

## CHAPTER II

### THEORY

#### 2.1 Supporting materials

The performance of many solid catalysts is directly proportional to their surface area. To maintain a high dispersion of the active compounds on the catalyst support, a property of high surface area of the support material is necessary required. A support material is usually a highly porous and thermally stable material. In addition, the support material might influence the catalytic activity of the active component or it might be a catalyst itself, thus forming a bifunctional catalyst together with the active compound.<sup>5</sup> Supports are most often used for metallic catalysts, especially for precious metals such as platinum, palladium and rhodium. Since unsupported metals usually have a very low dispersion, it would be very uneconomical to use expensive metal catalysts without supports. Using an appropriate support can increase the dispersion of the active metal. To function as a support for dispersed metal particles, the support must have a high surface area. The surface area greater than  $100 \text{ m}^2/\text{g}$  is preferable.<sup>28</sup> Any solid material can be used as a support in principle, however in practice preference is given to metal oxide supports and to a lesser extent carbon supports. The dominance of metal oxide supports is a consequence of their generally high thermal and chemical stability, and the knowledge of how to prepare these materials with high surface area.

The surface of metal oxides are composed predominantly of oxygen atoms, hydroxyl groups and exposed metal atoms. The chemical properties of these species and the manner in which they interact with metal-bearing precursors are strongly affected by the amount of charge localization. Oxygen anions behave as Lewis bases, metal cations behave as Lewis acids and hydroxyl groups can act either as acids or bases. The strength and surface concentration of acidic and basic center depends strongly on the nature of the Metal-Oxygen bond: Acidic oxides have mainly a covalent bond while basic oxides have an ionic bond. The behavior of hydroxyl groups at an oxide surface is strongly dependent on the composition of the oxide and the local chemical environment. Supporting the surface composition of an oxide as  $MO_m(OH)_n$ , when  $m$  increases in a value, the O-H bond in the hydroxyl groups is weakened and the Brønsted acid strength of these group increases. The charge of  $M$  also influences the acid strength of the hydroxyl groups. As the charge increases, the acidity increases and the basicity is reduced. For example,  $Mn_2O_7$  is an acidic oxide but  $MnO$  is a basic oxide.

The choice of a support material is usually governed by several factors.<sup>5</sup> The important factors are thermal stability, stability toward the feed, the chemical nature of the active phase, mechanical strength, acidity, surface area and price. An advantage of using amorphous supported is that they are commercially available. These supports can offer a simple and easy procedure, to be handled and purified. In contrast to amorphous or lamellar inorganic solids, zeolites have well-defined three-dimension crystalline structures. Although they are widely recognized as effective molecular sieves and drying agents, zeolites have received attention as catalysts or reagent supports as well. The characteristic properties of zeolites, such as variable acidity, shape-selectivity and thermal stability, make them attractive supporting materials. Indeed, they have already fulfilled important roles in the petrochemical and oil processing industries.<sup>29</sup> Although zeolite-supported reagents are air and moisture sensitive materials and require storage in air-tight containers, they offer the potential for shape-selective control of chemical reactions, and

consequently present new avenues for catalysis and synthetic methodology. In addition, mesoporous materials of which synthesis method has recently been developed can be prepared and used as supports in alternative ways.<sup>17-20,30</sup>

## 2.2 Types of Supporting materials

Three general types of useful solids can be distinguished:<sup>29</sup> (a) amorphous solids with random pores, so that reaction takes place at the irregular surface; (b) sheet or layered materials of which interlamellar region is useful for catalytic activity; and (c) the three-dimensional structure comprises a regular array of channels. For examples, amorphous silica and amorphous alumina fall into the first category, clay and graphite into the second, and zeolites into the third.

There are many useful supporting materials. The most frequently used supports are alumina, mostly as  $\gamma\text{-Al}_2\text{O}_3$ , silica, activated carbon and oxide supports that are usually prepared via precipitation of sol-gel process. In addition, microporous crystalline materials such as zeolites were of interest to replace the conventional amorphous support because of their molecular sieve properties of porous materials. Specific channel structures results in molecular shape selectivity where the size and shape of a diffusing substrate or products are closely matched to a pore diameter of the support. Nowadays, the research for finding new high surface area supports was required due to limitation by the pore size in zeolites, mesoporous materials have gained increasing attention. These materials began with the discovery of M41S family<sup>17</sup> in 1992, and subsequently followed by other mesoporous families.<sup>18-20,30</sup> These materials can be used as supports and can be modified to be catalysts by incorporation of heteroelements into the framework of silica.<sup>23</sup>

Table 2.1 shows properties of some supporting materials.

**Table 2.1** Properties of some supporting materials.<sup>28,31</sup>

Support	Crystallographic phase	Surface area (m <sup>2</sup> /g)	Acidity
Alumina	Mostly $\alpha$ and $\gamma$	100-300	Amphoteric
Silica gel	Amorphous	300-600	Weakly acidic or basic
Silica-Alumina*	Amorphous	364*	Acidic
Zeolites	Crystalline with various structure	300-600	Acidic
HMS	Hexagonal	600-1000	Weakly acidic

\*10% molAl<sub>2</sub>O<sub>3</sub>

### 2.2.1 Amorphous Silica

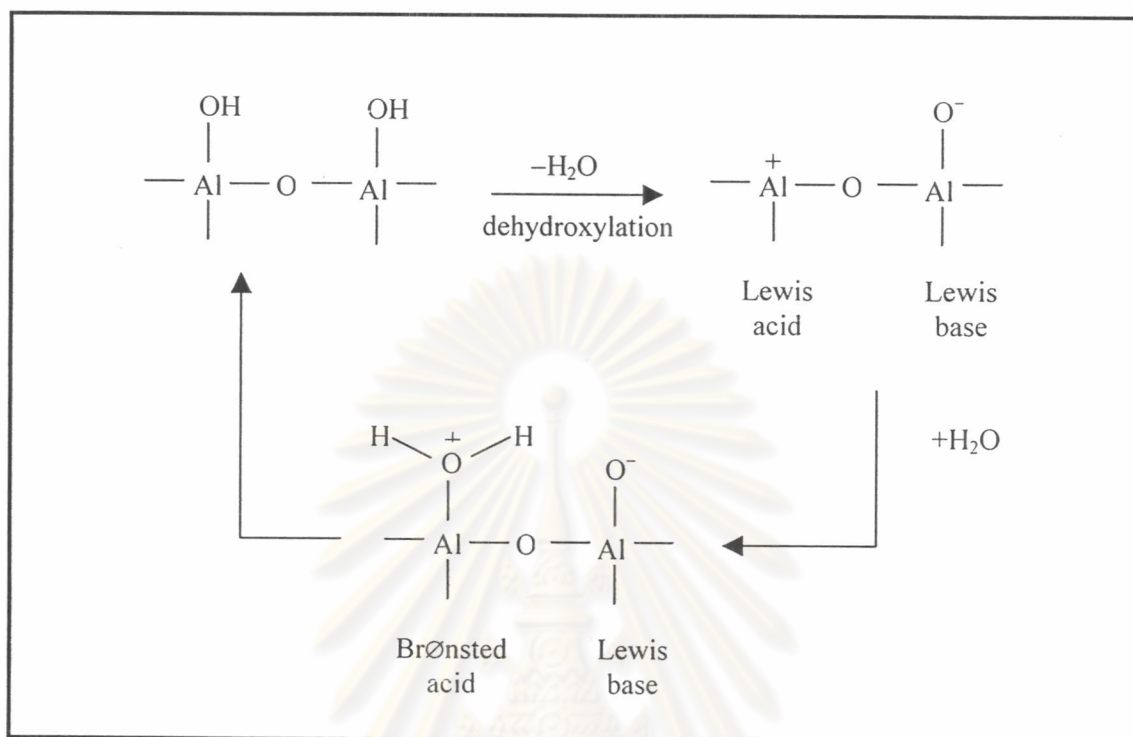
Amorphous silica has no long-range crystalline order.<sup>29</sup> However, short-range order maybe present depending on the method of preparation. The surface of amorphous silica consists of siloxane (Si-O-Si) and silanol (Si-OH) group. Silanol groups are hydrophilic, giving silica gels their characteristic water sorption properties. In addition, silanol groups are also weakly acidic so that amorphous silica can be used as catalyst for facile acid-catalyzed reactions. Although the silica surface is too weakly acidic to participate chemically in catalysis, physisorption of reactants from solution or gas phase onto the silica surface can lead to a local increase in concentration, thereby increasing the rate of reaction. Impurities within the structure of amorphous silica such as aluminum or magnesium lead to the increased surface acidity.



### 2.2.2 Amorphous Alumina

Aluminum oxide or alumina is usually prepared from the dehydration of aluminum hydroxide at the temperature of 900°C in a stream of CO<sub>2</sub>. The resulting alumina particles are coated with a thin layer of aluminum oxycarbonate. This corresponds to a basic grade of alumina. However, water content and alkalinity can be adjusted by washing with acid to give different grades. Thus, alumina is available as basic, neutral and acidic grades. In case of activated alumina, flash calcination of hydrated alumina results in the explosive release of steam. The steam generates an internal pressure, which opens up channels and cavities within the hydrated alumina precursor, giving rise to the high surface area.<sup>29</sup> Activated alumina is an amphoteric, containing either acidic or basic sites as shown in Figure 2.1. Surface acidity can be increased by impregnation with promoters<sup>28,29</sup> such as Cl<sup>-</sup> and F<sup>-</sup>. The strength of acidic and basic sites on surface is strongly dependent on the local environment of the site, and it is usual to find acidic and basic sites coexist. It is nicely illustrated by considering the changes in the acidity of alumina as it undergoes progressive dehydroxylation. Increasing of the temperature causes a decrease in the concentration of Brønsted acid sites as a consequence of dehydration.

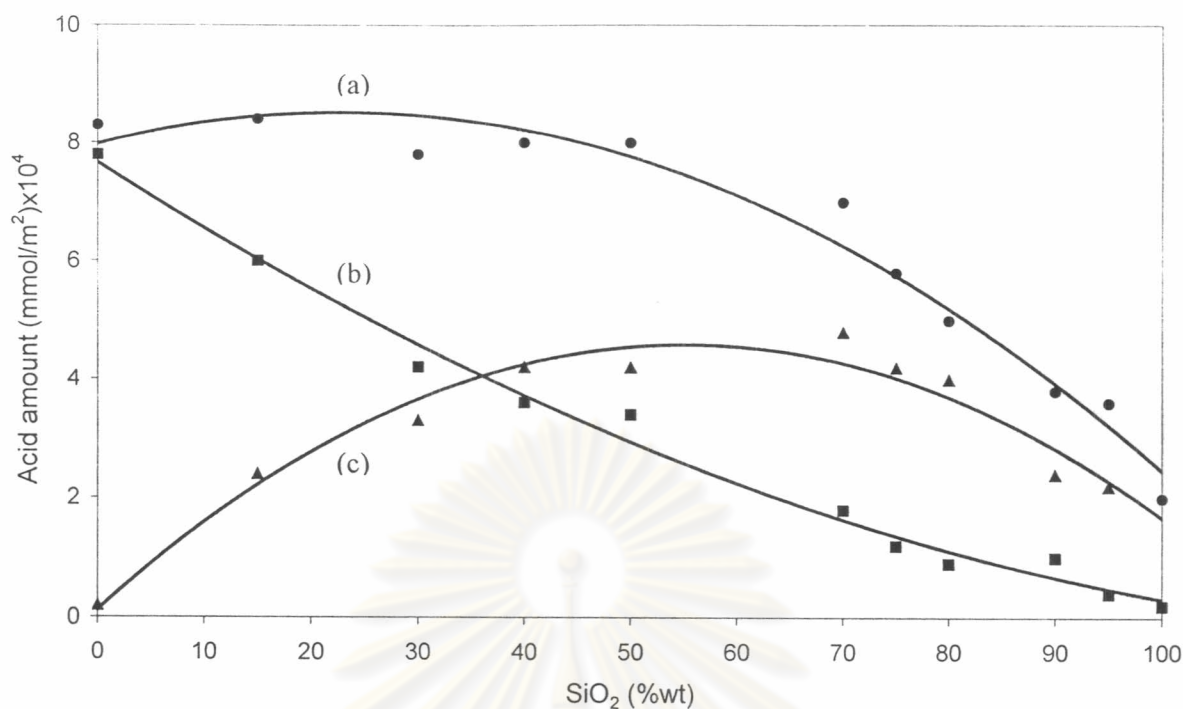
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**Figure 2.1** Acidic and basic sites on alumina.<sup>29</sup>

### 2.2.3 Amorphous Silica-Alumina

The Brønsted and Lewis acid-base properties of a support can also be altered by incorporation of a second metal atom into the framework of a host oxide, or by substitution of surface OH groups by more electrophilic group such as Cl or F. A classic sample of the influence of mixed oxide composition on acid-base properties is that of silica-alumina.<sup>28,29</sup> Figure 2.2 shows that the Lewis and Brønsted acidity of silica-alumina varied with the proportion of silica. Remarkable result is the very high concentration of Brønsted sites formed in the range of 60-80% SiO<sub>2</sub>.

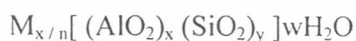


**Figure 2.2** Acid amount of  $\text{SiO}_2\text{-Al}_2\text{O}_3$  versus proportion of  $\text{SiO}_2$ : (a) Total amount of acid, (b) Lewis acid amount and (c) Brønsted acid amount.<sup>28</sup>

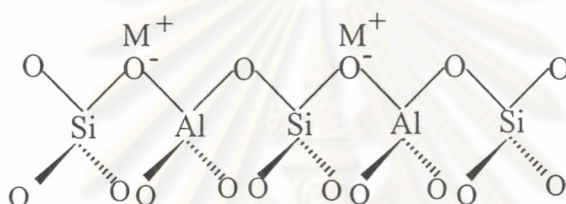
Amorphous silica-alumina is more acidic than either pure silica or pure alumina. When  $\text{Al}^{3+}$  replaces  $\text{Si}^{4+}$  in the structure, it results in the formation of an acidic hydroxyl group  $[(\text{AlO}(\text{OH}))_x (\text{SiO}_2)_{1-x}]$ . Acidic amorphous silica-alumina was used on a large scale as a cracking catalyst before the introduction of zeolite catalysts.

#### 2.2.4 Zeolites

A zeolite is crystalline microporous aluminosilicate with a structure based on an extensive three-dimensional framework which formed by connection of tetrahedral  $[\text{AlO}_4]^{5-}$  and  $[\text{SiO}_4]^{4-}$  linkage.<sup>32</sup> The  $\text{AlO}_4^{5-}$  tetrahedra, or empirically  $\text{AlO}_2^-$ , in the structure determines the framework charge and which is balanced by cations occupied nonframework positions. A representative general formula for a zeolite is written as:



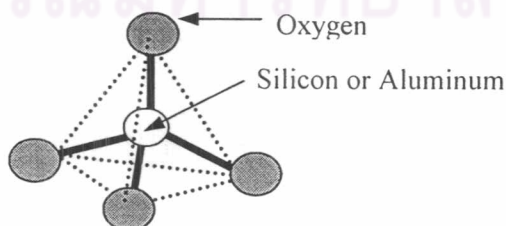
M represents the exchangeable cations, generally from group I or II in the periodic table of elements, and  $n$  represents the cation oxidation state. The value of  $x$  is equal to or greater than 1 because  $Al^{+3}$  does not occupy adjacent tetrahedral sites, otherwise it results in the negatively charged units next to each other. The framework of a zeolite is represented in Figure 2.3. The framework contains channels and interconnected voids which are occupied by the cation M and water molecules.



**Figure 2.3** Framework of zeolites.

#### 2.2.4.1 Structure of Zeolites

The structure of zeolite consisted of a three-dimension framework of the tetrahedral primary building units when tetrahedral atoms are silicon or aluminum. as shown in Figure 2.4



**Figure 2.4** A primary building unit of zeolites.



Adjacent tetrahedra are linked at their corners via oxygen atoms, generating a variety of secondary building units (SBU). A secondary building unit consists of selected geometric groupings of these tetrahedra. There are sixteen SBUs as shown in Figure 2.5, which can be used in describing all of the known zeolite structures.

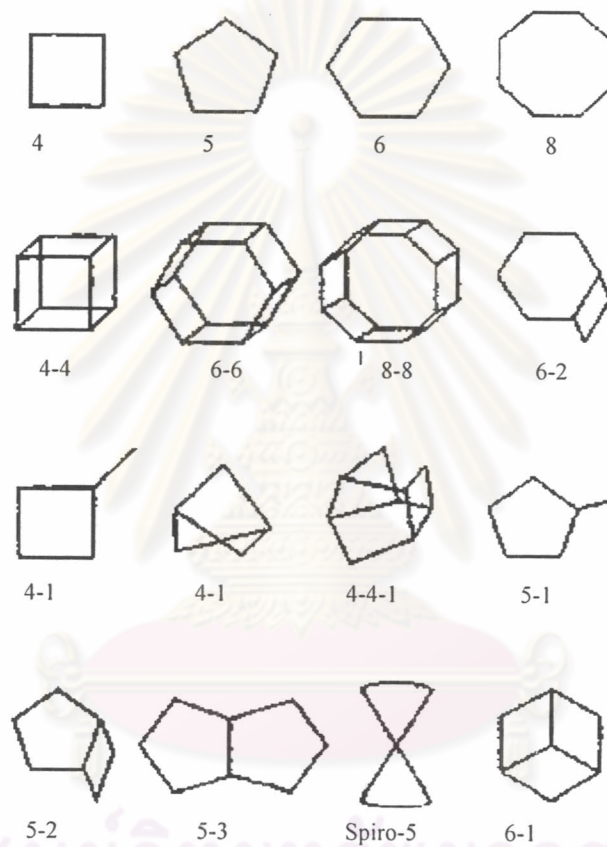
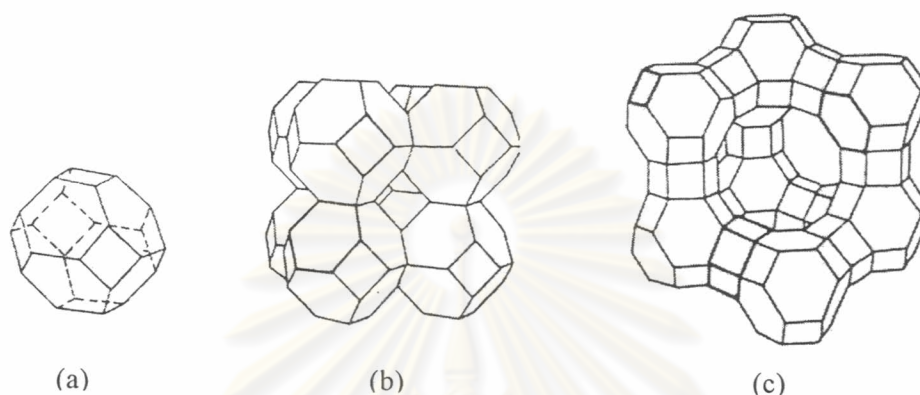


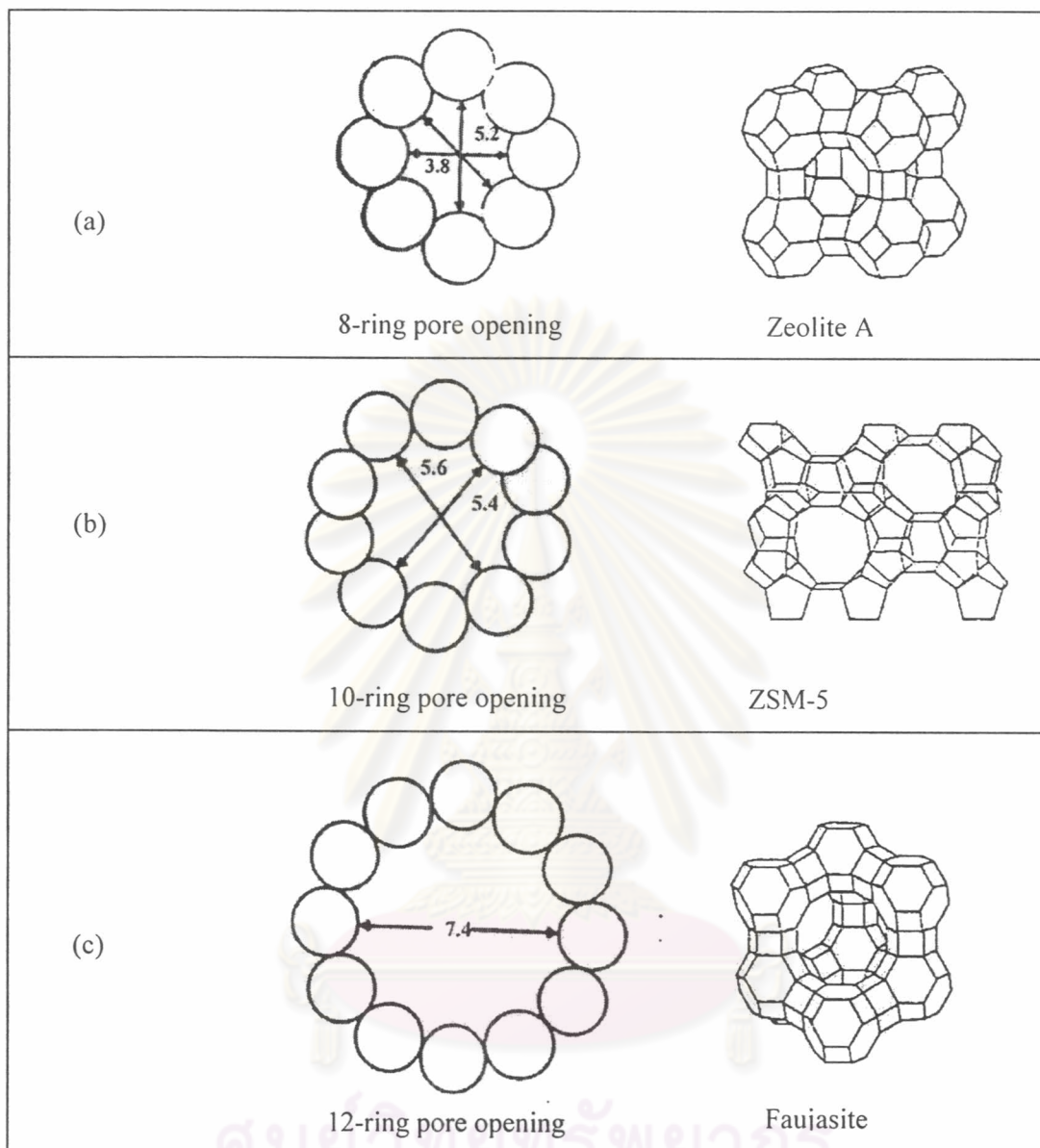
Figure 2.5 Secondary building units of zeolites.<sup>32</sup>

Most zeolite frameworks can be generated from several different SBUs. For example, the sodalite unit can be linked together through the single 4-membered ring, and the single 6-membered ring as shown in Figure 2.6, to form a framework of sodalite or faujasite structure.

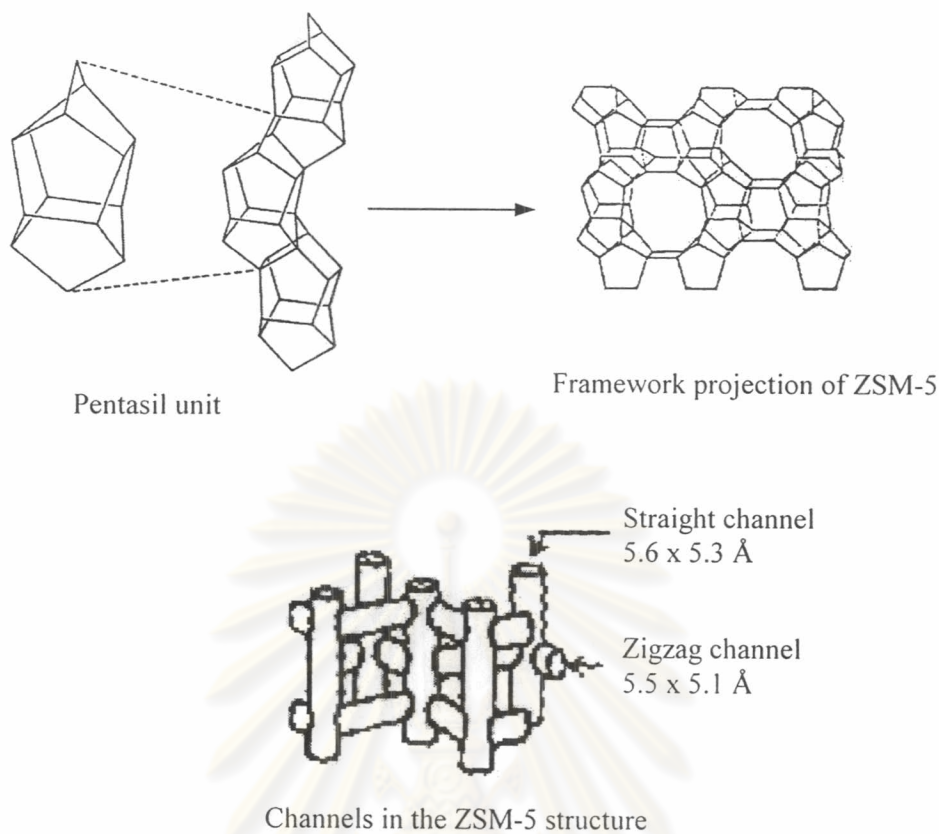


**Figure 2.6** Formation of important fundamental frameworks from the sodalite unit (a), resulting in either sodalite framework (b) or faujasite framework (c).<sup>33</sup>

The different pore sizes found in zeolites were due to the different number of tetrahedral atoms defining the opening, as shown in Figure 2.7. The ring sizes are often mentioned as the number of oxygen atoms which are equal to the number of tetrahedral atoms. One of family of 10-membered oxygen ring zeolites, the ZSM-5 typed zeolite (MFI structure) is probably the most useful one. The formation of pentasil unit resulting ZSM-5 structure is described by the 5-1 secondary building units. The ZSM-5 typed zeolite has two types of channel systems, one with straight channels of pore opening  $5.3 \times 5.6 \text{ \AA}$  and the other with zigzag channels of pore opening  $5.1 \times 5.5 \text{ \AA}$  as shown in Figure 2.8. These intersecting channels are perpendicular to each other, generating a three-dimensional framework. In addition, ZSM-5 has the greatest number of industrial applications.



**Figure 2.7** Example of the three types of pore openings in the zeolite molecular sieve, (a) small pore zeolite, (b) medium pore zeolite and, (c) large pore zeolite.<sup>32</sup>



**Figure 2.8** Formation of the ZSM-5 structure and channel systems.<sup>32,34</sup>

Three variables play important roles on zeolite structures: reactant mixture components, temperature, and time.<sup>32</sup> In general, there are also some other factors such as aging period, stirring, nature (either physical or chemical) of the reaction, and the order of mixing. These factors are sometimes called history-dependent factors.

**(a) Reaction mixture components**

Each component in the reactant mixture contributes to specific characteristic properties of the gel and to the final material obtained. For examples, zeolite ZSM-5 can be synthesized by preparing mixture of tetrapropyl ammonium ion, sodium oxide, an



oxide of silica or germanium, an oxide of aluminum or gallium, and water. The reactant ratio of mixture preferring for ZSM-5 phase formation is shown in Table 2.2

**Table 2.2** Details of the reactant ratio in the gel mixture for ZSM-5 synthesis<sup>35</sup>

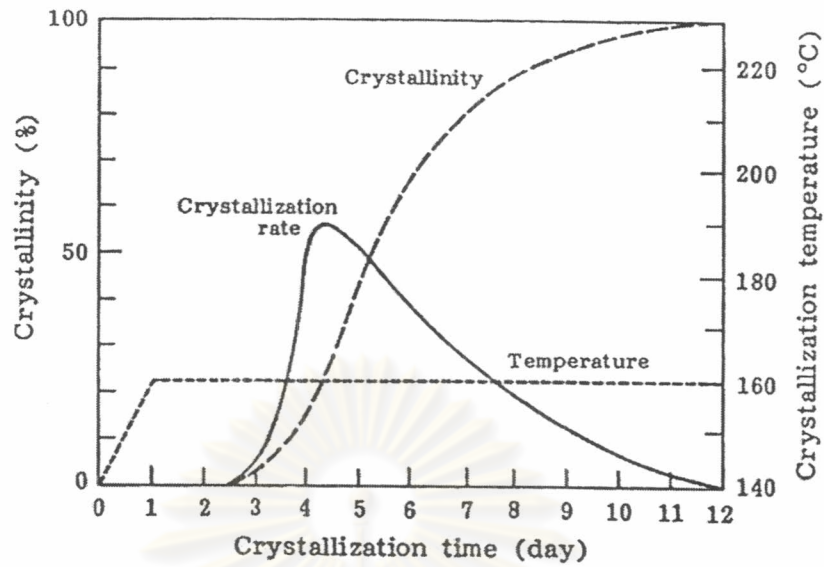
Reactant ratio*	Broad	Preferred	Particular preferred
$\text{OH}^-/\text{YO}_2$	0.07-10	0.1-0.8	0.2-0.75
$\text{R}_4\text{N}^+(\text{R}_4\text{N}^++\text{Na}^+)$	0.2-0.95	0.3-0.9	0.4-0.9
$\text{H}_2\text{O}/\text{OH}^-$	10-300	10-300	10-300
$\text{YO}_2/\text{X}_2\text{O}_3$	5-100	10-60	10-40

\*R is propyl, X is aluminum or gallium and Y is silicon or germanium

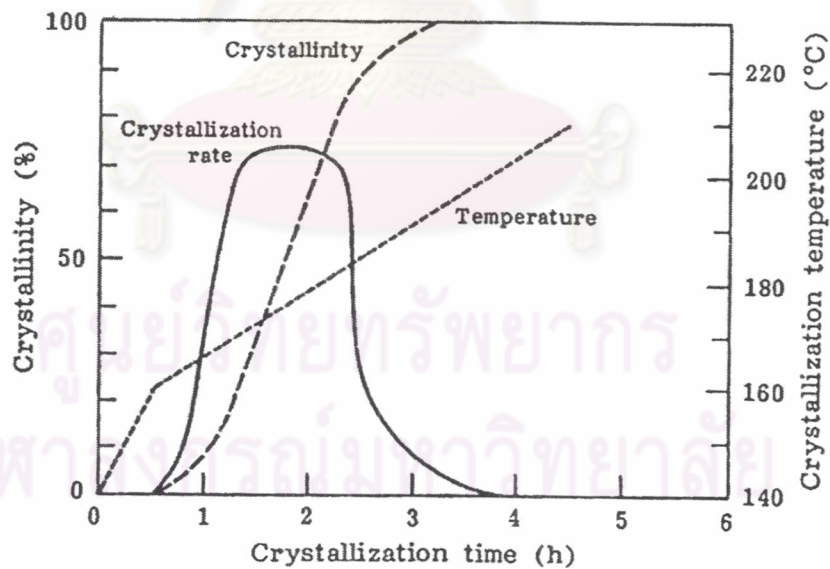
In addition, for template free synthesis when using silica sol as silica source, it was found that at high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  and high  $\text{Na}_2\text{O}/\text{SiO}_2$  ratio, the mixed phase of ZSM-5 and mordenite zeolites is preferred.<sup>36</sup> On the other hand, when the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  was low but  $\text{Na}_2\text{O}/\text{SiO}_2$  ratio still high, the mixed phase of zeolites become the pure phase of mordenite zeolite. The optimal condition for ZSM-5 formation is  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 50-70$  and  $\text{Na}_2\text{O}/\text{SiO}_2 = 0.13-0.20$  while mordenite formation is  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 20-25$  and  $\text{Na}_2\text{O}/\text{SiO}_2 \geq 0.20$ . Therefore, a suitable condition has to be carefully selected in order to obtain a pure phase of the wanted zeolite product.

### (b) Temperature

Temperature influences the zeolite phase obtained and crystallization time. The crystallization period decreases with increasing temperature. However, as the temperature changes, conditions may favor formation of other phases. The rate of crystallization and changing of temperature is shown in Figure 2.9 and 2.10..



**Figure 2.9** Conceptual for the changing of crystallization rate and crystallinity with time on hydrothermal treatment at constant temperature.<sup>37</sup>

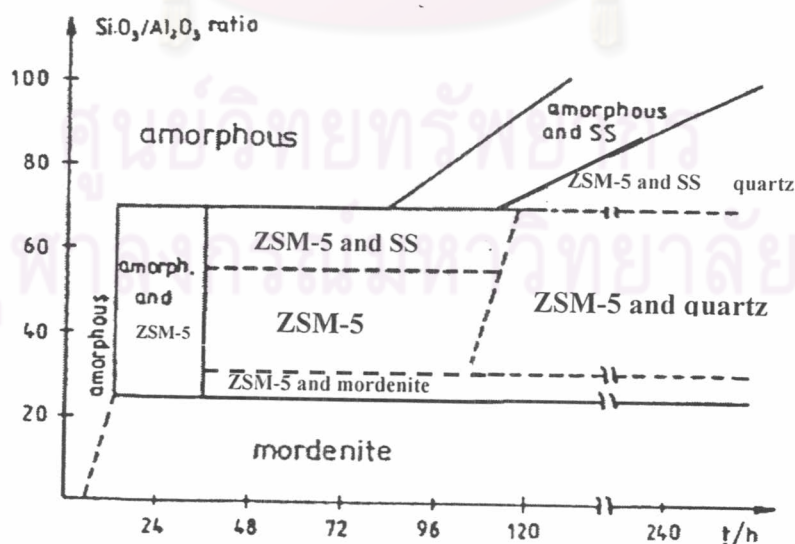


**Figure 2.10** Conceptual for the changing of crystallization rate and crystallinity with time on hydrothermal treatment with programmed temperature rise.<sup>37</sup>

In case of the ZSM-5 synthesis, the temperature range is 100-170°C for a period ranging from 6 to 60 days.<sup>35</sup> However, the preferable condition is 100-170°C for 12 h to 8 days. The higher temperature, the shorter crystallization time is needed. The conventional synthesis of zeolite ZSM-5 can be modified to rapid crystallization method<sup>37</sup>, applying the temperature program for crystallization of the ZSM-5 from the concept as shown in Figure 2.10.

### (c) Time

Zeolites are metastable phase and can recrystallize to other more stable phase which can be observed with prolonged crystallization time. Crystallization parameters must be adjusted to minimize the production of other undesired phase and also to minimize the time needed to obtain the desired crystalline phase. This parameter correlated with temperature in that the period of time can be reduced by increasing temperature. Figure 2.11 shows the effect of time on phase transformation in template free synthesis of ZSM-5.



**Figure 2.11** Isothermal phase transformation diagram of the template free synthesis of ZSM-5, SS denotes sheet structure.<sup>38</sup>

### 2.2.4.2 Acid Sites in Zeolites

Classical Brønsted and Lewis acid models of acidity can be used to classify the acid sites in zeolites. Brønsted acidity is at the proton donor site, and electron deficient atom that can accept an electron pair behaves as a Lewis acid site. Both types of acid sites occur in zeolites as shown in Figure 2.12.

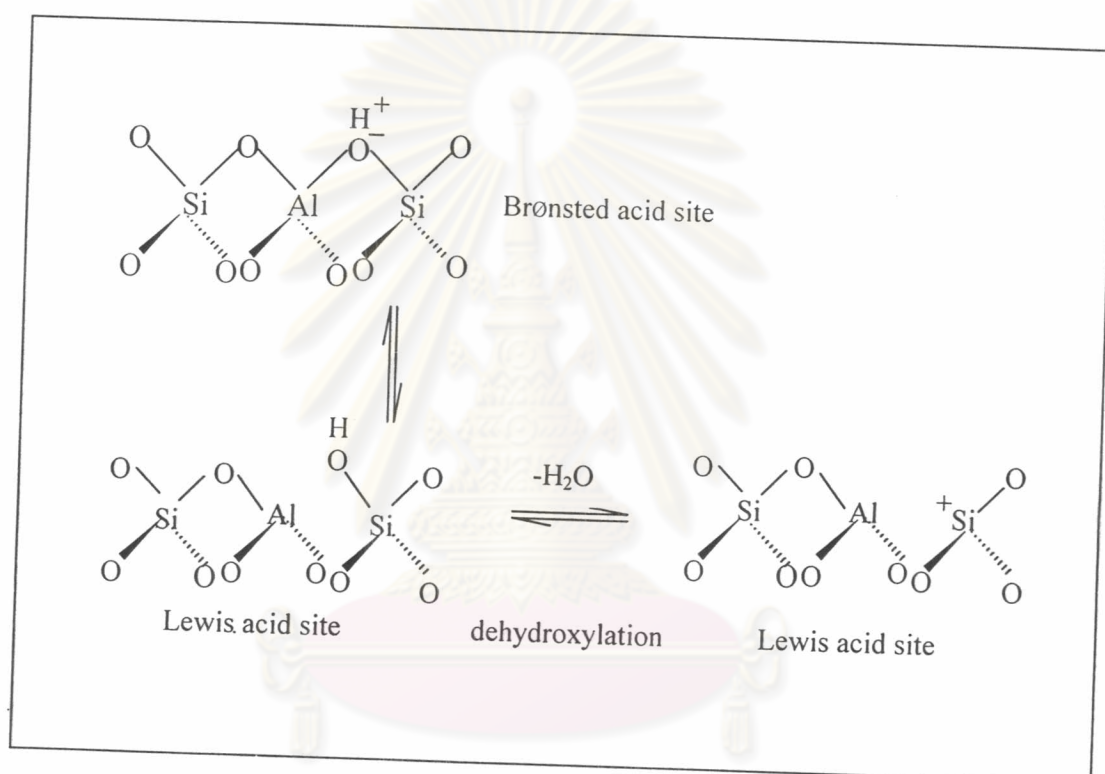


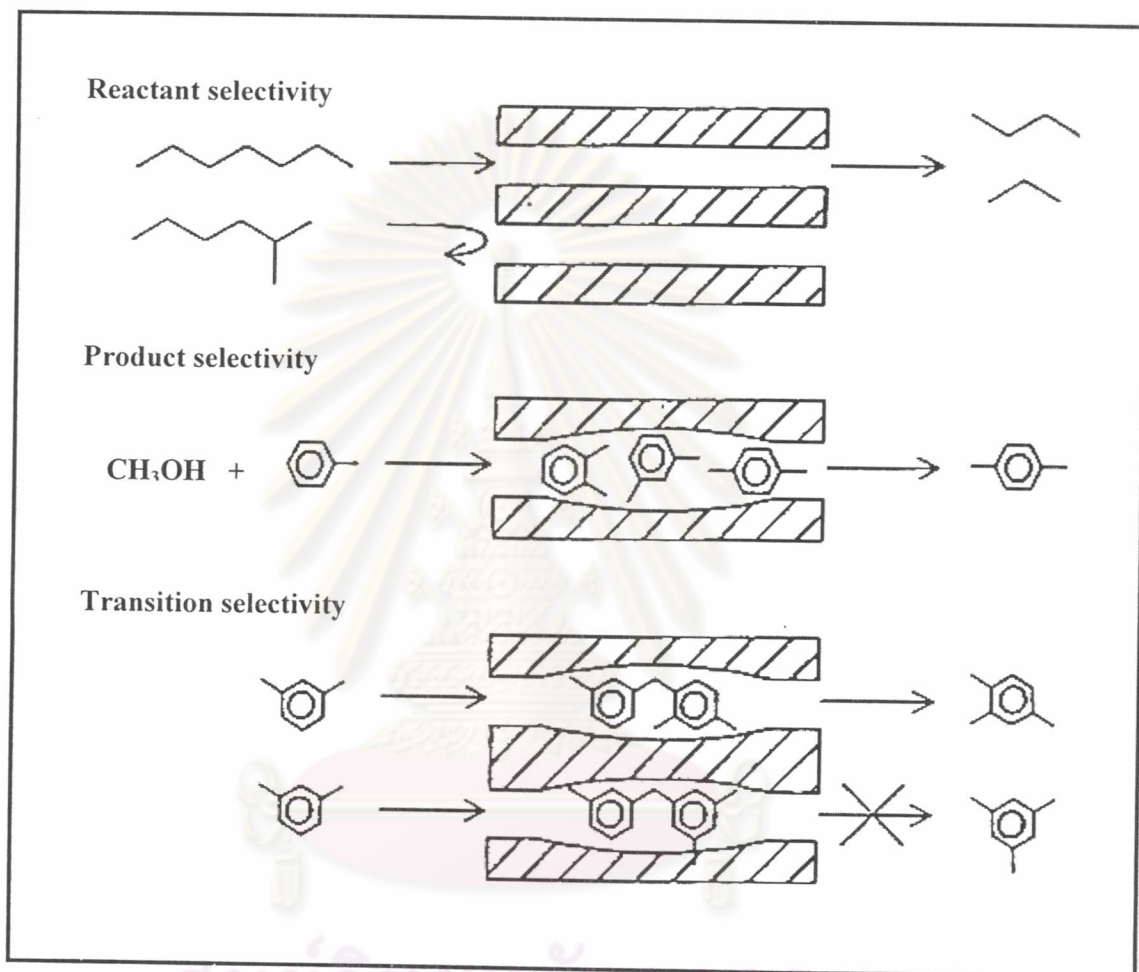
Figure 2.12 Brønsted and Lewis acid sites in zeolites.<sup>11</sup>

### 2.2.4.3 Shape Selectivity

The combination of high internal surface area, acid sites, selective sorption and molecular sieve properties, makes zeolites the most useful among versatile heterogeneous catalysts. High internal surface area and acidity give rise to high activity, while selective sorption and molecular sieve properties result in high reaction selectivity. Reaction selectivity may be diffusionally controlled (reactant or product



selectivity) or may be geometrically controlled (transition state selectivity). Figure 2.13 shows the models for the three types of selectivity observed in zeolites.



**Figure 2.13** Diagram depicting three types of selectivity: reactant, product and transition-state shape selectivity.<sup>32</sup>

### 2.2.5 Mesoporous Materials

Two classes of materials that are used extensively as heterogeneous catalysts and adsorption media are microporous and mesoporous materials. Well-known members of the microporous class are zeolites. Although zeolites exhibit excellent catalytic properties, their applications are limited by the relatively small pore openings, which constraint pore-size ( $<15 \text{ \AA}$ ) of microporous zeolites. Until 1992, Mobil corporation researchers<sup>17</sup> discovered a new family of mesoporous silicate molecular sieves called M41S. These mesoporous silicate materials have well-defined pore sizes of 15-100  $\text{\AA}$ . The extremely high surface areas of greater than  $1,000 \text{ m}^2/\text{g}$  and the ability to precisely tune the pore sizes are among the many desirable properties that have made such materials the focus of great interest. The M41S family is classified into several members. The most useful one is MCM-41 with hexagonal structure. Since the synthesis of M41S was reported, there are a considerable development to search for new mesoporous materials and to investigate their properties. Recently there are many families of mesoporous materials.<sup>17-20,23,30</sup> Especially, new mesoporous member with hexagonal structure was discovered, such as HMS<sup>19,30</sup> (Hexagonal Mesoporous Silica), FSM-16 (Folded Sheets Mesoporous Materials)<sup>18</sup> and SBA-15 with straight hexagonal structure.<sup>20</sup> Because different types of templates can be used for synthesizing hexagonal mesoporous materials at various pH of gel, the new hexagonal materials can be obtained.<sup>39</sup> The interaction of various types of template with inorganic species for assembling these materials are different as summarized in Table 2.3, together with the condition typically employed for a synthesis.

**Table 2.3** Various synthesis condition of hexagonal mesoporous materials and the type of interaction between template and inorganic species.

Material	Template	Assembly	Media (pH)
MCM-41	Quaternary ammonium salt	Electrostatic	Basic or Acid
FSM-16	Quaternary ammonium salt	Electrostatic	Basic (pH = 8.5)
SBA-15	Amphiphilic triblock copolymer	Hydrogen bonding	Acidic (pH = 1-2)
HMS	Primary amine	Hydrogen bonding	Neutral

MCM-41 and FSM-16 can be synthesized using quaternary ammonium salt as a template. In case of SBA-15, amphiphilic triblock copolymer can be modified as a template and must be synthesized in acid condition of hydrochloric acid. On the other hand, HMS can be prepared in neutral and environmentally benign condition using primary amine as a template. Although these materials have the same hexagonal structure, some properties are different as shown in Table 2.4.

**Table 2.4** Properties of some hexagonal mesoporous materials.<sup>17,30,40-42</sup>

Material	Pore size (Å)	Wall thickness (nm)	BET specific surface area (m <sup>2</sup> /g)	Framework structure
MCM-41	15-100	1	>1000	Honey comb
FSM-16	15-32	-	680-1000	Folded sheet
SBA-15	46-300	3-6	630-1000	Rope-like
HMS	29-41	1-2	640-1000	Wormhole

### 2.2.5.1 Characterization of Hexagonal Structure by XRD

Reliable characterization of the porous hexagonal structure requires the use of X-ray powder diffraction (XRD). The XRD patterns of hexagonal mesoporous materials show typically three to five reflections of two theta ( $2\theta$ ) between  $2^\circ$  and  $5^\circ$ . The reflections are due to the ordered hexagonal array of parallel silica tubes, and can be assigned to the corresponding lattice planes of Miller indices (100), (110), (200), (210) and (300). Since the materials are not crystalline at the atomic level, no reflections at higher angles are observed. The wall thickness can be calculated by determining the difference between the lattice parameter ( $a = 2d_{100}/\sqrt{3}$ ). From Bragg's law, when an X-ray beam strikes a crystal surface at some angle  $\theta$ , a portion is scattered by the layer of atoms at the surface. The unscattered portion of the beam penetrates to the second layer of atoms<sup>43</sup> as shown in Figure 2.14, where  $d$  is the interplanar distance of the crystal. Thus, the conditions for constructive interference of the beam at angle  $\theta$  can be described by Bragg equation which is written as Equation (2.1).

$$n\lambda = 2d \sin\theta \quad (2.1)$$

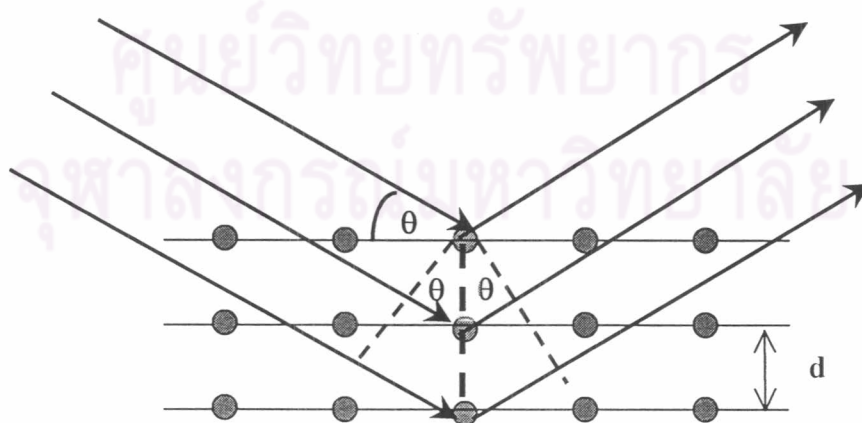


Figure 2.14 Diffraction of X-ray by a crystal.<sup>43</sup>



Hexagonal structure have characteristics of d-spacing ratio as follows :

$$d_{100}/d_{110} = d_{200}/d_{220} = 1.732 = \sqrt{3} \quad (2.2)$$

$$d_{100}/d_{200} = d_{200}/d_{400} = 2.000 \quad (2.3)$$

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (2.4)$$

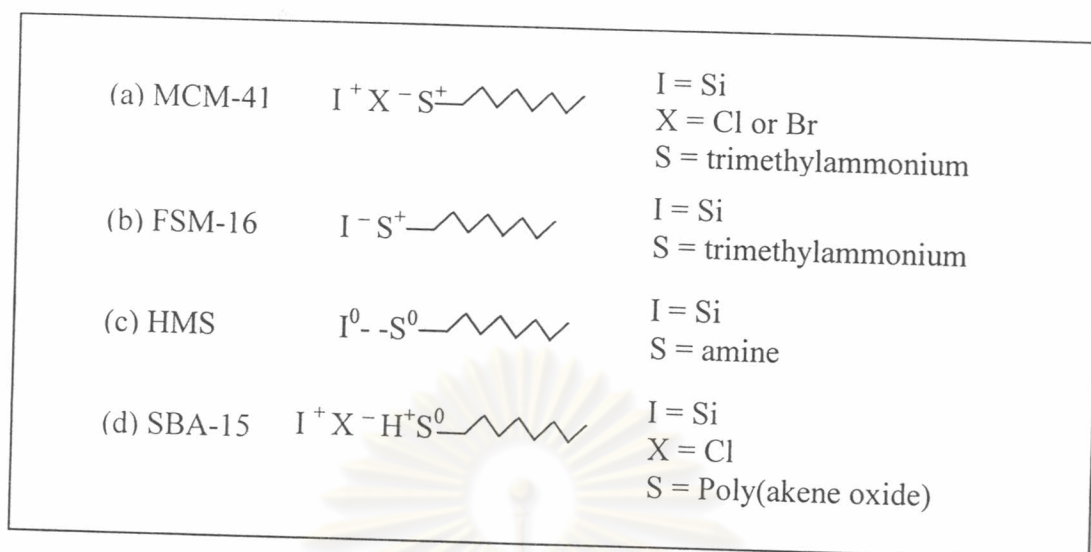
From Equation (2.2), (2.3), and (2.4)

$$a = 2d_{100}/\sqrt{3} \quad (2.5)$$

In addition, characteristic peaks in XRD patterns indicates order of hexagonal structure. HMS has long-range order hexagonal structure owing to the very weak 110, 200, 210 peaks in XRD pattern compared to other hexagonal phase. Only 100 peak occurs in XRD pattern of HMS. It means HMS has low scattering domain size.<sup>23,30</sup>

#### 2.2.5.2 Mechanism of Mesostructure Formation

A number of models have been proposed to explain the formation of mesoporous materials and to provide a rational basis for the various synthesis routes.<sup>39</sup> On the most common level, these models are predicted upon the presene of surfactants in a solution to direct the formation of the inorganic mesostructure from the solubilized inorganic precursors. The type of interaction between the surfactant and the inorganic species was significantly different depending on the various synthesis routes as shown in Figure 2.15.

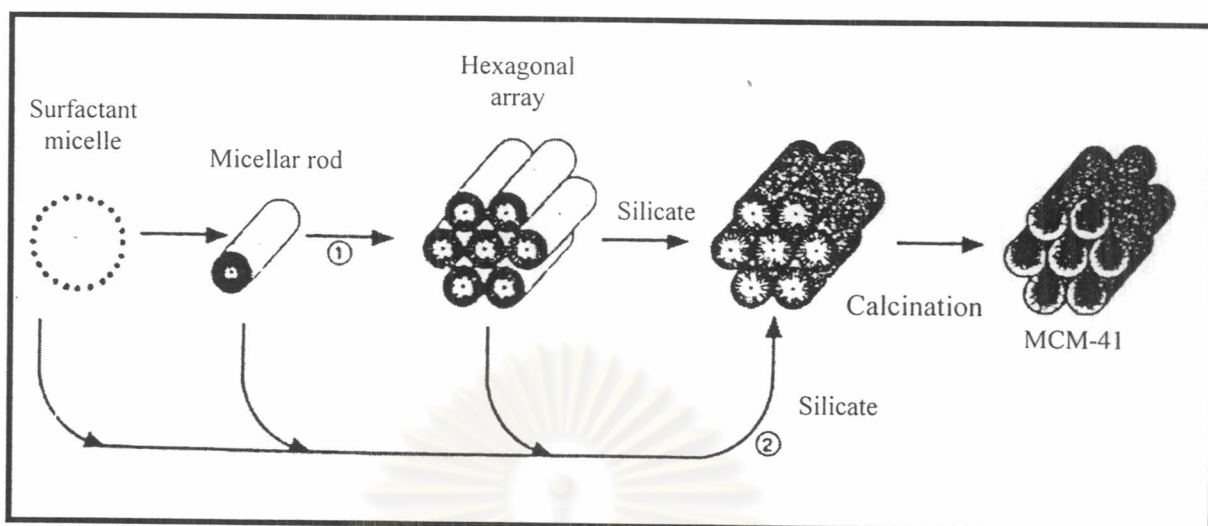


**Figure 2.15** Schematic representation of various types of interaction of surfactant head group with inorganic species: electrostatic in MCM-41 (a)  $I^+ X^- S^+$  and FSM-16 (b)  $S^+ I^-$ , hydrogen bonding in HMS (c)  $S^0 I^0$  and SBA-15 (d)  $I^+ X^- H^+ S^0$ .

In case of MCM-41 and FSM-16, the interaction between template and inorganic species is electrostatic interaction while hydrogen bonding interaction occurs in HMS and SBA-15 synthesis.<sup>44</sup> The pore diameter of these materials were controlled by alkyl chain length of surfactant. Mechanism of mesoporous formation were different depending on synthesis route for each material.

### (a) Liquid Crystal Templating Mechanism

A liquid crystal templating (LCT) mechanism was proposed by the Mobil researchers that firstly reported M41S material. The variation of surfactant concentration plays a significant role to control the structure. When surfactant / Si ratio was lower than 1, hexagonal mesophase was obtained. Figure 2.15 shows two possible pathways for the LCT mechanism for hexagonal MCM-41 synthesis.

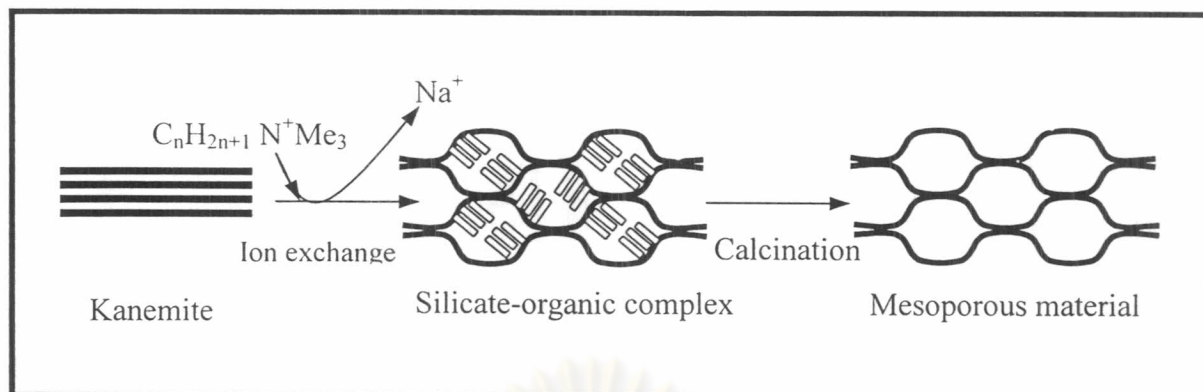


**Figure 2.16** Two possible pathways for the LCT mechanism.

There are two main pathways, in which either the liquid-crystal phase was intact before the silicate species were added (pathway 1), or the addition of the silicate results in the ordering of the subsequent silicate-encased surfactant micelles (pathway 2).

### (b) Folding Sheet Formation

The intercalation of ammonium surfactant into hydrated sodium silicate, which composed of single-layered silica sheets called kanemite, produced the lamellar-to-hexagonal phase in FSM-16 material preparation. After the surfactants were ion-exchanged into the layered structure, the silicate sheets were thought to fold around the surfactants and condense into a hexagonal mesostructure. The final product was claimed to be very similar to MCM-41. However, Vartuli *et al.* found that the layered structures were still retained in the kanemite-derived mesoporous materials.<sup>39</sup> Folding sheet formation is illustrated in Figure 2.17.



**Figure 2.17** Folding of silicate sheets around intercalated surfactant molecules.

### (C) Hydrogen Bonding Interaction

Tanev and Pinnavaia<sup>30</sup> showed that mesoporous silica could be prepared by the hydrogen-bonding interaction of alkylamine ( $S^0$ ) head group and hydroxylated tetraethylorthosilicate ( $I^0$ ) as shown in Figure 2.18. The materials lacked long-range order of pore, but had higher amounts of interparticle of mesoporosity, because the long-range effects of the electrostatic interaction that would normally control the packing of micellar rods were absent. This neutral templating synthesis route produced mesoporous silicates with thicker walls and higher thermal stability compared to the LCT-derived silicates. The silicate framework in the resulting mesophase was neutrally charged. From this reason, the surfactant can be easily removed by solvent extraction.





## 2.6 Hexagonal Mesoporous Silica (HMS)

HMS was discovered in 1994 by Pinnavia *et al.*<sup>19</sup> This material can be synthesis at room temperature by neutral templating route. In this case, primary amine can be used as a template, alcohol such as ethanol or propanol was used as a cosolvent.<sup>30</sup> Although alcohol behaves as a cosolvent in HMS synthesis, it make a different of polarity of mixed solvent, resulting different hydrolysis rate and nucleation rate. Pinnavaia and coworker revealed the different properties of HMS between the water rich system (water : ethanol = 90 : 10 v/v) and ethanol rich system (water : ethanol = 35 : 65 v/v). Textural mesoporosity or the porosity arising from intraaggregate void and spaces formed by interparticle contacts of HMS using water rich system is higher. In the ethanol rich system, HMS with low textural porosity was obtained and the particles are composed of macroscale spheroidal particles aggregate into the larger particles while water rich system yields mesoscale particle aggregate into larger particles.<sup>45</sup>

The pore size of HMS can be controlled by alkyl chain length between C<sub>8</sub>-C<sub>18</sub> in primary amine templates<sup>30</sup> and also modified with auxiliary structure modifier such as mesitylene to expansion the pore of HMS.<sup>45</sup> Due to the interaction between template and inorganic species is hydrogen bonding, the organic phase can be totally removed from as-synthesized samples by solvent extraction, which is not possible in the case of the other pathways where strong electrostatic interactions exist between organic and inorganic phase. The solvent extraction can prevent the partial degradation of the mesoporous structure that could occur during calcination in air at a relatively high temperature. In addition, the environmentally synthesis condition make many researcher focused on HMS synthesis and its potential application.<sup>23</sup>

Pure silica HMS was limited its application to catalysis, supports or adsorbents. In order to provide HMS with potential catalytic application, it was possible to modify the nature of framework by incorporation of heteroelement.<sup>23</sup> When trivalent metal cations like  $\text{Al}^{3+}$ ,  $\text{B}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Fe}^{3+}$  were incorporated to framework of silica, negative charges were occurred that can be balanced with proton. These solid catalyst can be used as acid catalyst or acid support. Acidity Adsorption of pyridine result on Al-HMS reported by Tuel *et al* showed that Al-HMS contain both Lewis and Brønsted acid sites. The Brønsted acid sites in Al-HMS were weaker and their strength was approximately the same as that of amorphous silica-alumina. In addition, Mokaya and Jones was found that directly calcined Al-HMS with Si/Al as 5 possessed acid sites very similar in strength to HY zeolite. To function as support material, Al-HMS was used as support in cracking, dehydrogenation, hydrodesulfurization<sup>46</sup>, selective catalytic reduction of NO with  $\text{NH}_3$ <sup>47</sup>, Fischer-Tropsch<sup>48</sup> etc.,.When other cations like  $\text{Ti}^{4+}$ ,  $\text{V}^{4+}$ ,  $\text{Sn}^{4+}$ ,  $\text{Zr}^{4+}$  substituted for silicon in the framework, the electroneutrally was maintained and the metal-containing can be used as oxidation catalyst.

## 2.7 Supported Homogeneous Catalysts

Although some of organometallic complexes exhibit remarkable catalytic properties, difficulting in separation from reaction media make them uneconomical. Thus, The heterogenization of homogeneous catalysts is a field of continuing interest. Many different strategies can be considered.<sup>49</sup>

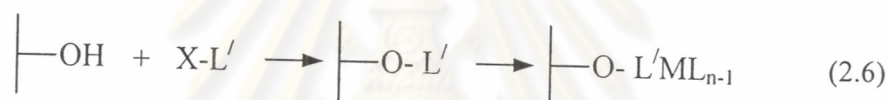
### (1) Physisorption

This method is applied to volatile uncharged organometallic compounds such as  $\text{Ni}(\text{CO})_4$ ,  $\text{Fe}(\text{CO})_5$  and  $\text{Mo}(\text{CO})_6$  using zeolite as a support. The molecules can be

adsorbed on the surface of zeolite by vapor deposition. The molecules loosely hold in zeolite cavities by weak Van der Waal interaction, classified as physical adsorption (physisorption). This interaction cannot prevent the leaching of metal complexes from pore into solution during catalytic reaction.

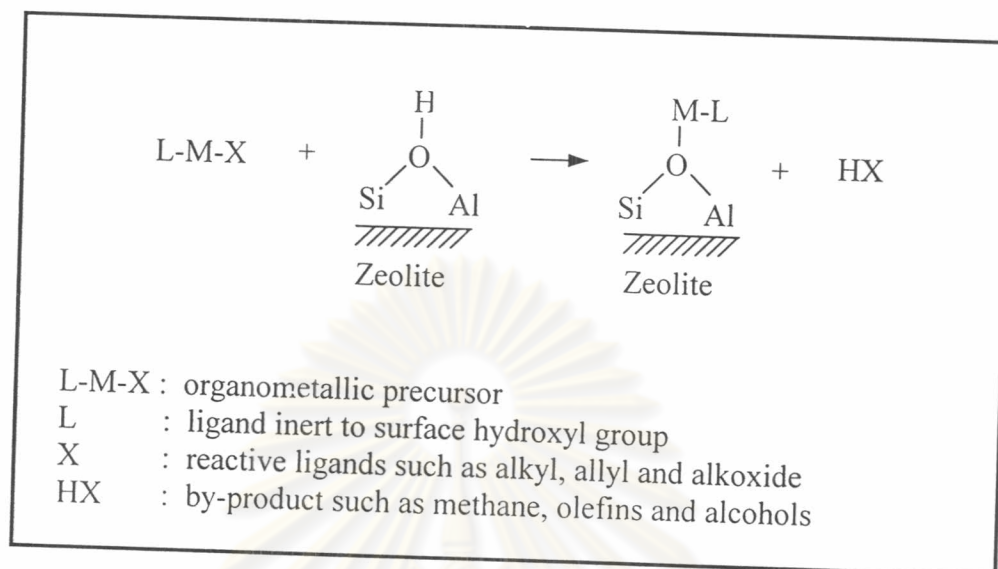
## (2) Anchoring

Most of the studies use silica as the support, because it is chemically inert, thermally stable and has hydroxyl groups which allow for ligand bonding. Two different approaches were used, which are represented below in equation 2.6 and 2.7.



The first approach shown in equation 2.6 consists of functionalizing the surface of silica by reaction between a bifunctional ligand (X-L') and the surface silanol. The second approach, shown in equation 2.7, consists of synthesizing the metal complex with desired functionalized ligand (L') which interacts to hydroxyl group on surface of silica. In case of using zeolite as a support, the precursor must have ligand such as methyl, allyl, alkoxide and chloride which are reactive to protons of acidic zeolite. The fragment of the metal species is stabilized by coordination between the metal center and oxygen of the zeolite framework as shown in Figure 2.19. However, disadvantage of this method is from the nature of moisture and air sensitive of organometallic compound, so making it difficult to handle.





**Figure 2.19** Anchoring of organometallic precursor on zeolite surface.

### (3) Encapsulation

Encapsulating or engaging the catalyst in the voids of porous materials is also known as “ship in the bottle” method, which was first used for preparing Nickel complex in pore of zeolite X. This method has been developed from the idea of assembling a ship in a glass bottle. Small parts of the ship were transferred into a bottle, the ship was built up from the parts within the bottle. This idea can be applied when synthesized complex is too large and rigid to migrate into the pore of support. There are two steps in preparing the size encapsulation product. The First step is ion exchange making a counter ion of the zeolite framework to be able to form a chelated complex for encapsulation in the second step. Examples of this approach were illustrated in Figure 2.20.

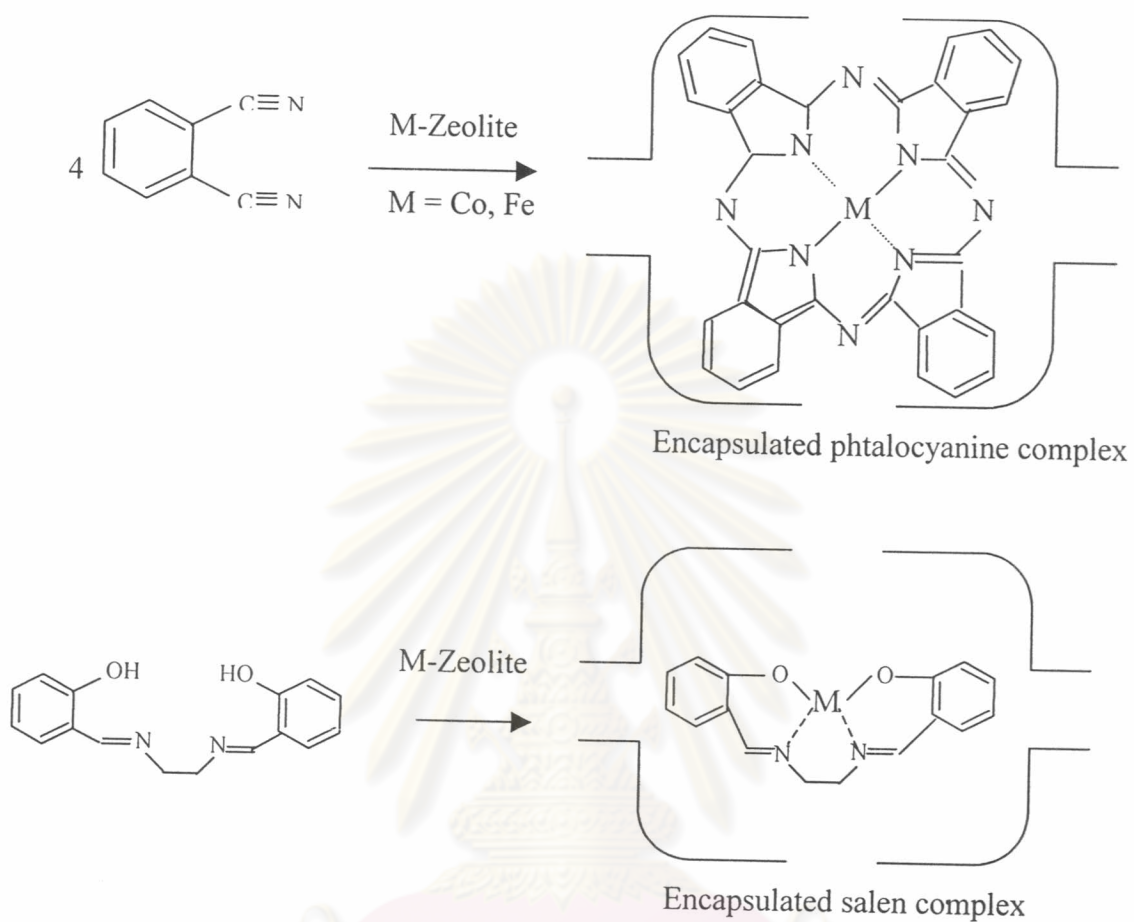
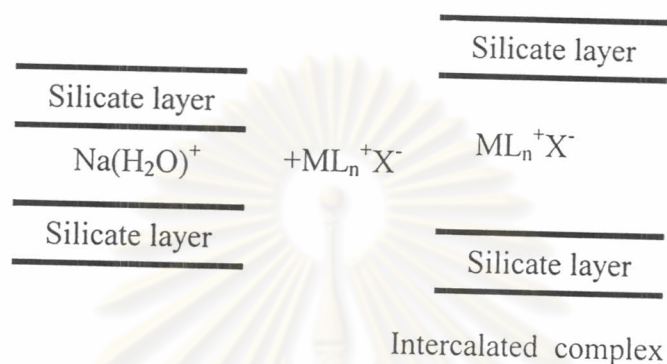


Figure 2.20 Encapsulated complex formation.<sup>49</sup>

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#### (4) Intercalation

This method introduces the cationic catalyst between the silicate layers of swelling clays by the conventional ion exchange procedure as shown in Figure 2.21.



**Figure 2.21** Synthesis of intercalated complexes.<sup>49</sup>

### 2.8 Supported Metal Catalysts

The term supported catalyst is used in a very wide meaning and not only in system which the transition metal compound is linked to the support. Metal catalysts are usually prepared by dispersing the metal onto a high surface area support, to assure that a high proportion of the metal atoms is available for interaction with gaseous reactants. Most of the supporting materials mentioned above are not purely oxidic unless treated at very high temperatures above 1000K, but contain varying amounts of water in the form of surface hydroxyl groups.<sup>5</sup> In general, the higher the treatment temperature of the support the lower the water content, but the surface area also usually decreases with the treatment temperature. The surface hydroxy groups are sites at which the precursor of the active species interacts with the support. A supports can be loaded with the active compound by various techniques. The most important ones being impregnation. In addition, ion exchange method can be used for the support having ion exchange properties such as

zeolites that are cation exchanger materials. According to the purpose for dispersing metal to support, highly dispersed metal catalysts can also be synthesized by means of modified metal atoms. The metal ions are in the gel mixture for preparing of support in sol-gel synthesis. It was called direct synthesis. For example incorporation of heteroatom into framework of pure silica mesoporous material using metal salts yields varied useful catalyst.<sup>23</sup>

### **(1) Impregnation**

Impregnation is the easiest method of making a heterogeneous catalyst.<sup>31</sup> A support or carrier, usually a porous material will be in contact with a solution of one or more suitable metallic compounds. The carrier is then dried, and the catalyst is activated as in case of precipitated catalysts. The size and shape of the catalyst particles are those of the carrier. The impregnation technique requires less equipment since the filtering and forming steps are eliminated and washing may not be needed. It is the economically desirable method in preparing supported metal catalysts in order to spread out the metal in a highly dispersed form as possible. Impregnation method can be divided into two types;

#### **(a) Wet Impregnation**

This method can be done by adding an excess amount of metal salt solution into supports. The composition of the solution will be changed slowly as the metal is absorbed on the surface. Thus, the metal content on the support will not be equal to the initial content in the solution. Besides, the release of support debris in the solution might form a mud, which makes it difficult to separate from the catalyst.

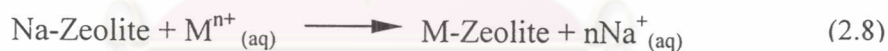
#### **(b) Dry Impregnation or Impregnation to Incipient Wetness**



This method is favored for industrial catalysts because the solution of metal salt will be dispersed by spraying on supports. The volume of solution should be equal to the pore volume of support in order to control the amount of active component. The required catalyst was obtained after drying and calcination step.

## (2) Ion Exchange

Zeolites are cation exchangeable materials. Metal ion and cationic complexes can occupy framework cation sites of zeolite as shown in Equation 2.8. Metal zeolite can be prepared by ion exchange with zeolite containing Na ions (Na-zeolite) with an aqueous solution of metal (M). The interaction is stronger than that on the case of physisorption. This method provides stronger coulombic interaction between cationic species and zeolite anionic framework.



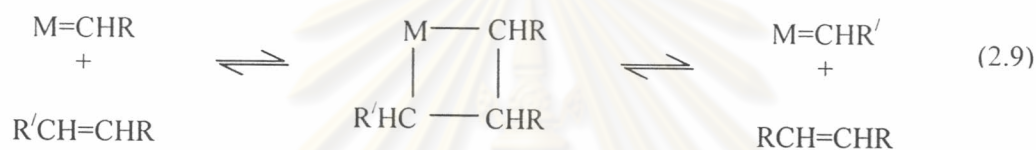
This method is simple and effective. However, it is limited to materials with exchangeable ions, mostly clays and zeolites.

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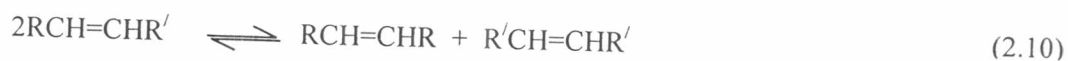
## 2.9 Olefin Metathesis

### 2.9.1 Definition of Olefin Metathesis

Olefin metathesis or olefin disproportionation<sup>50</sup> is a reaction in which alkenes are converted into new form products via the reformation C-C double bonds in the presence of metal carbene. Each half of one olefin can become attached to either half of the other olefin. The general form of olefin metathesis reaction is shown in Equation (2.9).



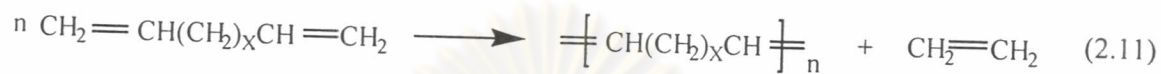
Exchange of the group around the double bond in the olefins, resulting in several outcomes: straight swapping of group between two acyclic olefins molecules, closure of ring, formation of dienes from cyclic olefins, polymerization of cyclic olefins, and polymerization of acyclic dienes. Depending on the starting olefins and the reaction parameters, different types of mono-olefin and diolefin undergo metathesis *via* contact with a suitable catalyst resulting in a wide variety of possible products as shown in Equations 2.10 to 2.13. In fact, many olefinic substrates can undergo metathesis in the presence of a suitable catalyst, resulting in a wide variety of possible products. These substrates include acyclic alkenes, dienes, polyenes, cyclic alkenes and also functionally substituted alkenes, such as unsaturated esters, nitriles, halogens etc.

Acyclic olefins

(R and R' = alkyl or H)

Diolefins

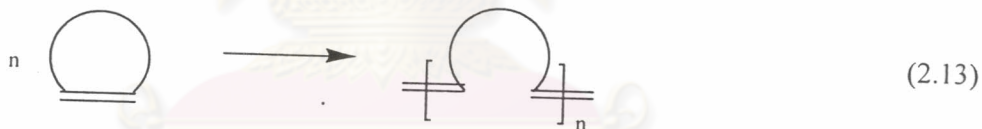
(a) Intermolecular Reaction : Acyclic diene metathesis polymerization (ADMET)




(b) Intramolecular Reaction : Ring-closing metathesis (RCM)

Cyclic Olefins :

Ring opening metathesis polymerization (ROMP)



(where ) represents a hydrocarbon chain with or without a heteroatom)

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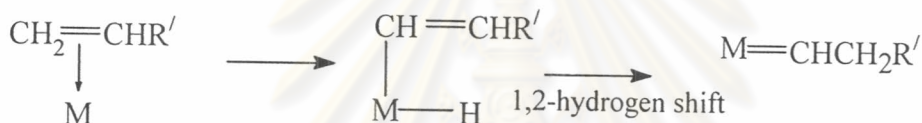
Metathesis reactions of acyclic mono-olefins can be classified into two groups: (1) a self-metathesis of a single olefin, and (2) a cross-metathesis of double-bond isomers of two different olefins. The self-metathesis reaction occurs between a pair of molecules of two original unsymmetric olefins in order to produce a pair of symmetric olefins; for example,  $R^1CH=CHR^2$  produces  $R^1CH=CHR^1$  and  $R^2CH=CHR^2$ . A simple example is the metathesis of propene into ethylene and 2-butene. The forward reaction is often called self-metathesis, while the reverse reaction, which is a reaction between two different alkene molecules, is called cross-metathesis.

Diolefins, such as  $\alpha,\omega$ -dienes, undergo intermolecular and intramolecular metathesis. Intermolecular reaction, as shown in Equation 2.11, eventually leads to the production of high polymers, known as acyclic diene metathesis (ADMET) polymers. If the diolefin couples undergo intramolecular to produce a cyclic alkene, as shown in Equation 2.12, the process is called ring-closure metathesis (RCM). RCM has become an important tool for organic synthesis and has been widely applied for the preparation of carbocyclic and heterocyclic intermediates. The reverse reaction of RCM is called ring opening cross-metathesis Equation 2.13 is an example of ring-opening metathesis polymerization (ROMP). The reaction is driven by the release of ring strain of the starting cycloalkene. Living polymerization occurs when the metal carbene catalyst reacts more rapidly with the cyclic olefin than those with a C=C bond of the growing polymer chain. All double bonds from monomer molecules are preserved in ROMP, resulting in the formation of polymers with highly unsaturated backbones.



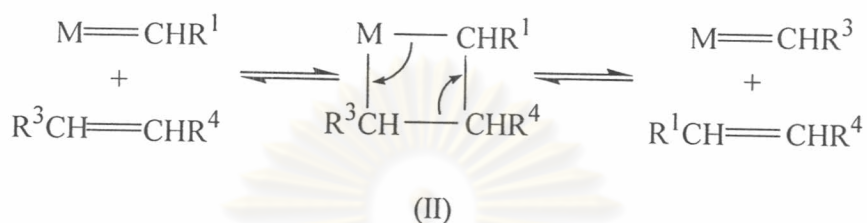
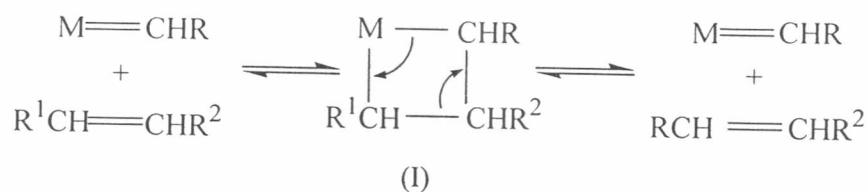
### 2.9.2 Olefin Metathesis Mechanism

The reaction mechanism proceeds *via* a metal carbene chain mechanism. The reactive initial metal carbene  $M=CHR$  can be formed by the a reaction of the substrate alkene with the transition metal center. The most accepted route to the first metal carbene include the formation of  $\pi$ -complex between the reacting alkene and the transition metal, followed by a 1,2-hydrogen shift mechanism. The forming step of metal carbene is shown in Sheme 2.1, where R described above is the  $CH_2R'$  group.



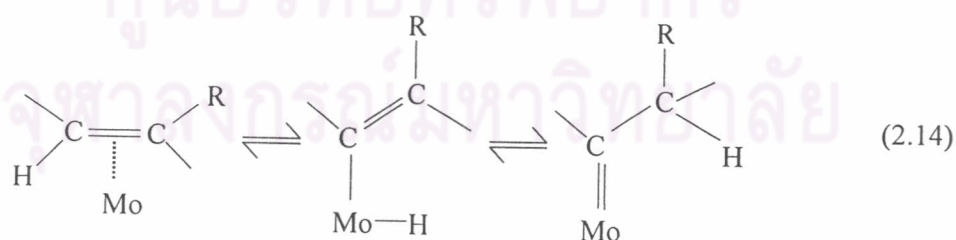
**Scheme 2.1** Metal carbene formation.<sup>51</sup>

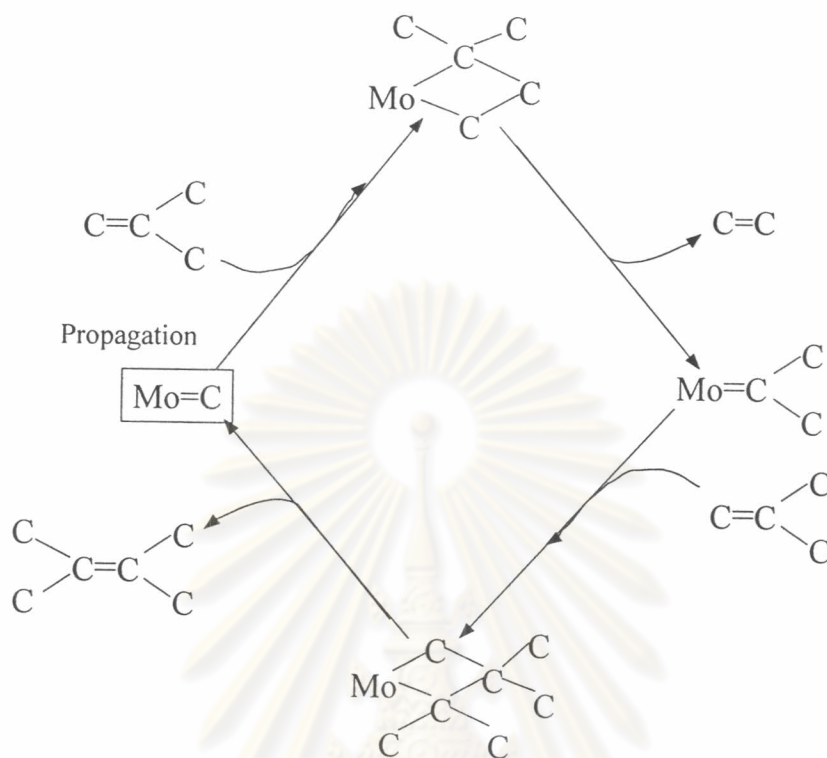
The propagation reaction involves a transition metal carbene as an active species with a vacant coordination site. The alkene coordinates at the vacant site and subsequently a metallacyclobutane intermediate is formed, which cleaves to form a new metal-carbene complex and a new alkene. For cyclic alkenes this mechanism results in unsaturated polymer chains. This mechanism was called The Chauvin mechanism<sup>52</sup> as illustrated in Sheme 2.2. It begins with formation of a metallacyclobutane (I), from the carbene complex and one of the olefin reactants. Fragmentation of I gives a new carbene complex and a new olefin. When the other olefin reactant is added, the new carbene complex forms another metallacyclobutane (II). Fragmentation of II finally gives an olefin which does not contain the carbene ligand of the catalyst. This mechanism is continuously operated.



**Scheme 2.2** The Chavin mechanism for olefin metathesis.<sup>52</sup>

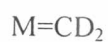
Consider, the mechanism of the molybdenum-containing catalyst which is molybdenum oxide supported on a solid matrix of aluminum oxide or silica as an example. The catalytically active metal-carbene intermediate was claimed to be formed by the 1,2-hydrogen shift of the alkenyl molybdenum complex and generated a catalytically active species. That can be expressed as Equation 2.14. The metal carbene proceeded metathesis reaction by the cycle as shown in Scheme 2.3.





**Scheme 2.3** Metathesis reaction cycle.<sup>53</sup>

Metathesis reaction can be distinguished into three different types:<sup>54</sup> (1) the productive metathesis yielding new products, (2) the degenerate or non-productive metathesis, in which the exchange of alkylidene groups does not result in new products, and (3) the cis-trans isomerisation. For metathesis of asymmetric internal alkenes, this reaction occurs simultaneously, while in the metathesis of 1-alkenes only the first two reactions occur. For example, considering the propylene metathesis mechanism of a mixture between  $C_3H_6$  and  $C_3D_6$ , the reaction of  $C_3D_6$  with the catalyst results in the metallocarbenes III and IV.



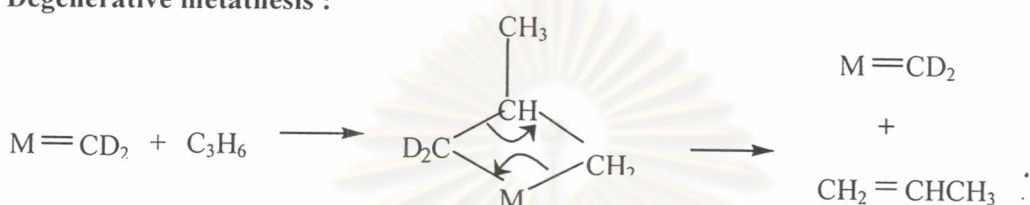
III



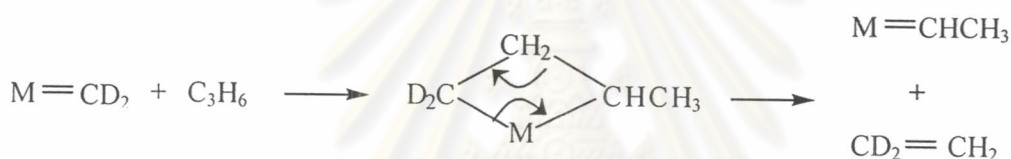
IV

The addition of propylene to species III generates a metallacyclobutane, which will be decomposed to either the degenerative or the productive metathesis, depending upon the orientation of the propylene molecule. The illustration of the degenerative and productive metathesis of propylene by  $M=CD_2$  are shown in Scheme 2.4. The analogous reactions can also be written for species IV.

**Degenerative metathesis :**



**Productive metathesis :**



**Scheme 2.4** The illustration of the degenerative and productive metathesis of propylene by  $M=CD_2$ .

### 2.9.3 Olefin Metathesis Catalysts

Traditionally, the large scale technologies employing alkene metathesis depending on heterogeneous catalysis. In these processes, the catalyst is supported on an insoluble, solid matrix that can stand high temperature and pressure. Often the pre-catalyst is loaded on the support and the active catalyst is generated by specific pre-treatment before metathesis initiated. Technological innovations were concerned with enhanced surface activity, identification of promoters and additives to improve conversions, recovery and regeneration of catalysts.

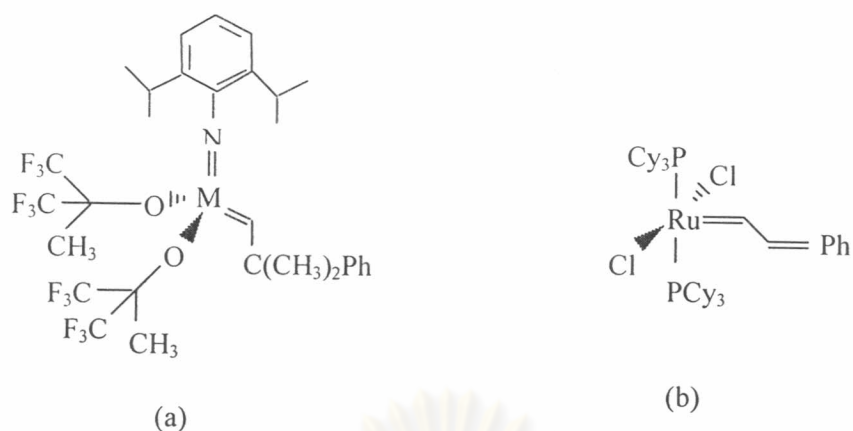


On the other hand, conventional homogeneous catalysts are extremely air and moisture-sensitive. Actual catalytic species are prone to decomposition on the slightest perturbation of original reaction parameters leading to inconsistent product yields. New generation homogeneous catalysts which are structurally well-defined metal-alkylidene complexes, are more tolerant of common organic functional groups. Some catalysts even perform in water and air. The emphasis of current research is on the development of mild and tolerant but highly efficient and selective catalysts.

### 2.9.3.1 Homogeneous Catalysts

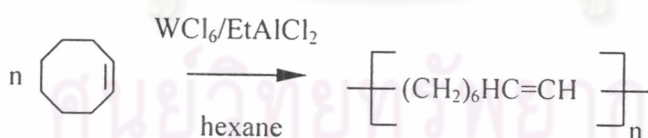
Homogeneous catalysts have been used more widely in polymerization reaction, predominantly ring opening metathesis polymerization (ROMP).<sup>53</sup> Access to pure structurally well-characterized catalysts reduce impurities in the obtained polymers to a great extent and reactions are normally carried out near ambient temperatures. Excellent functional group compatibility of some of the recent catalysts brought the metathesis reaction is useful in the synthetic organic chemistry.

The current chemistry is dominated by molybdenum and ruthenium. There are two well-known major classes of metathesis catalysts that are widely used. A molybdenum carbene developed by Schrock and a ruthenium carbene developed by Grubbs as shown in Figure 2.22. Both compounds are now commercially available and have been applied to a wide range of synthetic application, especially in ROMP.



**Figure 2.22** Schrock carbene (a) and Grubb carbene (b).<sup>53</sup>

Schrock's catalyst and Grubb's catalyst are well-known for use as the living polymerization catalyst. These catalyst catalyzed polymerization of norbornene or other cyclic alkenes. In fact, tungsten complex can catalyze the ROMP reaction, Ziegler-type catalyst prepared from  $\text{WCl}_6$  in excess of  $\text{EtAlCl}_2$  was used in ROMP of cyclooctene, producing polyoctenamer product, which is widely used as elastomer<sup>54</sup> as illustrated in Scheme 2.5. The reaction can be carried out in an inert solvent like hexane at ambient temperature and pressure.



**Scheme 2.5** Ring opening metathesis polymerization of cyclooctene.<sup>55</sup>

### 2.9.3.2 Heterogeneous Catalysts

Heterogeneous catalysts seem more suitable for industrial applications, because they are more favorable with respect to the separation of the catalysts from the reaction products and to the regeneration in continuous process application. The heterogeneous metathesis catalysts generally consist of a transition metal oxide (rhenium, molybdenum, or tungsten oxide) supported on a high surface area inorganic oxide such as alumina, silica or other inert surfaces. These supported metal oxide catalysts are commonly formulated as  $\text{Re}_2\text{O}_7/\text{support}$ ,  $\text{MoO}_3/\text{support}$  or  $\text{WO}_3/\text{support}$ . The catalysts are usually prepared by impregnation of the support with an aqueous solution of the ammonium salt of the transition metal, then dried in air at  $110^\circ\text{C}$  and calcined at temperatures between  $500$  and  $550^\circ\text{C}$ . The reactivity of the reaction is enhanced by the addition of other catalytically active metal derivatives, additives, or promoters. Several parameters can affect the performance of these catalyst systems, such as (i) the transition metal loading; (ii) the kind of support; (iii) the calcination procedure or a special activation procedure; (iv) using cocatalyst; etc.<sup>55</sup>

#### (a) Rhenium-Based Metathesis Catalysts

Rhenium-based metathesis catalysts are composed of rhenium oxide dispersed over oxide support, such as alumina or silica-alumina. This type of catalyst show high activity and high selectivity at low temperatures ( $20$ - $100^\circ\text{C}$ ), while they are also active for the metathesis of functionally substituted olefins when promoted with a tetraalkyltin or -lead compound.

A remarkable dependence of the rate of propylene metathesis over a  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst on the percentage of rhenium was observed.<sup>51</sup> At the low rhenium content the catalytic activity is extremely low, but the activity increases exponentially above a rhenium loading of about  $6\%$ wt  $\text{Re}_2\text{O}_7$ , the highest activity is reached at  $18\%$ wt  $\text{Re}_2\text{O}_7$ . The catalytic

activity is probably only limited by the maximum amount of rhenium oxide that can be anchored on the alumina surface. The catalytic performance of  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  can be increased by treating alumina first with an acid capable of reacting with the basic OH groups of alumina. In the region of low rhenium loading, which is economically preferable. The catalyst can be improved by (i) the incorporation of a third metal oxide such as  $\text{V}_2\text{O}_5$ ,  $\text{MoO}_3$  or  $\text{WO}_3$ ; (ii) the use of mixed support such as  $\text{SiO}_2\text{-Al}_2\text{O}_3$  or  $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$ ; (iii) the use of phosphate alumina.<sup>51</sup>

The catalytic activity of  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  increases with the rhenium loading. A positive correlation between the catalytic activity and the surface acidity of such system has been observed, mainly the Brønsted acidity. The activity of  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst can be explained on the basis of the activity of the surface  $\text{ReO}_4$  groups which have reacted with Lewis acid sites and with the different aluminium-bonded OH group during the preparation of the catalyst. The most active sites arise from the reaction between  $\text{ReO}_4^-$  ions and the most acidic OH groups on the alumina surface to form Al-bonded  $\text{ReO}_4^-$  species. Such reactions are favoured only after the basic and neutral OH groups have reacted to some extent.<sup>7</sup>

On the other hand, when  $\text{SiO}_2\text{-Al}_2\text{O}_3$  is used as the support, the catalytic activity decreases as the rhenium loading is increased because there are two types of hydroxyl groups on  $\text{SiO}_2\text{-Al}_2\text{O}_3$ : hydroxyl groups attached to a silicon atom and bridging hydroxyl groups attached to both a silicon and aluminium atom. The reaction of  $\text{ReO}_4^-$  ions with the bridging hydroxyl groups would generate active rhenium. Thus higher rhenium loadings would favour the formation of inactive sites of the types  $\equiv\text{Si-O-ReO}_3$ , as it is known that  $\text{Re}_2\text{O}_7/\text{SiO}_2$  has no activity in olefin metathesis.<sup>7,51</sup>

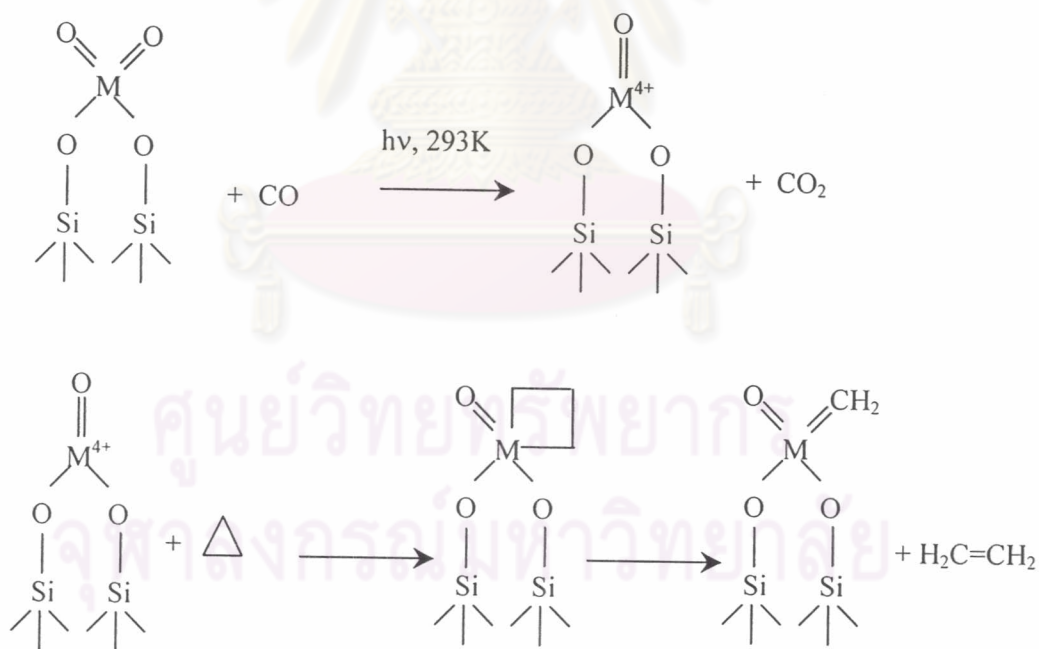
## (b) Molybdenum-Based Metathesis Catalysts

The variations in catalytic performance of molybdenum catalyst are due to the mode



of generation of molybdenum oxide from different precursor and different processing parameters. A recent study pointed out the oxidation state of molybdenum active species for metathesis of propylene. The formation of  $\text{Mo}^{4+}$  monooxo active species on  $\text{MoO}_3/\text{SiO}_2$  were formed by prereduction with CO under photoirradiation<sup>26,53</sup> while  $\text{Mo}^{4+}$  monooxo species on  $\text{MoO}_3/\text{Al}_2\text{O}_3$  were generated by  $\text{H}_2$  prereduction, resulting active metathesis catalyst. Whereas some reports showed that  $\text{Mo}^{5+}$  dioxo-species on  $\text{SiO}_2$ , which produced by photo-reduction with CO is also effective for metathesis.

Photoreduction of  $\text{MoO}_3/\text{SiO}_2$  can be operated with Hg lamp in a CO atmosphere lead mainly to  $\text{Mo}^{4+}$ . The resulting system is active for the metathesis of propylene. Treatment of this system with cyclopropane results in a sharp increase of its specific activity. This strategy is illustrated in Scheme 2.6.



**Scheme 2.6** Generation of molybdenum active species for metathesis reaction.

For molybdena, the activity also depends on the type of support. Using of  $\text{Al}_2\text{O}_3$  or  $\text{TiO}_2$  as support, generating active catalysts while using of  $\text{SiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Cr}_2\text{O}_3$  or  $\text{ZnO}$  resulting less active catalyst.

**(c) Tungsten-Based Metathesis Catalyst**

Because of chemistry of tungsten and molybdenum is identical, the observed applications are similar in metathesis application. The series of alumina-supported Mo- and W-based catalyst with the wide range of metal loading in metathesis of propylene were compared activity.<sup>27</sup> The selectivity to metathesis products varies as a function of the metal oxide at reaction temperature  $500^\circ\text{C}$  and propylene flow at 20ml/min. At 3% metal oxide loading, both  $\text{WO}_3$  and  $\text{MoO}_3$  yielded similar ethylene/butylene ratio. When the metal loading was increased, this ratio was decreased. This indicates that after the metathesis reaction, dimerization of ethylene occurs. Tungsten-based catalyst can be also used in propylene production *via* cross metathesis between ethylene and butene. The required reaction temperature is  $330^\circ\text{C}$  approximately, yielding 55% equilibrium conversion.<sup>2</sup>

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