CHAPTER 3

LITERATURE SURVEY

Many studies on the hydroisomerization of paraffinic hydrocarbons over dual-function catalysts have been done extensively. These catalysts generally consist of noble metals deposited on an acidic support such as silica-alumina. The properties of these catalysts depend strongly on the state and dispersion of a metal component. Therefore as soon as crystalline aluminosilicates (zeolites) were synthesized and became available, their specific properties (ion exchangeability, high adsorption capacity, crystalline structure with regular pores of molecular size) were utilized to prepare catalysts containing highly dispersed metals, to show molecular-sieve selectivity, and to develop polyfunctional action.

Voorhies and Bryant (1968) studied the hydroisomerization of n-pentane over a zeolite catalyst. They reported that the most active zeolite hydroisomerization catalyst found during the course of a series of experiments was palladium impregnated hydrogen-mordenite. The high activity of hydrogen-mordenite catalyst was also reported by researchers of the Shell Oil Company. Typical conditions used in this study are 550^OF, 450 lb/in^2 gauge, 8 grams of n-pentane fed/hour/gram of catalyst, and a hydrogen/pentane molar ratio of 3.4. Process-variable studies have shown that neither gas to particle

mass transfer, intraparticle (macro-pore)diffusion, nor the chemical reactions at the palladium sites are rate limiting. The data can be correlated by a mathematical model based on the assumptions that a first-order, reversible isomerization reaction on the mordenite acidic sites is rate-controlling, and the apparent rate constant is an Arrhenius function of the temperature of the system. The pressure dependency of the reaction rate constant is consistent with a dual-site mechanism and the Langmuir adsorption isotherms.

Beecher and Voorhies (1969) reported that a synthetic hydrogen-mordenite catalyst, with and without a dispersed noble metal, had the same very high hexane isomerization activity. This unique crystalline zeolite, without metal, was investigated by using the five isomeric hexanes to develop a kinetic model. Other paraffins were tested, and for n-pentane isomerization the nonmetal hydrogen-mordenite was more active than the metal-containing hydrogen-mordenite. But for n-heptane isomerization the nonmetal hydrogen-mordenite was essentially inactive while the metal-containing mordenite showed excellent isomerization and hydrocracking activity. Process-variable studies were made with n-hexane over synthetic hydrogen-mordenite by testing at various space velocities, temperatures, and pressures. The data obtained at various space velocities were correlated by using a first-order, reversible isomerization reaction model. The calculated reaction rate constants fitted an Arrhenius function of temperature with an apparent activation energy of 24.4 kcal.per mole. The effect of pressure on

the reaction rate constant was again consistent with the dual-site catalytic mechanism and the Langmuir adsorption isotherms.

Bolton and Lanewala (1970) investigated a mechanism for the isomerization of the hexanes using zeolite catalysts. The isomerization of the hexane isomers was studied at low conversion levels using a palladium-loaded zeolite catalyst. The primary products derived from the individual hexane isomers could not be explained in terms of an intramolecular rearrangement of a carbonium ion intermediate. It was observed that isomerization was invariably accompanied by hydrocracking, but the hydrocracked products were not consistent with a simple cleavage of the hexane molecules. A bimolecular mechanism is proposed which satisfactorily explains both the observed products from the isomerization and hydrocracking reactions as well as the presence of heptanes in the product.

Hosten and Froment (1971) studied the isomerization of n-pentane on a commercial reforming catalyst (Pt/Al_2O_3) in an isothermal, bench-scale, fixed-bed reactor. The influence of total pressure, molar ratio of hydrogen/hydrocarbon, chlorine content in the feed, and space time was investigated in the temperature range of 375° to 425^OC. Reaction rate equations of the Hougen-Watson type were derived on the basis of the generally accepted mechanism for skeletal isomerizations. Discrimination among rival models was based upon significance tests for the overall regression and for each parameter separately. The experimental data were treated by both the

differential and the integral method of kinetic analysis. Linear and nonlinear least squares techniques were used in the parameter estimation.

Sakai et al.(1975)investigated kinetically the isomerization of heptane isomers,namely, n-heptane, 2- and 3-methylhexane, 3-ethyl pentane, and 2,3- and 2,4-dimethylpentane over a palladium-zeolite catalyst in the presence of hydrogen at 280-350°C. First-order rate constants of 11 reaction paths were given along with their activation energies and pre-exponential factors. The reaction scheme network including 22 isomerization steps among 9 isomers was constructed through the detailed analysis of primary and secondary reaction products from the individual isomers. Finally, several proposed isomerization mechanisms were examined on the basis of the obtained experimental results.

Saito and Iwasaki (1976) studied the isomerization of pentanes on platinum/rare earths-hydrogen-zeolite Y catalysts. This reaction was carried out in the presence of H_2 in a flow system at 1-50 atm and 270-330°C, and the catalyst was prepared by ion exchange. They have found that the isomerization of n-pentane to isopentane and that of isopentane to n-pentane were accompanied by disproportionation to hexane and butane isomers, hydrogenolysis to lower molecular weight paraffins, and isomerization to neopentane.

Braun, Fetting, and Schoeneberger (1977) reported that Pt/Ca-Y zeolite, Pd/Ca-Y zeolite, Pt/H-mordenite, and Pd/H-mordenite were the most active catalysts for hexane and pentane isomerization. Re-, Ir-, and Ni-loaded catalysts were less active. Kinetic studies showed that intraparticle mass transfer limitations in the secondary pore system were significant for Pt/Ca-Y zeolite, but not for Pt/H-mordenite.

Chick, Katzer, and Gates (1977) reported that the rate of cracking of hexane on Pd/H-mordenite at H_2 partial pressure 1 atm and 250°C decreased as the Pd content was increased, the rate of isomerization increased with increasing Pd content. The rate of catalyst deactivation increased with the rate of cracking.

Ribeiro et al. (1980) studied influence of platinum content on the catalytic activity of Pt/H-Y and Pt/H-M zeolites. They found that at low platinum contents, the effect of platinum on the catalytic activity of Pt/H-Y and Pt/H-M was beneficial: platinum slowed coke formation, and the formation and hydrogenolysis of coke precursors on the metal were negligible. At higher platinum levels, this beneficial effect was counterbalanced by the formation of coke orginating from the metal. The test reaction used was hydroisomerization of hexane.

Aodul-Gheit et al. (1982) studied the effect of promoting gamma-alumina before and after calcination at 1130 K and silica-alumina with 0.35%(w/w) Pt and/or 3.87%(w/w) Cl upon the selectivity

of n-heptane isomerization in a high pressure continuous flow reactor. They have found that chlorination of Pt on γ-alumina increased its catalytic activity but decreased its isomerization selectivity, whereas chlorination of Pt on γ-alumina calcined at 1130 K enhanced both activity and selectivity. Pt on silica-alumina was the most active but the least selective among catalyst containing Pt plus Cl. The larger the surface area of a support, the larger the dispersion of Pt in it. Pt dispersion and distribution on the support increased markedly if impregnation was associated with chlorination. The isomerization selectivity of a catalyst did not appear to depend on dispersion of platinum, whereas hydrocracking increased as dispersion increased.

Ribeiro, Marcilly, and Guisnet (1982) studied the hydroisomerization of n-hexane on platinum zeolites to compare between the reaction mechanisms on platinum/Y-zeolite and on platinum/mordenite. The transformation of n-hexane was carried out under hydrogen pressure, on platinum/mordenite and platinum/Y-zeolite with platinum areas ranging from 10-15 $m^2 \, g^{-1}$. For both series, as can be expected from the conventional bifunctional process, the isomerization activity was proportional to the platinum area for small platinum areas and almost independent of it for large platinum areas. However, the primary products of n-hexane and 3-methylpentane isomerization were notably different: the selectivity of platinum/Y-zeolite with the platinum area equal to or more than 0.5 $m^2 \, g^{-1}$ was typical of a bifunctional reaction with, as limiting step, the skeletal isomerization of intermediate olefins; that of platinum/mordenite, even

with a platinum area equal to 15 $m^2 g^{-1}$, remained intermediate between those of platinum-free zeolites and large platinum area Y catalysts. These differences were clearly related to the higher activity of platinum/mordenite, to its lower hydrogenation activity as well as to diffusional limitations in the practically unidimensional porous structure of mordenite.

Spivey and Bryant (1982) investigated the hydroisomerization of n-C_5 and n-C_6 mixtures on a Pt/H-mordenite and a Pd/H-faujasite catalysts. A different type of anomalous behavior was observed on each catalyst in the conversion of mixtures relative to the conversion of pure components. Statistical analysis of various Langmuir-Hinshelwood type models for the hydroisomerization rate constant show that this behavior could be related to the adsorption parameters of each system.

Weitkamp (1982) investigated the isomerization of long-chain n-alkanes on a Pt/Ca-Y zeolite catalyst. In this study the pure n-alkanes with 6 to 15 carbon atoms were isomerized on a Pt/Ca-Y zeolite catalyst in the presence of hydrogen. A detailed analysis of the i-alkanes formed was achieved by capillary GLC. Up to ca. 40% conversion, isomerization was virtually free from hydrocracking, but at elevated conversion severe hydrocracking occurred. At low conversion monobranched i-alkanes, i.e., methyl, ethyl, propyl, and butyl isomers, were formed exclusively. Dimethyl isomers were formed in consecutive reactions. The rate of formation of 2-methyl isomers was

surprisingly low. This effect is shown to be consistent with a branching mechanism via protonated cyclopropanes while it cannot be explained by a classical mechanism via alkyl and hydride shifts.

El-kady, Menoufy, and Hassan (1983a) studied the isomerization of n-heptane over platinum catalysts supported on silica-alumina. They have found that the catalyst containing 0.4% Pt was the most active and selective catalyst for n-heptane isomerization. The increase in Pt content on the catalyst decreased the number of the isomerization sites and increased the olefin content on the catalyst surface which led to side reactions, such as cracking.

El-Kady, Menoufy, and Hassan (1983b) reported that both the reaction temperature and total hydrogen pressure affected the hydroisomerization activity of the catalyst to different extents. While the isomerization of n-heptane attained a maximum at 375 ^{O}C, it dropped sharply at higher temperatures. In addition, the isomerization activity of the platinum catalyst increased as the total pressure increased. The rate of n-heptane hydroconversion depended on the partial pressures of H_2 and n-heptane. At lower H_2 partial pressure, the reaction rate increased in proportion to the partial pressure of n-heptane. As the partial H_2 pressure increased, the reaction decreased. A total hydrogen pressure and reaction temperature of 45 atm and 375 ^{O}C, respectively, were selected as the most favorable for n-heptane isomerization.

El-Kady, Menoufy, and Hassan (1983c) studied the reaction mechanism and reaction order of n-heptane isomerization. They have found that the mechanism of hydroisomerization went through an olefin intermediate formation on the hydrogenation-dehydrogenation sites. The concentration of this olefin depended on the initial partial pressures of both n-heptane and H_2. The reaction was considered to be a first order one having an activation energy equal to 24.3 kcal.per mole.

Ribeiro (1984) investigated the behavior of the catalysts Pt/HM and Pt/HY in the hydroisomerization of n-hexane and concluded that Pt/HM had a higher isomerizing activity and selectivity for the dimethylbutanes of high octane number. These properties could explain the preference that was given to the use of Pt/H-mordenite in the Hysomer Shell process.

Giannetto, Perot, and Guisnet (1986) studied the transformation of n-heptane at 250°C, 1 atm, and H_2/heptane pressure ratio = 9 on a series of Pt/H-Y catalysts containing from 0.1 to 1.5 wt% platinum and having Si/Al atomic ratios of 3, 9, or 35. The activities, stabilities, and selectivities of the catalysts were clearly governed by the number of their acid sites (n_A) and hydrogenating sites (n_{Pt}). n_A is defined here as the number of acid sites on which the adsorption heat of NH_3 is greater than 100 kJ mol^{-1} and n_{Pt} as the number of accessible platinum atoms. For $n_A/n_{Pt} < 10$ (i.e., with catalysts with about 1 wt% Pt and Si/Al atomic ratio of 9 or 35) the

formation of monobranched, bibranched, and tribranched isomers and cracking products was a step by step process. Such catalysts presented the best possible hydroisomerization selectivity, the cracking products appearing only at conversion rates of over 50% and the yield in isomers reaching 65% for a total conversion rate of 75-80%. Thus they could be considered as "ideal hydroisomerization catalysts".

Mahos, Nakamura, and Niiyama (1986) investigated the isomerization of n-heptane on a series of platinum-hydrogen mordenite catalysts of various silica-alumina ratios over a wide range of operating conditions. Based on experimental results and simple statistical considerations, a classical mechanism appeared more likely than the protonated cyclopropane one. An apparently direct formation of dibranched isomers and a non-zero intercept of the reaction rate vs n-heptane partial pressure plot could be interpreted in view of a "modified" bifunctional mechanism.

Nasution (1986) studied the hydroisomerization of cyclohexane and n-heptane using Ni-Mo and Ni-W catalysts supported on silica-alumina. An experiment has been carried out to study the influence of hydrogenating site of bi-functional and of n-butylamine on the hydroisomerization of cyclohexane and n-heptane. The observed data show that a high activity of hydrogenating site of of bi-functional catalyst, tends to increase the catalytic activity of hydroisomerization reaction and n-butylamine acts as catalyst poison, which reduces the isomerized products.

Shil and Bhatia (1986) studied the isomerization of n-hexane in the presence of excess hydrogen at 643 K in a flow reactor over Ni/Ca-Y (nickel on calcium Y type faujasite) and Ni/H-M (nickel on hydrogen-mordenite) catalysts. Catalysts were prepared by ion exchange, and nickel concentration was varied from 1 to 5 wt%. Nickel crystallite size distribution was affected by the degree of nickel exchange and the type of parent cation present in zeolite. Ni/Ca-Y containing 1.86 wt% nickel exhibited maximum isomerization activity and selectivity. Ni/H-M catalysts showed lower conversion and activity compared to Ni/Ca-Y catalysts because of higher acidity and the presence of large-sized nickel crystallites. The average nickel crystallite size was calculated by using electron microscopy and X-ray line-broadening techniques. The isomerization activity of nickel over the zeolites was probably due to the interaction of small nickel crystallites and the polarizing entities of the intra-zeolitic matrix.

Zou (1986) investigated the preparation and properties of a series of solid super acids, Fe_2O_3/SO_4^{2-}. The Fe_2O_3/SO_4^{2-} catalyst, prepared from $Fe(NO_3)_3$ and H_2SO_4, had a strong acidity. The isomerization of heptane was studied at 25°C. After 0.5 hour, conversion of heptane was 75%.

Aboul-Gheit et al. (1987) investigated the hydroconversion of n-heptane in a high-pressure continuous plug-flow reactor system using catalysts containing hydrogen mordenite (HM): Pt/H-M, Re/H-M, PtRe/H-M and PtTh/H-M. Pt/H-M was found most selective for n-heptane

isomerization, whereas PtRe/H-M and PtTh/H-M possessed comparable intrinsic isomerization activities and excellent central hydrocracking selectivities. PtTh/H-M gave the highest $i-C_4/n-C_4$ ratio. The Thiele modulus and effectiveness factor were calculated as diffusion parameters over the temperature range studied (250°-400^oC) for all catalysts. A correlation of these parameters with catalytic behaviour shed some light on the migration of metals during catalyst preparation. Platinum appeared to migrate away from the pore mouth to the pore interior via promotion with either rhenium or thorium.

Anderson, Burch, and Cairns (1987) investigated the hydrogenolysis and skeletal rearrangement reactions of n-hexane on Pt catalysts supported on silica and titania. The results showed that the product distribution was dependent on the choice of support but that Pt/titania catalysts in the "normal" state were similar to Pt/titania catalysts in the "strong metal-support interaction"(SMSI) state. It was observed that in the SMSI state, when more than 99% of the Pt was inaccessible to hydrogen, the activity was only slightly reduced. Surprisingly, the selectivity for hydrogenolysis versus skeletal isomerization was almost the same in normal and in SMSI catalysts. The results provided evidence that the same active center was involved in both the hydrogenolysis and the skeletal rearrangement reactions, and do not support the contention that hydrogenolysis required a larger ensemble of Pt atoms than skeletal rearrangement. The results were interpreted in terms of an active center consisting of a single Pt atom located in the planes

of the small Pt crystallites. The precise selectivity observed might depend on the local environment of the Pt atom during the sojourn of the n-hexane molecule on the active center.

Rodriguez-Reinoso et al. (1987) investigated the isomerization and hydrogenolysis of n-butane over platinum catalysts supported on activated carbons. A series of carbon-supported Pt catalysts prepared using different precursors and methods and covering a wide range of metal dispersion (0.08-0.51) were studied in the reaction of n-butane with hydrogen. These were basically hydrogenolysis catalysts in which the splitting of the terminal C-C bond predominated. The hydrogenolysis of n-butane was a reaction sensitive to the structure of the catalysts, whereas this was not the case for isomerization. The selectivity for hydrogenolysis increased with decreasing mean Pt particle size. The apparent activation energies for the two reactions (larger for isomerization) were independent of particle size.

Urbanovich, Komarov, and Shirinskaya (1987) reported that Sn-modified Pt/Al_2O_3-zeolite catalysts were very active and selective for hexane isomerization, due to an optimum ratio of dehydrogenation and acidic properties. Pt catalysts modified with Ce, Sn, and B were even more selective.

Vazquez, Escardino, and Corma (1987) studied the hydrocracking and hydroisomerization of n-heptane on a series of Ni-Mo/HY zeolite catalysts at 300-350°C reaction temperature and 25 kg.cm^{-2}

of total pressure. The product distribution in the isomerized fraction and in the cracked fraction has been discussed from the point of view of a typical bifunctional mechanism. It has been found that the Ni/(Ni+Mo) atomic ratio of the catalyst has a strong influence on the activity, and a maximum is found for a Ni/(Ni+Mo)= 0.5. The selectivity of hydroisomerization, hydrocracking, and hydrogenolysis also depends on the Ni/(Ni+Mo) ratio and any of them could be maximized by an adequate combination of the hydrogenating and the acid function.

Abbot and Wojciechowski (1988) studied catalytic reactions of n-hexane on H-Y zeolite at 500°C. An examination of initial product selectivities showed that monomolecular processes were dominant. These included cracking to produce either C_3+C_3 or C_2+C_4 and skeletal isomerization. Bimolecular cracking processes accounted for only 5% of the total initial selectivity. Methane was identified as an initial reaction product, but its formation was due to concurrent thermal processes. Molecular hydrogen was observed only as a secondary product. The conversion of n-hexane was fitted by a kinetic model previously applied to various n-alkanes in the range C_8-C_{16}. In all these cases, the model shows that adsorption of reactants was strongly inhibited by product olefins. Addition of small amounts of olefins to the n-hexane feed had no accelerating effect, which did not confirm results of previous studies.

Chen, Martin, and John (1988) reported that the hydroisomerization of hexane to methylpentanes and dimethylbutanes was inhibited by the presence of aromatics (C_6H_6, p-xylene, and mesitylene) in the feed, probably because of blockage of the pores in the zeolite catalyst.

Giannetto, Alvarez, and Guisnet (1988) studied the transformation of n-heptane at 250°C, 1 atm, and H_2/heptane pressure ratio= 9 on a series of Pt/H-offretite catalysts(Pt/HOFF) containing from 0.06 to 1.25 wt% platinum with a dispersion equal to or higher than 90%. Adsorption measurement showed that platinum did not modify the crystallinity of offretite but caused a blockage of some of the large channels. This explained why platinum had only a slight positive effect on the rate of n-heptane transformation. The reaction products can be divided in two families: (i)linear cracking products formed in the gmelinite cages and in the large channels inaccessible to branched hydrocarbons because of the platinum (their distributions, 55-60 mol% C_3, 30-35% n-C_4, and 5-10% n-C_5) can be explained by cracking and alkylation reactions whose linear products alone could diffuse in the gas phase); (ii) isomers and isobutane plus an equimolar amount of propane formed through the classical bifunctional mechanism in the unobstructed large channels.

Mahos, Nakamura, and Niiyama (1988) studied the effect of heptane isomer cofeeding on heptane isomerization over a platinum-loaded mordenite catalyst. A monobranched (3-methylhexane, 3MH), a

dibranched (2,3–dimethylpentane, 23DMP), and a multibranched (2,2,3–trimethylbutane, 223TMB) heptane isomers were separately added to heptane feed, and the reaction mixture was converted on a platinum–loaded hydrogen–mordenite catalyst. The cofeeders were chosen so as to represent typical isomerized products, at concentrations close to those obtained in the conversion of a pure feed. The reaction of heptane occurred free of any diffusion limitations. The presence of 3MH or 223TMB did not affect the reaction, whereas a multiple effect was obtained by 23DMP addition. In the latter case, the reaction was found to proceed autocatalytically. The results were interpreted in view of a mass–transport mechanism and the ease of the cofeeder for carbocation formation. In light of these considerations, the effect of contact time on heptane conversion was discussed, and potential practical applications were delineated.