

CHAPTER II

LITERATURE SURVEY

2.1 Mechanism of Catalytic Cracking over Zeolite

The catalytic cracking of hydrocarbons is a chain reaction that is believed to follow the carbocation theory. This chain mechanism involves three elementary steps: initiation, propagation, and termination. The initiation step is represented by the attack on an active site by the reactant molecule to produce the activated complex that corresponds to the formation of a carbocation. The chain propagation is the transfer of a hydride ion from a reactant molecule to an adsorbed carbenium ion. Finally, the termination step is a desorption of the adsorbed carbenium ion to give an olefin whilst restoring the initial active site. In general, for components with equal carbon numbers, the rate of cracking decreases in the order: *i*-olefins > *n*-olefins > *i*-paraffins \approx naphthenes > *n*-paraffins > aromatics.

Corma and Orchilles (2000) summarized the catalytic mechanism for the reaction over zeolite catalysts. After the olefin interacts with zeolite, Bronsted acid sites are active, when a proton has attacked an olefin the reaction can occur, if the cracking of the C-C bond located in β position with respect to the carbon supporting the positive charge the reaction called β -scission. The cracking of paraffins can be initiated by the direct attack of a Bronsted acid site on a C-C bond, forming a surface activated complex, it called carbonium ion. When this carbonium ion is formed, it can crack paraffins via protolytic cracking. The protonic attack occurs on the most nucleophilic center of the molecule, i.e. on the σ C-C and C-H bond. After the C-C bond is broken, a carbenium ion is left on the surface. This ion can either desorb, giving one olefin or one paraffin depending upon the cracking occurs via β -scission or protolytic respectively, or it can interact with one molecule of reactant for performing propagation step. When a carbenium ion abstracts a hydride ion from a reactant the chain propagation will occur. The reactant molecule will be converted into a carbenium ion that will be able to crack, therefore keeping the reaction chain

going. The chain transfer is terminated when the surface carbenium ion is desorbed and the Bronsted acid site of the zeolite is regenerated.

Experimentally, it has been observed that alkane cracking on small and medium pore zeolite (such as FER and MFI) occurs predominantly via the protolytic cracking mechanism. This is generally believed to be due to steric limitations as smaller micropores hinder the formation of the hydride transfer transition state. This is an example of a so-called “shape-selectivity” effect. In addition, protolytic cracking is favoured under conditions where the concentration of alkenes is low since alkenes are better proton acceptors than alkane (Anderson *et al.*, 2002).

In alkene cracking some of the key steps that are postulated to occur at acid sites in zeolite catalysts involve the initial adsorption of the alkene on the acid site of the zeolite Z-O-H to form the ‘carbenium ion’ species:



β -scission of the C-C bond at the beta position relative to the cationic site to form a smaller alkene and another carbenium ion:



and chain termination by deprotonation of the product cation, the reverse of the adsorption reaction (Hay *et al.*, 1999).

Hollander *et al.* (2002) illustrated cracking mechanism by the reaction of *n*-heptene, the formation of carbenium ions from olefins can easily precede by addition of the proton from a Bronsted acid site of the catalyst to the carbon-carbon double bond. Cracking of the adsorbed carbenium ion proceeds through the β -scission mechanism or through the protonated cyclopropane mechanism. Figure 2.1. illustrates this mechanism.

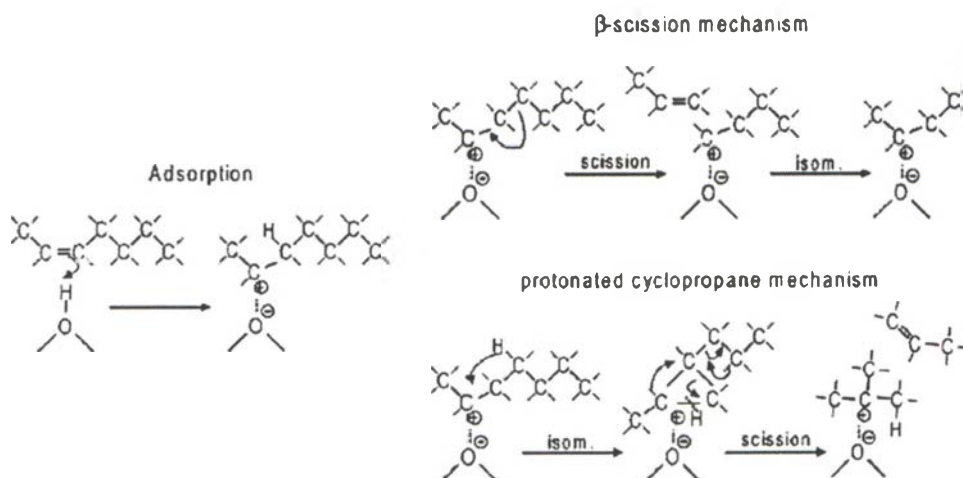


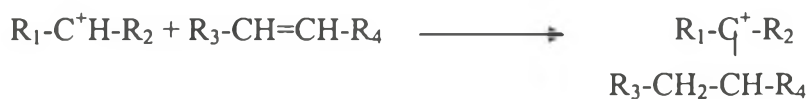
Figure 2.1 Cracking mechanisms illustrated by the reaction of *n*-heptene; adsorption at a Bronsted acid site.

Other reactions of the adsorbed carbenium ion are:

(I) Isomerization to a more stable carbenium ion, for example, through a methyl shift:



(II) Oligomerization with olefin in a bimolecular reaction to form a larger adsorbed carbenium ion:



(III) Desorption with deprotonation to form an olefin (the opposite of adsorption):



(IV) Desorption with hydride abstraction from paraffin to form new paraffin from the carbenium ion and new carbenium ion from the new paraffin (H-transfer reaction):



(V) Desorption with hydride abstraction from (cyclic) olefins or coke (precursors) to form paraffin and a bigger aromatic compound (H-transfer reaction):



The bimolecular reactions (II), (IV) and (V) can occur if the pore size of the catalyst is large enough to accommodate the reactive intermediates, or they should occur on the outer surface of the zeolite particles. If the pores are too small, as in the case of ZSM-5 (0.53 nm×0.56 nm), these reactions cannot take place with larger components e.g. gasolines, although oligomerization or dimerization of small (C₂-C₄) olefins could be possible. With ZSM-5, cracking dimeric intermediates has only been reported in the reactions of relatively small *n*-olefin. Abbot and Wojciechowski (1985) have studied cracking of *n*-olefins from C₅ to C₉ at 678 K with ZSM-5 and found that cracking of pentene solely took place through a dimeric/disproportionation mechanism. Cracking of heptane and larger molecules proceeded mainly through monomolecular cracking, and at 678 K, hexane represented the transition case of the two mechanisms and was cracked by both monomolecular cracking and through dimeric intermediates.

At higher temperature and lower pressure, adsorption of hydrocarbon decreases and the monomolecular mechanism will become more important and dominates over the dimeric cracking mechanism. From equilibrium calculations (regarding the formation and cracking of olefins) it was found that the thermodynamic equilibrium favors the formation of small olefins such as propylene, when ZSM-5 catalyst is used at FCC reaction conditions.

Catalytic processes have been developed to take advantage of the unique transport and molecular sieving properties of zeolite. The zeolite that are widely used in many applications is the medium-pored ZSM-5.

2.2 ZSM-5 Zeolite

The three-dimensional network of ZSM-5 pores is represented in Figure 2.2.

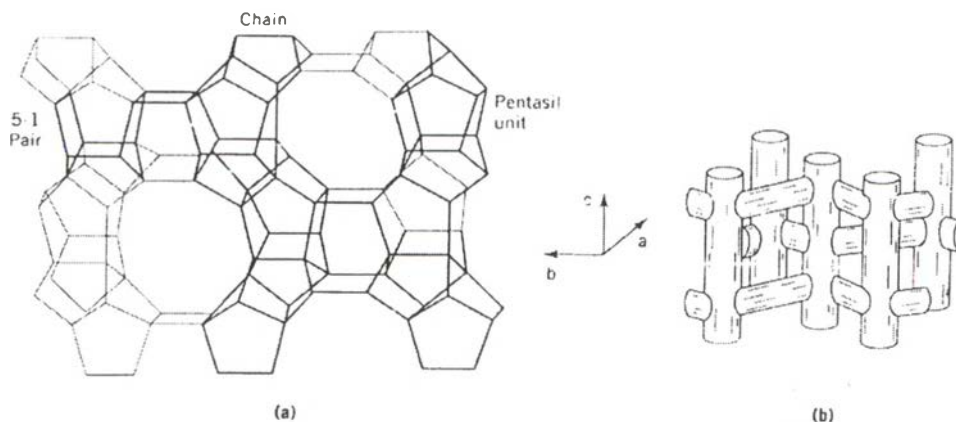


Figure 2.2 Structure of the zeolite ZSM-5: (a) framework of the zeolite; (b) schematic representation of the pore structure.

ZSM-5 can be viewed as a set of straight parallel pores intersected by a set of perpendicular zigzag pores. ZSM-5 is classified as a medium pore and as acidic zeolite catalysts. This zeolite is not very strong acid at low temperatures, but at 500 °C, it is such strong acid that they can protonate paraffins. Almost all the catalytic applications of zeolite take advantage of the acidic property. Activities of ZSM-5 zeolites with different Si:Al ratios have been studied (Buchanan, 1998). When the Al contents in the zeolite are low, the catalytic activity is proportional to the Al content of the zeolite, this relation is a linear function for a wide range of compositions. These results identify the proton donor sites for the cracking reaction. At higher concentrations of Al in the zeolite, the dependence is no longer linear.

One of the main characters of zeolite is the pore size. The pore size of the zeolites is determined by the number of oxygen atoms that form the pore aperture and by the possible obstruction of the pores by cation. The pore structure of zeolite controls the diffusion of reactants and products, and the stability of the transition state (TS), or in other words, the activation energy has influences the catalytic activity and particularly selectivity. The pores in ZSM-5 (Figure 2.3) consist of 10-rings of oxygen atoms.

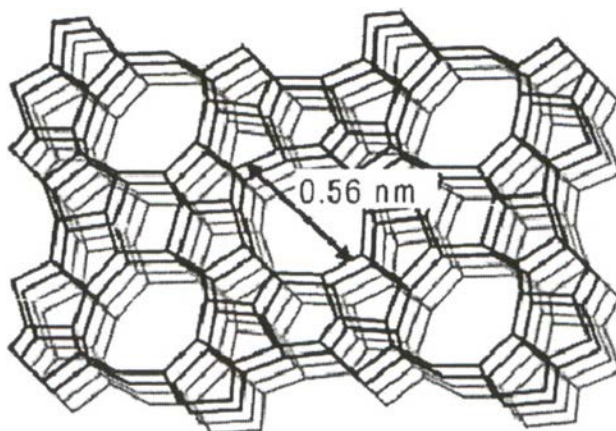


Figure 2.3 Structure of ZSM-5.

The ZSM-5 consists of two types of pore; straight channels with pore sizes of $0.53\text{nm} \times 0.56\text{nm}$ and cross-linked sinusoidal channels of $0.51\text{ nm} \times 0.55\text{ nm}$.

Investigations by Viswanadham *et al.* (1997) suggested that:

- (1) Linear aliphatic molecules diffuse freely in ZSM-5 framework and can be adsorbed in both types of the channels.
- (2) Iso-aliphatic compounds experience steric hindrance effects, which may restrict their diffusion in sinusoidal channel system.
- (3) Aromatic compounds and methyl-substituted aliphatics have a strong preference for diffusion and/or adsorption in the linear elliptical channels. This implies that flat and large molecules prefer to diffuse in wider elliptical channels.

Under the cracking conditions, ZSM-5 zeolite is very active for the cracking of all the components in the gasoline range. Many previous researchers have especially paid attention to the cracking reaction mechanism involved with ZSM-5 and its effectiveness to increase lighter olefins yield. Zhao and Harding (1999) have studied the impact of the hydrogen transfer characteristics of the base cracking catalysts and feed stock on the performance of ZSM-5 additives. To find the relative rate of olefin cracking reaction versus hydrogen transfer reactions determines the effectiveness of ZSM-5 additive in FCC process and propose that maximizing light olefins by using ZSM-5, which more effective in systems with lower hydrogen

transfer activity. On the Bronsted sites of ZSM-5, the carbenium ions are easily isomerized or cyclized to form naphthenes especially cyclohexenes, due to the shape-selectivity, and in the meantime the carbeniums can also undergo β -scission to obtain light olefins. If the catalyst has higher hydrogen transfer activity, that means strong capacity for hydride ions, it can quickly accommodate the hydride ions that are released by the dehydrogenation of naphthenes, resulting finally in formation of aromatics and paraffins. If the catalyst has lower hydrogen transfer activity, it cannot easily catch and hold of the hydride ions set free by the dehydrogenation of naphthenes, resulting in β -scission of carbeniums to the formation of lighter olefins.

2.3 Role of ZSM-5 in Cracking Process

A number of clean fuels are typically made from light olefins such as propylene or butene. The fluid catalytic cracking (FCC) units in petroleum refineries are a major source of these olefins. Olefins are useful building blocks for making clean fuels, because olefins are relatively reactive. It is relatively easy to oligomerize them, alkylate them, or add alcohol or water to make various oxygenates. To increase the amount of these clean fuels, it is necessary to increase the supply of olefins used to make them. Adding ZSM-5 to catalytic crackers has been found to be an effective means of increasing olefins production.

In FCC unit, the powdered catalyst continuously circulates between a riser-type reactor, and a regenerator. The base FCC catalyst is a stabilized Y zeolite, bonded in a spray-dried matrix such as silica-alumina. Liquid feed is introduced at the base of the riser, catalyst is separated out with cyclones, stripped with steam, and flowed to the regenerator, where coke is burned off from the spent catalyst.

Buchanan (2000) studies the effect of adding ZSM-5 in the FCC unit. When a large amount (25% of the total catalyst) of ZSM-5 containing additive was added to a pilot FCC unit, the results show that, the adding ZSM-5 can increase the gasoline octane rating, this result comes from the decreasing of gasoline range (typically C_5 - C_{12} hydrocarbons) and increasing in C_3 - C_4 gas products. The C_{5+} species that drop are mainly the paraffins and olefins drop by about half. Comparing

between paraffins and olefins, ZSM-5 has higher activity with paraffin than olefin. Reaction patterns over two unbound ZSM-5 catalysts, with 55:1 and 450:1 silica/alumina ratios were studied, in order to gain more insight into the effects of silica/alumina ratio. It was found that, for pure hexane and pure octane feeds, the propylene/butene ratio from the 450:1 ZSM-5 in cracking of these alkanes feed was significantly lower than from the 55:1 ZSM-5. For hexane cracking, the activation energy over the 55:1 catalyst was about 15.3 kcal/mol, while 450:1 catalyst was about 20.5 kcal/mol. For octane cracking, activation energies were 2.8 kcal/mol for the 55:1 catalyst, and 4.1 kcal/mol for the 450:1 catalyst. The lower activation energies for the 55:1 ZSM-5 are consistent with mass transfer limitation over the catalyst. In general, compared to reactions over the 55:1 ZSM-5, the rates of the fastest reactions (which tend to boost octane with little or no gasoline yield), are accelerated over the 450:1 ZSM-5 relative to slower reactions, which tend to reduce gasoline yield with less gain in octane.

Hollander *et al.* (2002) studied the cracking of a straight-run FCC gasoline using a thermal, ZSM-5 catalyst, and base catalyst (zeolite Y). The results show that ZSM-5 gives the highest olefin yield as shown in Figure 2.4.

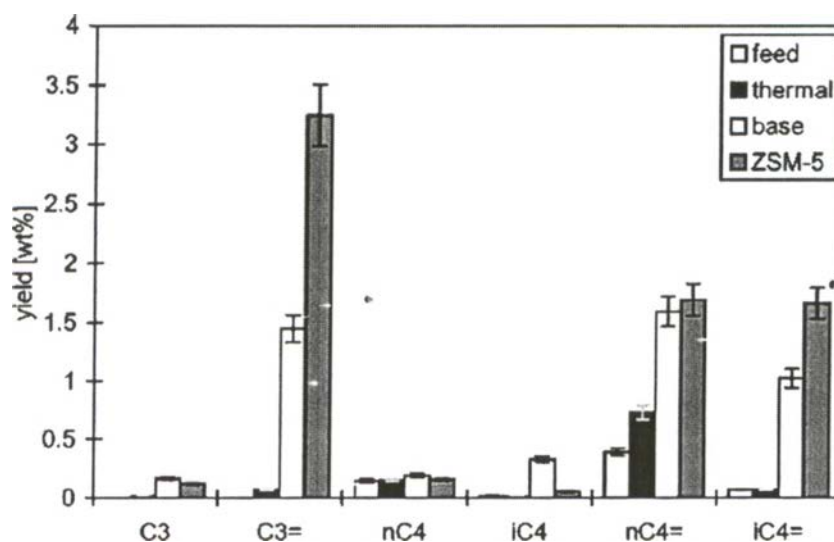


Figure 2.4 Composition of LPG obtained from gasoline cracking without catalyst (thermal), with FCC base catalyst, and with ZSM-5.

The FCC base catalyst produces mainly LPG-range olefins, but propane and *n*-butane are also produced in significant amounts. Propylene is the main product. ZSM-5 produces no significant amounts of LPG-range paraffins, but the yield of the olefins, especially propylene, is higher than that of the base catalyst. The cracking products from ZSM-5 have a higher olefinicity than those of the base catalyst. This high olefinicity could be caused either by a relatively high yield of olefin or by a relatively low yield of paraffins. The former is the case for the C₂ and C₃ fraction of ZSM-5, the C₄ fraction of ZSM-5 has a higher olefinicity than that of the base catalyst due a lower concentration of paraffins (*i*-butane) with ZSM-5. The reason is that hydrogen transfer reaction that produce paraffins only take place with the base catalyst. All result can be explained by the existence of shape selectivity in the case of ZSM-5. Due to the relatively small pore size of ZSM-5, only monomolecular reactions take place and the interaction between the reactants and the catalyst is higher. The cracking reactions are restricted to adsorption of olefins, followed by isomerization or β -scission and desorption and the catalytic surface has to be visualized by the acid sites as such. No hydrogen transfer takes place and the only possible products from cracking with ZSM-5 are light olefins. The small pore size of ZSM-5 restricts the entry of large hydrocarbons and enables a higher interaction with the reaction intermediates. Therefore, the conversion of gasoline feed to olefins is higher with ZSM-5 than with the base catalyst.

Based on the literature cited above, it is to be expected that with ZSM-5, the cracking reactions of larger, C₇⁺, olefins are restricted to simple β -scission reactions; relatively straight chains (or part of it) can enter the pores, are adsorbed, split-off small olefins, and desorbed. As an example, the reaction of *n*-heptene over ZSM-5 (for simplicity only the β -scission mechanism) is shown in Figure 2.5. The adsorbed C₇-carbenium ion is cracked to propylene and an adsorbed C₄-carbenium ion. The latter can desorb as butene or be cracked to two ethane molecules.

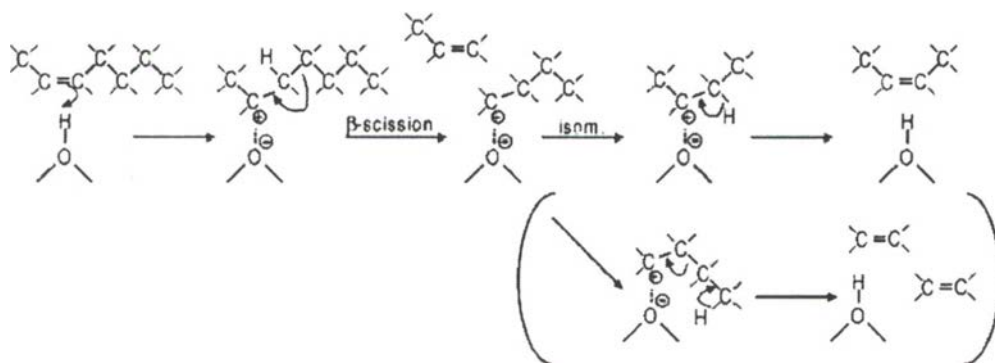


Figure 2.5 Monomolecular cracking mechanism (only possible with ZSM-5).

Generally, the second reaction, formation of ethane, is energetically less favorable because it involves the formation of two primary carbenium ions. However, due to the small pores of ZSM-5, the electrical field in the pores is larger and a relatively large interaction between the catalyst and the adsorbed carbenium ions shall exist. It is believed that the oxygen atoms of a zeolite structure play a role in solvating carbocations, delocalizing the positive charge into the framework. The smaller the sizes of the pores of the zeolite, the closer the different oxygen atoms are to the adsorbed reaction intermediates and the higher the possible interaction. So possibly, as a result of increased stabilization of the intermediates, the formation of ethylene is enhanced when small pore-zeolites such as ZSM-5 are involved. The main cracking reactions on ZSM-5 can be envisaged as follows: olefins adsorb, and can undergo cracking or isomerization reactions before they desorb and leave the catalytic site available for adsorption of a new olefin. On the FCC base catalyst, the olefins adsorb on the catalytic site and, in addition to the reactions on ZSM-5, the adsorbed carbenium ion can dimerize with other hydrocarbons to form a larger adsorbed carbenium ion that can split-off a fragment like in a chain-transfer mechanism. According to this proposed mechanism, the active site of ZSM-5 is the acid site itself, while the active site in zeolite Y can be represented by the adsorbed carbenium ion. The reaction intermediates with ZSM-5 contain at maximum the number of carbon atoms of the feedstock (C_5 - C_{11}), while the (surface) intermediates with the base catalyst can be much larger. As a result, the cracking products from

ZSM-5 will be mainly C₃, C₄, and to some extent also C₂ olefins, while the zeolite Y base catalyst larger fragments can be formed. This agrees with the results that can be found that, the main products from *n*-olefins and *i*-olefins cracking on ZSM-5 are light olefins with a high selectivity for propylene.

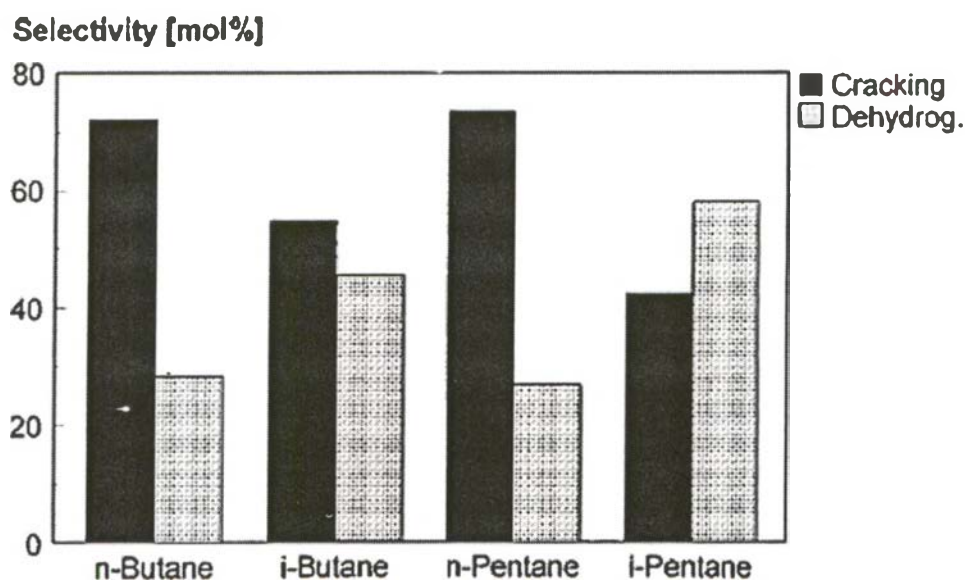


Figure 2.6 Selectivities to cracking and dehydrogenation for *n*-butane, *i*-butane, *n*-pentane, and *i*-pentane on ZSM-5 at 733 K.

The catalytic conversion of light hydrocarbons (propane, *n*-butane, *i*-butane, *n*-pentane, and *n*-hexane) over on ZSM-5 were investigated by Narbeshuber's group (1997). In their experiment was used ZSM-5, having a Si/Al ratio of 35 and a particle size of approximately 1 μm . Infrared spectroscopy showed two characteristic hydroxyl adsorption bands at 3610 and 3745 cm^{-1} . They were assigned to Bronsted acid sites and terminal hydroxyl groups, respectively. Lewis acid sites were not detected. Steady state and transient response experiments were carried out in a plug flow reactor using a quartz glass tube with an inner diameter of 4 mm. The reactions were investigated between 733 and 823 K. Propane or *n*-butane was used as 10 or 20% mixture in He. Pentane and hexane were added to the carrier gas via a syringe pump. Partial pressures of the reactants ranged from 10 Pa to 10 kPa. The

catalyst weight was varied from 0.002 to 0.05 g. Flow rates were adjusted from 10 to 100 ml/min, so that the reactor operated under differential conditions.

The reactions can undergo to cracking and dehydrogenation, the product selectivity for the conversion of *i*-pentane and *n*-pentane at 773 K are added in Figure 2.6. Methane and butene, ethane and propylene, propane and ethane, and pentene were the primary products in the conversion of *n*-pentane. The conversion of *i*-pentane yielded the same primary products as *n*-pentane with the exception of propane.

As observed for the conversion of the butanes, the selectivity to dehydrogenation was higher for *i*- than for *n*-pentane. Table 2.1 and 2.2 reflect the rates of reaction and the energies of activation for the monomolecular cracking and dehydrogenation processes. The energies of activation for *n*-butane and *i*-butane show a similar trend. The E_A for dehydrogenation was somewhat smaller than the value for cracking. In contrast, the comparison of the activation energies for *n*- and *i*-pentane showed a distinctly different behavior. With *i*-pentane the activation energy for cracking was much higher than that for *n*-pentane, while the activation energy for dehydrogenation was the same for both hydrocarbons. These data suggest a change in the rate determining steps of both processes. Looking closer to the activation energies for cracking and breaking down the overall value to $E_{A \text{ Methane}}$ and $E_{A \text{ Ethane}}$, a clear distinction can be made between the two cracking processes, (i) the formation of methane and butanes and (ii) the formation of ethane and propenes, denoted as C_5-1 and C_5-2 in Table 2.2. Note that in the conversion of *i*-pentane, the step producing butenes showed apparent activation energy, which was 25 kJ/mol higher than the step producing propenes. Suggesting that the rate determining step for C_5-1 is the desorption of the olefins while for C_5-2 it should still be protolysis of the C-C bond.

Table 2.1 Conversion of *n*- and *i*-butane on ZSM-5 at 773 K; Rates of Production Formation $\times 10^9$ [mol/gs mbar]; E_A [kJ/mol]

R. no.	Reaction	<i>n</i> -Butane	<i>i</i> -Butane
C ₄ -1	$C_4H_{10} \rightarrow C_1 + C_3^=$	3.7	4.5
C ₄ -2	$C_4H_{10} \rightarrow C_2 + C_2^=$	3.6	0
C ₄ -3	$C_4H_{10} \rightarrow H_2 + C_4^=$	2.7	4.0
C ₄ -4	$C_4^= \rightarrow 2 C_2^=$	0.1	0.1
$r_{Cracking}$		7.3	4.5
$r_{Dehydrog.}$		2.8	4.1
E_A Cracking		135	125
E_A Dehydrog.		115	100

Table 2.2 Conversion of *n*- and *i*-pentane on ZSM-5 at 773 K; Rates of Product Formation $\times 10^9$ [mol/gs mbar]; E_A [kJ/mol]

R. no.	Reaction	<i>n</i> -Pentane	<i>i</i> -Pentane
C ₅ -1	$C_5H_{12} \rightarrow C_1 + C_4^=$	9.4	17
C ₅ -2	$C_5H_{12} \rightarrow C_2 + C_3^=$	21	6.6
C ₅ -3	$C_5H_{12} \rightarrow C_3 + C_2^=$	7.2	0
C ₅ -4	$C_5H_{12} \rightarrow H_2 + C_5^=$	12.2	21
C ₅ -5	$C_5^= \rightarrow C_2^= + C_3^=$	9	12.5
$r_{Cracking}$		37.6	23.6
$r_{Dehydrog.}$		12.2	21
E_A Cracking		115	150
E_A Methane		115	155
E_A Ethane		115	130
E_A Dehydrog.		150	150

In order to determine the influence of olefins on the rates and product selectivity of *n*-butane conversion, small amounts of *i*-butene were added to the *n*-butane feed. The quantities added to the feed stream were increased linearly as the conversion was increased, and were in the range of the amount produced via dehydrogenation of *n*-butane. The selectivity of the products is compiled in Figure

2.7 for the cracking of *n*-butane on ZSM-5 at 803 K with and without addition of *i*-butene in the feed, respectively. The selectivity to the butene isomers increased from 15% to approximately 22% upon addition of *i*-butene to the feed. This level represents the amount of *i*-butene co-feed.

It was observed that the butene isomers were always close to thermodynamic equilibrium suggesting that isomerization of the olefins is much faster than all other surface processes involved in olefin *trans*-formation. The equilibrium selectivity was maintained during cofeeding of pure *i*-butene indicating that isomerization of the butenes is fast compared to desorption.

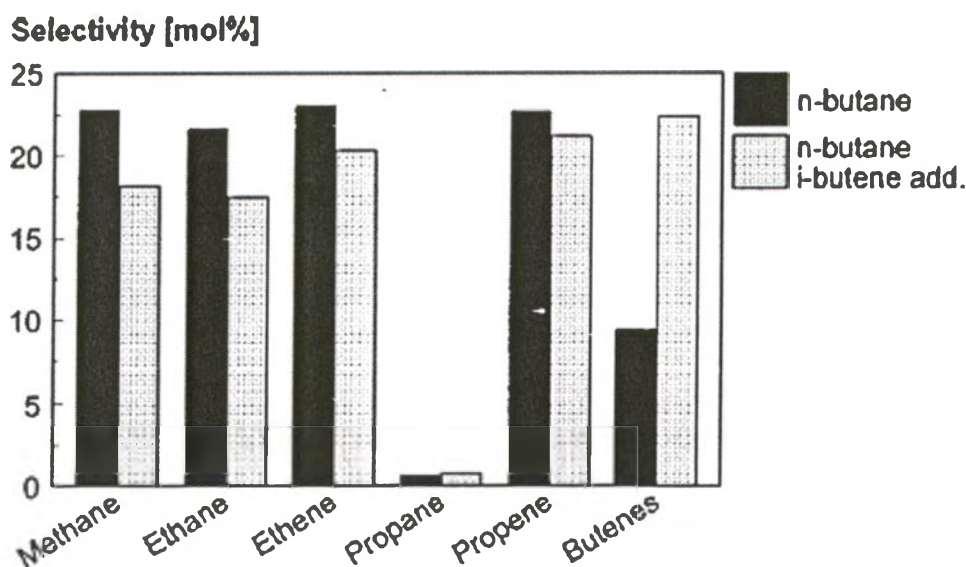


Figure 2.7 The influence of the addition of *i*-butene upon conversion of *n*-butane at 803 K.

At higher conversion levels, the formation of butene increased drastically. At this level of conversion, also the selectivity of the cracking products changed. The rate of production of ethylene and propylene was higher than that of methane and ethane.

2.4 Techniques of Zeolite Characterization

Information on the structural, chemical and catalytic characteristics of zeolite is essential for deriving relation between their chemical and physical properties for catalysts development. In general, the characterization of a zeolite has to provide information about (i) its structure and morphology, (ii) its chemical composition, (iii) its ability to sorp and retain molecules and, (iv) its ability to chemically convert these molecules. A major difficulty arises from the fact that the latter two surface chemical properties. The micropore surface of a zeolite is a periodic three-dimensional intrinsic property of the material and can not be straightforwardly probed with surface sensitive techniques. Therefore, many of the approaches chosen rely on bulk characterization techniques and focus on the description of the interaction of the zeolite with atomic or molecular probes.

Compared to many other analytical techniques, temperature programmed desorption (TPD) provides information which is closely related to the catalytic properties and the reactions in question. With the proper choice of probe molecule, it is frequently possible to relate TPD curves to the catalytic activity and selectivity of a particular catalyst and to determine the probable state of the catalyst under working conditions. The principle of TPD is to monitor the changes in the surface coverage (i.e., the rate of desorption) of probe molecules, which adsorbed on the sample as a function of the temperature by following the partial pressure of the probe molecules in the gas phase over the sample with, e.g., a mass spectrometer. The changes in the partial pressure are directly proportional to the desorption rate under the assumptions: (i) the rate of removal of the molecules from the gas phase over the sample is significantly higher than the desorption rate and (ii) the re-adsorption of the probe molecules does not occur. Note that both criteria are not (ideally) fulfilled for most zeolite samples.

One of the popular probe molecules is ammonia. The comparison of the NH_3 -TPD on mordenate, ZSM-5, SAPO-11 and ALPO-11, shown in Figure 2.8, indicate that the each sorption site of different acidity is reflected by maximum in the desorption rate. On all materials weakly acid sites are present, which result in the maximum at lower temperature (~ 373 K). On mordenite, ZSM-5 and SAPO-11

additionally strongly acid sites are present, the different in the position of the second desorption maximum indicate that the SiOHAl groups on ZSM-5 and mordenite are more strongly acidic than those on SAPO-11.

While the example discussed reflects the trends in the acidity for four samples, significant limitation exist for NH_3 -TPD. First, it can not differentiate between Bronsted and Lewis acid sites and second, the strong interaction of ammonia with the acid sites might result in a partial re-adsorption of NH_3 , which can cause a shift of the desorption maxima of up to 150 K, depending on the experimental conditions and the particle size of the sample. Therefore, it might be preferable to use reactive amines such as isopropylamine as probe molecules.

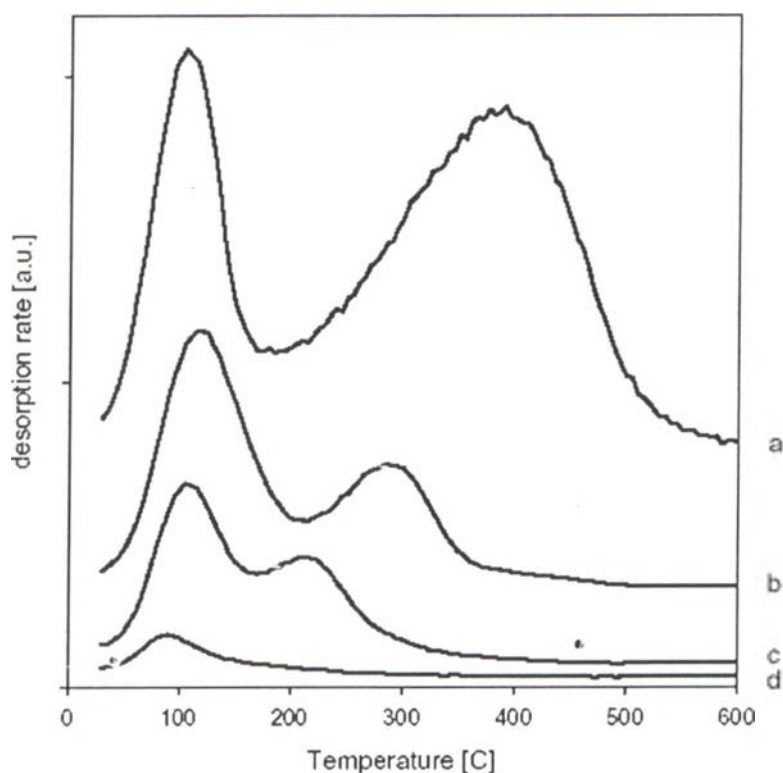


Figure 2.8 Comparison of the NH_3 -TPD on (a) Mordenite, (b) ZSM-5, (c) SAPO-11, and (d) ALPO-11.

During TPD, the desorption of propylene and ammonia results from the decomposition of the amine occurring only at Bronsted type acid sites, while the desorption of isopropylamine indicates the presence of Lewis type acids sites.

An alternative approach is to follow the desorption of NH_3 after ion exchanging the zeolite in a 1 molar NH_4OH solution for 24 h at room temperature. During the liquid phase ion exchange, the protons are replaced by NH_4^+ ions. These act as the charge balancing cations and, therefore, are only bound to the Bronsted type acid sites, while on Lewis type acids sites ammonia is not bound. Thus, during TPD only ammonia desorbing from Bronsted type acid sites is observed (Jentys and Lercher, 2001).

Gorte (1996) suggested that, the most useful probe molecules for measuring Bronsted acid site concentrations are simple alkyl amines, other than methylamine. These molecules are protonated to form ammonium ions by the acid sites and decompose to olefin and ammonia products. Methylamine is not a good probe molecule because it cannot decompose to an olefin product without at first going through a bimolecular reaction. Typical results for a TPD-TGA measurement of isopropylamine in ZSM-5 zeolite are shown in Figure 2.9. ZSM-5 is an ideal sample for demonstrating the technique because it contains one Bronsted acid site for each framework Al. In Figure 2.9, this 1:1 adsorption complex is clearly visible as the desorption of propylene and ammonia between 575 and 650 K.

TGA indicates that the amount desorbing from this region is close to the Al content of the sample. The amount of unreacted amine desorbing was shown at lower temperature, below 500 K. Finally, it should be noted that the amine desorption technique is extremely sensitive to very small Bronsted site concentrations, having been used to quantify site densities down to $2 \mu\text{mol/g}$, a site density equivalent to an ZSM-5 catalyst with a Si/Al ratio of $\sim 16,000$. Given the high sensitivity of this technique, and its ability to discriminate between Bronsted and Lewis acids sites, it would appear that TPD of amines should find wide application to the characterization of solid acid like zeolite.

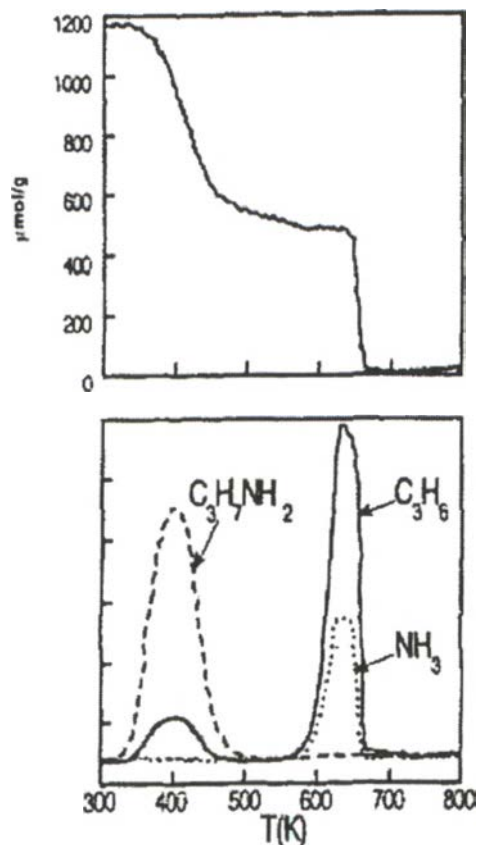


Figure 2.9 TPD-TGA curves for isopropylamine from ZSM-5 catalyst containing approximately 500 $\mu\text{mol/g}$ of Bronsted acid site. A mass spectrometer was used to determine the products, with signals for isopropylamine ($m/e = 30$ and 40), propylene ($m/e = 41$), and ammonia ($m/e = 17$).

The zeolite ZSM-5 is well known for its unique intersecting channel system. This channel system has an important bearing on the shape selective properties and the long life times of ZSM-5. The internal surface of ZSM-5 plays a major role in shape selective catalysis. The acid sites on the external surface will play a greater role in the reaction of large molecules than in the reaction of molecules that readily diffuse through the channels, as larger molecules have greater diffusion resistances. Even though the number of acid sites on the external surface is only approximately 1% of the total number of acid sites, depending on the crystal size, these easily accessible, non-shape selective acid sites may provide a high turnover rate for non-

shape selective reactions. In addition, the smaller aromatic molecules formed in the channel of ZSM-5 can diffuse out of the channels with relative ease due to the intersecting channel system of this zeolite. However, when coke formation on the external surface becomes dominant, the poly-aromatic molecules on the external surface block access to the channels. This coverage of the external surface which is the main cause of the deactivation of ZSM-5. The deposition of coke on/in zeolite catalysts has been extensively investigated. Various techniques have been employed to characterize the coke species on the catalyst, e.g., IR, MS, conventional Raman spectroscopy, NMR. Despite many attempts to elucidate the formation and the structure of the coke deposited on catalysts, this matter is still not well understood. Recently developed ultraviolet (UV) Raman spectroscopy show great advantages over the conventional techniques for the characterization of coke deposits. This technique is possible to identify the type of coke species and the deactivation mechanism.

Xiong *et al.* (2000) presented the UV Raman spectra of coke species formed during the methanol conversion to propylene on ZSM-5 zeolites at various temperatures. The UV Raman spectra can definitely characterize the different coke species formed in zeolite under reaction conditions as shown in Figure 2.10.

From Figure 2.10-A, the band at 384 cm^{-1} is characteristic for ZSM-5, 1023 cm^{-1} is assigned to the C-O stretching vibration, and the band at 1467 cm^{-1} is a deformation mode of the CH_3 group. The two bands at 2849 and 2954 cm^{-1} can be attributed to symmetric and asymmetric stretching vibrations of C-H group. The band of adsorbed methanol disappear upon raising the temperature to 523 K (Figure 2.10-B) meanwhile the new bands are produced. The band at 1392 cm^{-1} is broad and actually composed of several components, indicating that there are several kinds of adsorbed species formed on the surface. The band at 1624 cm^{-1} is attributed to the C=C stretching vibration of olefin species. Figure 2.10-C and D is the spectra recorded after a reaction at 773 K for 1 h and 2 h, respectively. Compared to Figure 2.10-B, the band at 1624 cm^{-1} shifts to lower wave numbers, and the C-H vibrational bands vanish. This suggestion that dehydrogenation and oligomerization of the adsorbed species take place at high temperature, i.e., some aromatic or alkyaromatic species are formed. The coke species formed on ZSM-5 are mainly olefin and

aromatic species. Figure 2.10-E shows that most of the coke species deposited in ZSM-5 can be removed by an oxidation treatment with O₂ at 773 K for 1 h. But a tiny band at 1623 cm⁻¹ due to coke species is still detected ever after the treatment indicating that some residual coke species still exists.

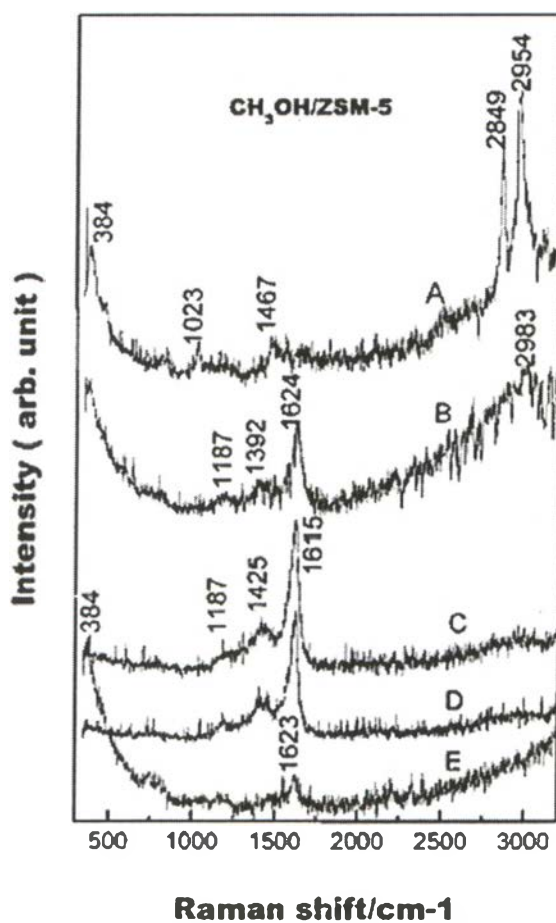


Figure 2.10 UV Raman spectra recorded during CH₃OH conversion on ZSM-5: (A) adsorption of CH₃OH on ZSM-5 for 30 min at room temperature; (B) at 523 K for 30 min; (C) at 773 K for 1 h; (D) for 2 h and, (E) pure O₂ flow at 773K for 1 h.