# CHAPTER III

# THEORY

This chapter briefly describes some basic theories concerning the overview of non-oxidative methane coupling over metal-containing Y-type zeolite catalysts.

## 3.1 Zeolite Y

The zeolites finding the largest-scale application in catalysis belong to the family of faujasites, including zeolite X and Y [Gates (1992)]. Zeolite Y was discovered by R.M. Milton and coworker between 1949 and 1954. Also in 1959 a zeolite Y-based catalyst was marketed by Union Carbide as an isomerization catalyst. Subsequently it found applications in many areas of catalysis and molecular sieve, generating interest in an industrial and academic laboratories. As catalyst, zeolite Y exhibits appreciable acid activity with sharp selectivity features not available in the compositional equivalent amorphous catalysts. In addition, these material can act as supports for numerous catalytically active metals. The porous framework of the zeolites enable them to act as molecular sieves i.e., they are used to separate molecular mixtures on the basis of size and shape molecule compounds or for the selective adsorption of gases. These unique properties are utilized in diverse industrial processes such as the purification of water as well as other liquids and gases, chemical separations, catalysis, and decontamination of radioactive wastes [Jiratthitikan (1997)].

### 3.1.1 Structures of Zeolite Y

Zeolite Y is a crystalline aluminosilicates which is a complex of a crystalline inorganic polymer based on an infinitely extending three-dimensional, four-connected framework of $[AlO_4]^{5-}$ and $[SiO_4]^{4-}$ tetrahedral (figure 3.1) linked to each other by the sharing of oxygen ions. Each $[AlO_4]^{5-}$ tetrahedron in the framework bears a net negative charge which is balanced by a cation. The framework structure contain

channels or interconnected voids that are occupied by the cations and water molecule. The cations are mobile and ordinary undergo ion exchange. The water may be removed reversibly, generally by the application of heat, which leaves intact a crystalline host structure permeated by the micropores and voids which may amount to 50% of the crystals by volume [Jiratthitikan (1997)].

The structural formula of zeolite Y is based on the crystallographic unit cell, the smallest unit of structure, represented by $Na_j[(AlO_2)_j(SiO_2)_{192-j}].zH_2O$, where z is about 260. The value of j is between 48 and 76.



Figure 3.1 $[SiO_4]^{4-}$ or $[AlO_4]^{5-}$ tetrahedral

The primary structural units, the $[SiO_4]^{4-}$ or $[AlO_4]^{5-}$ tetrahedral, are assembled into secondary building units (SBUS) which are shown in Figure 3.2. It denotes only the aluminosilicate skeleton (i.e. the Si, Al and O positions in space relative to each other) and excludes consideration of the cation and water moieties sited within the cavities and channels of the framework. The final structure framework consists of assemblages of secondary units. The most favored is the use of tetrahedral arrays, adopted by organic chemists, where the oxygen atoms are drawn as single bonds joining together tetrahedral centers depicting silicon and aluminium. The SBUS are joined to create the infinite lattices they can produce a large ring containing 12 linked tetrahedral ( ring of 12 oxygen atoms). The ring is obviously important structural features and is often called "oxygen windows" (Figure 3.3).
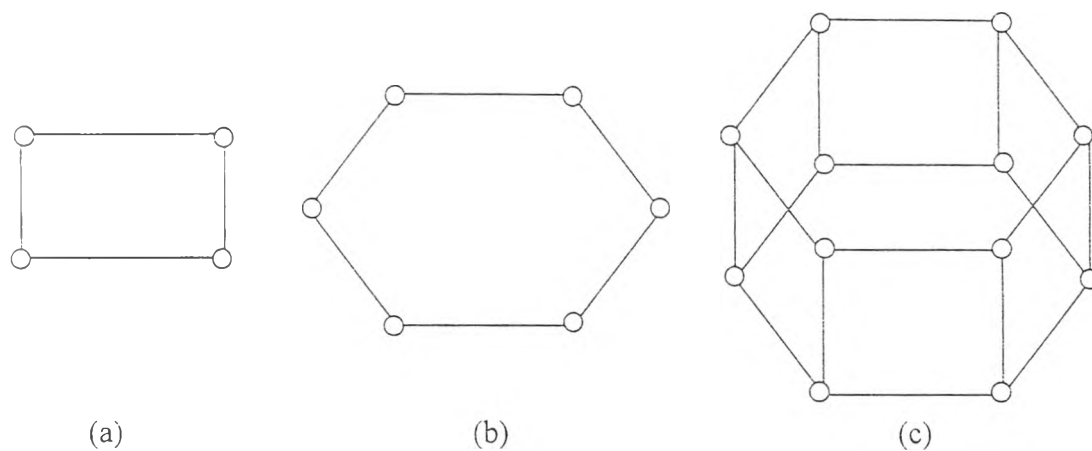
**Figure 3.2** Secondary building units (SBUS) of zeolite Y; (a) single four ring (S4R) , (b) simple six ring (S6R) , (c) double six ring (D6R)
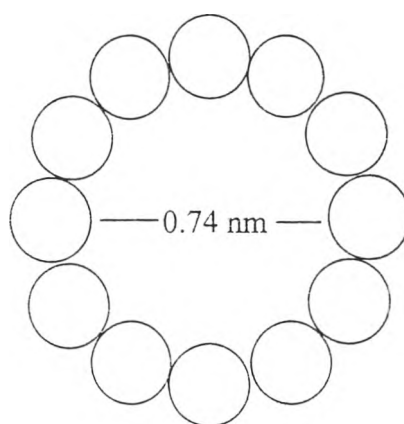


**Figure 3.3** zeolite Y pore geometry [Jiratthitikan (1997)].

Zeolite Y has 0.74 nm apertures (12 membered oxygen rings) and a three-dimensional pore structure, they admit even hydrocarbon molecules larger than naphthalene. Their chief application is in catalytic cracking of petroleum molecules (primarily in the gas oil fraction), giving smaller, gasoline-range molecules [Gate (1992)].
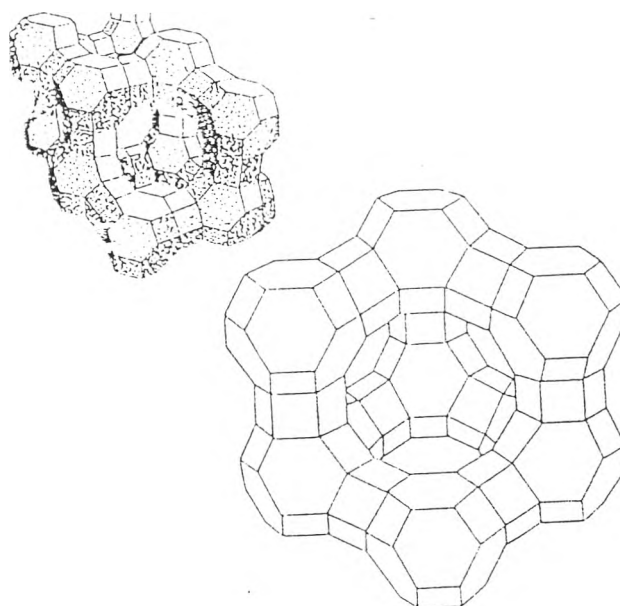


**Figure 3.4** Structure of zeolite Y [Gate (1992)].

The framework structure of zeolite Y (figure 3.4) is closely related to that of zeolite A. The sodality cages in zeolite Y is arranged in an array with greater spacing than in zeolite A. Each sodality cage is connected to four other sodality cages; each connecting unit is six bridging oxygen ions linking the hexagonal faces of two sodality units, as shown in figure 3.4. The bridging oxygen form what is called a hexagonal prism. The supercage in this structure, surrounded by 10 sodality units, is large enough to contain a sphere with a diameter of about 1.2 nm. The three-dimensional pore structure is large enough to admit reactant molecules like the

hydrocarbons in gas oil, but the 0.74 nm pore apertures are still small enough that some transport restrictions are expected. The excess negative charge of the $[AlO_4]^{5-}$ tetrahedral. is balanced by such as $Na^+$, $H^-$. Four cation sites are illustrated in figure 3.5. Type I sites are located at the centers of the hexagonal prisms, type I' sites are located in the sodality cages across the hexagonal faces from type I sites, type II sites are located in the supercages near the unjoined hexagonal faces, and type II' sites are located in the supercages, farther from the hexagonal faces than the type II sites [Gate (1992)].

Since these cations are largely responsible for the catalytic activity of a zeolite, their locations are important. Cations in type II and II' sites are readily implicated in catalysis, since they are accessible to reactants. The type I and I' sites, being less accessible, are less important for catalysis.
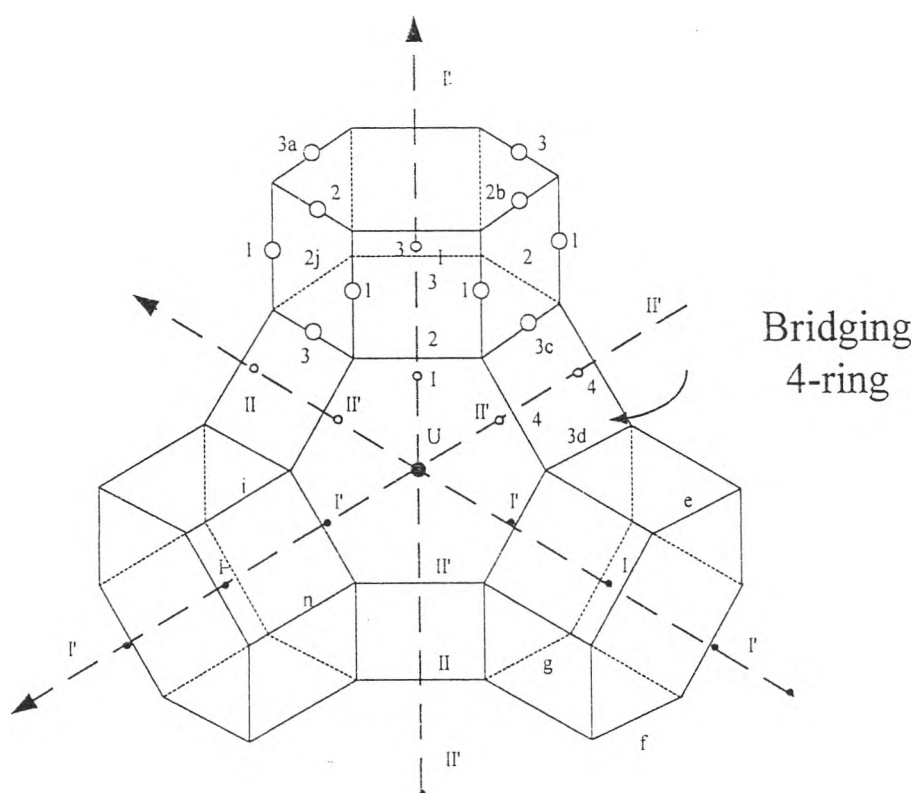


**Figure 3.5** Locations of cation sites in Y zeolites [Gate (1992)].

### 3.1.2 Active sites of Zeolite Y

#### 3.1.2.1 Acid sites

Most industrial applications of zeolites are based upon technology adapted from the acid silica/alumina catalysts originally developed for the cracking reaction. This means that the activity required is based upon the production of Brönsted and Lewis acid sites. Brönsted acidity is a proton donor activity; a tridiagonally co-ordinated alumina atom is an electron deficient and can accept an electron pair, therefore acts as a Lewis acid. In general, the increase in Si/Al ratio will increase acidic strength and thermal stability of zeolite. Since the number of acidic OH groups depend on the number of aluminum zeolite's framework, decrease in Al content is expected to reduce catalytic activity of zeolite. If the effect of increase in the acidic centers, increase Al content, shall result in enhancement of catalytic activity [Jiratthitikan (1997)].

Based on electrostatic consideration, the charge density at a cation site increases with increasing Si/Al. It was conceived that these phenomena are related to reduction of electrostatic interaction between framework sites, and possibly to difference in the order of aluminum in zeolite crystal-the location of Al in crystal structure [Jiratthitikan (1997)].
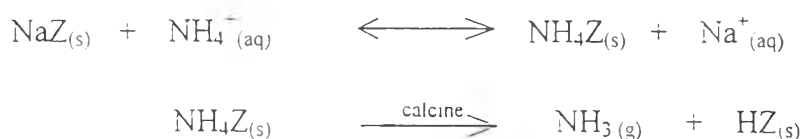
Recently it has been reported that the mean charge on proton was shifted regularly towards higher values as the Al content decreased. Simultaneously the total number of acidic hydroxyls, governed by the Al atoms, were decreased. This evidence emphasized that the entire acid strength distribution (weak, medium, strong) was shifted towards stronger values. That is the weaker acid sites become stronger with the decrease in Al content.

An important in thermal and hydrothermal stability has been described to the lower density of hydroxyls groups which is parallel to the Al content.
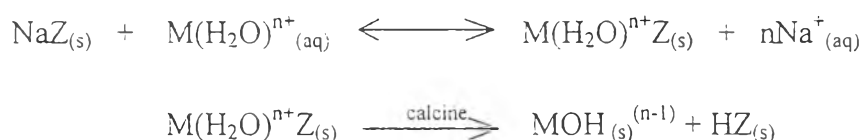
A longer distance between hydroxyl groups decreases the probability of dehydrogenation that generates defects on structure of zeolite.

Bronsted site arise from the creation 'hydroxyls' within the zeolite Y pore structure. These hydroxyls are usually formed either by ammonium or polyvalent cation exchange followed by a calcination step:

Ammonium ion exchange

$$NaZ_{(s)} + NH_4^+{}_{(aq)} \longleftrightarrow NH_4Z_{(s)} + Na^+{}_{(aq)}$$

$$NH_4Z_{(s)} \xrightarrow{calcine} NH_{3\,(g)} + HZ_{(s)}$$

Polyvalent ion exchange

$$NaZ_{(s)} + M(H_2O)^{n+}{}_{(aq)} \longleftrightarrow M(H_2O)^{n+}Z_{(s)} + nNa^+{}_{(aq)}$$

$$M(H_2O)^{n+}Z_{(s)} \xrightarrow{calcine} MOH_{(s)}^{(n-1)} + HZ_{(s)}$$

In high-silica zeolites (e.g. ZSM-5 and clinoptilolite) these 'protonated' zeolites (HZ) can be made by direct exchange with mineral acid. Ideally the 'protonated' form contains hydroxyls which are protons associated with negatively charged framework oxygens linked into alumina tetrahedral. i.e. Bronsted sites are created:
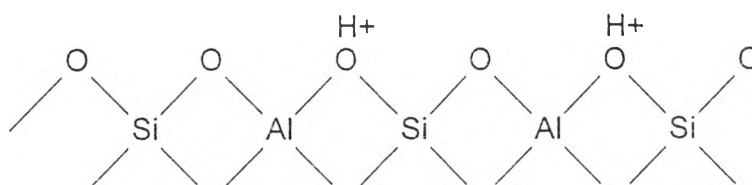


The protons have great mobility when the temperature is above 200 °C and at 550°C they are lost as water (clearly seen by thermal analysis) with the consequent formation of Lewis sites:



Bronsted site            Lewis site
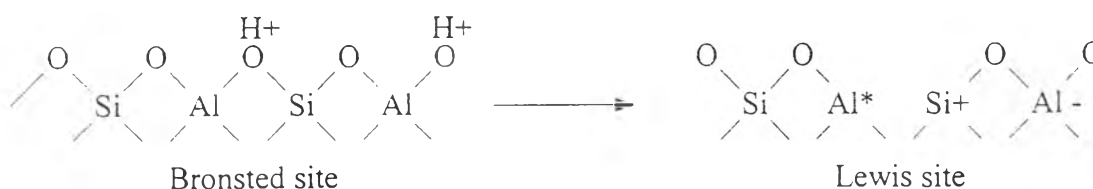
The lewis sites in turn are unstable, especially in the continue presence of water vapor and an annealing process stabilizes the structure. This produces the so-called 'ture' lewis sites by ejecting Al species from the framework, i.e.:

$$\underset{\text{Lewis site}}{\overset{\displaystyle \overset{O}{\diagup}\overset{O}{\diagdown}\quad\overset{O}{\diagup}\overset{O}{\diagdown}\overset{O}{\diagup}}{\diagup \ \underset{\diagup}{\overset{\diagup}{Si}} \ \underset{\diagdown}{\overset{\diagdown}{Al^*}} \ \underset{\diagdown}{\overset{\diagup}{Si+}} \ \underset{\diagdown}{\overset{\diagdown}{Al-}} \ \underset{\diagdown}{\overset{\diagup}{Si}}}} \quad\longrightarrow\quad \underset{\text{'True' Lewis site}}{\overset{\displaystyle (AlO)+\atop \overset{O}{\diagup}\overset{O}{\diagdown}\overset{O}{\diagup}\overset{O}{\diagdown}\overset{O}{\diagup}}{\diagup \ \overset{Si}{} \ \overset{Si}{} \ \overset{Al}{} \ \overset{Si}{} \ }}$$
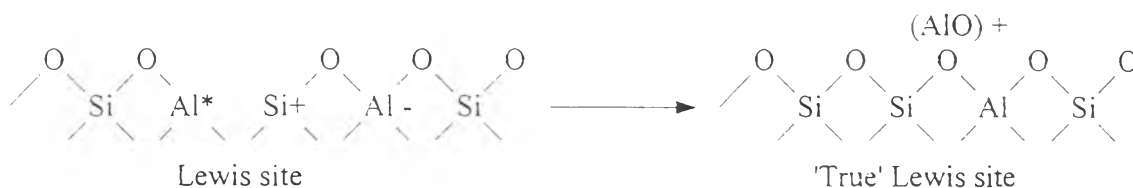
This extra framework aluminium can be identified by Magic Angle Spinning Nuclear Magnetic Resonance (MASNMR), but is in at least two forms. Theoretical calculations support the idea that $(AlO)^+$ species are the source of useful Lewis activity, whilst suggesting that the tricoordinated Al of the Lewis site ($Al^*$ above) acts as a weak acid. (There is, however, no direct evidence for the existence of tricoordinated Al). Electron spin resonance (ESR) studies propose that, when Bronsted sites interact with near by Lewis sites, 'super acid' sites are formed. The evidence is that these seem likely to be due to displaced aluminium species. The uniqueness of zeolites as cracking catalysts lies in the high density of these active sites coupled with the zeolite inherent stability and amenability to regeneration [Dyer (1990)].

### 3.1.2.2 Bifunctional catalysis

Bifunctional zeolite catalyst, generally metal load acid zeolite are employed in numerous processes in petroleum refining and in petrochemical industries : hydrocracking , selectroforming , dewaxing , hydroisomerization of $C_5$-$C_6$ alkanes , hydroisomerization of $C_8$ aromatics. The catalysts used in this processes present two types of site : metallic site to main function is to hydrogenate and to dehydrogenate and acid site whom main function is to crack or to isomerize. Hydrocracking requires catalyst with a high acidity counterbalanced by a high hydrogenation activity, which implies the use by a Y zeolite in which the sodium ion have been replaced by

hydrogen, by rare earth or by divalent cations and dehydrogenating function is provided by noble or non-noble metals. In marked contrast to amorphous silica – alumina catalysts, zeolite catalysts can operate in the present of substantial amount of ammonia and other nitrogen compounds. This greater ability of the zeolites to tolerate these compounds can be attributed to their greater number of acid sites. Moreover this greater acidity enhances the resistance of hydrogenating function to poisoning by sulfur compound and hydrocracking catalysts show a high stability with regards to sulfur poisoning.

Generalities, in bifunction catalysts, reactions occur in successive steps involving two different types of sites. As an example, the conventional bifunctional process for isomerization of n-hexane into methylpentanes found on platinum-silica alumina is shown in figure 3.6. this catalyst presents two types of site:

1. platinum site whose function is to hydrogenate n-hexane into n-hexenes (reaction 1) and to hysrigenate methylpentenes in to methylpentanes (reaction5).

2. acid site whose function is to isomerize hexenes into methylpenthanes

(reaction 3).

Beside these chemical steps, a bifunctional process requires diffusion steps of the intermediates species. In this case , olefin intermediates diffuse from the metallic to the acid sites (step 2) and from the acid to the metallic sites (step 4).
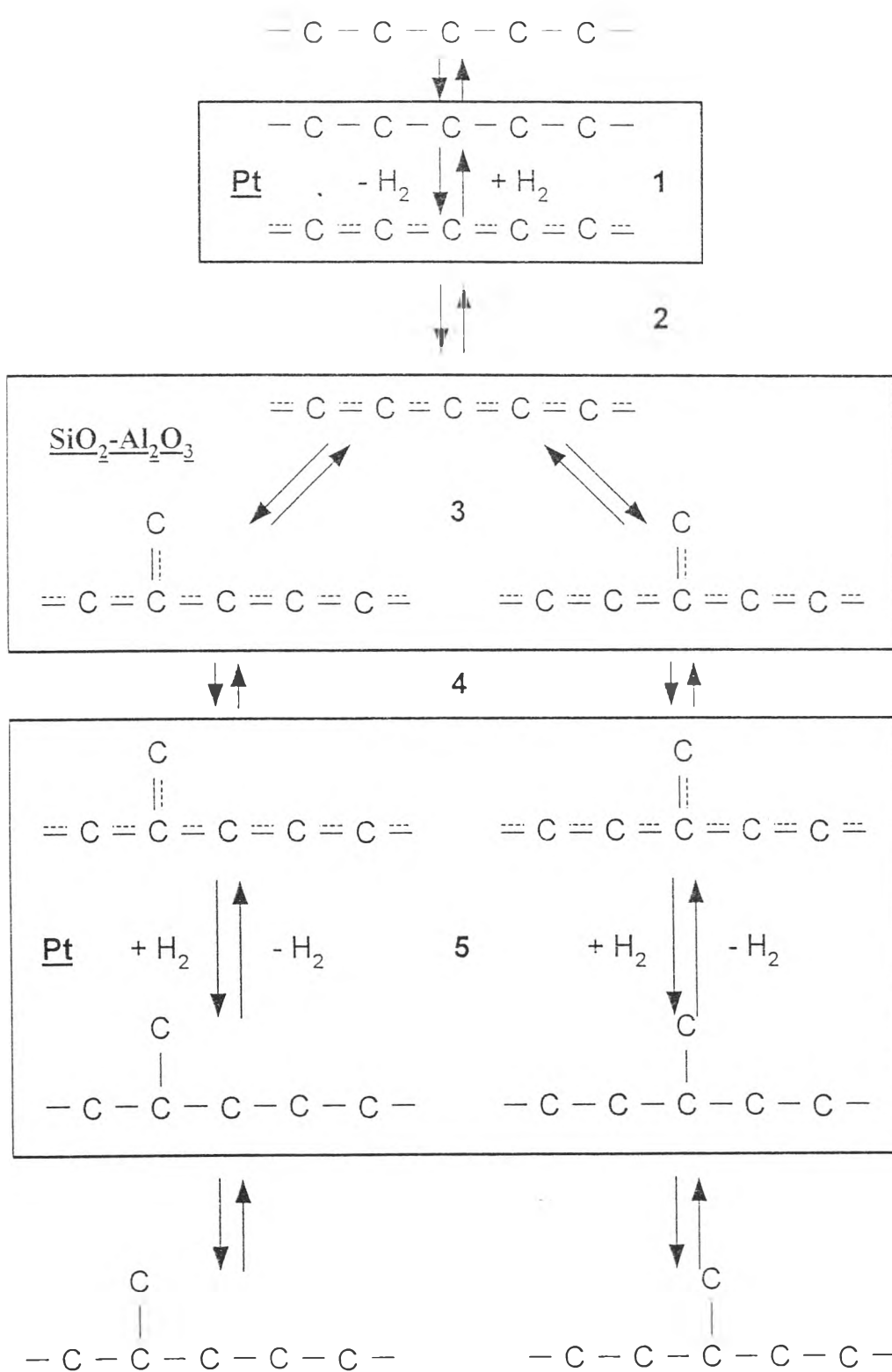
**Figure 3.6**  Bifunctional procedure of n-hexane isomerization on platinum-silica alumina.

The existence of this bifunctional process is now well established:

- although highly unfavoured thermodynamically under the usual operating conditions, the intermediate olefins were detected by GLC and mass spectrometry. Moreover, the skeletal isomerization of olefins (reaction 3 in figure 3.6) is known to occur very readily on acid catalysts;

- the participation in the reaction of both acid and hydrogenating centers was clearly demonstrated by using physical mixtures of an catalyst and of a metal deposited on an inert carrier : the activities of the mixtures were definitely greater than the sum of the activities of the components;

- the change in the isomerization activities of bifunctional catalysts (differing by their platinum content) as a function of their hydrogenation activities was the change expected from the multi-step bifunctional process.

The activity, the stability and the selectivity of bifunctional zeolite catalysts are clearly governed by the characteristics of their acid and hydrogenating sites. As was shown for alkane isomerization and cracking, the highest activity would be obtained if all the acid sites were the active and working at their maximum. For this to occur, the acid sites must be sufficiently supplied with olefinic intermediates which requires numerous and well distributed active hydrogenating sites. In the "ideal" case, the diffusional path of olefins(between two hydrogenating sites) will contain only one active site. Here the catalyst will also be the most selective one in the series of consecutive reaction : thus, when transforming n-alkanes, it will give the best yield of monobranched isomers and the most selective isomerization. On such the catalyst, coke formation will be very slow and consequently the stability very great. Zeolite are perfectly adapted to the preparation of "ideal" bifunctional catalysts : their acid sites are numerous and highly active ; moreover, a high dispersion and a high activity of hydrogenating sites can be obtained when introducing the metal by an ion-exchange process.

## 3.2 Methane Coupling

The methane coupling reaction is a two-step route in which methane is first thermally activated. It is decomposed by a reduced group VIII metal catalyst into hydrogen and adsorbed surface carbonaceous species (1) ($CH_x$ when $1 \leq x < 4$) at low temperature. In a second reaction step a particular surface carbonaceous intermediate produces hydrocarbons upon hydrogenation at low temperature (2).

$$2CH_4 + 6M \longrightarrow 2M_3C + 4H_2 \qquad\qquad (1)$$

$$2M_3C + 3H_2 \longrightarrow C_2H_6 + 6M \qquad\qquad (2)$$

where M = zero-valent transition metal [Koerts *et al.* (1992)].
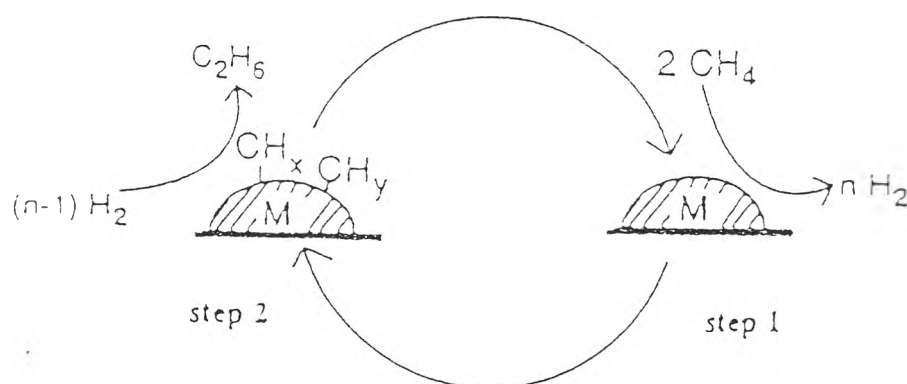


**Figure 3.7**   Schematic presentation of the two-step route of methane conversion into ethane or higher hydrocarbons using transition metal catalysts [Koerts *et al.* (1992)].