



CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Octane Number

Octane number provides an indication of the ability of a gasoline to resist knocking as it burns in the engine. There are two test methods to measure the octane number of a gasoline. These methods use different engine conditions, mainly the intake temperature and the engine speed. The Research Octane Number (RON) method represents engine operations typical of mild driving, without consistent heavy loads on the engine, while the Motor Octane Number (MON) method represents severe, sustained high speed, and high load driving. The pump octane number is the average between the two methods $(RON+MON)/2$. For most gasoline fuels, RON is higher than MON. The difference between the two $(RON-MON)$ is called "Sensitivity". Modern fuels are expected to have low sensitivities. Therefore, refiners are concerned about keeping both high RON and high MON.

2.2 Strategies for the Improvement of Octane Number

As illustrated in Figure 2.1, a direct ring opening (RO) of the C₆-ring is not desirable because all of the resulting RO products have low octane number. By contrast, some ring contraction (RC) products (dimethylcyclopentanes DMCPs) and some secondary ring opening products of the DMCPs (see Figure 2.2) have relatively high octane number and would be a desirable product in gasoline. In general, the RC products have higher RON, while the RO products trend to have higher MON.

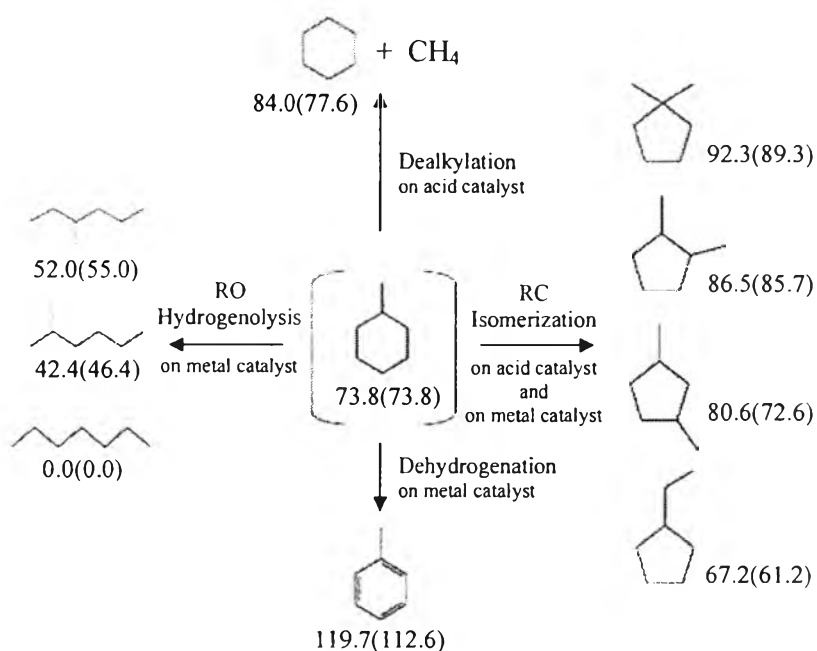


Figure 2.1 Possible products from methylcyclohexane and their research octane number (RON) and their motor octane number (MON). (Santikunaporn *et al.*, 2006)

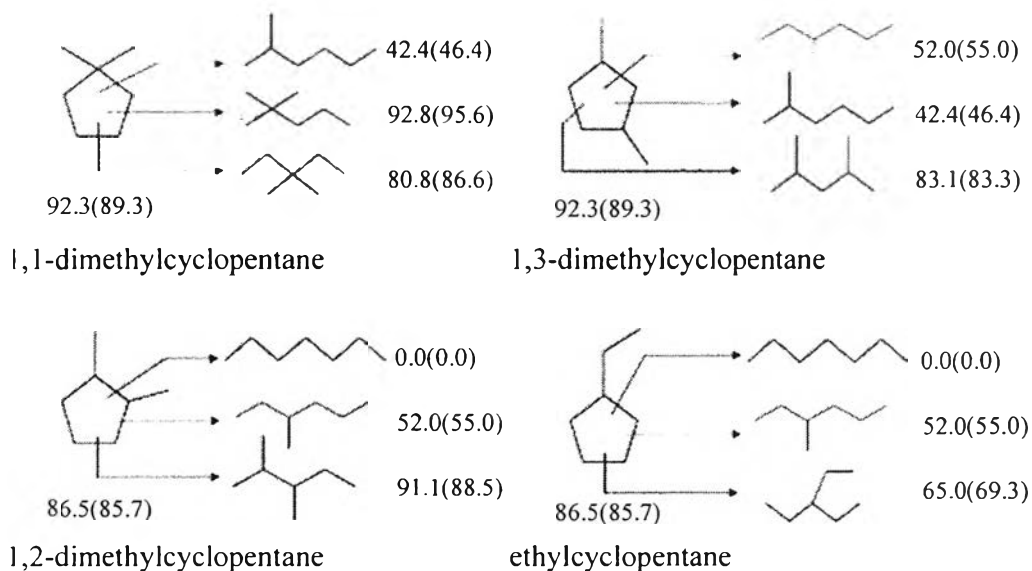


Figure 2.2 Hydrogenolysis on metal catalysts: product from ring opening reactions of C₇ ring contraction compounds and their corresponding research octane number and motor octane number. (Santikunaporn *et al.*, 2006)

2.3 Methylcyclohexane Ring-Contraction

Solid acid catalysts are extensively used by the petroleum industry for the production of motor fuels and a wide range of petrochemicals. Since a large number of hydrocarbon conversion reactions are involved, it is important to establish reliable test protocols that correlate the physical and compositional properties of solid acids with the acidity requirements of the specific reaction being catalyzed. Well-designed probe reactions can identify subtle differences in both metal and acid functions, aid process condition optimization, and provide insight into catalyst activation, deactivation, and regeneration processes. McVicker *et al.* (2005) have described the use of a simple solid acid promoted hydrocarbon conversion reaction, namely, ring-contraction of methylcyclohexane (MCH) to a mixture of ethylcyclopentane (ECP) and dimethylcyclopentane (DMCP) isomers, as a probe reaction for characterizing the acidity parameters of a wide range of platinum-loaded solid acids. MCH ring-contraction rates and product patterns can be used to appraise not only the relative number and relative strength of acid sites in both amorphous and crystalline solid acids, but can additionally evaluate subtle shape selectivity differences in zeolites and microporous materials. Figure 2.3 summarizes the relationships observed among MCH conversions and product selectivities and the three key acidity parameters attributed to solid acids.

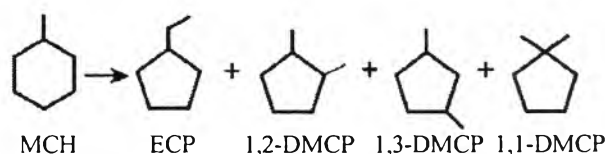


Figure 2.3 Methylcyclohexane ring-contraction isomers. (McVicker *et al.*, 2005)

First, the relative number of effective acid sites can be ascertained by comparing overall ring-contraction activities under a given set of reaction conditions. For example, if catalyst “A” under a specific set of reaction conditions selectively converted 50% of MCH to ring-contraction products, while catalyst “B” under identical conditions selectively converted only 25% of MCH catalyst it is reasonable

to suggest that catalyst "A" contains twice as many effective acid sites as catalyst "B". Second, relative strengths of solid acids can be estimated by comparing selectivity differences shown toward a particular ring-contraction product. At low MCH conversion levels (10-20%) weaker acid strength solid acids typically exhibit >70% selectivities toward the nonbranching ECP isomer while stronger acid strength solid acids produce larger quantities (50-70%) of the doubly branched DMCP isomers. The relative ease of forming ECP is rationalized as resulting from the facile rearrangement of a tertiary carbocation. Formation of DMCP isomers, which demands stronger acid sites and furthermore cannot be formed by a tertiary carbocation route, is assumed to occur via parallel, nonclassical carbocation (ionic) routes utilizing protonated cyclopropane transition states (Figure 2.4). Postulated carbocation transition states for the various MCH ring-contraction products are listed in the order of decreasing stabilities.

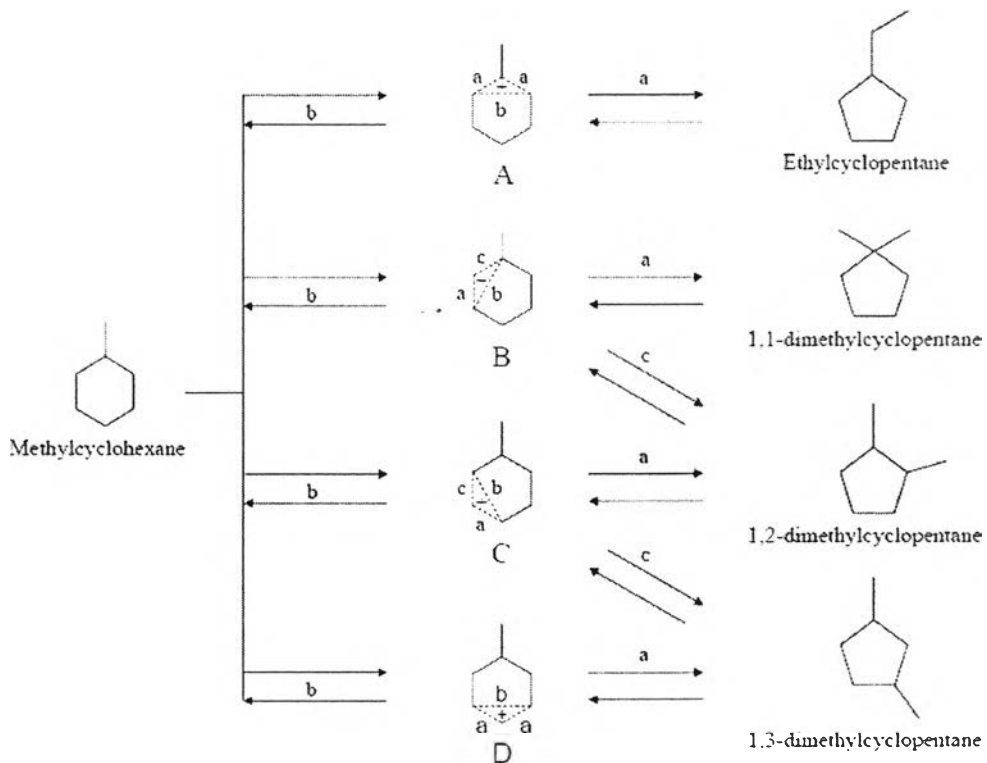


Figure 2.4 Carbocation chemistry for the ring-contraction reactions.

Increasing acid strength should enhance the extent to which the individual DMCP isomer concentrations approach equilibrium. Based upon this postulate, ECP selectivity, at a given MCH conversion, can be used as a relative measure of acid strength. Last, the *trans*-1,2-DMCP/*trans*-1,3-DMCP isomer ratio was found to vary between 0.1 and 2.4 over a large number of representative solid acids. The substantial variability exhibited by this ratio is consistent with a product shape selectivity dependence resulting from differences in the transport capabilities of the 1,2- and 1,3-DMCP isomers. The less bulky 1,3-DMCP isomer would likely experience a smaller transport inhibition than the bulkier 1,2-DMCP isomer through the intracrystalline channels and pore mouths of 10- and 12-ring zeolites and microporous materials. Ten-ring zeolitic and microporous materials typically display *trans*-1,2-DMCP/*trans*-1,3-DMCP ratios in the 0.1 to 0.5 range, while larger pore size 12-ring zeolites and amorphous solid acids exhibit much higher values for this isomer ratio, ranging from 1.2 to 2.4. Over the rather broad temperature range utilized throughout these studies the equilibrium value for the *trans*-1,2-DMCP/*trans*-1,3-DMCP ratio remains near 1.8-1.9 (see Figure 2.5).

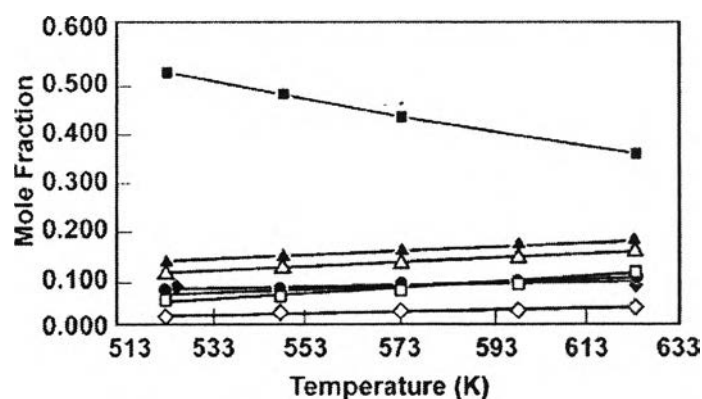


Figure 2.5 Equilibrium distributions of MCH ring-contraction products. Symbol codes: ■ MCH, □ ECP, ◆ 1,1-DMCP, ◇ *cis*-1,2-DMCP, ▲ *trans*-1,2-DMCP, △ *cis*-1,3-DMCP, and ● *trans*-1,3-DMCP. (McVicker *et al.*, 2005)

2.4 Ring-Opening Catalysis

2.4.1 Cracking on Solid Acid Catalysts

Selective ring opening of naphthenes with minimum cleavage of side chains is very complex and represents a challenge to catalyst researchers. It is known that ring opening can be catalyzed by the acid sites, e.g. the Brønsted sites, via carbenium intermediates (Galperin *et al.*, 2003). The reaction is initiated by protolytic cracking, accompanied by protolytic dehydrogenation, hydride transfer, skeletal isomerization, β -scission and alkylation, as in the cases of cracking of aliphatics over acid catalysts. The latter mechanisms have been extensively studied (Cumming and Wojciechowski, 1996). The cracking of endocyclic C–C bonds in cyclic hydrocarbons, however, is much slower than those of aliphatics, presumably because of a higher tendency of the alkenyl cation, formed by β -scission of a cycloalkyl cation, to recyclize, or because of a lower β -scission rate in cycloalkylcarbon ions caused by an unfavorable orientation of the p-orbital at the positively charged carbon atom and the β -bond to be broken (Figure 2.6). As a result, the overall reaction is predominated by isomerization and subsequent hydrocracking (β -scission) of side chains of cyclic hydrocarbons, particularly of those having substituents with more than five carbon atoms, leading to significant dealkylation of pendant substituents on the ring.

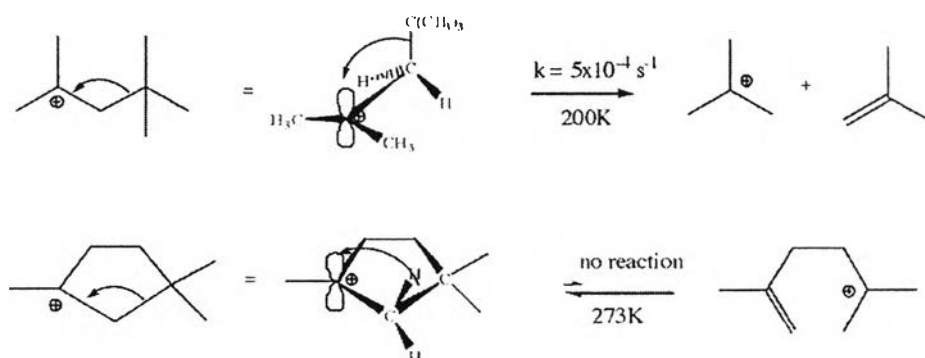


Figure 2.6 β -scission of linear and cyclic hydrocarbons. (Du *et al.*, 2005)

2.4.2 Hydrocracking on Bifunctional Catalysts

Starting in the 1950s, bifunctional catalysts consisting of highly dispersed metal particles for hydrogenation or dehydrogenation and an acidic support for cracking or isomerization were introduced in refining processes, such as catalytic reforming of naphtha, hydrotreating, hydrocracking and hydroisomerization (Marcilly, 2003). These processes improved fuel quality and at the same time avoided catalyst decay and the formation of coke deposits. Early studies by Mills *et al.*, (1953) and by Weisz and Swegler (1957) described the reactions over the bifunctional catalysts as proceeding over two distinct catalytic sites: the reactants are first converted into olefins on the metal site via hydrogenation/dehydrogenation reactions (Eq. (1)); then the formed olefins are protonated at the acid sites, leading to the formation of carbenium ions, which subsequently undergo skeletal isomerization, cracking or alkylation (Eq. (2)). The products are finally desorbed from the acid sites as olefins, which are hydrogenated on the metal sites in the presence of hydrogen (Eq. (3)).



It was later recognized that the reactions could also occur on one reaction site, owing to activated hydrogen species, i.e. spillover hydrogen (Roessner *et al.*, 1997). The metal co-catalyst provides spillover hydrogen, which migrates to the acid sites and saturates the carbenium intermediates. In other words, the acidic support cannot only initiate the formation of carbenium ions pyrolytically or by the addition of protons to olefins, but also hydrogenate carbenium ions with hydride ions

and promote their desorptions as the saturated products. In addition, the ring opening of naphthenes can also proceed on certain metal sites via direct hydrogenolysis of an endocyclic C–C bond (Galperin *et al.*, 2003), i.e. cleavage of a C–C bond with the addition of hydrogen. This issue will be discussed in detail further.

Overall, the activity and selectivity of ring opening on bifunctional catalysts are strongly dependent on the properties of the metal and support as well as on reaction conditions. These parameters include the type of metal, metal particle size, acidity of the support, pore size of the support, the interface length and strength balance between the metal and acid sites, working conditions, such as temperature, hydrogen pressure, etc. This has provided opportunities to devise catalysts for highly selective ring opening of naphthenic compounds in fuel without significant dealkylation of any pendant substituents on the ring.

2.4.3 Catalytic Ring Opening of Methylcyclohexane

To begin with, the salient mechanistic features of catalytic ring opening of cycloalkanes are briefly sketched (see Figure 2.7): On bifunctional catalysts, methylcyclohexane is dehydrogenated on metallic sites, and the resulting cycloalkenes are protonated to carbenium ions on acidic sites. Usually, skeletal isomerization into highly branched isomers occurs first, whereupon classical β -scission can proceed. Finally, (Weitkamp *et al.*, 1984) the diene formed is hydrogenated on a metal site (Figure 2.7, top). On monofunctional acidic catalysts, two different mechanisms can be operative (Hagg *et al.*, 1985): On the one hand, β -scission of classical carbenium ions is possible, but the latter can now only form through a bimolecular hydride transfer (Figure 2.7, bottom). On the other hand, methylcyclohexane can be directly protonated forming a nonclassical carbonium ion with a three-center, two-electron bond in the transition state (Haag - Dessau cracking, Figure 2.8).

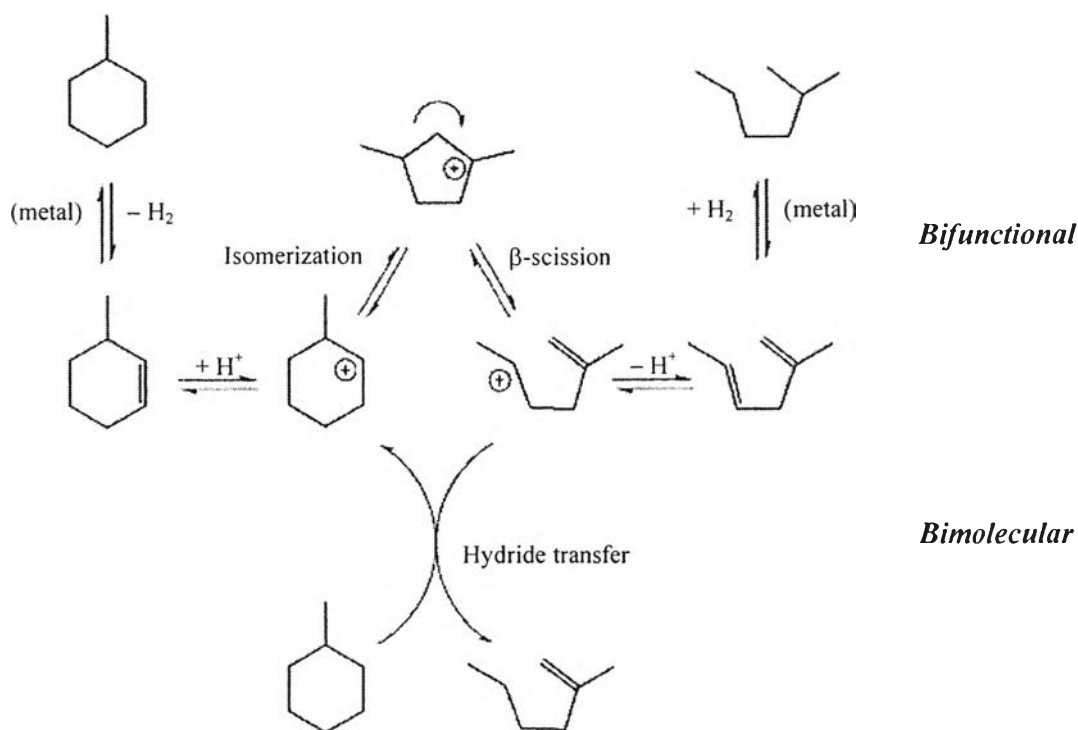


Figure 2.7 Mechanisms for ring opening of cycloalkanes: classical (bifunctional or bimolecular).

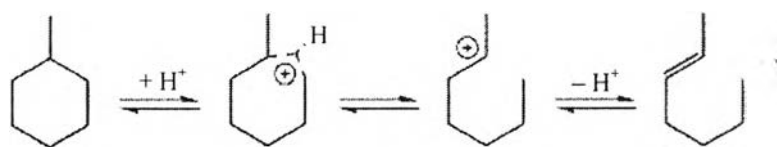


Figure 2.8 Mechanisms for ring opening of cycloalkanes: nonclassical cracking.

If ring opening is accompanied by secondary cracking steps, isoalkanes (no methane and ethane due to the instability of primary carbenium ions) will predominantly be formed in the first case due to the preceding isomerization, while n-alkanes (including methane and ethane) will be the dominant products in the second case. Under increased pressure of hydrogen, only saturated compounds and no alkenes are obtained in the product stream, even on the metal-free acidic catalysts. This can be accounted for by activation of hydrogen on the acid sites (Weitkamp *et al.*, 2000).

2.4.4. Hydrogen Spillover

The classical model for bifunctional catalysis Mills *et al.*, (1953) and by Weisz and Swegler (1957) envisaged the reaction in three steps (Eqs. (1)–(3)), involving a gas phase diffusion of olefinic intermediates between the two catalytic sites. The model successfully explained a number of experimental observations, but failed to account for the role of hydrogen and the synergy between the two catalyst components in controlling the selectivity and activity (Roessner *et al.*, 1997). The extension of the classical model by incorporating the hydrogen spillover concept allows a better interpretation of experimental results, including those that did not fit into the old theorem. The new model involves the formation of mobile hydrogen surface species, i.e. spilt-over hydrogen that allows the hydroconversion of the hydrocarbon at a certain distance from the metal so that all reaction steps can occur on one reaction site.

Spillover is now a well-known phenomenon in heterogeneous catalysis, involving the transport of active species adsorbed or formed on one surface onto another that does not adsorb or form the active species under the same conditions. Several small molecules have been known to exhibit spillover effects upon interactions with noble metals, including hydrogen, oxygen, nitrogen, carbon monoxide and organic species (Roland and Roessner, 1997). Hydrogen spillover plays an important role in petroleum processes, e.g. in hydrotreating, hydrocracking, hydrogenation and hydroisomerization.

The nature of the spilt-over hydrogen species has been discussed in the literature. Depending on the system studied, different species have been claimed, including H atoms, H ions, ion pairs, H₃ species and bound species. (Roland and Roessner, 1997) proposed a model that describes the spilt-over species as electron donors adsorbed on the surface, which corresponds to H atoms (occupied, weakly chemisorbed) or H⁺ ions (empty, strongly chemisorbed). Their ratio is determined by the chemical properties (e.g. the presence of Lewis and Brønsted acid sites) and the electronic properties (e.g. electron density) of the solid. In bifunctional catalysts, spilt-over hydrogen can donate an electron to the support to form a proton on a Brønsted site, and a hydride ion may form on a Lewis site in the process of charge balancing (Cumming and Wojciechowski, 1996). An olefin formed on the metal by

dehydrogenation can react with the proton on a Brønsted site to form a carbenium ion, which may then combine with the migrated hydride ion from a Lewis site to produce a saturated compound. Alternatively, the carbenium ion formed by addition of a proton to an olefin on a Brønsted site can migrate to a Lewis site where it reacts with a hydride ion.

The creation of catalytic active sites by spill-over hydrogen has been recognized and used in supported metal catalysts for hydrogenation (or dehydrogenation), hydrocracking and hydroisomerization. For instance, spillover of hydrogen from a metal under certain conditions can make the inert silica, or alumina, or carbon support active for hydrogenation of olefin or benzene. A number of studies showed that mechanical mixtures of supported metal catalyst and a support exhibited higher hydrogenation activities than the supported metal catalyst alone. The increased activities have been attributed to hydrogen spillover. Without activation by hydrogen spillover, neither silica nor alumina will adsorb hydrogen and both are inert for hydrogenation catalysis.

2.5 Selective Ring Opening of Single-Ring Compounds

2.5.1 Activity and Selectivity

When adsorbed on metal surface at certain conditions, hydrocarbon molecules undergo dehydrogenation/hydrogenation, skeletal isomerization and hydrogenolysis, including ring opening/cyclization, and ring contraction/enlargement. Certain noble metals, such as Pt, Pd, Ir, Ru and Rh have been found to be selectively active for the ring opening for cyclic hydrocarbons to the corresponding paraffins with the same carbon number. The activity and selectivity depend mainly on the metal catalysts, such as the type of metal, particle size, crystal morphology, etc. The ring opening of cyclic hydrocarbons on noble metals is highly sensitive to the catalyst structure.

The ring opening of methylcyclopentane (MCP) on supported metal catalysts has been extensively studied (Gault, 1981). The reaction produces *n*-hexane (*n*Hx), 2-methylpentane (2MP) and 3-methylpentane (3MP). The product distribution is dependent on the properties of the metal. Over supported Pt catalysts with small

particle sizes, e.g. low loading and highly dispersed Pt, the ring opening of MCP is non-selective (the rupture of endocyclic C–C bonds is statistical, producing 2MP, 3MP and *n*Hx in a ratio of 2MP:3MP:*n*Hx = 40:20:40 related to the number of bond types in the molecule) as illustrated in Figure 2.9. On the other hand, the ring opening of MCP on large metal particles and metal surfaces with low Miller index produces selectively 2MP and 3MP, but no *n*Hx. In some cases, the ring opening does not follow the “selective” or “non-selective” mechanism, instead producing unusually high amount of *n*Hx or 3MP relative to its statistical ratio. These “partially selective” mechanisms compete with the non-selective and selective mechanism, occurring on high loaded 10% Pt/Al₂O₃ at high-temperature (Gault, 1981), or Pt/zeolite (Arribas and Martinez, 2002).

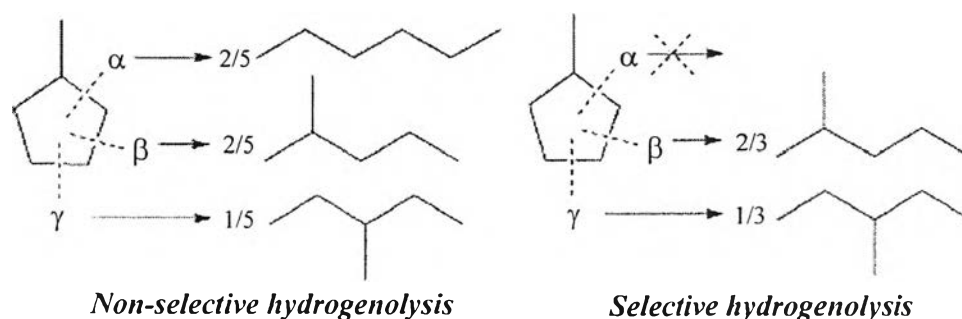


Figure 2.9 Non-selective and selective hydrogenolysis of methylcyclopentane.

The ring opening of MCP on Ir (Galperin *et al.*, 2003) and Rh (Teschner *et al.*, 2003), on the other hand, is less sensitive to the particle size of the metals in comparison with Pt catalysts. However, these metals exhibit higher activity and selectivity to open the C₅ ring in bissecondary positions (McVicker *et al.*, 2002). Other metal catalysts, such as Co, Ni, Ru and Os, show extensive hydrogenolysis, yielding a significant amount of fragments (Teschner *et al.*, 2003).

Generally, the ring-opening activities of alkylcyclopentanes on metal catalysts decrease with increased number of ring substituents (Zimmer and Paál 1989). This is especially the case for Ir, and to lesser extent Ru, Rh and Ni (McVicker *et al.*, 2002), all of which show a preference for cleaving unsubstituted ring C–C bonds. A significant decrease in activity was observed for cleaving

substituted ring C–C bonds over these metals. In comparison, Pt is better able to break substituted ring C–C bonds than Ir, Ru, Rh and Ni. However, the ring-opening rate over Pt catalysts is sensitive to the *cis*-/*trans*-isomer ratio, decreasing with increasing *trans*-isomer concentration. In other words, Pt requires a *cis*-substitution of isomers when breaking a tertiary–tertiary C–C ring bond.

The reaction conditions have also been found to affect the product distribution. Changes in selectivity and activity of MCP ring opening on supported Pt metal catalysts with hydrogen pressure have been reported (Zimmer and Paál 1989). Higher hydrogen pressures favor ring opening further from the substituents. The increase in hydrogen partial pressure leads to increased ring-opening activity on supported Pt catalysts at relatively low temperatures (<300°C). This reaches a maximum and thereafter shows a steady decline or a very broad plateau with further increase in hydrogen partial pressure. The hydrogen pressure at which the maximum activity is obtained is a function of the support. However, these volcano-type plots of ring-opening activity versus hydrogen pressure are independent of the support and the reduction temperature. The latter determines the particle size, morphology and structure of the metal particle on the support, and influences the activity. These results were attributed to the competitive adsorption of hydrogen and hydrocarbon on the metal surface. Increase in hydrogen pressure diminishes dehydrogenation activity, leading to an increase in the overall selectivity towards the ring-opening reaction.

Hydrogen pressure dependence on activity and selectivity of ring opening has also been observed over other transition metal catalysts (Teschner *et al.*, 2003). The relationships between the product formation rate and hydrogen pressure varies with catalytic systems, reflecting differences in reaction mechanism. Over Rh catalysts (Török *et al.*, 1996), the ring opening of 1,2-dimethylcyclopropane goes through a maximum, and then a minimum and then a continuous increase along with the increase in hydrogen pressure. On Pd, Ni and Cu catalysts (Pálinkó, 1997), the formation rates of one product increases and levels off with increasing hydrogen pressure, while for the other product the curve passes through a maximum. These observations were attributed to the changes of formation of adsorbed intermediates at different hydrogen pressures. A dissociative adsorption of hydrocarbon via the

rupture of the C–H bond(s) was assumed at low hydrogen pressure. An increase in hydrogen pressure inhibits this C–H dissociation, slowing down the reaction rate. In the case of Rh catalyst, new adsorbed species were presumably formed via scission of the ring C–C bond at high hydrogen pressure. These species were desorbed to produce ring-opening compounds.

Compared to the five-membered ring cyclopentanes, the ring opening of the four-, and six-membered ring compounds are less extensively studied. Cyclobutanes are more reactive towards ring opening than cyclopentanes due to higher ring strain. The reactions can take place at low temperature (<100°C), exhibiting relatively low selectivity, i.e. statistical product distribution (Török *et al.*, 1995). On the other hand, the ring opening of cyclohexanes over metal catalysts (Figueras *et al.*, 1997) is much slower than five-membered rings, even over the most active metal Ir (McVicker *et al.*, 2002). Instead, cracking and aromatization dominate the total reaction. For a significant conversion of six-membered rings into alkanes without loss of molecular weight, additional acid function is required to convert the six-membered rings to the five-membered rings via skeletal isomerization. The latter then readily undergo selective ring opening on acid or metal sites.

2.5.2 Proposed Mechanism

There have been several mechanisms proposed to account for ring opening on metal surfaces, two of which are well recognized: the multiplet mechanism and the dicarbene mechanism (Hayek *et al.*, 1997). The two mechanisms differ mainly in how the reaction intermediate forms on the metal surface.

In the multiplet mechanism, cyclic hydrocarbons physically adsorb either edgewise on two metal atoms, or flat-lying on the metal surface. The former is called the “doublet” mechanism, and the latter called the “sextetdoublet” mechanism. Both mechanisms compete with each other in the reaction. The doublet mechanism is thought to occur on small metal particles, and is used to explain the selective hydrogenolysis of bissecondary C–C bonds. According to this mechanism, cyclic hydrocarbon is adsorbed perpendicular to the metal surface via a bissecondary C–C bond, which then reacts with chemisorbed hydrogen in a push–pull manner to produce ring-opening products. Due to steric hindrance, the edge-wise adsorption of

the tertiary–secondary or tertiary–tertiary C–C bonds is limited. In the “sextet–doublet” mechanism, on the other hand, the cyclic molecule is physically adsorbed flat-lying on the metal surface, with the carbon atoms of the ring located over the interstices of the metal plane, e.g. Pt(111). For the five-membered ring cyclopentanes, one C–C bond has to be stretched (Figure 2.10), and this bond is readily attacked by neighboring, adsorbed hydrogen, leading to hydrogenolysis of the ring. The tertiary–secondary C–C bonds in alkylcyclopentane could be ruptured via the five-atom adsorbed mode. For cyclobutanes, all four C–C bonds are stretched, resulting in higher reactivity but lower selectivity. In contrast, there is no stretching when cyclohexanes and paraffin adsorb on the metal surface, as all the carbon atoms can fit the interstices of the Pt(111) plane. As a result, cyclohexanes and paraffin are usually not hydrogenolyzed, but preferably dehydrogenated or isomerized.

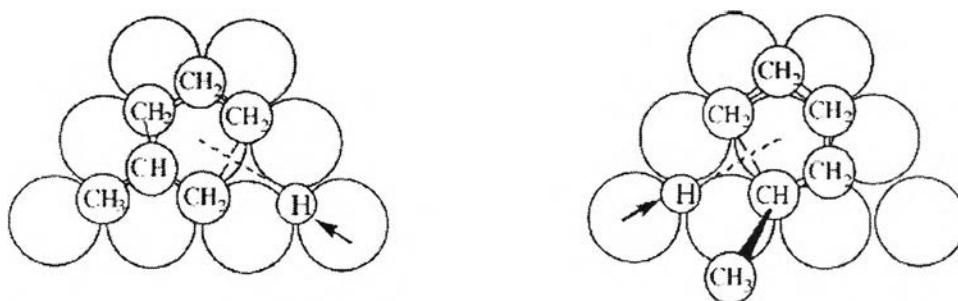


Figure 2.10 Hydrogenolysis of methylcyclopentane via the multiplet mechanism. (Gault, 1981)

Alternatively, the dicarbene mechanism involves the chemisorption of the cyclic hydrocarbon molecules on the metal surface after the rupture of several C–H bonds, forming carbon–metal bonds or π -adsorbed olefins (Figure 2.11). The nonselective ring opening of MCP on metal catalysts can be accounted for by the π -adsorbed olefin mechanism. Similar to that in the sextet–doublet mechanism, MCP is adsorbed parallel to the metal surface, but in a quasi-planar manner involving only one metal atom. The selective ring opening of MCP, on the other hand, involves 1,2-dicarbene complexes that bond to several metal atoms and stand perpendicular to the metal surface. Owing to steric hindrance, the hydrogenolysis of the tertiary–

secondary C–C bonds is retarded. On some occasions, however, an exocyclic alkyl substituent participates in the formation of a metallocyclobutane intermediate, resulting in the selective breaking of tertiary–tertiary and tertiary–secondary C–C bonds (Figure 2.11(b)).

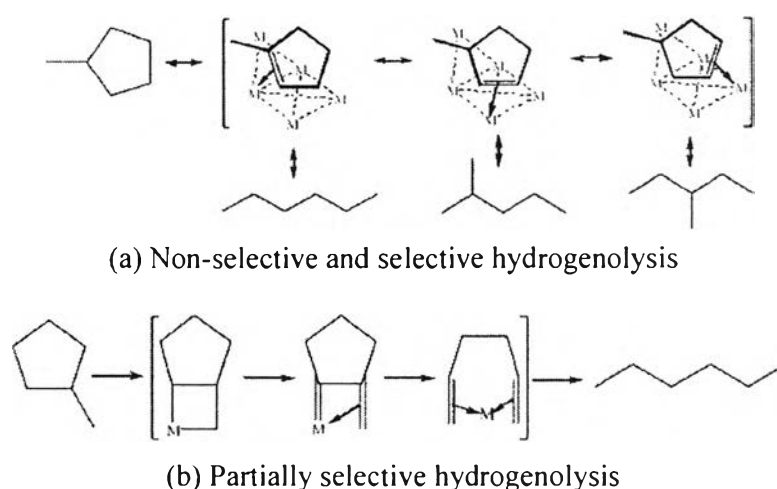


Figure 2.11 Hydrogenolysis of methylcyclopentane via the dicarbene mechanism. (Gault, 1981)

2.4.3 Electronic Effect

Various mechanisms were proposed to account for experimental facts such as selectivity, structural effect and kinetic data, the nature of the catalyst–reactant interactions remains unknown. In ring opening (cyclization), and isomerization catalysis, metallocyclobutanes, metallocarbenes and metallocarbynes were postulated as the possible reaction intermediates, depending on the nature of the sites. To generalize and simplify the reaction mechanisms, Garin *et al.* (1997) proposed an agostic precursor as the first species adsorbed on the metal surface, which consists of an $M \leftarrow H-C$ with a hydrogen atom bonded simultaneously to both a carbon atom of a reactant and a transition metal atom (Figure 2.12). This species initiates the formation of a σ -alkyl or carbene species that further reacts to give rise to products of ring opening (cyclization), hydrogenation (dehydrogenation) and/or isomerization. It was proposed that an electronic (or ligand) effect governs the relative contribution of σ -alkyl or carbene precursor, while a geometric (or ensemble

size) effect determines the pathway to the bond shift (isomerization), the cyclic, and the hydrogenolysis reactions.

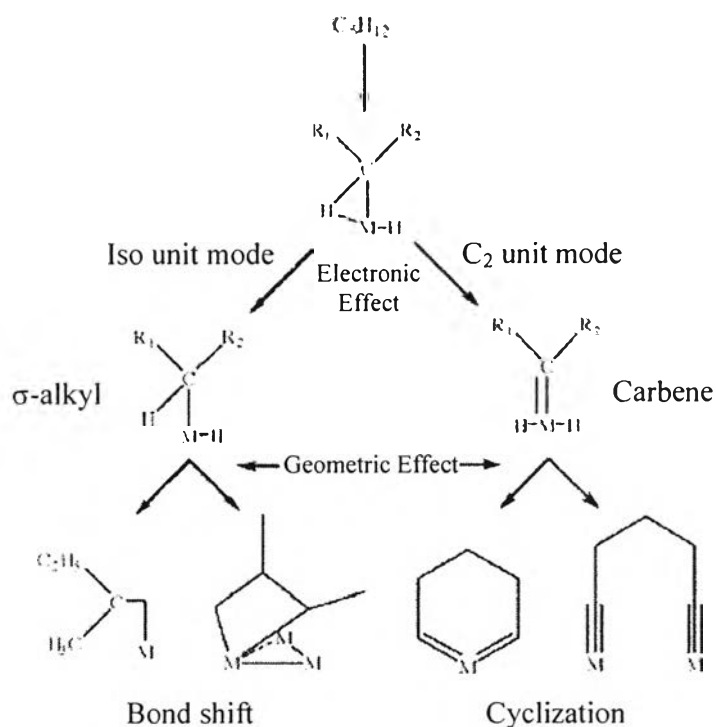


Figure 2.12 Proposed reaction mechanism of $n\text{-C}_5\text{H}_{12}$ on a metal catalyst, involving an agostic precursor species. (Garin *et al.*, 1988)

In hydrocracking/isomerization of 2-methyl- and 3-methylpentane on several group VIII metal catalysts (Garin *et al.*, 1988), studies have shown that Co and Ni tend to cleave multiple bonds, leading to extensive cracking, while Pd, Pt and Ir selectively rupture primary–secondary/tertiary, secondary–secondary/tertiary (demethylation) and secondary–secondary C–C bonds, respectively. The differences in the selectivity and activity of metals in hydrogenolysis and isomerization may be related to their electronic structure (density of states), as proposed by Saillard and Hoffmann (1984). When a H_2 or a hydrocarbon molecule (e.g. CH_4) approaches a metal surface, the electron transfer from d orbitals of the metal M to a C–H σ^* antibond ($\text{M} \rightarrow \sigma^*$) dominates the early stages of the reaction, which weakens the C–H σ bond and forms the M–H bond. This is different from transition metal complexes in which $\sigma \rightarrow \text{M}$ electron transfer leads the reaction because of the higher

energy of the occupied metal orbitals on the surface. For transition metals at the left side of the periodic table, the surface is positive relative to the bulk, while for metals at the right side of the periodic table, the metal surface is negative. This is in accordance with the fact that the heats of chemisorption of hydrogen on metal surfaces decrease from left to right across a periodic row (Baetzold, 1983). These metals are more likely to form metallocarbynes or carbenes, leading to multiple C–C rupture. Within the same series of transition metals, e.g. group VIII metal, the charge transfer from the bulk to the surface decreases as d level occupancy for a metal surface increases in traversing a periodic row (Baetzold, 1980). Consistently, the heats of chemisorption for hydrogen atoms on the metal surface decrease in going from 3d to 4d to 5d (i.e. decrease with increased atomic weight).

Based on the product distribution, hydrogenolysis reaction on metal catalysts can be classified into two groups (Garin *et al.*, 1988): the C₂-unit mode, involving rupture of C–C bonds between primary and secondary carbon atoms; and the isounit mode, involving rupture of a C–C bond with a tertiary carbon atom. In the C₂-unit mode, metallocarbene species may be formed upon removing at least two hydrogen atoms, which lead to hydrogenolysis over isomerization. On the other hand, in the iso-unit mode where only one H atom is available on the tertiary carbon, σ -alkyl species are formed, leading to higher isomerization than hydrogenolysis. The relative contribution of the two modes is determined by the electronic effect, i.e. the nature of the metal catalyst.

The C₂-unit mode is favored on monometallic Ru, Ir and bimetallic Pt-Ru, Pt-Co, Pt-Ir and Pt-Mo catalysts. The C₂-unit mode-dominated reactions, e.g. catalyzed by Ir catalysts, were thought to proceed via a dicarbene (or doublet) mechanism. The reactant bonds perpendicularly to the metal surface. The reactions are usually not sensitive to the particle size of metals but to the number of substituents because of steric hindrance. On the other hand, the iso-unit mode is dominant on Ni, Pt, Pd, Pt-Ni, Pt-W and Pt-Pd catalysts. In this case, the reactant is adsorbed parallel to the metal surface, and the reaction proceeds via a multiplet mechanism. The particle size of metal influences the selectivity of the reactions.

It is now widely accepted that the reactions of hydrocarbon on metal are initiated by dissociative adsorption of the alkanes on the metal surface and followed by subsequent hydride elimination from adsorbed alkyl intermediates. The former is the rate-determining step in the reaction, while the latter is thought to determine the selectivity. Zaera (2002) proposed that β -hydride elimination from the surface intermediate accounts for the production of olefins, γ -hydride elimination is responsible for isomerization and cyclization, and α -hydride elimination leads to hydrogenolysis products (Figure 2.13). The relative rates for α -, β - and γ -dehydrogenations determine selectivity of metal catalysts in hydrocarbon reforming. In general, the reactivity for α -, β - and γ -dehydrogenations increase with early transition metals and with decreasing hydrocarbon chain lengths. The β -hydride elimination is the most favorable. However, the relative rates for α -, β - and γ -dehydrogenations within the metal also change across the periodic table, which results in the different catalytic performance of different metals in hydrocarbon reforming. For instance, Pt(111) displays comparable rates for α - and γ -dehydrogenations, while Ni(100) only shows α -dehydrogenation. These results explain the unique ability of Pt for catalyzing hydrocarbon reforming as opposed to Ni, which facilitates extensive cracking.

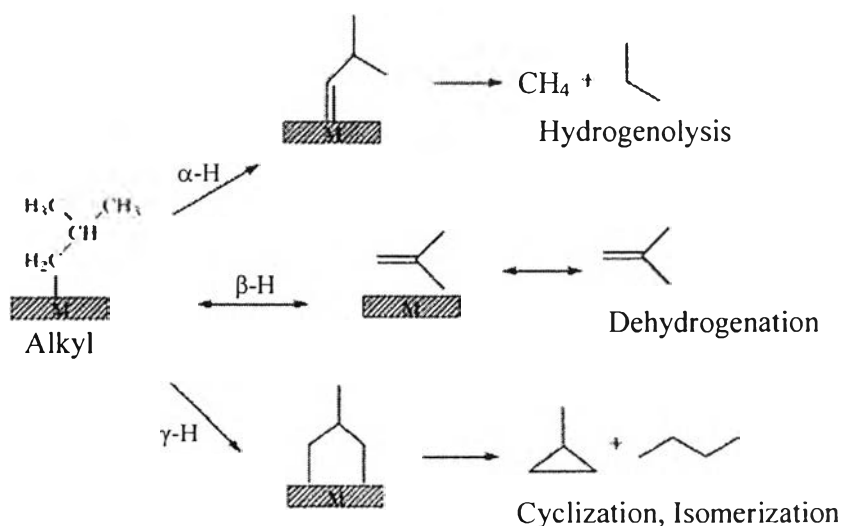


Figure 2.13 Simplified reaction mechanisms for the catalytic reforming of hydrocarbons on transition metal surfaces. (Zaera, 2002)

2.5.4 Geometric Effect

The geometric effect on the catalytic properties is exemplified by the particle size effects, which have been extensively studied (Coq and Figueras, 1998). In hydroconversion of hydrocarbons, large metal particle size promotes selective hydrogenolysis, and small particle size favors non-selective isomerization and hydrogenolysis. For instance, ring opening on supported Pt metal catalysts exhibit pronounced particle size effects on the selectivity. As illustrated by the hydrogenolysis of MCP, catalysts with large Pt particle size lead to selective ring opening, favoring 2MP, and 3MP with the formation of nHx suppressed. Small Pt particle size produces non-selectively nHx , 2MP and 3MP in a statistical ratio. Other metals, e.g. Rh and Ir, favor the selective hydrogenolysis with little effect of particle size.

The particle size has also affected the turnover rate (activity) in the hydrogenolysis of cyclic hydrocarbons (Bennett and Che, 1989). On Pt/Al₂O₃, the turnover rate of the hydrogenolysis of cyclopentane was shown to decrease with decreased particle size. Similar results were observed on Rh/Al₂O₃. On Ir/Al₂O₃, however, the hydrogenolysis of cyclopentane is insensitive to the particle size. Pd/Al₂O₃, on the other hand, presented a slight increase in the hydrogenolysis of cyclopentane with decreasing particle size.

The origin of particle size effects is not clear. Some possible explanations include electronic effects, morphology, and support effects (Gault, 1981). As the particle size is reduced, the electronic bands of the metal particle become distinct, and the electron energies increase. For most metal particles, the electron energies begin to increase as the particle size is reduced below 5 nm. For some metals, the energies level off below a certain size, e.g. Pd at about 1 nm, while for others, e.g. Pt, the increase in energies continue with the decrease in particle size. As a result, the electronic configurations of the surface atoms are different from those of large particles, leading to changes in the catalytic properties. On the other hand, the decrease in particle size likely changes the morphology of the metal particle, which could influence the catalytic properties. For instance, a large fcc metal particle crystallizes in an octahedron geometry (8 faces), while most small fcc metal particles ($d = 10$ nm) adopt cubooctahedral geometry (14 faces) as

demonstrated by quantum-mechanical calculations and experimental studies. For even smaller particles a non-fcc arranged icosahedron (20 faces) might become more stable (Bennett and Che, 1989). As the particle size decreases, the number of atoms of low coordination at the edges or corners of the crystallites increases, while the fraction of face atoms diminishes. Therefore, small particles would favor catalysis by atoms of low coordination, e.g. the non-selective, statistical hydrogenolysis, giving higher rates. Large particles would favor catalysis by face atoms of high coordination numbers, e.g. selective hydrogenolysis. The effect of surface atom coordination on the catalytic properties of the metal can also account for the changes in the selectivity of the ring opening of MCP over different metal surfaces. In controlled tests using metal films with oriented faces (Rupprechter *et al.*, 1998) or supported metal catalysts where the specific facets of the metal particles were selectively prepared (Pirault-Roy *et al.*, 2003), studies showed that the hydrogenolysis activity and product selectivity varied from facet to facet of metal crystal. High activities and non-selective hydrogenolysis were observed on small polycrystalline particles with disordered surfaces, or on flat, stepped, and kinked noble-metal single-crystal surfaces of high Miller index containing high concentrations of low-coordination sites. This particle size phenomenon observed in heterogeneous catalysis is the basis of the current interest in nanotechnology related to chemistry and materials.

2.5.5 Support Effect

Besides the above-mentioned electronic and geometric effects, catalyst supports also play an important role in heterogeneous catalysis. As demonstrated in many catalytic processes, the supports are not inert in selective ring opening catalysis as previously thought, but alter the catalytic properties of the metal particles through electronic interactions, or by space confinements. The support effect has attracted much attention and stimulated extensive research worldwide. Excellent reviews have been published on this subject (Breysse *et al.*, 2005).

A “partly” selective mechanism for ring opening of MCP was observed on noble metals supported on acidic oxides, which produced a higher proportion of $n\text{Hx}$ than the theoretical ratio, according to a non-selective mechanism.

The formation of $n\text{Hx}$ appeared to increase with increasing support acidity (McCarthy *et al.*, 1996). Kramer and Zuegg (1983) used the adlineation model to account for the partial selectivity for $n\text{Hx}$ and 2MP. The model assumed that ring opening occurs at the phase boundary of metal and support. The support, i.e. an acidic site, interacts with the tertiary C–H of MCP because this H atom is most susceptible to attack by an acidic or cationic site, while the neighboring carbon is attached to the metal site. Ring opening of MCP adjacent to the methyl group occurs, leading to the formation of additional $n\text{Hx}$ (Figure 2.14). This partly selective mechanism competes with a nonselective mechanism occurring exclusively on the metal surface. Alternatively, the partly selective ring opening of MCP may be explained by electronically asymmetric pairs of metal atoms resulting from strong metal–support interactions. The cationic sites of the support in bifunctional catalysts exert an electric field on adjacent metal sites, leading to the formation of partially charged metal atoms that have been confirmed by various methods (Kramer and Fischbacher, 1989). The resulting $\text{M}^{\delta-} - \text{M}^{\delta+}$ exhibits functionalities similar to those of the acid site–metal pair to selectively produce $n\text{Hx}$ and 2MP but not 3MP (Figure 2.14) (Anderson *et al.*, 1987).

Another “partly” selective mechanism for ring opening of MCP has been observed over zeolite-supported metal catalysts, for example, on SAPO-11 (Hoffmeister and Butt, 1992), LTL (Alvarez and Resasco, 1996) and FAU (Garin *et al.*, 1997). Over these catalysts, significantly higher selectivities to 3MP were observed compared to other supported metal catalysts of similar particle size. These enhanced selectivities were attributed to the constraint of the one-dimension pores of zeolites that result in a preferred orientation of the incoming MCP molecule with its long axis parallel to the direction of the pores. When the MCP molecule reaches a metal particle inside a zeolite pore, ring opening preferentially takes place through one of its ends, resulting in a 3MP/2MP product ratio higher than the statistical value of 0.5 (Figure 2.14). Similarly, a higher 3MP/ $n\text{Hx}$ ratio than that the statistical value of 0.5 can be explained by the steric hindrance of the methyl group of MCP in zeolite pores that restrict the rotation of the molecule when it approaches the metal particle with its methyl end.

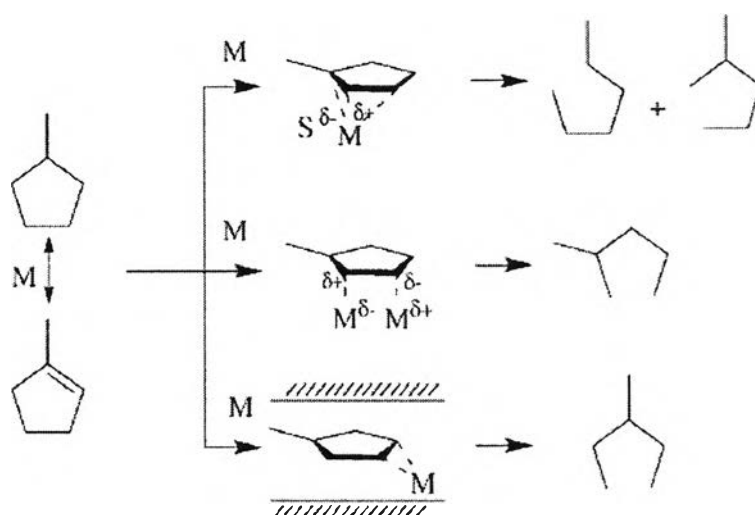


Figure 2.14 Partly selective ring opening of methylcyclopentane.

2.6 Catalytic Reactions for the Methylcyclohexane (MCH)

Previous researchers have studied the reaction paths and the role of catalyst structure on product distribution for MCH reaction. For example, Mignard *et al.* (1994) have studied the conversion of MCH on Pt/USY catalysts. They found that MCH is first isomerized via ring contraction (RC) into ethylcyclopentane (ECP) and dimethylcyclopentanes (DMCPs) and then transformed into C_7 iso-alkanes and cracking ($<C_7$) products, respectively, as the reaction temperature increases. In that study the individual RC products were lumped, but as shown in Figure 2.1, different RC products have very different ON. The intermediate RC step has been made evident in several other studies on acidic catalysts, both zeolitic and non-zeolitic (Figueras *et al.* 1997). In some cases, the RC reaction has been proposed to occur by a bifunctional path, involving dehydrogenation on metals. For example, Belatel *et al.* (2004) investigated the MCH reaction on Pt-Ir/sulfated zirconia catalysts and showed that no isomerization was found to take place in the absence of metals.

On zeolitic catalysts, the structure of the zeolite can be used to greatly modify the product distribution. The role of shape selectivity in determining the product distribution of isomerization of naphthenic rings was pointed out by Weitkamp *et al.* (1984). In their work on Pt/HZSM-5 catalysts, they found that on

these small-pore catalysts, no 1,1- or 1,2-dimethylcyclopentane were formed while cis/trans-1,3-dimethylcyclopentane appeared even at very low conversions

The role of metals is not only the dehydrogenation/hydrogenation steps. It may also participate in ring opening of naphthenic molecules. The principal path for ring opening on catalysts with only the metal function is hydrogenolysis. In this reaction, the cleavage of a C-C bond of alkylcycloalkanes depends on the nature of the catalyst, the type of ring, and the presence of alkyl substituents. Gault (1981) identified three different paths for ring opening via hydrogenolysis. The most common pathway involves a dicarbene intermediate with cleavage at the unsubstituted secondary-secondary C-C bond. In the other two reaction paths the cleavage occurs at substituted C-C bonds through π -adsorbed olefin and metallocyclobutane intermediates, respectively. The product distribution from the hydrogenolytic ring opening over metals (i.e. Pt, Ir, Rh and Ru) is strongly dependent on the nature of reactants and catalyst structure, which in turn can be modified by parameters such as particle size or metal-support interactions (Resasco and Haller 1984). For example, the products obtained from ring opening of methylcyclopentane on high loading, low dispersion Pt/Al₂O₃ catalysts were mostly 2-methylpentane (2-MP) and 3-methylpentane (3-MP) with no n-hexane (*n*-Hx). The first two products result from a dicarbene intermediate, the third one requires cleavage of a substituted C-C bond. By contrast, significant amounts of *n*-Hx were found in the products when the catalyst was a highly dispersed, low loading Pt/Al₂O₃.

In addition to zeolitic catalyst, the case of tungsten-containing zirconia (WO_x-ZrO₂) is of particular interest in catalysis because of its good combination of activity and selectivity. The catalytic activity is associated with interconnecting polyoxotungstate clusters on the surface of tetragonal zirconia. The polyoxotungstate species increase the acid strength of the catalyst relative to that of unmodified zirconia, but the acid strength is still less than that of zeolites and far below the superacidic range. The addition of platinum to the catalyst and H₂ to the feed drastically improves the catalytic activity, selectivity, and stability. The platinum enhances the desorption of reaction intermediates and minimizes the condensation reactions, so that mono-molecular isomerization predominates (Torres-Gracia *et al.*, 2004).

Figueras *et al.* (1997) studied in the conversion of methylcyclohexane (MCH). The main reaction observed is the isomerization to alkylcyclopentanes (ACP), the slow step of which is the acid-catalyzed contraction of the ring. The positive order with respect to hydrogen pressure is tentatively assigned either to a nonclassical bifunctional mechanism where hydride transfer steps play a key role or to the increased formation of active Brønsted sites, coming from the reduction of Lewis sites by hydrogen. Some ring opening products (ROP), i.e., C₇ alkanes are formed from ACPs either by hydrogenolysis on the Pt sites or more probably by bifunctional acid catalysis. Besides, Zimmer and Paal (1989) suggested that the ROPs clearly appeared as secondary products. A possibility is metal-catalyzed hydrogenolysis, not of the cyclohexane ring, but of the cyclopentane ring of product ACPs, which is much easier.