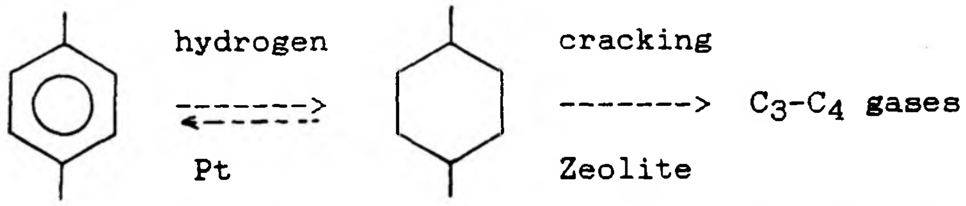
Pressure : 0.1 MPa

Component	Feed (wt%)	Product at TOS 6 (wt%)	Product at TOS 24 (wt%)	Product at TOS 66 (wt%)
Aliphatics:				
C_1-C_4	0.00	15.63	13.16	11.91
C_5	15.47	2.48	3.85	5.05
C_6	6.07	0.58	1.19	2.20
C_7	3.03	0.25	0.73	1.38
C_8	2.85	0.18	0.65	0.69
C_9	0.08	0.00	0.00	0.00
Aromatics:				
C_6	34.04	31.75	32.09	32.31
C_7	24.52	30.41	29.34	27.82
C_8	2.04	11.82	11.98	10.72
C_9	12.00	6.87	6.94	8.33
Aromatics:	72.60	80.85	80.35	79.18

TOS = Time on stream.

mentioned earlier, of the oligomerization of the lighter components (C_3 and C_4 alkanes and alkenes) produced from the cracking of the heavier hydrocarbons. We do find a large decrease of the C_5-C_9 alkanes and alkenes in the product (from 27.5 to 3.49), the rest of the hydrocarbons having been transformed into the lighter fraction (C_1 to C_4 gases) and aromatics. As the colour of the product was light brown, further experiments were carried out in the presence of hydrogen and Pt was included in the catalyst.

In the studies reported in the next few pages, the feeds used are the ones already reported in table IV.1. The feeds were obtained from two different petrochemical plants which used two different naphthas for cracking. Also, the severity of cracking in the two plants were different. Hence, the differences in the composition of the two feedstokcs. The feedstocks are designated as PG 1 and PG 2. For reasons already explained in chapter II, different batches of the feeds were used. As the compositions of these varied, the composition of the feed will always be presented along with product compositions in all the tables. When experiments were carried out in hydrogen at higher pressures, aromatic gain became very small due to hydrogenation of the aromatics (by the Pt in the catalyst) and the subsequent cracking of the cycloalkanes by the zeolite. Also high hydrogen pressures suppressed the oligomerization reaction.



Eventhough, only a small amount of the cycloalkanes may be favoured by thermodynamics, their subsequent cracking by the zeolite pushes the reaction to the right, converting more aromatics. To minimize the cracking of the cycloalkanes, and to reduce aromatic loss, lower amounts of zeolites [ZSM-5 or (Fe)-ZSM-5] were used in the preparation of the catalysts used in the following studies.

In table IV.3, the results of the reforming of PG 1 over a conventional, monometallic reforming catalyst and a similar catalyst containing 5 wt% ZSM-5 are reported. The data were obtained at atmospheric pressure over a period of ten hours. The composition of the feed has also been presented in the table for comparison purposes. It is noticed that both Pt-alumina and the zeolite containing Pt-alumina create extra aromatics. However, the BTX (benzene, toluene, xylenes + ethyl benzene i.e., C_6 + C_7 + C_8 aromatics)[*] gain is negligible after 10 hours in the case of the conventional catalyst (Pt-alumina) while it continues to be high (about 7 % gain) in the case of the zeolite containing catalyst. At at a time on stream of 1.5 hours the zeolite

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[*] **Please note that the acronym BTX will be used for Benzene + Toluene + xylenes + ethylbenzene i.e., C_6 +C_7 + C_8 aromatics except where noted.**

Table IV.3

Reforming of pyrolysis gasoline

Comparison between Pt-alumina and ZSM-5-Pt-Alumina catalysts

Feed : PG 1

Conditions:

Temperature : 763 K
Pressure : 0.1 MPa
WHSV : 2.25 h^{-1}
H_2/HC : 6 mole ratio

Component	Feed	$Pt-Al_2O_3-Cl$*			$Pt-Al_2O_3-Cl$ + ZSM-5**		
		Products at TOS[#] (h)					
		1.5	5.5	10.0	1.5	5.5	10.0
C_1+C_2	0.00	0.35	0.32	0.23	0.97	1.10	1.56
C_3	0.00	0.64	0.55	0.41	4.16	4.44	5.85
C_4	0.00	0.73	0.62	0.49	2.89	3.05	3.50
C_5	3.13	3.83	5.13	5.37	0.84	1.04	1.73
C_6	7.10	7.13	6.48	6.73	1.78	3.22	3.71
Aliphatics in BTX	13.02	5.57	7.49	9.68	0.43	1.31	1.67
Benzene	58.20	64.33	62.98	58.76	68.67	65.52	61.04
Toluene	14.05	12.18	11.70	13.48	16.91	16.94	17.59
C_8 aro.	0.23	0.54	0.50	0.60	1.56	1.62	1.74
C_9+***	4.26	4.69	4.21	4.24	1.76	1.77	1.61
BTX	72.48	77.05	75.18	72.84	87.14	84.08	80.37

* 0.6 wt% Pt and 1.1 wt% Cl.

** 0.6 wt% Pt, 1.0 wt% Cl and 5.0 wt% ZSM-5.

*** Mostly aromatics.

[#] TOS = Time on stream.

catalyst produces even more BTX (87.14 wt % for zeolite catalyst and 77.05 wt % for Pt-alumina). The Pt-alumina catalyst is found to transform far less C_6 and BTX range aliphatics (C_7-C_9) than the zeolite catalyst. The increased conversion of C_6-C_9 aliphatics results in more aromatics and C_1-C_4 gas fraction. As explained earlier, the increased production of BTX in the case of the zeolite containing catalyst can be attributed to (1) oligomerization reactions (2) enhanced dehydrocylization and (3) dealkylation of the C_9 + aromatics.

The results of the studies on the influence of varying the zeolite content on product yields are presented in figure IV.1. The feed used was PG 1, the pressure being 1.0 MPa and the temperature being 753K. The yields of C_1-C_4 (gases), total aromatics (Σ Aro.) and the aliphatics (C_8 +) present in the BTX fraction are presented. The aliphatics boiling in the BTX range assume significance because if they are totally eliminated by cracking, a simple fractionation will yield BTX of high purity. If they are totally (or near totally) removed, an expensive solvent extraction step will not be necessary to obtain BTX of good purity. The boiling point of benzene, the lightest component in the BTX cut, is 353.3K and that of o-xylene, the heaviest component in the cut is 418.2K. As the reaction is being carried out on a Pt catalyst in the presence of H_2, the non-aromatics boiling between 353 and 418K are C_6,C_7,C_8 and C_9 alkanes and cycloalkanes. The only C_6 hydrocarbon boiling after benzene is cyclohexane (boiling point = 354.3 K).

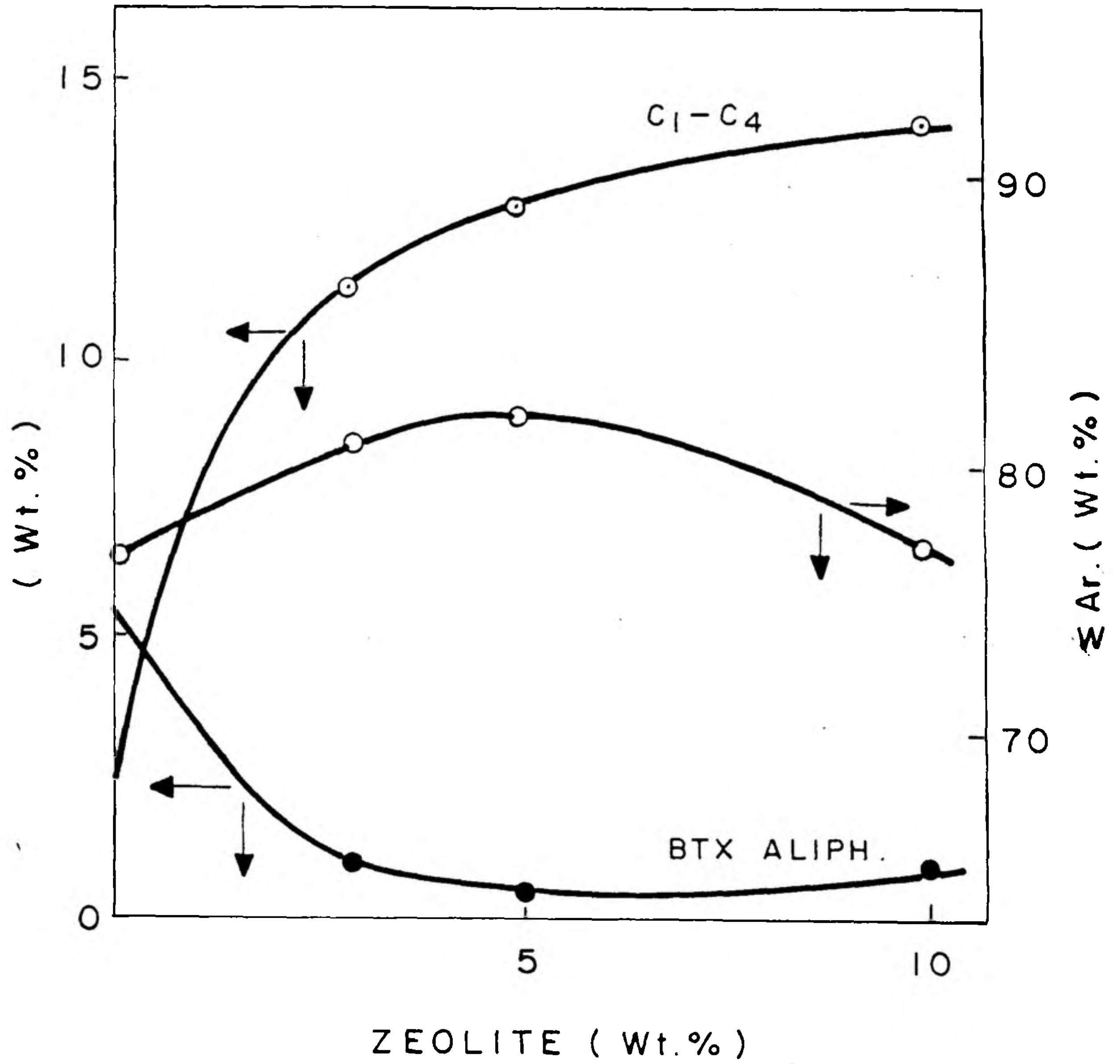


FIG. IV. I.

INFLUENCE OF ZEOLITE CONTENT ON PRODUCT DISTRIBUTION

(Feed PG 1, Pressure: 1.0 MPa; WHSV: 2.25 h^{-1}; Temperature:753K
Hydrogen/oil (mole) :6.0)

It is observed that the yield of C_1-C_4 gases increases as the zeolite content is increased and the concentration of the aliphatics in the BTX range decreases. However, the yield of aromatics goes through a maximum . The aromatics yield increases on addition of zeolite upto almost 5%, presumably due to oligomerization or increased amounts of dehydrocylization. The concentration of BTX aliphatics becomes quite low (~0.4 wt%) at 5% zeolite level and increasing the zeolite content further does not appear to reduce their concentration any further. The reason for the loss of aromatics at high zeolite levels is the rapid cracking of the cycloalkanes produced from the hydrogenation of the aromatics at the high pressure used. While, hydrogenation is a fast reaction, cracking is a slow one and the destruction of aromatics is determined by the rate of cracking of cycloalkanes. Thus, the studies indicate that incorporation of more than 5 % ZSM-5 in the catalyst could be counter productive.

The next part of the study relates to the comparison between ZSM-5 and (Fe)-ZSM-5. Pt-alumina containing 10 wt% of (Fe)-ZSM-5 and ZSM-5 were used used in these studies. The experiments were carried out at pressure of 0.1MPa. Table IV.4 presents the results. It is noticed that both (Fe)-ZSM-5 and ZSM-5 containing catalysts produce more aromatics, the yield of aromatics being more in the case of the ZSM-5 catalysts. Further, the stability of the ZSM-5 catalyst is also better and the aliphatics in the BTX range are also lower. Both (Fe)-ZSM-5 and ZSM-5 deactivate, the aliphatics content going up from 2.63 at one hour on stream

Table IV.4

Reforming of pyrolysis gasoline

Comparison of ZSM-5 and (Fe)-ZSM-5 catalysts

Feed : PG 1

Conditions:

Temperature : 773 K
Pressure : 0.1 MPa
WHSV : 2.25 h^{-1}
H_2/HC : 6 mole ratio

Catalysts:

Zeolite content: 10.0 wt%
Pt : 0.6 wt%
Chlorine : 1.1 wt %
γ-alumina : 88.4 wt %

Component	Feed (wt%)	ZSM-5*		(Fe)-ZSM-5**	
		Product distribution at TOS# (h)			
		1	10	1	10
C_1+C_2	---	1.72	1.20	0.78	0.91
C_3	---	5.71	3.67	3.07	2.65
C_4	---	3.01	1.98	2.42	2.19
C_5	3.37	0.64	0.52	3.17	3.52
C_6	7.80	1.65	3.64	4.80	7.53
Aliphatics in BTX	12.92	0.62	2.33	2.63	4.41
Benzene	57.43	62.20	62.21	63.80	62.09
Toluene	14.20	19.26	17.62	15.05	13.57
C_8 arom.	0.27	2.60	3.90	1.63	1.10
Others	4.01	2.48	2.92	2.63	1.99
BTX	71.90	84.15	83.74	80.49	76.78

* (0.1 μm crystallite size, SiO_2/Al_2O_3 = 84).

** (0.5 μm crystallite size, SiO_2/Al_2O_3 =108).

\# TOS = Time on stream

to 4.41 in the case of (Fe)-ZSM-5 and from 0.62 to 2.33 in the case of ZSM-5. The greater cracking activity of ZSM-5 when compared to (Fe)-ZSM-5 is evident from the lower content of BTX range aliphatics in the products from ZSM-5 catalyst.

IV.3. INFLUENCE OF FEED CHARACTERISTICS

As seen from table IV.1, the composition of pyrolysis gasoline depends on its source, being a function of the characteristics of the naphtha feed and the conditions of steam cracking. The aromatics gain, the amount of BTX-aliphatics cracked and the life of the catalyst will depend on the composition of the pyrolysis gasoline. The results of the reforming of pyrolysis gasoline from two different sources are presented in table IV.5. PG 1 is a lighter fraction than PG 2. PG 1 is less olefinic (bromine no. 20.5) than PG 2 (bromine no.79). PG 2 also has a large amount of the catalyst deactivating material dicyclopentadiene (DCP). Being a lighter fraction, DCP is absent in PG 1, but its aromatic content is higher. Reforming the two feedstocks using an ZSM-5 containing catalyst leads to increased yields of BTX for both feedstocks. The zeolite content was 5 wt% in both cases. The results were obtained at a time on stream of 10 hours. In order to offset thermodynamic limitations on aromatics formation, the pressure has been kept low at 0.45 MPa. At this slightly higher pressure, catalyst deactivation is reduced and hydrocracking of C_6-C_9 aliphatics (BTX range aliphatics) is more than at 0.1 MPa (cf. Table IV.4). Because PG

Table IV.5

Reforming of pyrolysis gasoline from different sources

Catalyst : ZSM-5* (5 wt%) + Pt (0.6 wt%) - Al_2O_3-Cl(1.1 wt%)

Conditions:

Temperature	773 K	753 K
Pressure	0.45 MPa	0.45 MPa
WHSV	2.5 h^{-1}	2.5 h^{-1}
Hydrogen/HC	7.0 mole ratio	8.0 mole ratio

Composition:

Component	PG 1 (wt%)	Product 1 (wt%)	PG 2 (wt%)	Product 2 (wt%)
C_5-C_6	11.00	15.96	25.60	30.23
Aliphatics in BTX range	8.18	0.10	3.67	0.11
Benzene	73.78	75.29	37.59	41.11
Toluene	7.02	8.30	15.20	17.09
Xylenes	0.02	0.35	3.38	3.31
Styrene	--	--	5.61	0.02
Ethyl benzene	--	--	1.45	5.72
Dicyclopentadiene	--	--	7.48	2.41
BTX** gain	--	3.12	--	5.32
Bromine number	20.50	1.90	79.00	1.40

* 0.1 μm crystallites, silica/alumina = 84

** Benzene+Toluene+Xylenes only (Ethyl benzene not included)

1 had a larger aromatics content (80.82 wt%) than PG 2 (63.25 wt%), it had to be reformed at a higher temperature (773 K) than PG 2 (753 K) inorder to achieve an aromatic gain.

The most interesting aspect of the results is the negligible amounts of BTX range aliphatics in the products (0.10 for PG 1 and 0.11 for PG 2) even though the feeds themselves had large quantities of those hydrocarbons. This is clearly evident from figure IV.2 which presents the partial gas chromatograms of the feed (PG 2) and the product. Figure IV.2 (a) is the chromatogram for the feed. It shows a large number of aliphatic components between benzene and toluene and between toluene and o-xylene. On the other hand, the product (figure IV.2 (b)) has very little of aliphatics components. Small amounts of the non-desired hydrocarbons present are cyclohexane, dimethylcyclopentane and dimethylcylcohexanes each one of them being less than 0.03 wt %. The overall purity of the BTX fraction (C_6+C_7+C_8 aromatics) is >99.8 wt%. The near lack of aliphatics boiling between benzene and o-xylene avoids the need for solvent extraction to separate the aromatics. The compounds boiling closest to benzene and o-xylene are methylcyclopentane (b.p. 345.2 K) and n-propyl benzene (b.p. 432 K). These are well separated from benzene and o-xylene. Therefore, it should be possible to obtain BTX of desired purity (>99.5 wt%) by a simple fractionation step. Thus reforming over ZSM-5 containing catalysts makes the extraction of aromatics from pyrolysis gasoline a two step operation instead of the four (or five) step process in commercial practice presently used.

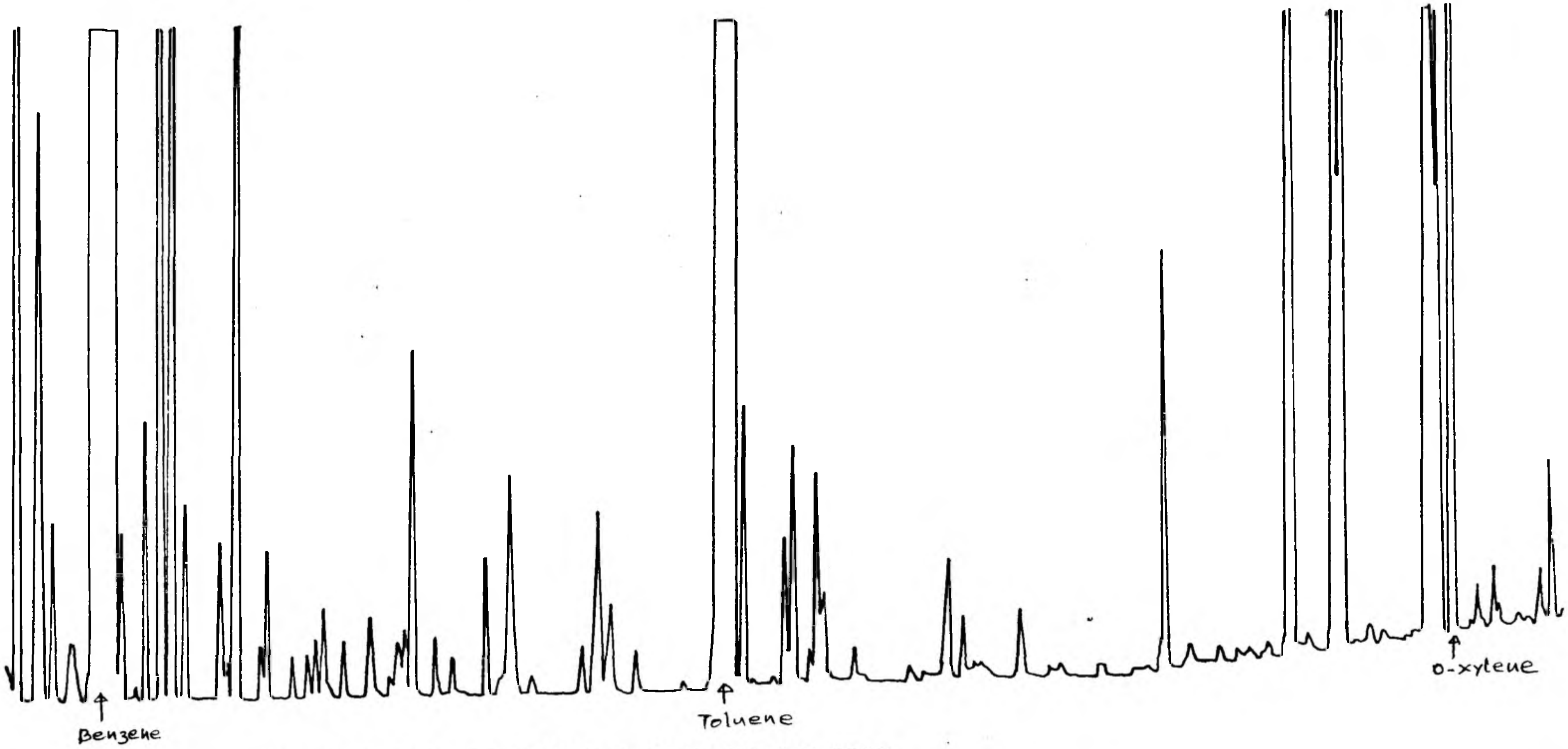


Fig IV.2 (a) GAS CHROMATOGRAM OF THE FEED

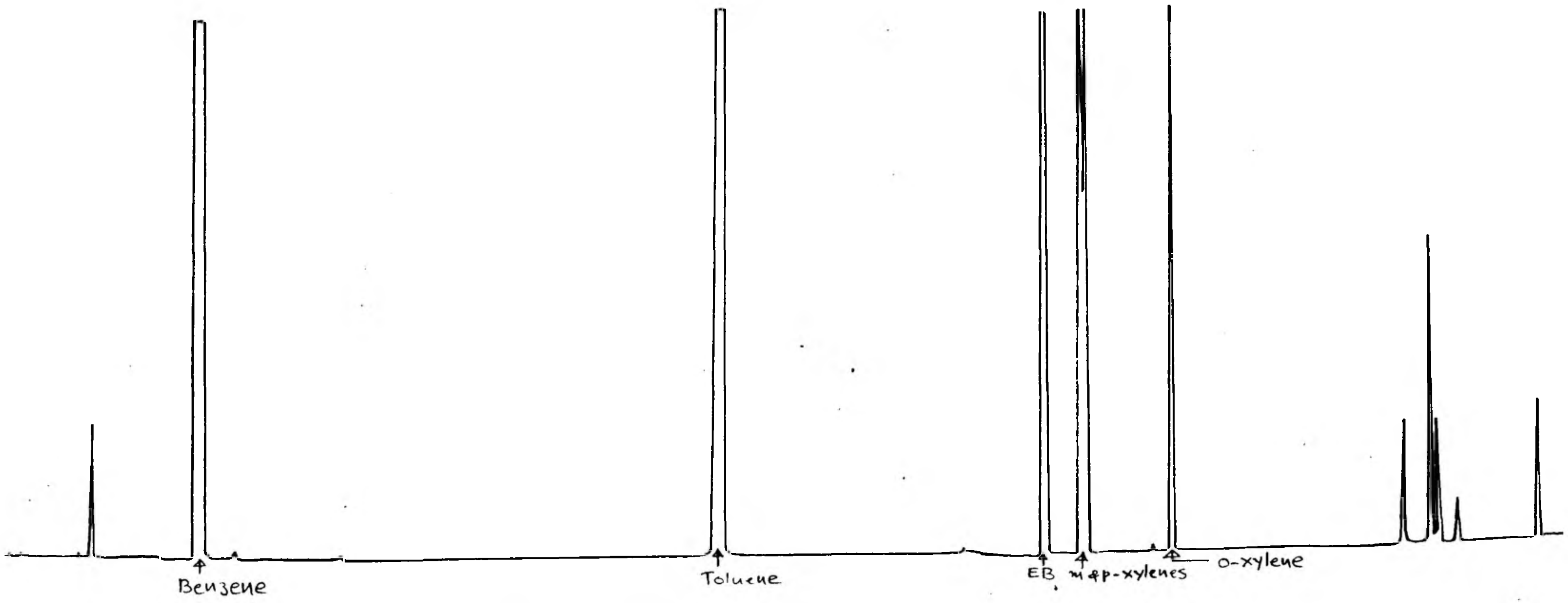


Fig IV.2 (b) GAS CHROMATOGRAM OF THE PRODUCT

IV.4. INFLUENCE OF DICYCLOPENTADIENE ON CATALYST AGING

Dicyclopentadiene (DCP) is often present in pyrolysis gasolines upto about 15 wt %. It is a very reactive hydrocarbon and transforms itself into coke rapidly over catalysts (at high temperatures). Experiments to study the influence of DCP on the activity of a ZSM-5 containing (5 wt%) Pt -alumina catalyst were carried out both at atmospheric pressure (0.1 MPa) and at high pressures (0.6 MPa). The cracking activity of the catalyst and the BTX gain were examined at two different DCP contents. In the case of atmospheric pressure experiments the feed used was PG 1 containing no DCP. DCP was added to get a feed with 13.66 wt% DCP. In the case of high pressure studies, PG 2 was used, and different levels of DCP was obtained by fractionation. As the composition of the total feed changed on addition of DCP, we will be comparing only the percentage cracking of the aliphatics and the BTX gain. The results of the studies are presented in table IV.6.

Examining the results, we find that DCP lowers the activity for cracking both at atmospheric and higher pressures. It also lowers the aromatic gain observed, especially at the lower pressure. The deactivation of the cracking function of the catalyst with time is more rapid when DCP is present. However, higher pressures reduce the influence of DCP. When 2.38 wt % DCP is present in feed, the cracking activity is 99 % even after 20 hours on stream at 0.6 MPa. However, if >99.5 wt % purity is desired for the BTX fraction, it is necessary that the DCP in the

Table IV.6

Influence of Dicyclopentadiene content on cracking activity and BTX gain

Catalyst : ZSM-5$^+$ (5 wt%) + Pt (0.6 wt%) - Al_2O_3-Cl(1.1 wt%)

Condtions:

Temperature : 773 K
WHSV : 2.0 h^{-1}
H_2/HC : 7 mole ratio

DCP in feed (wt%)	% cracking of aliphatics in BTX range(wt%)	BTX gain (wt%)
Case 1 (Pressure = 0.1 MPa)*		
0.0	88 (74)	13.0 (10.0)
13.66	65 (45)	7.9 (6.8)
Case 2 (Pressure = 0.6 MPa)**		
0.0	99.5	0.7
2.38	99.0	0.7
8.11	87.0	0.3

* At TOS = 1 hours and 7 hours for bracketed values.
Feeds : PG 1 and PG 1 + added DCP.

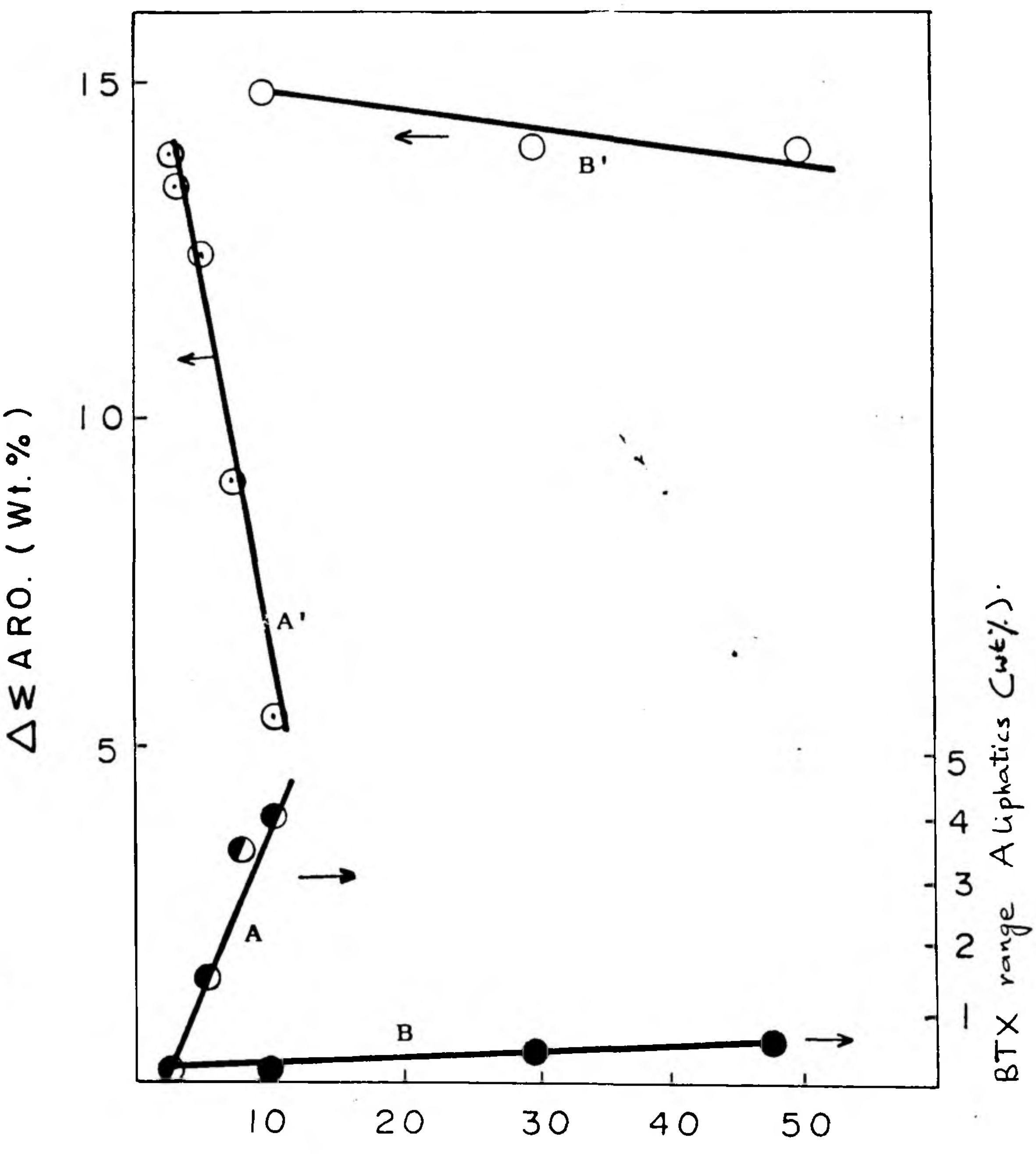
** At TOS = 20 hours.
Feeds : PG 2 fractionated to contain different levels of DCP.
\+ 0.1 μm crystallites, silica/alumina = 84.

feed is very small. As many pyrolysis gasolines have >5 wt% of DCP, it is necessary to fractionate the feed to exclude DCP (b.p.of DCP = 442 K).

IV.5. CATALYST AGING CHARACTERISTICS

As discussed in the earlier section, catalyst life is increased at higher pressures and in the absence of dicyclopentadiene. Table IV.7 and IV.8 present the results obtained at atmospheric pressure on the cracking of PG1 with and without added DCP. At atmospheric pressure, the catalyst deactivates rapidly, (BTX gain decreases and BTX-aliphatics increase) even in the absence of DCP, the deactivation becoming more pronounced when DCP is present. At higher pressures, the deactivation is less (cf. table IV.9). The high pressure studies were carried out using PG 2, and data for two times on stream viz.6 hours and 21 hours have been presented. It is noticed that during 15 hours of operation (6-21 hours), the loss in BTX gain is only 0.3 wt% and the increase in BTX-ailiphatics is only 0.15 wt%.

In order to understand better the function of ZSM-5 in reducing deactivation, experiments were carried out with a Pt-alumina catalyst alone. A comparison of the activities of Pt-alumina and Pt-alumina-ZSM-5 is made in figure IV.3. Plots of total aromatic gain and aliphatic content in BTX range with time on stream have been made for the two catalysts. The experiments were carried out with PG 1 at 773 K at 0.45 MPa. The results



FIG· IV 3

COMPARISON OF AGING RATES BETWEEN Pt-Al_2O_3-Cl AND ZSM-5 -Pt-Al_2O_3-Cl CATALYSTS

(Feed: PG 1, Temperature: 773 K; Pressure: 0.45 MPa; WHSV: 2.25 h^{-1}; H_2/oil (mole) : 6)

Table IV.7

Influence of Time on stream in the reforming of pyrolysis gasoline

Feed : PG 1

Catalyst : ZSM-5* (5 wt%) + Pt (0.6 wt%) - Al_2O_3-Cl(1.1 wt%)

Conditions:

Temperature : 773 K
WHSV : 2.25 h^{-1}
Pressure : 0.1 MPa
H_2/HC : 6.0 mole ratio

Component	Feed (wt%)	Product distribution at TOS (h) (wt%)			
		1	3	4.5	7.25
C_1+C_2	---	0.46	0.42	0.36	0.60
C_3	---	1.60	1.45	1.46	1.63
C_4	---	1.57	1.39	1.08	1.49
C_5	3.84	2.85	3.33	3.05	3.78
C_6	7.00	4.38	4.79	4.44	4.59
C_7	13.53	1.58	2.83	3.08	3.48
Benzene	62.08	73.16	72.83	70.47	66.07
Toluene	10.87	12.52	11.33	13.42	16.19
C_8 arom.	0.65	0.91	0.92	1.42	1.15
Others	2.03	0.93	0.67	1.32	1.15
BTX	73.60	86.59	85.08	85.31	83.41

* 0.1μm crystallites, silica/alumina = 84.

Table IV.8

Influence of Time on stream in the reforming of pyrolysis gasoline*

Catalyst :ZSM-5+ (5 wt%) + Pt (0.6 wt%) - Al_2O_3-Cl(1.1 wt%)

Conditions :

Temperature : 773 K
WHSV : 2.25 h^{-1}
Pressure : 0.1 MPa
H_2/HC : 6.0 mole ratio

Component	Feed (wt%)	Product distribution at TOS (h) (wt%)			
		1	3	5	7
C_1+C_2	---	0.60	0.66	0.37	0.38
C_3	---	0.88	0.81	0.42	0.37
C_4	---	0.89	0.81	0.52	0.42
C_5	3.79	8.79	11.87	11.56	13.34
C_6	5.85	5.23	3.55	3.77	4.14
C_7	10.75	3.78	4.86	5.91	6.10
Benzene	52.16	59.77	57.62	59.90	59.72
Toluene	11.00	11.09	11.81	10.92	10.01
C_8 arom.	0.18	1.08	0.85	0.66	0.44
DCP	13.66	0.34	0.34	0.27	0.22
Others	2.61	7.53	5.78	5.69	4.83
BTX	63.34	71.94	70.28	71.48	70.16

* DCP was added to the pyrolysis gasoline (PG I).
+ 0.1 μm crystallites, silica/alumina = 84.

Table IV.9

Influence of Time on stream in the reforming of pyrolysis gasoline*

Catalyst : ZSM-5 (5 wt%) + Pt (0.6 wt%) - Al_2O_3-Cl(1.1 wt%)

Conditions:

Temperature : 773 K
WHSV : 2.5 h^{-1}
Pressure : 0.5 MPa
H_2/HC : 8.0 mole ratio

Component	Feed (wt%)	Product distribution at TOS (h) (wt%) 6	21
C_1-C_6	25.6	28.99	27.38
Aliphatics in BTX range	3.67	0.16	0.32
Benzene	37.59	41.20	38.50
Toluene	15.22	17.38	18.41
Xylenes	3.38	4.37	5.70
Ethyl benzene	1.45	5.64	6.94
Styrene	5.61	0.03	0.04
DCP	7.48	2.29	2.71
BTX gain	---	6.76	6.42
Bromine no.	68.60	~ 1.00	~ 1.00

* PG 2 fractionated to contain 7.48 wt% DCP.

show that the ordinary reforming catalyst (Pt-alumina) deactivates very rapidly while the zeolite catalyst deactivates slowly. The reasons for the slower deactivation of the zeolite catalyst have already been discussed. They are (1) the resistance of ZSM-5 to accumulate coke inside the pores and (2) the ability of ZSM-5 to crack away the coke precursors preventing them from building up on the catalyst surface. The coke contents of the zeolite containing catalyst (figure IV.3) at the end of 52 hours on stream was 4.3 wt% while that of Pt-alumina at the end of 12 hours on stream was 8.7 wt%.

IV.6. INFLUENCE OF PROCESS PARAMETERS

IV.6.A. EFFECT OF TEMPERATURE

The influence of temperature on BTX gain ($\Delta\Sigma$ BTX) and BTX aliphatics content at two different pressures (0.1 and 1.0 MPa) are plotted in figure IV.4. The catalyst used was a 5 wt% ZSM-5 containing Pt-alumina. The feed was PG 1. The detailed product analyses are presented in tables IV.10 and IV.11. It is noticed that at both 0.1 MPa and 1.0 MPa, increasing the temperature increases the yield of aromatics and decreases the BTX-aliphatics. As already discussed, the aromatic gain is more at 0.1 MPa than at 1 MPa, while the BTX-aliphatics content is less at 1 MPa than at 0.1 MPa.

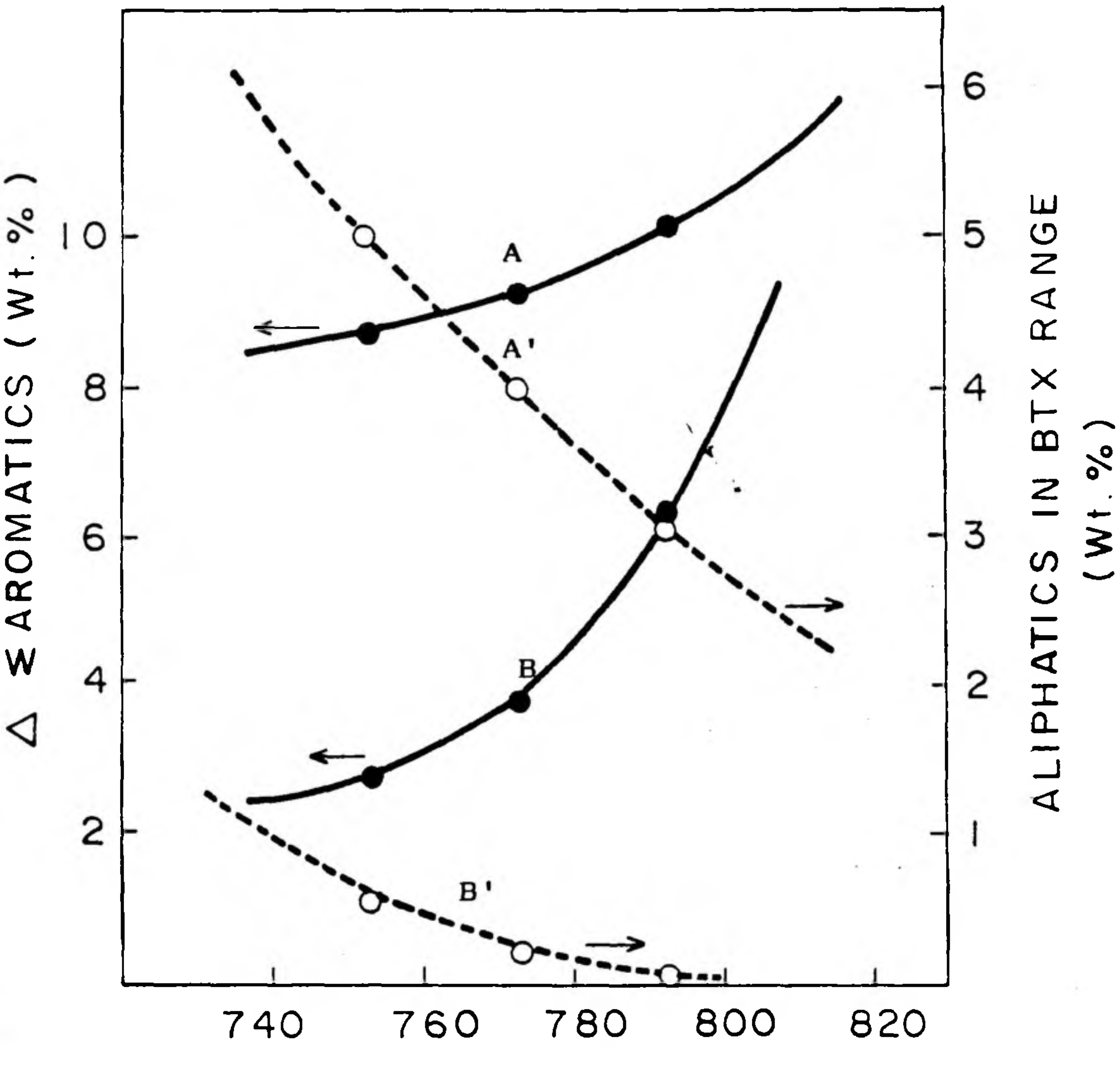


FIG. IV. 4

INFLUENCE OF TEMPERATURE ON PRODUCT DISTRIBUTION

(Catalyst: ZSM-5 (5 wt%)-Pt-Al_2O_3-Cl: see tables IV.10 and IV.11 for process parameters)

A,A': 0.1 MPa; B,B': 1.0 MPa

Table IV.10

Pyrolysis gasoline reforming: Effect of temperature

Catalyst : ZSM-5$^+$ (5 wt%) + Pt (0.6 wt%) - Al_2O_3-Cl(1.1 wt%)

Conditions:

WHSV : 2.0 h^{-1}
Pressure : 0.1 MPa
H_2/HC : 6.0 mole ratio
TOS : 2 hours

Component	Feed (wt%)	Product distribution at Temp.(K) (wt%) 753	773	793
C_1+C_2	---	0.32	0.54	0.70
C_3	---	1.05	1.70	1.71
C_4	---	1.04	1.47	1.58
C_5	1.35	2.21	2.33	2.95
C_6	6.69	5.94	5.01	4.04
C_7	12.95	5.00	3.76	3.08
Benzene	59.47	66.92	67.40	68.35
Toluene	14.12	14.78	14.59	13.94
C_8 arom.	0.23	0.87	1.05	1.60
Others	5.18	1.85	1.06	2.31
BTX	73.82	82.57	83.05	83.89

+ 0.1 μm crystallites, silica/alumina = 84.

Table IV.11

Influence of temperature in the reforming of pyrolysis gasoline

Catalyst : ZSM-5^{+}(5 wt%) + Pt (0.6 wt%) - Al_2O_3-Cl(1.1 wt%)

Conditions:

WHSV : 2.5 h^{-1}
Pressure : 1.0 MPa
H_2/HC : 6.0 mole ratio
TOS : 5-20 hours

Component	Feed (wt%)	Product distribution at Temp. (K) (wt%)		
		753	773	793
C_1+C_2	---	0.12	0.17	0.22
C_3	---	9.52	9.40	8.00
C_4	---	2.91	2.71	1.90
C_5	3.26	1.23	0.78	0.42
C_6	6.06	1.01	0.13	0.23
Aliphatics in BTX range	7.94	0.54	0.20	0.05
Benzene	67.94	68.60	69.49	71.53
Toluene	13.70	14.95	15.25	15.81
C_8 arom.	0.17	1.02	0.81	0.81
Others	0.94	0.90	0.76	0.80
BTX	81.81	84.57	85.55	88.15
BTX gain	---	2.76	3.74	6.34

+ 0.1μm crystallites, silica/alumina = 84.

IV.6.B. EFFECT OF PRESSURE

The effect of pressure at two typical pressures of operation viz. 0.1 MPa and 1.0 MPa can also be understood by examining the tables IV.10 and IV.11 and figure IV.4 which compare activities at two different pressures and different temperatures. As expected increasing the pressure decreases aromatic gain while improving the life of the catalyst. At the same time higher pressures favour the cracking of BTX range aliphatics.

IV.6.C. EFFECT OF WHSV

The influence of WHSV on the reforming of pyrolysis gasoline at atmospheric pressure (0.1 MPa) is presented in table IV.12. The yield of aromatics, surprisingly, increases with increasing WHSV in the low WHSV range (0.9 to 2.25 h^{-1}) studied. A more clear picture of the effect of WHSV is obtained from figure IV.5 which compares the WHSV effect at 0.1 MPa and at 1.0 MPa. The 1.0 MPa results are interesting. At very low WHSV (< 1.5 h^{-1}), there is actually an aromatics loss caused by hydrogenation of aromatics and their subsequent slow cracking by the zeolite. At high pressures the hydrocracking rate goes up but the oligomerization reactions which produce aromatics are suppressed due to the hydrogenation of the olefins as schematically shown below:

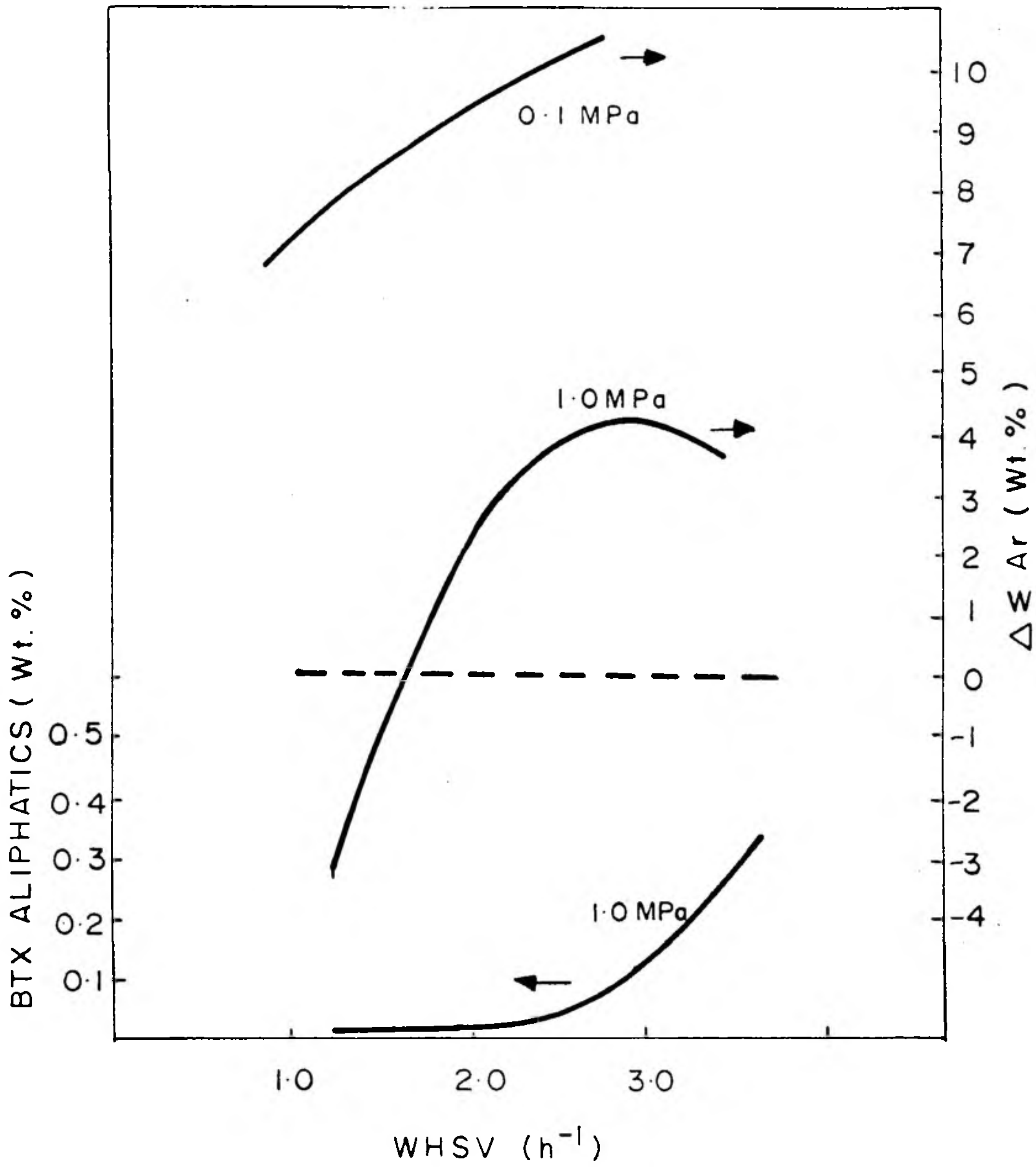


FIG. IV. 5.

INFLUENCE OF SPACE VELOCITY ON PRODUCT DISTRIBUTION

(Temperature: 773K; H_2/oil (mole): 6)

Catalyst: ZSM-5 (5 wt%)-Pt-Al_2O_3-Cl

Table IV.12

Influence of WHSV in the reforming of pyrolysis gasoline

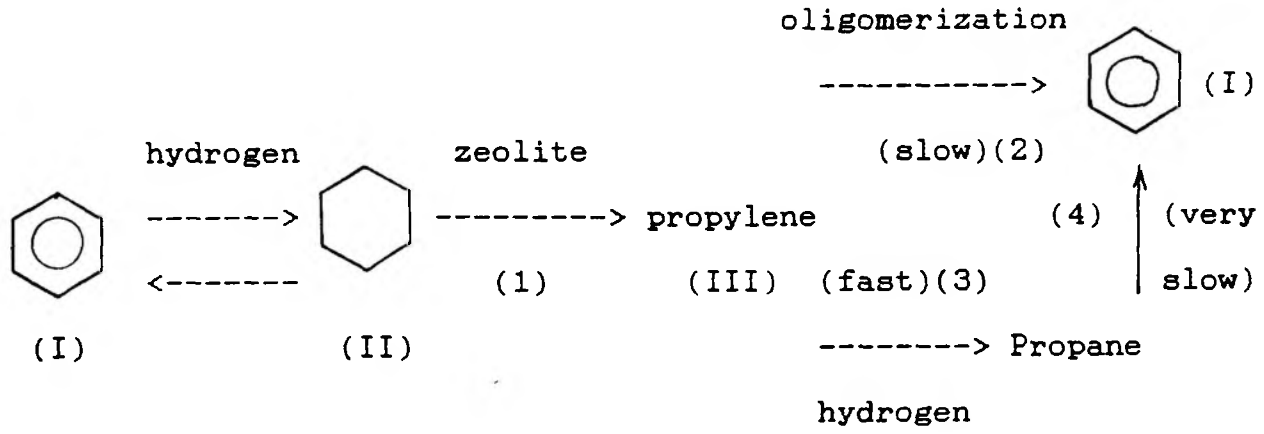
Catalyst : ZSM-5+ (5 wt%) + Pt (0.6 wt%) - Al_2O_3-Cl(1.1 wt%)

Conditions:

Temperature : 773 K
Pressure : 0.1 MPa
H_2/HC : 6.0 mole ratio
TOS : 2.0 hours

Component	Feed (wt%)	Product distribution at WHSV (h^{-1}) (wt%) 0.90	1.69	2.25
C_1+C_2	---	1.08	0.76	0.53
C_3	---	2.43	1.47	1.08
C_4	---	2.21	1.65	1.25
C_5	3.24	3.47	5.15	3.21
C_6	6.97	6.92	5.85	6.86
C_7	12.89	3.99	4.68	4.52
Benzene	55.05	61.78	63.12	63.72
Toluene	13.81	12.31	12.39	13.88
C_8 arom.	0.27	1.47	0.82	0.85
Others	7.78	4.52	4.11	3.68
BTX	69.13	75.56	76.33	78.46

+ 0.1 μm crystallite size, silica/alumina= 84.



At high pressures, thermodynamics favours formation of II, and the cracking of II by zeolites pushes the equilibrium to the right as explained in an earlier section. Further, at high pressures, reaction 3 overrides reaction 2 and reaction 4 being slow, the formation of benzene (by oligomerization) is suppressed. At higher WHSV's (1.5 to 3) there is a net aromatics gain, though at still higher WHSV's (>3) the aromatics gain goes down. The drop in aromatics yield at very high WHSV's is due to the decrease in the reforming and oligomerization reactions. The content of BTX-aliphatics in the product increases with WHSV (figure IV.5). This is to be expected as cracking reactions are slow and are prone to decrease with decreasing contact time.

IV.7.CONCLUSIONS

The above studies have established a new route for the utilization of pyrolysis gasoline. The new route is a simple two stage route involving a cracking-cum-reforming step and a fractionation step. The new route has been possible due to the unique properties of ZSM-5 like resisting deactivation by coke deposition, propensity to crack hydrocarbons and oligomerizing light olefins.

The studies have revealed the following:

1. The addition of ZSM-5 reduces the deactivation of conventional Pt-Al_2O_3 catalysts during the reforming of pyrolysis gasoline.
2. ZSM-5 present in the catalyst oligomerizes cracked products into aromatics. This effect is significant when the ZSM-5 contents are large and when the hydrogen partial pressure is low.
3. The Fe-isomorph of ZSM-5 is less active in cracking the aliphatics in pyrolysis gasoline.
4. The presence of dicyclopentadiene in the feed deactivates the catalyst faster, though at higher pressures the effect is less.
5. In general, due to thermodynamic reasons, low pressures lead to higher aromatics yield, but shorter catalyst life.
6. At high pressures, the space velocity has to be maintained high enough to prevent aromatics loss.

CHAPTER V

SELECTIVE HYDROCRACKING OF PETROLEUM OILS USING ZEOLITE CATALYSTS

In chapter III, the hydrocracking of some simple hydrocarbons like n-hexane, n-heptane, n-octane and n-hexadecane over shape selective zeolites (ZSM-5 and its derivatives) was reported. In chapter IV, the hydrocracking of aliphatic components of pyrolysis gasoline using, again, the shape selective zeolite ZSM-5 was studied. Further, its oligomerization activity was also examined. In this chapter the studies on the shape selective hydrocraking of much heavier hydrocarbons present in heavy petroleum fractions will be reported. The catalysts used will be metal loaded ZSM-5.

V.1. HYDRODEWAXING

Hydrodewaxing refers to the process of removing the 'waxy' molecules from petroleum fractions using hydrogen and in the presence of a solid catalyst. Long chain normal alkane molecules due to their uniform zig-zag structures, tend to form close packed units which crystallize as solid 'wax' at low temperatures thus reducing the fluidity of petroleum fractions such as diesel and lubricating oils. In the petroleum industry, the fluidity of an oil is expressed in terms of its pour point which may be defined as the temperature at which it begins to flow and is measured by the ASTM D-97 test[180]; lower the pour point of an oil, lower is the temperature at which it can be used in a fluid form. Pour point specifications of petroleum fractions depend on their end use and vary with climatic conditions. The wax content varies with the source of the crude oil. Thus Bombay High Crude oil is more ´waxy´ than those from the Middle East. In the heavier fractions, in addition to the normal alkane molecules, branched alkanes also crystallize out as wax (microcrystalline wax). Hence, to reduce the pour point of an oil, these normal and slightly-branched alkanes should be removed.

Shape selective zeolites are used commercially to dewax petroleum oils by hydrocracking the normal and slightly-branched alkanes. There are two principal developers of dewaxing catalysts/processes. These are British Petroleum and Mobil, USA. The catalysts offered by British petroleum are believed to be based on mordenite and erionite[152-154] while those offered by Mobil are based on pentasil zeolites, principally ZSM-5[156-159]. Generally one or more metallic components are incorporated into commercial dewaxing catalysts in order to improve their performance, eventhough the cracking of normal alkanes readily occurs in the pores of the zeolite even in the absence of metallic components.

V.2 CATALYTIC DEWAXING OVER ZSM-5

In this chapter, the studies carried out on the dewaxing of a series of lube raffinates over ZSM-5 based catalysts will be reported. A number of aspects relating to the characteristics of the zeolite, the feed, and the products will be examined. The properties of the oils used in this study have already been reported in chapter II. The preparation of the zeolites and the catalysts and the experimental procedures adopted have also been reported earlier (chapter II). The various studies will be presented in the different sections which follow.

V.3. SHAPE SELECTIVITY IN DEWAXING

The gas chromatograms of equal quantities of spindle raffinate (pour point = 290 K) and its dewaxed product (pour point = 273 K) are presented in figure V.1 The dewaxing was done over Ni-ZSM-5. The spikes in the gas chromatograms are due to n-alkanes. The n-alkanes content estimated using 4A molecular sieves by the method of Barton and Hajnik[195] was 16 wt% in the case of the spindle oil feed, the major fraction of the n-alkanes lying in the range C_{15}-C_{25}. The unresolved portion is due to the unseparated components, mainly branched alkanes, naphthenes and some aromatics. A fraction of n-alkanes are also included in the envelope. It is observed that the area of the envelope is *nearly* the same in both the gas chromatograms, but the spikes are much less in the chromatogram of the dewaxed oil. This shows that selective removal of the n-alkanes without significant cracking of other components has taken place. The small decrease observed in the area of the envelope is probably due to the removal of the n-alkanes or slightly branched alkanes in the envelope. Shape selective cracking of n-alkanes on ZSM-5 is a typical example of reactant shape selectivity[167].

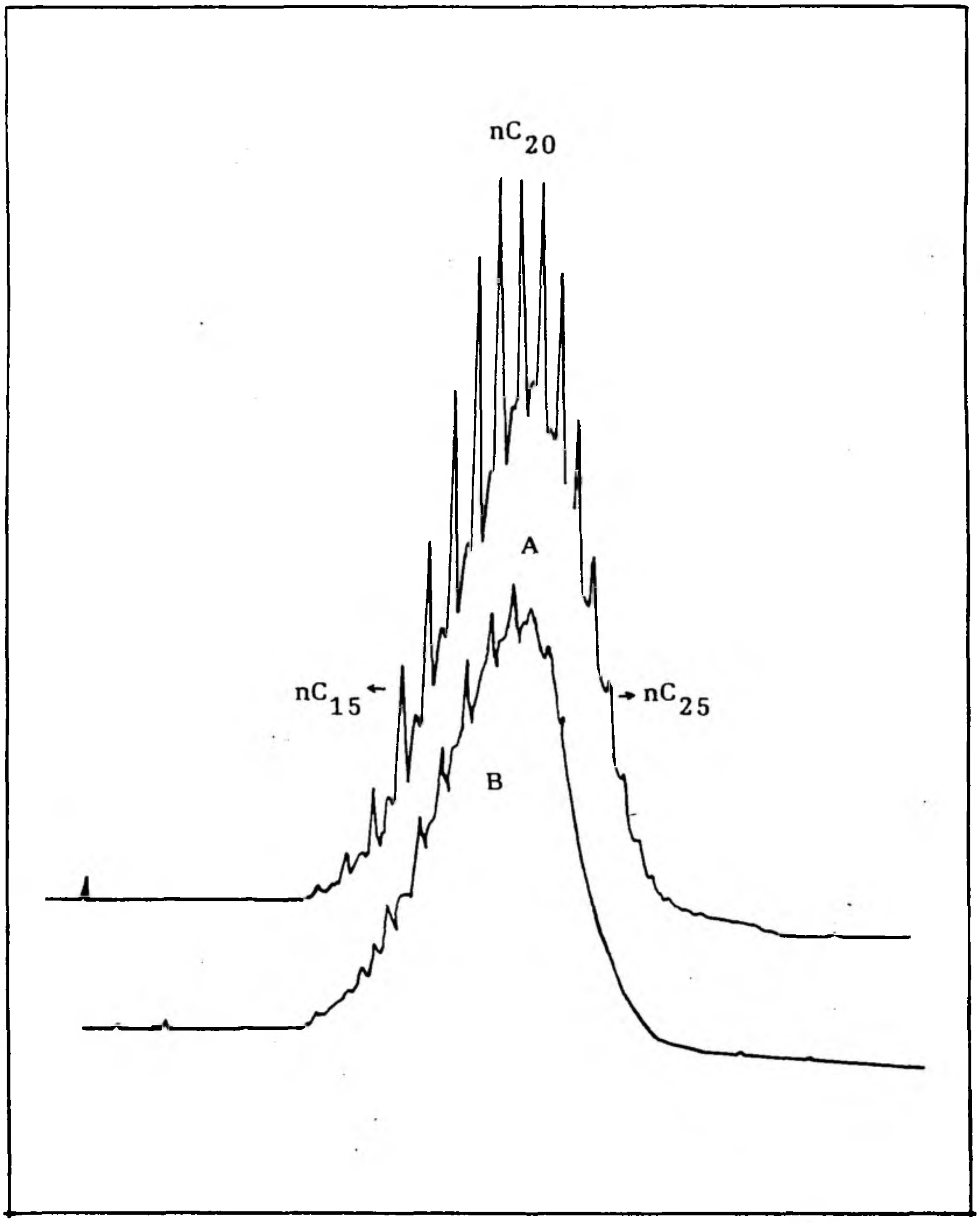


Fig. V.1 SHAPE SELECTIVITY IN DEWAXING

(Gas Chromatograms of spindle raffnate (A), pour point: 290K, Dewaxed spindle raffnate (B), pour point: 273K)

V.4. INFLUENCE OF PHYSICO-CHEMICAL PROPERTIES OF ZSM-5 ON CATALYTIC DEWAXING

In reactions involving zeolites, a number of parameters like crystallite size, silica/alumina ratio and isomorphous substitutions affect the conversion level, the product selectivity and the life of the catalyst. The influence of variations in zeolite crystallite size in the case of a number of reactions like the disproportionation of m-xylene[196], residue cracking[197], xylene isomerization[198] and methanol to gasoline reaction[199], have already been reported. Similarly, the influence of variation in silica/alumina ratio on different reactions involving different zeolites are available in the literature.[200] Typical examples are (i) the linear relationship established between catalytic activity for the cracking of n-hexane and the aluminium content of ZSM-5 by Haag *et al*[119], (ii) the effect of Al^{3+} content in Y-zeolite on the activity, selectivity and stability of cracking catalysts[201,202] and (iii) the linear relationship between Al content and xylenes isomerization activity of ZSM-5.[203] The influence of isomorphous substitution in zeolites, is less well documented, though the effects of Fe^{+3} and B^{+3} substitution in ZSM-5 on its activity for a number of reactions have been published recently[195].

V.4.A. INFLUENCE OF SILICA/ALUMINA RATIO

The results of hydrodewaxing of spindle raffinate over two samples of Ni-ZSM-5 with different silica/alumina ratios (58 and

94) and the same crystallite size of 0.1μm, are presented in table V.1. The results show that in the dewaxing of spindle oil silica/alumina ratio has a significant effect. The catalyst with silica/alumina ratio of 58 has a higher activity than that of the sample with silica/alumina ratio of 94 in that the former produces a product with a lower pour point than the latter. As the experiments were conducted at atmospheric pressure, rapid deactivation (pour point increase with duration of run) is noticed.

Earlier reports[204,205] had, however discounted any effect of silica/alumina ratio (in the range 32-84) on the dewaxing of heavy neutral feedstock. The discrepancy between the two results is due to the difference in the feeds. The present study has used a lighter feed stock containing n-alkanes in the range C_{15}-C_{25} (see figure V.1) whereas the earlier workers[204] had used a much heavier feed stock, containing larger n-alkanes (range C_{30}-C_{50}). Also the n-alkane content of spindle oil is 16 wt%, while that of heavy neutral (used by earlier workers) is 4 wt%. Thus, whereas the reduction in pour point of spindle raffinate requires primarily the removal of its n-paraffin fraction, the lowering of the pour point of heavy neutral requires also the removal of considerable quantities of branched alkanes. Cracking of the lighter n-alkanes (in spindle oil) is free from diffusion effects and a variation in silica/alumina ratio (variation in number of active centers), has an influence on the rate of the reaction (and the pour point of the product). On the other hand,

Table V.1

Influence of Silica/alumina ratio in dewaxing

Catalyst : Ni-ZSM-5^{+}; Feed : Spindle Raffinate

Conditions:

Temperature : 533 K
Pressure : 0.1 MPa
WHSV : 1.98 h^{-1}
H_2/oil : 400 v/v

SiO_2/Al_2O_3 ratio of ZSM-5	Time on stream (h)	Product distribution		pour point of C_5+ fraction (K)
		C_1-C_4	C_5+	
58	2.0	21.6	78.4	265
	3.5	21.5	78.5	269
94	2.0	14.0	86.0	280
	3.5	13.4	87.6	284

+ 0.1 μm crystallites; silica/alumina ratio 84.

the cracking of the large molecular weight alkanes and branched compounds present in heavy neutral was diffusion controlled and variation in the number of active centers (silica/alumina ratio) did not have any influence on the pour point of the product.

V.4.B. INFLUENCE OF ZEOLITE CRYSTAL SIZE

ZSM-5 possesses pores of dimension (~5.5 Å) just adequate for the entry of only normal and mildly branched alkanes, the cause of reactant shape selectivity[185]. Since the diffusion of large alkane molecules into the ZSM-5 pores is slower than their cracking rates, the reaction tends to be the diffusion limited, when dewaxing the heavier cuts of oils containing large alkane molecules (carbon numbers > 30) with greater amounts of chain branching. This leads to a situation where the zeolite crystallite size affects the activity of the catalyst.

The hydrodewaxing of a Bright stock raffinate was carried out on ZSM-5 zeolites having the same silica/alumina ratios (~80) but possessing two different crystallite sizes. Table V.2 summarizes the results obtained. The activity of the catalyst increases as the crystallite size is decreased. For example, to obtain a dewaxed product of nearly the same pour point (267 ± 2 K), the catalyst containing the zeolite with larger crystallite size (2.0 μm) has to operate at a 22 degree higher temperature than the small particle (0.2 μm) catalyst. This is mainly due to the easier accessibility of a larger number of active acid sites in the smaller zeolite crystal than in the larger ones. The

Table V.2

Influence of Crystallite size in dewaxing

Catalyst : Ni-ZSM-5$^+$; Feed : Bright stock raffinate

Conditions:
Pressure : 4.5 MPa
WHSV : 0.8 h^{-1}
H_2/oil : 400 v/v
TOS : 50-100 h

zeolite	Zeolite crystallite size (μm)	Temp.of reaction^1 (K)	Product distribution (wt%)		
			C_1-C_4	C_5-DWO	DWO*
ZSM-5	0.2	581	9.2	7.4	83.2
ZSM-5	2.0	603	10.5	5.1	84.4

1 Average temperature required to obtain a DWO pour point of 267K
* Dewaxed oil pour point 267 K.
\+ 2.0 wt% Ni, silica/alumina ratio = 84

greater accessibility of acid sites in the smaller crystallites arises from the shorter path length in them. The larger crystallites also produce (table V.2) more gaseous fractions (C_1-C_4) (10.5 and 9.2 for the 2.0 and 0.2 μm zeolites) through greater secondary cracking due to the longer residence of the primary cracked molecules inside the zeolite crystallites.

Using similar heavy feedstocks, earlier workers[206] have also reported similar crystallite-size effects. They have also observed that smaller crystallites had a lower deactivation rate than larger crystallites. Haag *et al*[170] have reported the lack of crystallite size effects in the cracking of dodecane over ZSM-5, but they found considerable diffusion effects while cracking branched molecules. They have reported an η (effectiveness factor) value of 1 for the cracking of dodecane on both small and large particle zeolites (0.025 and 1.35 μm) and η values of 1 and 0.3 in the cracking of 2,2-dimethylbutane over the small and large particles. This report confirms our earlier explanation for the presence of crystallite size effects during dewaxing of heavy petroleum fractions which contain large quantities of branched alkanes.

V.5. INFLUENCE OF ISOMORPHOUS SUBSTITUTION OF Al^{3+} IN ZSM-5

The isomorphous substitution of Al^{3+} by Ga^{3+}, Fe^{3+} and B^{3+} in ZSM-5 has been shown to decrease acid strengths in the order: (Al)-ZSM-5 > (Ga)-ZSM-5 > (Fe)-ZSM-5 > (B)-ZSM-5. Of these, the (B)-ZSM-5 was found to be too weakly acidic to crack alkanes[12].

The hydrodewaxing of a gas oil fraction was carried out on samples of (Pt)-Al-ZSM-5, Pt-(Fe)-ZSM-5 and Pt-(B)-ZSM-5. The results are presented in table V.3. The characteristics of the three zeolites and the conditions of the experiments are also presented in the table. As expected, activity decreases in the same order as above, the (Fe)- and (B)-ZSM-5 isomorphs requiring higher temperatures to dewax the oil to obtain products with similar pour points (264 ± 2 K). Interestingly, the selectivity for gasoline (C_5-443 K fraction) increases when Al is substituted by Fe or B. Since all the three zeolites have the same pore structure and void volume, the enhanced selectivity for gasoline indicates the suppression of secondary cracking of the intermediate gasoline, into C_1-C_4 products according to the scheme:

$$\text{gas oil} \text{ ----> } \text{gasoline} \text{ ----> } C_1\text{-}C_4 \text{ products}$$

The moderate activity possessed by (B)-ZSM-5 is surprising in view of earlier reports that (B)-ZSM-5 does not have enough acidity to crack alkanes. Even the (Fe)-ZSM-5 appears to be more active than one would expect for a sample with high SiO_2/Fe_2O_3 ratio (184). The reason for this may be the insertion of Al^{3+} ions into lattice positions of (Fe)- and (B)-ZSM-5 during the preparation of the extrudates with alumina binder. The Al^{3+} incorporation could have occurred during the blending of the zeolite and peptized (acid) alumina hydrate and during the calcination steps. Similar observations of Al^{3+} incorporation into (B)-ZSM-5 (during catalyst preparation) increasing its

Table V.3

Influence of isomorphous substitution

Feed : Atmospheric Gas oil

Conditions:
Pressure : 5 MPa
WHSV : 2.0 h^{-1}
H_2/oil : 300 v/v

Catalyst*	Temp. (K)	Conv. (wt%)	product distribution			Pour Point of 443^+ K fraction
			C_1-C_4	C_5-443	443^+	
Pt-(Al)-ZSM-5	623	50.9	29.4	21.5	49.1	263
Pt-(Fe)-ZSM-5	628	45.7	12.5	33.2	54.3	264
Pt-(B)-ZSM-5	663	42.8	8.5	34.3	57.2	266

* Pt content : 0.3 wt%,
SiO_2/M_2O_3 in zeolite :
ZSM-5 : 186
(Fe)-ZSM-5 : 184, Al impurity 380 ppm (as Al_2O_3)
(B)-ZSM-5 : 174, Al impurity 240 ppm (as Al_2O_3)
Average crystallite size 5.0-6.0 μm for all zeolites.

catalytic activity has already been reported[207]. However, patent literature on the use of (B)-ZSM-5 for catalytic dewaxing is available[208]. Another reason for the activity of (B)-ZSM-5 could be the ease of cracking of the large molecular weight hydrocarbons present in the oil.

V.6. INFLUENCE OF FEED CHARACTERISTICS

Different petroleum fractions have different amounts of waxes. To achieve a certain product pour point, the amount of wax to be converted will depend on the wax content of the oil.

The results of dewaxing of six different feed stocks to obtain a dewaxed oil with pour point 268 ± 5 K are presented in table V.4. The characteristics of the feedstocks have already been reported in chapter II. Except the straight run gas oil feed (GO) which was obtained from Bombay High crude, the others were a series of lube raffinates obtained by furfural extraction of different vacuum gas oil cuts from a persian crude. The n-alkane content decreases as the boiling point of the fraction increases as seen from the gas chromatograms (figure II.1) presented in chapter II. The spikes in the chromatograms which are due to n-alkanes decrease as the oil becomes heavier.

In table V.5, the n-alkane contents of the different oils determined by adsorption by 4 A sieves[203] are also presented along with the yields of dewaxed oils (fraction boiling > IBP) from them. The depth of dewaxing (Δ PP) being the difference between the feed and product pour points is also reported. The

Table V.4

Influence of Feed characteristics

Catalyst : Ni-ZSM-5[+]

Conditions:
Pressure : 4.0 MPa
H_2/oil : 400 v/v
Temp. and WHSV varied.

Feed	n-alkanes[*] (wt%)	DWO pour point	Δ P.P.[1] (K)	DWO yield (wt%)
GO	30	266	46	62.3
SP	16	263	27	72.5
LN	12	263	46	75.0
IN	8	266	54	79.0
HN	4	273	58	83.3
BS	-	273	60	86.9

[*] Estimated by the method of Barton and Hajnik.[195]

[1] Δ P.P = P.P. of feed - P.P. of DWO.

[+] 0.1 μm crystallites, silica/alumina ratio 84

Table V.5

Influence of feed characteristics on product distribution

Catalyst : Ni-ZSM-5$^+$

Conditions :

Pressure : 4.0 MPa
H_2/oil : 400 v/v
WHSV : varied
Temp. : varied

	Product distribution (wt%)						DWO pour point (K)
Feed	C_1	C_2	C_3	C_4	C_5+ to IBP	DWO	
IN	0.10	0.43	5.01	4.59	11.60	78.27	267
HN	0.09	0.38	4.72	3.50	7.60	83.71	273
BS	0.08	0.29	3.17	3.25	6.91	86.30	267

+ 0.1μm cyrstallites, silica/alumina ratio 84.

results indicate that the yield of dewaxed oils increases as the n-alkane contents decrease, even when pour point lowering (Δ PP) increases.

The complete product distributions obtained for three feedstocks (IN, HN and BS) while dewaxing them using a Ni-ZSM-5 catalyst are reported in table V.5. The pour points of the oils (DWO) are also reported in the table. It is observed that both the gaseous and gasoline fractions decrease as the feed becomes heavier. It is interesting to note that the C_1+C_2 yields are very low. This is one of the characteristics of cracking over ZSM-5.

V.7. PRODUCT CHARACTERISTICS FROM DEWAXING

The specifications for a lube oil base stock are determined by (1) its application and (2) the properties of the feedstock. Three important properties are pour point, viscosity and viscosity index. The required pour point of the oil is generally achieved by adjusting dewaxing parameters. The yield of the product (DWO) will depend on its pour point, the lower the pour point the lower its yield. The viscosity required is generally met by adjusting ˊcut pointsˊ of the oil. Viscosity index (VI) which is an inverse measure of the temperature viscosity coefficient is determined by the molecular composition of the oil. In this section we will report the relationship between pour point and yield of different oils and also their VI properties.

V.7.. RELATIONSHIP BETWEEN YIELD AND POUR POINT

The pour point of the dewaxed oil depends on the extent of removal of the waxes (normal and slightly branched alkanes). It is therefore, natural that the yield of the dewaxed oil depends on its pour point. Three oils viz. inter neutral, heavy neutral and bright stock were dewaxed to different levels by varying the process parameters. The relationship between the DWO yield and its pour point in the case of heavy neutral is presented in figure V.2a. The scatter in the points is due to the inaccuracy in the pour point measurements, which is ± 3 degrees. A linear relationship between yield and pour point is apparent. In figure V.2b, the linear regression plots of yield versus pour point for three oils (IN, HN, and BS) are shown.

The equations for the three feeds are

Inter neutral

$$Y = 80.1 + 0.54\ t_{PP}$$

Heavy neutral

$$Y = 83.1 + 0.50\ t_{PP}$$

Bright stock

$$Y = 86.0 + 0.20\ t_{PP}$$

where, Y is the yield of the dewaxed oil and t_{PP} is the pour point of the dewaxed oil in degrees celsius.

The yield of the dewaxed oil decreases, as expected, with decreasing pour point. The yield drop is larger in the case of the lighter oils than in the case of the heavier ones. The yield

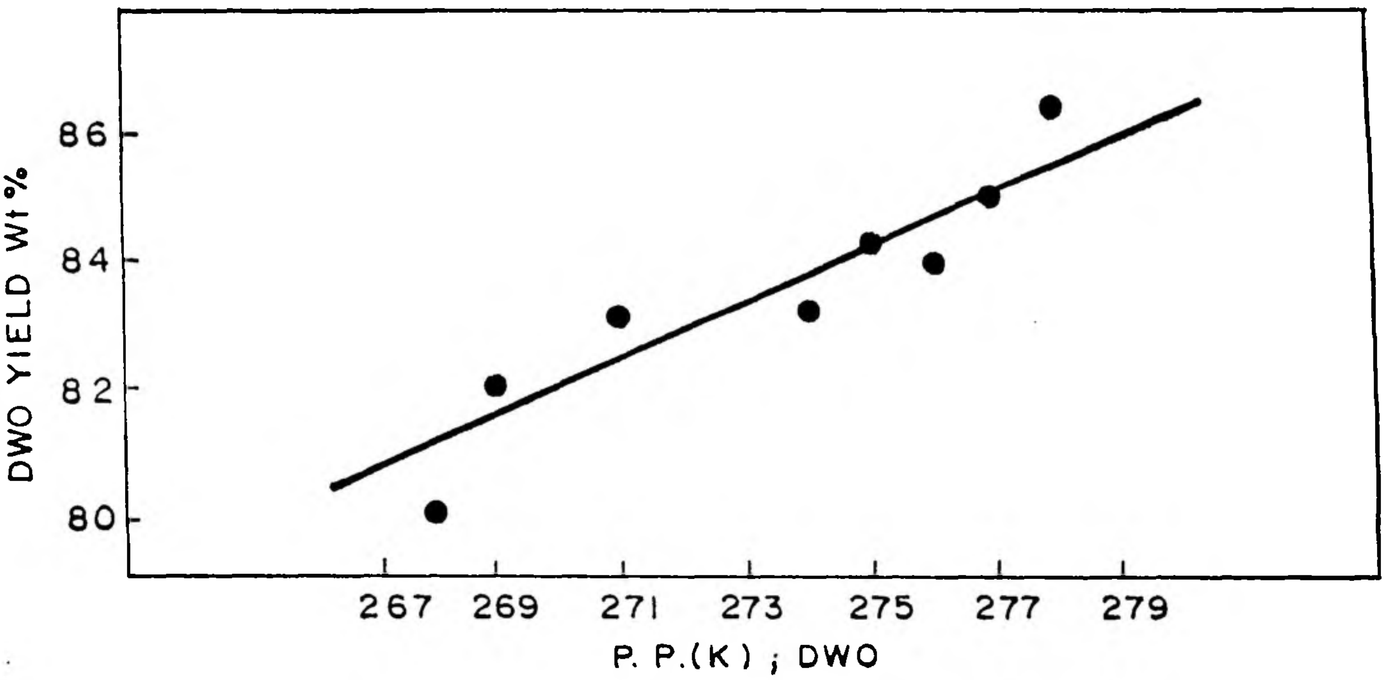


FIG. II.2 A

THE INFLUENCE OF THE POUR POINT OF DWO ON ITS YIELD

(Feed : Heavy neutral)

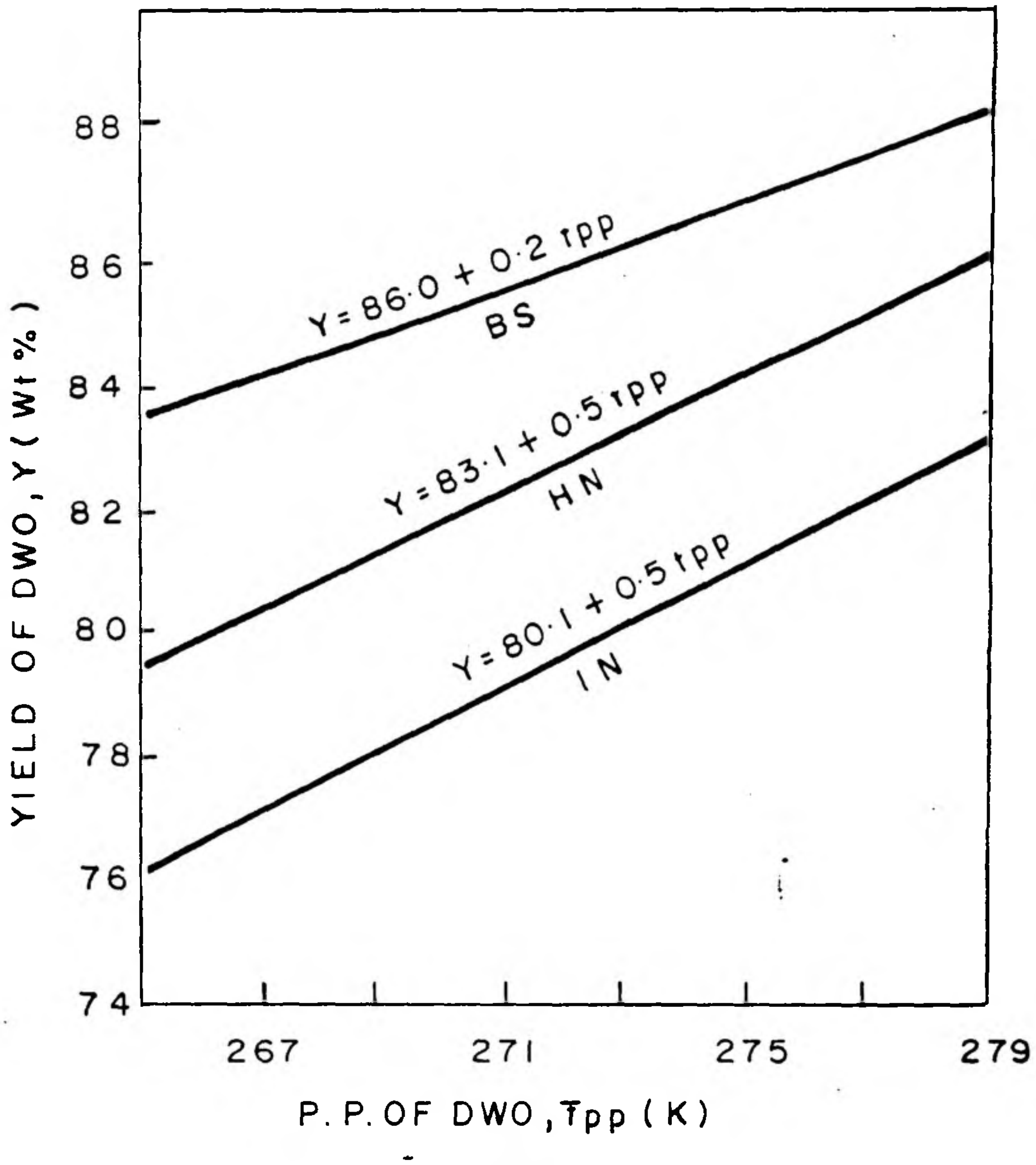


FIG.V 2 B

YIELD VERSUS POUR POINT RELATIONSHIPS FOR
IN, HN AND BS

drop per degree decrease in pour point is 0.54, 0.50 and 0.20 for interneutral, heavy neutral and bright stock respectively.

It should be remembered that the data refer to a short range of pour point values viz., 273 ± 6 K. Linearity of the yield versus pour point relationship has not been observed for wider pour point ranges[209].

V.7.B. VISCOSITY INDEX OF CATALYTICALLY DEWAXED OILS

Viscosity Index is a series of numbers which reflect the temperature-coefficient of viscosity of oils[210]. It is based on reference compounds, which are two families of oils. The one whose viscosity varies greatly with temperature is assigned a VI of zero; the other whose viscosity varies little with temperature is given a VI of 100. The viscosity index of any oil is a numerical comparison of the difference between its viscosities measured at 373 and 313 K with the variation of the viscosities of the two reference oils having the same viscosity at 373 K. The method of calculation of the viscosity index of oils is described in ASTM method D 2270-79[183]. The viscosity of lubricating oils used in automotive engines should not change significantly with changes in the crank case temperature. This is possible only in the case of oils with large VI values. Thus, VI is a very important parameter in evaluating the quality of a lubricating oil; the higher the VI the better is the lubricating oil.

The viscosity characteristics of three catalytically (Ni-

ZSM-5) dewaxed oils are reported in table V.6. The corresponding properties for conventional solvent dewaxed oils[211] are also reported in the same table. It is observed that the viscosity of catalytically dewaxed (CDW) oils is slightly higher at 313 K than the solvent dewaxed (SDW) oils, the viscosity at 373 K being similar. The VI values of the CDW oils are lower than those of the SDW oils, especially for the lighter fractions. The value for the heavy Bright Stock is nearly the same (94 for CDW and 95 for SDW).

Many explanations[159,164] have been offered for the lower VI values of CDW oils when compared to the SDW oils. To understand the VI differences noted above, one has to understand the chemistry of dewaxing of the oils. In the case of the lighter feedstock (inter neutral), the main reason for pour point lowering is the destruction of long chain alkanes by shape selective cracking[164]. In the case of inter neutral, ZSM-5 being highly shape selective, is more selective in cracking the n-alkanes and mono-branched alkanes, whereas SDW procedures do not remove n-alkanes as well, more paraffins being left behind in the oil. Ramage *et al*[164] have reported that in the case of an inter neutral dewaxed oil, the approximate number of methyl branching (branching index as measured by proton NMR) was 3.5 and 4.1 for SDW and CDW oils, confirming the greater removal of less branched alkanes by CDW when compared to SDW. (However, SDW achieves the same level of pour point reduction by removing more of the bulkier cycloalkyl and aromatic derivatives than CDW does).

Table V.6

Viscosity characteristics of catalytic dewaxed oils (Comparison with solvent dewaxing)

Feed:	IN		HN		BS	
Process:	SDW	CDW	SDW	CDW	SDW	CDW
Viscosity (CST) at 313 K	70-80	98.4	190-210	207.9	620-640	650
at 373 K	8-10	10.6	16-18	17.4	37	37.4
Viscosity Index	95	89	90	88	95	94
Pour point (K)	267	267	273	273	267	267

SDW = solvent dewaxing (information supplied by Madras Refineries limited, Madras, India).

CDW = Catalytic dewaxing (Catalyst: Ni-ZSM-5, conditions varied).

Alkanes with less branching have higher VI and also have higher pour points than the more branched alkanes. For example, n-hexacosane (n-C_{26}) has a high VI of 188, but its pour point is 329 K. On the other hand, the branched molecule 5-n-butyl docosane ($C_{26}H_{54}$) has a VI of 136 and a pour point of 293.8 K. 9-n-dodecyl phenanthrene ($C_{26}H_{54}$) has a low VI of about 61 but a high pour point 349 K. SDW leaves a larger fraction of the alkanes with larger VI in the dewaxed oil but removes more of the alkyl cycloalkanes and alkyl aromatics which have low VI and high pour points[210]. The overall effect is that the VI of SDW oils are more than that of CDW oils (for the same pour point of the oil); the yield of dewaxed oil being similar.

In the case of bright stock, as normal and mono-branched alkanes are nearly absent,[164] the cause of pour point reduction by CDW is the destruction of long side chains associated with cycloalkanes and aromatics. The wax present in bright stock is called microcrystalline wax. The fact that the VI values of both SDW and CDW oils are similar suggests that both CDW and SDW remove the same type of molecules. However, because microcrystalline wax (multiply branched alkanes) trap more oil, the yield of DWO in the case of bright stock is less if SDW methods are used.

The situation in the case of heavy neutral is intermediate between that of interneutral and bright stock and the difference in VI between SDW and CDW is moderate.

V.7.C. IMPROVING VISCOSITY INDEX BY INCREASING SHAPE SELECTIVITY

One more reason for the lower VI of oils obtained from ZSM-5 is the presence of acid centers on the external surface of the crystallites. These acid centres crack the relatively high VI and low pour fractions without discrimination resulting in a lower VI of the product. One solution to this problem is the use of a large crystallite zeolite having a lower external surface area. However, such a zeolite will have a low activity due to lesser accessibility of the internal surface area to the reacting paraffinic molecules. On the contrary,small crystallites will be more active and will need a lower operating temperature for a given pour point reduction than larger crystallites. The other benefits of small crystallites such as longer life and better product selectivities have already been discussed (cf.table V.2).

One way of benefitting from the advantages of small crystallite zeolites and at the same time incorporate the advantages of the large crystallite zeolites is to suppress the acid centres on the external surface of small crystallites by surface passivation methods. Such passivation can be achieved by replacing the aluminium ions, which are the seats of the acid centres, by inactive silicon ions by decomposing on the external surface a large molecular weight silicon compound which cannot enter the pores of the zeolite. Such a decomposition will also cover the external surface containing the aluminium ions by layers of inactive silica, thereby also reducing the activity of the external surface of the zeolite crystallites.

Table V.7 presents the results of dewaxing a bright stock raffinate over three zeolites, ZSM-5(0.2), ZSM-5(S)(0,2) and ZSM-5 (2.0). All the zeolites were loaded with 2% Ni. ZSM-5(0.2) and ZSM-5(2.0) were zeolites with crystallites sizes of 0.2 μm and 2.0μm, respectively.

ZSM-5(S)(0.2) had 15 wt% silica deposited on its external surface by a procedure described already in chapter II. The bulk silica/alumina ratios of the samples ZSM-5(0.2) and ZSM-5(S)(0.2) estimated by chemical analysis were 82 and 90.8, respectively. Their surface silica/alumina ratios estimated by XPS were 70.6 and 128.6, the larger silica/alumina ratio on the surface for the ZSM-5(S)(0.2) sample indicating that silica was deposited preferentially on the external surface of the zeolite crystallites. Adsorption experiments gave similar values for the adsorption of n-hexane on both the samples (11.3 wt% and 10.9 wt% for ZSM-5(0.2) and ZSM-5 (S) (0.2), respectively at a p/p_o of 0.5) confirming that silica did not enter the pores of the zeolite. The silica/alumina ratio of ZSM-5(2.0) was 84 (chemical analysis). The above zeolites were blended with alumina (35 wt%) and loaded with 2 wt% Ni as per standard procedures to obtain the final catalysts which were used for dewaxing studies. The catalysts Ni-ZSM-5(0.2) and Ni-ZSM-5(2.0) are the same as those reported in table V.2.

The VI of the dewaxed oil obtained from small crystallite catalyst Ni-ZSM-5(0.2) is lower than that of the dewaxed oil obtained from the large crystallite Ni-ZSM-5(2.0). The reasons

Table V.7

Influence of surface passivation on viscosity index

Catalyst : Ni-ZSM-5+; Feed : Bright stock raffinate

Conditions:

Pressure : 4.5 MPa

WHSV : 0.8 h^{-1}
H_2/oil : 400 v/v
TOS : 50-100 h

Catalyst/ zeolite	Zeolite crystallite size (μm)	Temp.of reaction[1] (K)	Product distribution			Viscosity index of DWO[3]
			C_1-C_4	C_5-DWO	DWO*	
ZSM-5	0.2	581	9.2	7.4	83.2	90.3
ZSM-5(S)[2]	0.2	578	8.1	7.2	84.7	92.0
ZSM-5	2.0	603	10.5	5.1	84.4	91.9

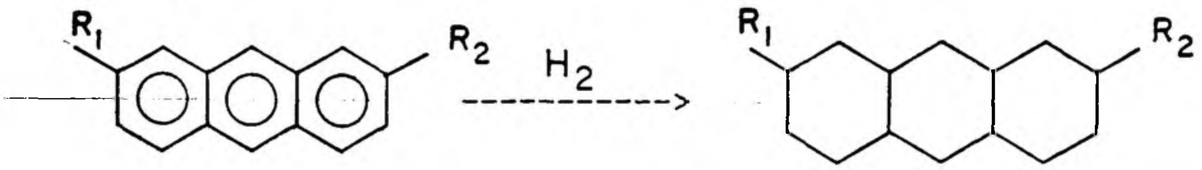
1 Average temperature required to obtain a DWO pour point of 267K
* Dewaxed oil pour point 267 K.
2 External surface passivated by silylation.
3 values accurate to ± 0.4 units.
\+ 2.0 wt% Ni, silica/alumina ratio 84.

for this have been explained already. On surface passivation, the small crystallite zeolite catalyst [Ni-ZSM-5(S)(0.2)] yields a product with a higher VI of 92 (equal to that of Ni-ZSM-5 (2.0)). Further, the yield of DWO is higher, being also similar to that of Ni-ZSM-5(2.0). The DWO yields are 83.2 for the small particle zeolite. It is higher, viz., 84.7 and 84.4 for the surface passivated small crystallite zeolite and the large crystallite zeolite. The temperature of the reaction (for obtaining the same pour point of DWO) is, however, similar for both the passivated small crystallites and for the non passivated small crystallites, and much lower than that of the large crystallites. Thus, surface passivation combines the benefits of both small crystallite and large crystallite zeolites.

In fact, it is surprising that the benefits of improved shape selectivity should be observed for dewaxing a very heavy petroleum oil, whose molecules may be much too large to enter the pores of ZSM-5. However, Ramage *et al*[164] have reported that reactant shape selectivity plays an important role in the dewaxing of bright stock also. They have observed that the dewaxed oils obtained from the catalytic dewaxing of bright stock have more number of branches per molecule (6.7) than the feed (5.5).

V.7.D. IMPROVING VISCOSITY INDEX BY HYDROFINISHING

Another reason for the slightly lower VI of the CDW oils is the presence of small amounts of polynuclear aromatic hydrocarbons created on the surface of zeolite crystallite by hydrogen transfer and by dehydrogenation over the metal component. Generally polynuclear aromatic rings have very low VI (even -ve values) and high pour points. Hydrogenating these structures leads to saturates which have higher VI and lower pour point values. For example, hydrogenation of compound I given below into compound II increases the VI and decreases pour point.[210]



VI = -60 VI = 20

Freezing point > 323 K Freezing point >= 293 K

I II

Therefore a simple strategy is to hydrotreat the DWO. Hydrotreatment using a Ni-Mo catalyst is found to increase VI of the oils by 2-3 units in the case of brightstock and haavy neutral. Table V.8 compares the VI of dewaxed oils obtained from bright stock before and after hydrotreatment. The VI values increase after hydrotreatment. Similar results have been reported by others also[212], who have found that VI of CDW oils increases by 3-4 points on hydrotreatment.

V.8. INFLUENCE OF NITROGEN POISON IN CATALYTIC DEWAXING

Basic nitrogen compounds poison acid sites of zeolites provided they can enter the pores. As the feed stocks (except the gas oil fraction) used in this study are raffinates obtained

Table V.8

VI of dewaxed oil from Bright Stock ; Influence of hydrofinishing

Dewaxing

Catalyst : Ni-ZSM-5^{+}
Press : 4.50 MPa
Temp. : 573-653 K
WHSV : 0.9 ± 0.1 h^{-1}
H_2/Oil : 550 v/v

Hydrotreating

Catalyst : Ni-Mo/$Al_2O_3^{*}$
Press : 5.00 MPa.
Temp. : 573 K
WHSV : 1 ± 0.1 h^{-1}
H_2/Oil : 600 v/v

Liquid	Sample No.	VI	P.P(K)	Viscosity (CSt)	
				313 K	373 K
DWO	1	92.2	265	610.1	35.5
	2	92.7	267	629.9	36.4
	3	93.1	266	610.4	35.8
HYDROTREATED DWO	1	94.8	264	570.0	34.8
	2	95.2	265	580.1	35.3
	3	95.8	267	563.7	34.9

+ 0.1 μm crystallites, silica/alumina ratio 84.

* commercial; composition: NiO, 5 wt%; MoO_3, 16 wt%.

by solvent extraction of the aromatic components, their nitrogen content is low (table II.2). Also, as the nitrogen containing molecules are quite large, they will be excluded from the pores of ZSM-5. This is one reason for the success of ZSM-5 dewaxing catalyst. In figure I.1, the exclusion of a large molecular nitrogen compound (5,6 benzoquinoline) by ZSM-5 is depicted.

Studies on the influence of nitrogen poison on the dewaxing of a heavy neutral feed (HN) over a Ni-ZSM-5 catalyst have been carried out. These studies were carried out by spiking HN with 1,8-octyldiamine to give 1000 ppm nitrogen content in the feed This high level of nitrogen was found to deactivate the catalyst rapidly. These results are reported in figure V.3. The pour point of the product increased rapidly from 261 K to 288 K in 4 hours during the injection of the nitrogen feed. After injecting the nitrogen poisoned feed for 5 hours, the feed was changed to a fresh feed without added nitrogen. Even after many hours of 'clean feed' and flushing in hydrogen (at 683 K), the catalyst did not get back to the original activity. However, it was possible to obtain the same product pour point by raising the temperature to 618 K from 573 K. This suggests the presence of strongly adsorbed ammonia on the catalyst deactivating a part of the active centres. Air oxidation (regeneration) of the catalyst brought it back to the old activity values showing that no permanent damage happened to the catalyst. Heavy neutral and bright stock contain 234 and 103 ppm of nitrogen, respectively. The nitrogen compounds present are large molecule aromatics which

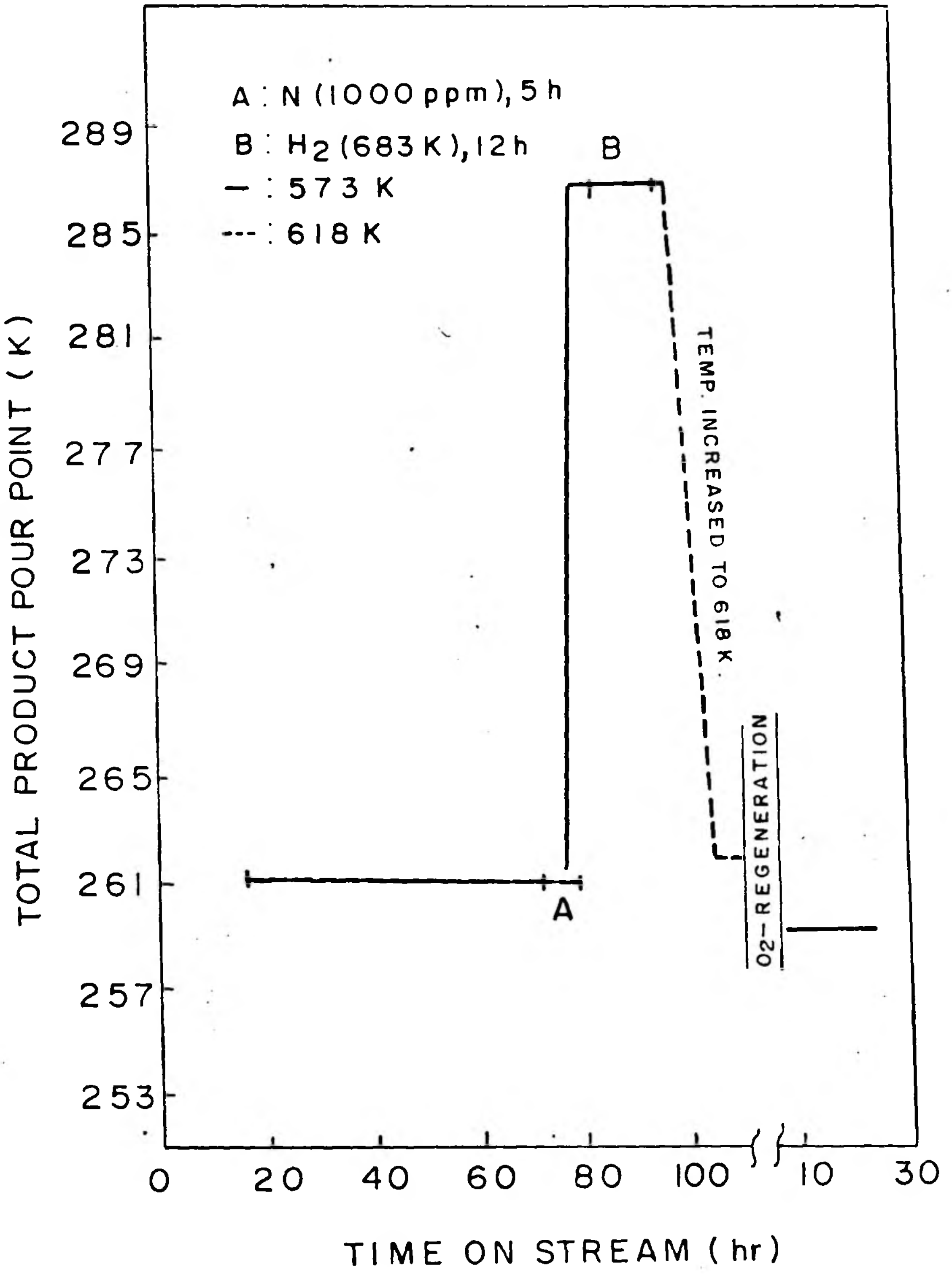


Fig V.3 INFLUENCE OF N-POISON DURING THE DEWAXING OF HEAVY NEUTRAL

(Refer text for details)

cannot enter the zeolite pores and decompose or poison the active centres. The dewaxed oils from HN and BS had nitrogen contents of 276 and 105 ppm, respectively, proving that the nitrogen compounds were not converted under the conditions of the experiment. Hence, the experiment shows that only easily decomposable normal alkyl amines (which are not generally present in heavier petroleum fractions) and ammonia gas poison the catalyst.

The desorption of ammonia preadsorbed on ZSM-5 at different temperatures has been presented in figure I.3. It is seen that a majority of the ammonia molecules are lost by the catalyst (ZSM-5) only when heated to about 753 K. Thus, to remove ammonia poison from the catalyst, hydrogen flushing should be carried out at temperatures around 723-753 K. The flushing carried out at 683 K during the present experiment is too mild to desrob the ammonia from the catalyst surface.

V.9. INFLUENCE OF PROCESS PARAMETERS

There are two process parameters which significantly affect the pour point of oils during dewaxing. These are temperature and space velocity. The other parameters like the pressure and hydrogen partial pressure (hydrogen/oil ratio) affect the pour point of the product to a smaller extent, though the product distribution is affected to a considerable extent. The above observations are, however, based on studies in a limited range of pressures (3.0 - 6.0 MPa) and H_2/oil ratios (300 - 600 v/v).

The influence of process parameters on the dewaxing of two feeds were investigated. The influence of temperature and space velocity (WHSV) (keeping other parameters constant) on the pour point of the dewaxed oil in the case of bright stock are presented in figure V.4 and V.5. Both the parameters are found to affect the pour point of the oil significantly.

Another approach to the evaluation of the influence of process parameters is to examine the influence of the different parameters at constant pour point of the product. The study reveals the influence of process parameters on the product distribution at constant pour point of the product (DWO)

Tables V.9 to V.12 present the influence of temperature, pressure, WHSV and hydrogen/oil (v/v) ratio on the product yields of heavy neutral. The influence of temperature has been obtained at different times on stream (as the catalyst deactivated, 10-800 h). Therefore, other parameters could be kept constant. As the catalyst deactivates, and the temperature is raised to obtain the required product pour point (273 ± 2 K), the yield of DWO decreases (table V.8 and figure V.4) while the yields of C_5+ -IBP increases. The yields of C_1-C_4 show only a very slight increase. The loss of DWO is due to larger contribution from non shape selective cracking on the external surface of the zeolites at the higher temperatures.

The influence of pressure (table V.9) indicates a similar influence on DWO yields. The yield of gases increases due to larger amount of hydrocracking. Table V.10 and figure V.5

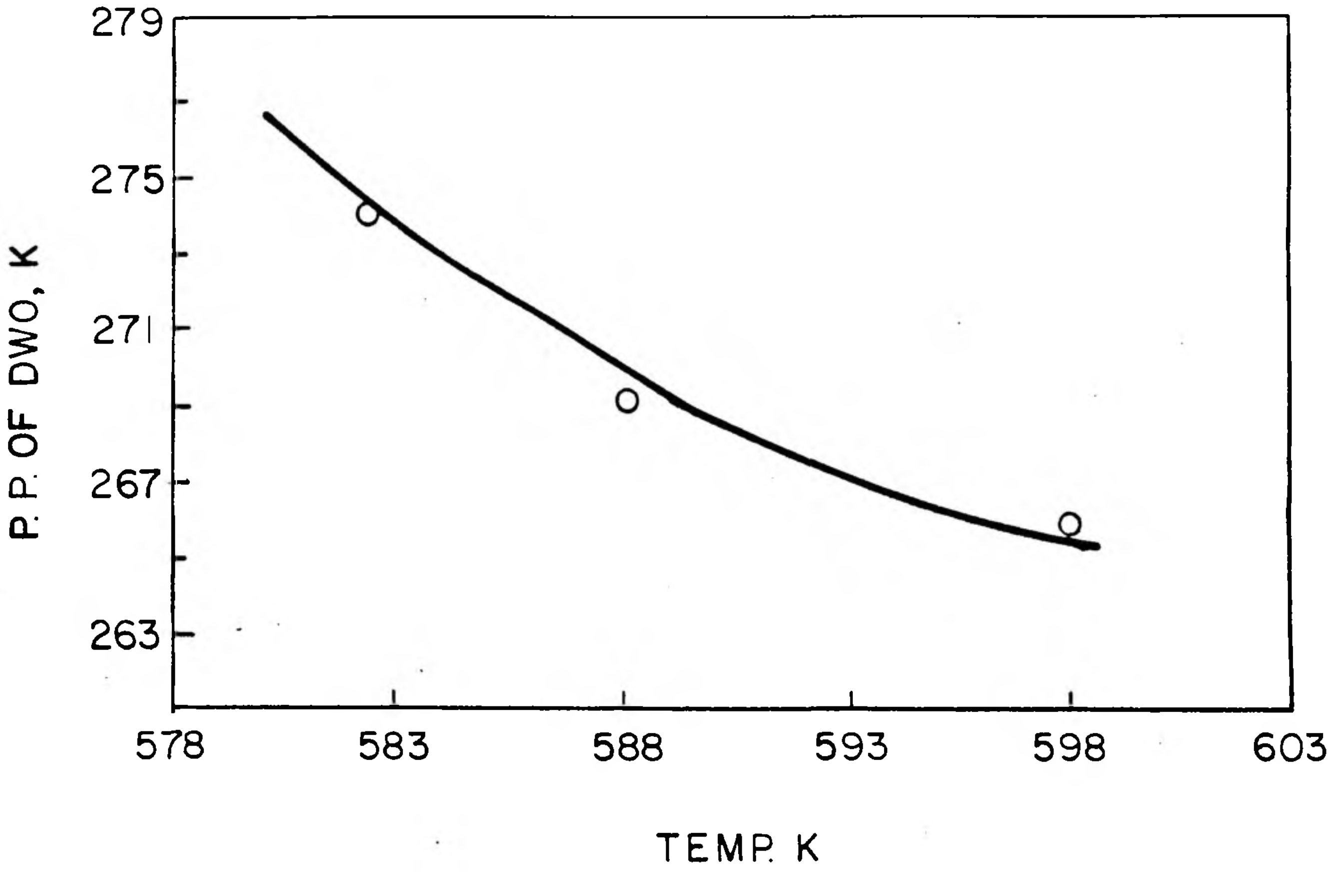


Fig. V.4 INFLUENCE OF TEMPERATURE ON POUR POINT OF DWO

(Feed: Bright stock; Catalyst: Ni-ZSM-5)

(P= 4·5 MPa, WHSV = 0·6 h^{-1}, H_2/oil (v/v) = 600).

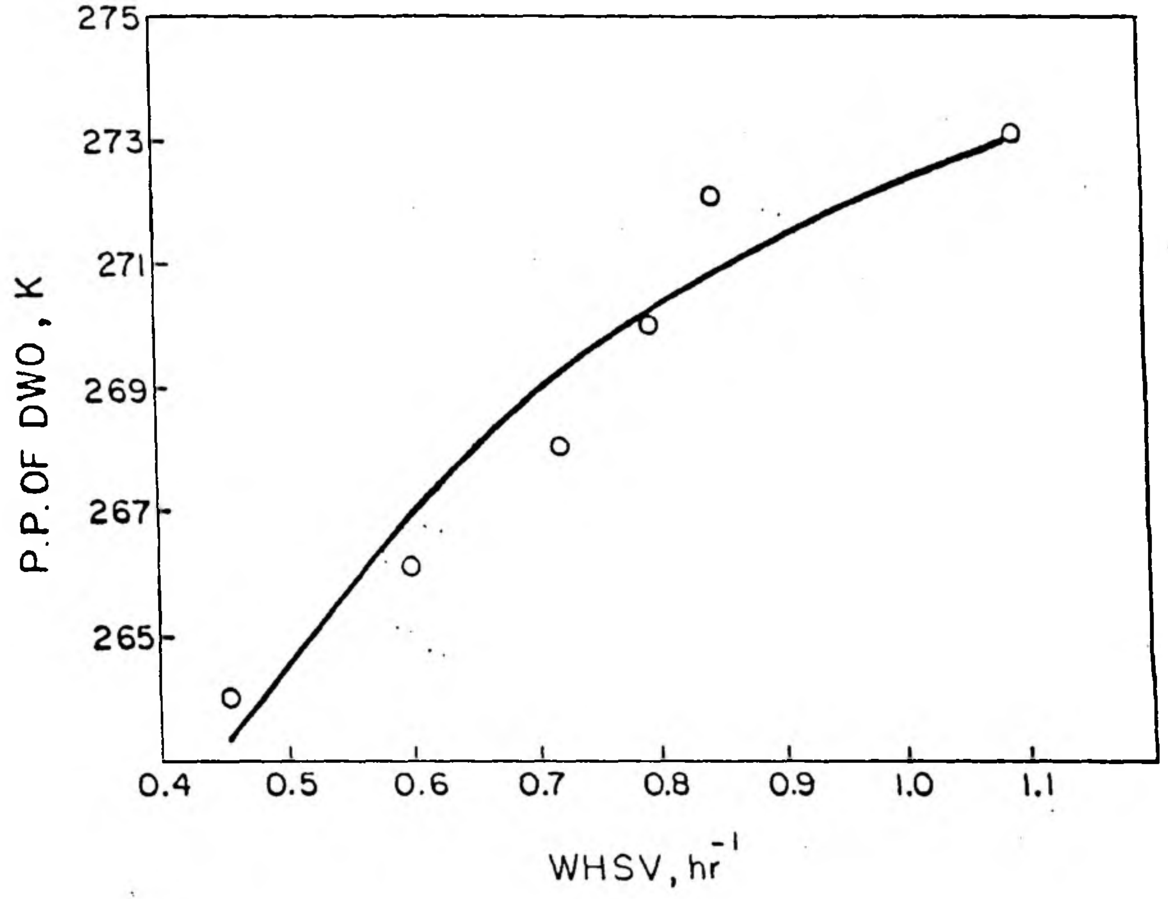


Fig. V.5 INFLUENCE OF WHSV ON POUR POINT OF DWO
(Feed: Bright stock)
(P = 4·5 MPa, Temp. = 593 K ; H_2/oil (v/v) = 600).

Table V.9

Influence of Temperature in hydrodewaxing

Catalyst : Ni-ZSM-5+
Feed : Heavy Neutral Raffinate;
Feed pour point = 329 K
Product pour point = 271 ± 1 K
WHSV = 0.87 ± 0.05
H_2/oil = 510 ± 18 v/v
Pressure = 4.5 MPa.

Temp. (K)	WHSV (h^{-1})	H_2/oil (v/v)	Product distribution (wt%) C_1	C_2	C_3	C_4	C_5+ -IBP[1]	DWO[2]
573	0.87	506	0.09	0.38	4.72	3.50	7.60	83.71
598	0.83	510	0.11	0.38	4.57	3.74	8.67	82.53
613	0.92	492	0.12	0.45	4.35	4.17	8.76	82.12
648	0.89	502	0.12	0.46	3.79	4.13	10.41	81.06
673	0.84	528	0.18	0.69	4.30	4.30	10.16	80.37

1 IBP of DWO = 673 K : Fraction collected between C_5+ to 673 K.

2 DWO estimated from G.C.analysis.

+ 0.1µm crystallites, silica/alumina ratio 84.

Table V.10

Influence of Pressure in hydrodewaxing

Catalyst : Ni-ZSM-5^{+}
Feed : Heavy Neutral Raffinate;
Feed pour point = 329 K
Product pour point = 271 ± 2 K

WHSV = 0.87 ± 0.04 h^{-1}
H_2/oil = 512 ± 14 v/v
Temp. = 596 - 601 K.

Press.	WHSV	H_2/oil	Product distribution (wt%)					
(MPa)	(h^{-1})	(v/v)	C_1	C_2	C_3	C_4	C_5+-IBP[1]	DWO[2]
3.5	0.91	498	0.07	0.20	4.04	3.66	8.05	83.96
4.5	0.83	510	0.11	0.38	4.57	3.74	8.67	82.53
5.0	0.88	526	0.12	0.43	5.09	3.90	8.31	82.05
5.5	0.87	514	0.13	0.44	5.34	3.82	8.87	81.40

1 IBP of DWO = 673 K : Fraction collected between C_5 + to 673 K.

2 DWO estimated from G.C.analysis.

+ 0.1 μm crystallites, silica/alumina ratio 84.

Table V.11

Influence of WHSV in hydrodewaxing

Catalyst : Ni-ZSM-5[+]
Feed : Heavy Neutral Raffinate;
Feed pour point = 329 K
Product pour point = 270 ± 2 K
Pressure = 4.5 MPa
H_2/oil = 510 ± 18 v/v

Temp.	WHSV	H_2/oil	Product distribution (wt%)					
(K)	(h^{-1})	(v/v)	C_1	C_2	C_3	C_4	C_5+-IBP[1]	DWO[2]
576	0.45	525	0.12	0.49	4.66	4.07	8.92	81.74
582	0.65	507	0.10	0.27	4.97	3.74	8.85	82.07
592	0.77	494	0.09	0.25	4.83	3.86	8.39	82.58
598	0.83	510	0.11	0.38	4.57	3.74	8.67	82.33

1 IBP of DWO = 673 K : Fraction collected between C_5 + to 673 K.

2 DWO estimated from G.C. analysis.

+ 0.1 μm crystallite size, silica/alumina ratio 84.

Table V.12

Influence of hydrogen/oil ratio in hydrodewaxing

Catalyst: Ni-ZSM-5$^+$
Feed : Heavy Neutral Raffinate;
Feed pour point = 329 K
Product pour point = 271 ± 1 K

WHSV = 0.86 ± 0.03 h^{-1}
Pressure = 4.5 MPa
Temp. = 597 ± 4 K

WHSV	H_2/oil	Product distribution (wt%)					
(h^{-1})	(v/v)	C_1	C_2	C_3	C_4	C_5+-IBP[1]	DWO[2]
0.86	328	0.86	0.34	4.52	3.37	9.12	82.56
0.83	510	0.10	0.38	4.57	3.74	8.66	82.53
0.89	682	0.12	0.43	4.62	4.11	8.55	82.17

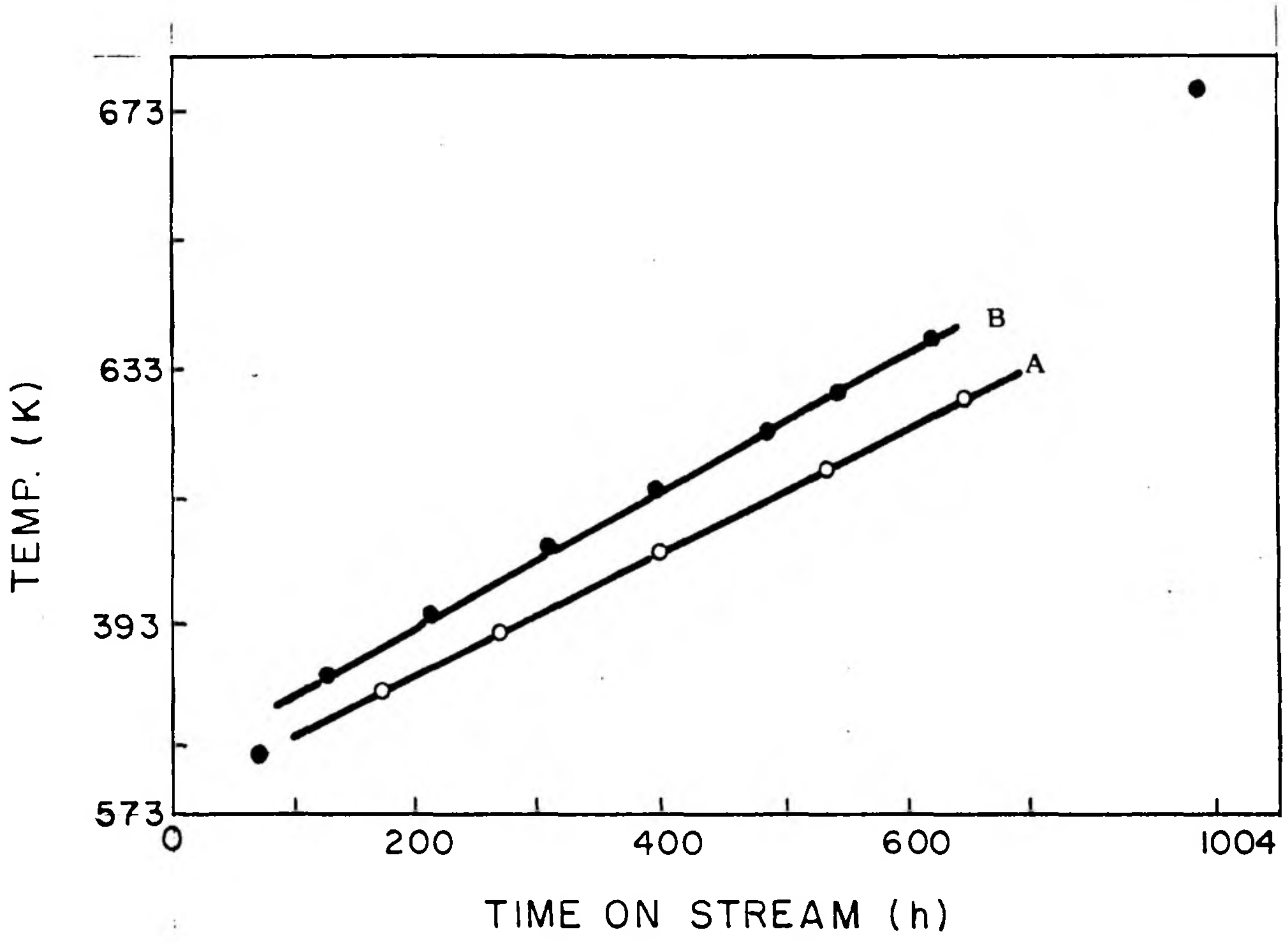
1 IBP of DWO = 673 K : Fraction collected between C_5 to 673 K.

2 DWO estimated from G.C.analysis.

+ 0.1μm crystallites, silica/alumina ratio 84.

Fig V.6 INFLUENCE OF PROCESS PARAMENTERS ON LIFE OF Ni-ZSM-5

(Feed: Bright stock, Product (DWO) Pour point : 266 ±2K)



A: Pressure : 4.5 MPa; WHSV: 0.9 h^{-1}; H_2/oil: 600v/v

B: Pressure : 3.0 MPa; WHSV: 0.6 h^{-1}; H_2/oil: 400v/v report the influence of WHSV. To maintain a constant pour point the temperature has been raised (table V.10), and higher WHSV yields slightly larger amounts of DWO. The influence of hydrogen/oil ratio in the range of 328 to 682 (v/v) has been studied and the results reported in table V.11. The studies show that the influence of hydrogen/oil ratio on product selectivity is very small.

The aging characteristics of a catalyst depend primarily on the process parameters and the feedstock employed. The deactivation rates of Ni-ZSM-5 when dewaxing Bright stock at two different process conditions are depicted in figure V.6. It is noticed that a higher total pressure and a higher hydrogen partial pressure leads to lower deactivation of the catalyst, even when throughput (WHSV) is higher. The rate of deactivation is measured from the rate of rise of temperature necessary to maintain the same product (DWO) pour point (266 ± 2 K in this case) with duration of run. It is noticed that the rate of rise in temperature is less for the high pressure (high hydrogen flow) case than for the low pressure (low hydrogen flow) case. This shows that total pressure and hydrogen partial pressure should be kept large to minimize deactivation.

V.10. CONCLUSIONS

The dewaxing of petroleum oils over shape selective catalysts is influenced by many parameters like, zeolite characteristics, feed properties, operating conditions and product specifications.

Influence of zeolite characteristics

1. During the dewaxing of light feedstocks like spindle oils, the zeolite silica/alumina ratio affects the activity.

2. Small zeolite crystallites have better activities, but yield less dewaxed oil, the dewaxed oil having lower VI than that observed for larger zeolite crystallites.

3. Isomorphous substitution by Fe and B reduces the activity of the zeolite, though product selectivities may be better.

Influence of feed characteristics

1. Heavier feeds contain less n-paraffins and yield more dewaxed oil for the same reduction in pour point.

2. The viscosity index (VI) of catalytically dewaxed oils (CDW) from lighter cuts are substantially lower than those obtained by solvent dewaxing (SDW) processes, though in the case of very heavy oils like bright stock, the VI of the oils from both CDW and SDW are similar.

Influence of process parameters

1. Temperature and space velocity have significant effects on the dewxing reaction, though pressure and hydrogen partial pressure effects are less marked.

Product specifications

1. The yield of DWO depends on the pour point of the product, the lower the pour point, the lower the yield.

2. Viscosity index of catalytically dewaxed oils can be improved by hydrogenation of the product or by surface passivation of small crystal zeolites.

SUMMARY

This thesis is a study of the shape selective cracking of some model hydrocarbons, aliphatics in pyrolysis gasoline and waxy material (primarily long chain alkanes) in heavy petroleum oils. The shape selective zeolite used is ZSM-5.

The studies on the hydrocracking of n-alkanes (hexane, heptane, octane and hexadecane) were aimed at establishing the influence of chain length on cracking characteristics, and deactivation rates in the presence and absence of nitrogen containing compounds. The influence of different metal components on the activity and product selectivity in the cracking of n-hexadecane was also investigated.

The cracking of pyrolysis gasoline was investigated with a view to increase the aromatic yield and also to eliminate all the aliphatic impurities in the BTX fraction. In order to achieve reduced deactivation, increased aromatic yield and better quality of product, the zeolite (ZSM-5) was supported on a matrix of alumina containing Pt (conventional reforming catalyst).

The fundamental aspects of the dewaxing of heavy petroleum oils were examined inorder to study the influence of zeolite and feed characteristics on the reaction. The inter relationship between feed properties and product properties and yield pattern was also investigated.

The results of the various studies are summarised below.

1) Hydrocracking of alkanes

- During the hydrocracking of n-hexane, deactivation increases with temperature and poison (N-compounds) content in the feed. The deactivation by coke deposition and poisoning are independent of one another, especially after the first one or two hours on stream.

- The crackability of the alkanes increases with chain length. The deactivation coefficient decreases, and so also the influence of nitrogen poisons. - The deactivation coefficient is found to be directly proportional to the nitrogen content of the feed in the cracking of n-hexadecane.
- The inclusion of a metal in ZSM-5 increases the activity for cracking even when enough S compounds are present in the feed.
- During the study of n-hexadecane cracking, an interesting "compensation effect" was observed. Whenever, activation energy changed, the Arrhenius parameter, A, also changed.
- The medium pore zeolites, ZSM-5 and its isomorph, (Fe)-ZSM-5 are more active than large pore zeolites Y and Beta. Also the product selectivities are different.

2) Hydrocracking of pyrolysis gasoline

- Inclusion of an alumina matrix along with Pt improves the product quality.
- Small quantities of ZSM-5 in Pt-Al_2O_3 matrix leads to an aromatic gain. The aromatic gain is more at lower pressures and higher temperatures.
- At high pressures of operation, the contact time has to be low to achieve aromatics gain.
- Fe-isomorph of ZSM-5 is less active in cracking the

aliphatics in pyrolysis gasoline.

- Presence of dicyclopentadiene in pyrolysis gasoline reduces the life of the catalyst.

3) **Shape selective cracking of heavy petroleum oils**

- During the dewaxing of light oils like spindle oil, the zeolite silica-alumina ratio has an influence on the activity.
- Small zeolite crystallites have better activities, but yield less dewaxed oils. Also the VI of the product (DWO) is less.
- Fe and B isomorph of ZSM-5 have lower activities.
- Heavy feeds contain less n-paraffins and yield more DWO for the same pour point lowering.
- The VI values of DWO from lighter fraction (inter neutral) are substantially lower than those obtained from solvent dewaxing. However, this difference is negligible in the case of heavy oils like bright stock.
- The yield of dewaxed oil is related to its pour point, the lower the pour point, the lower the yield.
- Improvement in VI of the DWO can be achieved by hydrofinishing the product and also by passivating the external surface of the zeolite crystallites.
- Temperature and space velocity have significant influence on activity and pour point reduction. However, the influence of presure and H_2 partial pressure are less marked, though they have considerable affect on aging characteristics of the catalyst.

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