



## CHAPTER II

### THEORY OF REACTIVITIES OF ALCOHOLS OVER CATALYSTS

#### 2.1 Papers and Publication Related to the Present Work

##### 2.1.1 Basic Knowledge of Alcohols ( $C_1O_H - C_4O_H$ )

##### 2.1.1.1 Methanol (6)

Methanol (methyl alcohol),  $CH_3OH$ , is a clear, water-white liquid with a mild odor at ambient temperatures. From its discovery in the late 1600S. methanol has grown to become the 21st largest commodity chemical with over  $12 \times 10^6$  metric tons annually produced in the world. Methanol has been called wood alcohol because it was obtained commercially from the destructive distillation of wood for over a century.

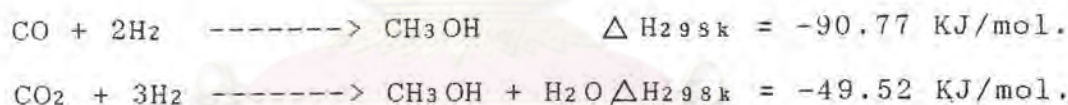
The physical properties of methanol are given in Table 2.1. The vapor pressure of methanol from 15.00 to  $64.50^\circ C$  is given by the following equation,

$$\ln P = 15.76 - 2.846 \times 10^3 T^{-1} - 3.743 \times 10^3 T^{-2} + 2.189 \times 10^7 T^{-3}$$

where  $P = \text{kPa}$  and  $T = \text{temperature in degree Kelvin}$ . An equation that covers a wider temperature range

from  $-67.4$  to  $240^{\circ}\text{C}$  is probably accurate enough for most purposes.

The eldest industrially significant method of methanol manufacture was destructive distillation of wood. Modern industrial scale methanol production is based exclusively on synthesis from pressurized mixtures of hydrogen, carbon monoxide, and carbon dioxide gases in the presence of metallic heterogeneous catalysts. The required synthesis pressure is dependent on the activity of the particular catalyst. The formation of methanol from mixtures of carbon monoxide, carbon dioxide and hydrogen which proceeds according to the following reactions :



Catalyst used in synthesis is zinc oxide - chromium oxide, copper - zinc oxide, zinc - chromium - and copper based catalyst.

One area of promise for methanol is its direct use in fuels. Potentially it can be used as a replacement for diesel fuel and gasoline or as a gasoline extender. Methanol can also be used to make gasoline in Mobil's MTG process. Methanol is also considered for use in many other areas. These include its use as feedstock to produce olefins.



### 2.1.1.2 Ethanol (7)

Ethanol or ethyl alcohol,  $\text{CH}_3\text{CH}_2\text{OH}$ , has been described as one of the most exotic synthetic oxygen - containing organic chemicals because of its unique combination of properties as a solvent, a germicide, a beverage, an antifreeze, a fuel, a depressant, and especially because of its versatility as a chemical intermediate for other organic chemicals.

Ethyl alcohol under ordinary conditions is a volatile, flammable, clear, colorless liquid. Its odor is pleasant, familiar, and characteristic, as is its taste when it is suitably diluted with water. The physical and chemical properties of ethyl alcohol are primarily dependant upon the hydroxyl group. This group imparts polarity to the molecule and also gives rise to intermolecular hydrogen bonding. A summary of physical properties of ethyl alcohol is presented in Table 2.2. The chemistry of ethyl alcohol is largely that of the hydroxyl group, namely, reactions of dehydration, dehydrogenation, oxidation, and esterification.

Fermentation, one of the oldest chemical processes known to man, is used to make a variety of products, including foods, flavorings, beverages, pharmaceuticals, and chemicals. At present, however, many of simpler products such as ethanol. Ethanol is made from a variety



of agricultural products such as grain, molasses, fruit, whey, and sulfite waste liquor. Generally, most of the agricultural products mentioned above command higher prices as foods and others, i.e., potatoes, are uneconomical because of their low ethanol yield and high transportation cost. The energy crisis of the early seventies may have generated renewed interest in ethanol fermentation.

Ethanol can be derived by fermentation processes from any material that contains sugar. The many and varied raw materials used in the manufacture of ethanol via fermentation are conveniently classified under three types of agricultural raw materials : sugar, starches, and cellulose materials. Sugar (from sugar cane, sugar beet, molasses, fruit), can be converted to ethanol directly. Starches (from grains, potatoes, root (crops) must first be hydrolyzed to fermentable sugars by the action of enzymes from malt or molds. Cellulose (from wood, agricultural residues, waste sulfite liquor from pulp and paper mills) must likewise be converted to sugar generally by the action of mineral acids.

Industrial ethanol is one of the largest-volume organic chemicals used in industrial and consumer products. The main uses for ethanol are as an intermediate in the production of other chemicals and as a solvent.

Table 2.1 Physical properties of methanol (6)

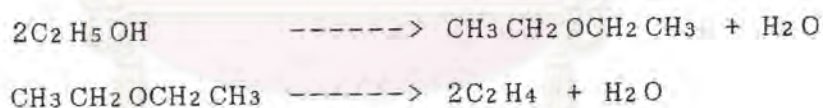
Property	Value	Ref.
freezing point, °C	-97.68	1
boiling point, °C	64.70	1
critical temperature, °C	239.43	1
critical pressure, kPa <sup>a</sup>	8096	1
critical volume, mL/mol	118	1
critical compressibility factor $z$ in $PV = znRT$	0.224	1
heat of formation (liquid) at 25°C, kJ/mol <sup>b</sup>	-239.03	2
free energy of formation (liquid) at 25°C, kJ/mol <sup>b</sup>	-166.81	2
heat of fusion, J/g <sup>b</sup>	103	1
heat of vaporization at boiling point, J/g <sup>b</sup>	1129	1
heat of combustion at 25°C, J/g <sup>b</sup>	22,662	1
flammable limits in air		
lower, vol %	6.0	3
upper, vol %	36	3
autoignition temperature, °C	470	4
flash point, closed cup, °C	12	4
surface tension, mN/m (= dyn/cm)	22.6	5
specific heat		
of vapor at 25°C, J/(g·K) <sup>b</sup>	1.370	1
of liquid at 25°C, J/(g·K) <sup>b</sup>	2.533	1
vapor pressure at 25°C, kPa <sup>a</sup>	16.96	6
solubility in water	miscible	
density at 25°C, g/cm <sup>3</sup>	0.78663	7
refractive index, $n_D^{20}$	1.3284	1
viscosity of liquid at 25°C, mPa·s (= cP)	0.541	8
dielectric constant at 25°C	32.7	9
thermal conductivity at 25°C, W/(m·K)	0.202	10

Table 2.2 Physical properties of ethanol, (7)

Property	Value
freezing point, °C	-114.1
normal boiling point, °C	+78.32
critical temperature, °C	243.1
critical pressure, kPa <sup>b</sup>	6383.48
critical volume, L/mol	0.167
critical compressibility factor, $z$ , in $PV = znRT$	0.248
density, $d_4^{20}$ , g/mL	0.7893
refractive index, $n_D^{20}$	1.36143
$\Delta n_D/\Delta t$ , 20-30°C, per °C	0.000404
surface tension, at 25°C, mN/m (= dyn/cm)	231
viscosity, at 20°C, mPa·s (= cP)	1.17
solubility in water, at 20°C	miscible
heat of vaporization, at normal boiling point, J/g <sup>c</sup>	839.31
heat of combustion, at 25°C, J/g <sup>c</sup>	29676.69
heat of fusion, J/g <sup>c</sup>	104.6
flammable limits in air	
lower, vol %	4.3
upper, vol %	19.0
autoignition temperature, °C	793.0
flash point, closed-cup, °C	14
specific heat, at 20°C, J/(g·°C) <sup>c</sup>	2.42
thermal conductivity, at 20°C, W/(m·K)	0.170
dipole moment, liq at 25°C, C·m <sup>d</sup>	$5.67 \times 10^{-30}$
magnetic susceptibility at 20°C	$0.734 \times 10^{-6}$
dielectric constant at 20°C	25.7

Chemicals derived from ethanol; where ethylene is in short supply and fermentation ethanol is made economically feasible, ethylene is manufactured by the vapor-phase dehydration of ethanol. The production of ethylene from ethanol using naturally renewable resources is an active and useful alternative to the pyrolysis process based on nonrenewable petroleum. This route may make ethanol a major raw material source for producing other chemicals.

Dehydration of ethanol has been effected over a variety of catalysts among the synthetic and naturally occurring aluminas, silica-alumina, and activated alumina. Operating space velocity is chosen to ensure that the two consecutive reactions, go to completion, avoiding the need



to recover and recycle unreacted ethanol. the dehydration is endothermic, and temperature is a critical operating parameter : high temperatures produce aldehydes and low temperatures, ethers. The catalyst is usually regenerated with steam and air every few weeks to remove carbon deposits.



### 2.1.1.3 Propyl Alcohol (8)

n - Propyl alcohol : 1 -propanol,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ , is a clear, colorless liquid with a typical alcohol odor, and it is miscible in water, ethyl ether, and alcohols. 1 - Propanol occur in nature in fuel oils and forms from fermentation and spoilage of vegetable matter.

A number of physical and chemical properties of 1 - propanol are listed in Table 2.3.

Isopropyl alcohol : (2 - propanol, sec - propyl alcohol) is the lowest number of the class of secondary alcohols.

A listing of physical properties are given in Table 2.4. Isopropyl alcohol is a colorless, volatile, flammable liquid. Its odor is slight, resembling a mixture of ethyl alcohol and acetone.

Isopropyl alcohol undergoes reactions typical of an active secondary alcohol. It can be dehydrated, dehydrogenated, oxidized, esterified, or otherwise modified at this site more readily than primary alcohols.

The basic process for the commercial manufacture of isopropyl alcohol, potential synthetic methods include fermentation (of certain carbohydrates. Large - scale, commercial biological production of propyl alcohol from

carbohydrate raw materials is being studied. Approximately 50 wt% of C<sub>3</sub> chemicals properly will be supplied by fermentation when carbohydrates become competitive with petroleum feedstocks in ca 2000.

#### 2.1.1.4 Butyl Alcohol (9)

There are four isomeric, 4 - carbon alcohols of molecular formula C<sub>4</sub>H<sub>9</sub>OH, two are primary, one is an unsymmetrical secondary alcohol, and one is tertiary.

The butyl alcohols are colorless, clear liquids with characteristic odors. The straight - chain primary alcohol is the highest boiling point and the highly branched tertiary alcohol is the lowest boiling point. With the exception of tert - butyl alcohol (mp. 25°C) the butyl alcohols have very low melting points. Their relative solubilities in water also correspond to their molecular structures, n - butyl alcohol has a solubility of approximately 8%, whereas the tertiary alcohol is miscible. The four butyl alcohols are miscible with most common organic solvents. Physical constants of the butyl alcohols are given in Table 2.5.

The chemical properties of the butyl alcohols are primarily a function of the hydroxyl group, and consequently their most important reactions are dehydration, dehydrogenation or oxidation, and esterification.



Table 2.3 Physical and chemical constants of 1 - propanol

(8)

Property	Value
freezing point, °C	-126.2
boiling point, °C	97.20
vapor pressure, kPa <sup>b</sup>	
at 20°C	1.987
at 40°C	6.986
at 60°C	20.292
at 80°C	50.756
Antoine eq. (2-120°C): $\log P_{\text{kPa}}^{\text{c}} = 6.97257 - \frac{1499.21}{(204.64 - t)}$ , $t = \text{°C}$	
vapor density (air = 1) <sup>d</sup>	2.07
density (at 20°C), g/cm <sup>3</sup>	0.80375
Francis eq. (-21 to 180°C): $\text{dens} = 0.8813 + (5.448 t \times 10^{-4}) - \left[ \frac{21.536}{(313.09 - t)} \right]$ , $t = \text{°C}$	
refractive index, $n_{\text{D}}^{20}$	1.38556
viscosity (at 20°C), mPa·s (= cP) <sup>d</sup>	2.256
surface tension (at 20°C), mN/m (= dyn/cm)	23.75
critical temperature, °C	263.56
critical pressure, kPa <sup>b</sup>	5169.60
critical density, g/cm <sup>3</sup>	0.275
heat capacity (liquid at 25°C), J/(mol·K) <sup>e</sup>	141
heat of vaporization, kJ/mol <sup>e</sup>	
at 25°C	47.53
at 97.20°C	41.78
heat of combustion (liquid at 25°C), kJ/mol <sup>e</sup>	-201.98
heat of formation (liquid at 25°C), kJ/mol <sup>e</sup>	-304.01
flash point (Tag open cup), °C <sup>d</sup>	29
autoignition temperature, °C <sup>d</sup>	371.1
explosive limit (in air), vol % <sup>d</sup>	
lower	2.1
upper	13.5
electrical conductivity (at 25°C), S (= mho) <sup>d</sup>	$2 \times 10^{-8}$

n - butanol can be manufactured by the selective bacterial fermentation of carbohydrate - containing materials such as molasses, corn, and grain fermentation processes using molasses instead of grain were developed. A number of other synthetic methods have been described in the patent literature. Ethyl alcohol may be converted directly to 1 - butanol at 325°C and 13 MPa over magnesium oxide - copper oxide.

One area of promise for butanol is its direct use in a butylene synthesis, the alcohols be passed over various dehydration catalysts at elevated temperatures. Thus butanol gives a mixture of 1 - and 2 - butenes at 175-400°C in the presence of such catalysts as alumina, tungsten oxide, and magnesium chloride. The ease of dehydration increase from primary alcohol to tertiary alcohol.

Table 2.4 Physical properties of isopropyl alcohol. (8)

Property	Grade	
	Anhydrous	91 vol %
molecular weight	60.10	60.10
boiling point (at 101.3 kPa), °C <sup>b</sup>	82.3	80.4
freezing point, °C	-88.5	-50
sp gr. 20/20°C	0.7881	0.8179
density (at 20°C), g/cm <sup>3</sup>	0.7849	
surface tension (at 20°C), mN/m (= dyn/cm)	0.0213	0.0214 <sup>c</sup>
specific heat (liquid at 20°C), J/(kg·K) <sup>d</sup>	2510.4	
refractive index, n <sub>D</sub> <sup>20</sup>	1.3772	1.3769
heat of combustion (at 25°C), kJ/mol <sup>d</sup>	2005.8	
latent heat of vaporization (at 101.3 kPa <sup>b</sup> ), kJ/mol <sup>d</sup>	39.8	
vapor pressure (at 20°C), kPa <sup>b</sup>	4.4	4.5
critical temperature, °C	235.2	
critical pressure (at 20°C), kPa <sup>b</sup>	4750	
viscosity, mPas (= cP)		
at 0°C	4.6	
at 20°C	2.4	2.1 <sup>c</sup>
at 40°C	1.4	
solubility (at 20°C)		
in water	complete	complete
water in	complete	complete
coefficient of expansion <sup>e</sup>	$V_t = V_0 [1 + (1.0743 \times 10^{-3}) t + (3.28 \times 10^{-7}) t^2]$	
flammability limit in air, vol %/		
lower	2.02	
upper	7.99	
flash point, °C		
Tag open cup	17.2	21.7
closed cup	11.7	18.3

Table 2.5 Physical properties of the butyl alcohols (9)

Properties	1-Butanol [71-36-3]	2-Methyl- propanol [78-83-1]	2-Butanol [78-92-2]	2-Methyl- 2-propanol [75-65-0]
formula	$\text{CH}_3(\text{CH}_2)_2\text{-CH}_2\text{OH}$	$(\text{CH}_3)_2\text{CH-CH}_2\text{OH}$	$\text{CH}_3\text{CH}_2\text{CH-}(\text{OH})\text{CH}_3$	$(\text{CH}_3)_3\text{COH}$
alternative name	<i>n</i> -butyl alcohol	isobutyl alcohol	<i>sec</i> -butyl alcohol	<i>tert</i> -butyl alcohol
classification	primary	primary	secondary	tertiary
mp, °C	-90.2	-108	-114.7	25.5
bp, °C	117.7	108.1	99.5	82.5
density, $d_4^t$ , g/mL	0.81337 <sup>15</sup>	0.80576 <sup>15</sup>	0.81089 <sup>15</sup>	0.77620 <sup>30</sup>
refractive index, $n_D^t$	1.39711 <sup>20</sup>	1.39768 <sup>15</sup>	1.39446 <sup>15</sup>	1.3811 <sup>25</sup>
flash pt, °C	35.0	27.5	24.4	8.9
viscosity, mPa·s <sup>t</sup> (=cP <sup>t</sup> )	33.79 <sup>15</sup>	47.03 <sup>15</sup>	42.10 <sup>15</sup>	33.16 <sup>30</sup>
heat of vaporization, J/g <sup>a</sup>	591.2	578.4	562.4	535.4
sp heat, J/(g·K) <sup>a</sup>	2.33 <sup>20</sup>	2.38 <sup>20</sup>	2.73 <sup>20</sup>	3.04 <sup>27</sup>
heat of fusion, J/g <sup>a</sup>	125			91.6
heat of combustion, J/g <sup>a</sup>	2674	2670		2633
critical temp, °C	287	265	265	235
critical pressure, kPa <sup>b</sup>	4890	4850		
vapor pressure, kPa <sup>b</sup>	0.628 <sup>20</sup>	1.173 <sup>20</sup>	4.132 <sup>32</sup>	4.079 <sup>20</sup>
electrical conductivity, ( $\Omega\text{-cm}$ ) <sup>-1</sup>	$9.12 \times 10^{-9}$	$8 \times 10^{-8}$		
dipole moment, C·m <sup>c</sup>	$1.66 \times 10^{-18}$	$5.97 \times 10^{-30}$		$5.54 \times 10^{-30}$
dielectric constant, $\epsilon^t$	17.7 <sup>17,2</sup>	17.95 <sup>25</sup>	15.5 <sup>19</sup>	11.4 <sup>19</sup>
solubility at 30°C, wt %				
in water	7.08	7.5	18	miscible
of water	20.62	17.3	36.5	miscible

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### 2.1.2 Literature Survey on reactivities of Alcohols (C<sub>1</sub> - C<sub>4</sub>) over Synthesis Catalysts

The hydrocarbon may be produced in many ways, from different raw materials. One of the processes is the catalytic cracking of the alcohols, in the presence of various catalysts, and under different reaction conditions.

Costa, et al. (10) studied the conversion of ethanol to hydrocarbons by use of a ZSM-5 zeolite catalyst. The effect of zeolite Si/Al ratio, ethanol dilution, and process variable were established. The hydrocarbons produced in the ethanol conversion were grouped in four fractions : gaseous paraffins, gaseous olefins, nonaromatic liquid hydrocarbons, and aromatic liquid hydrocarbons. Effect of Zeolite (Si/Al ratio = 34, 85, 323,  $\infty$ ) ; the formation of liquid hydrocarbons was favored by the increase, in the aluminum content. On the other hand, if the silicon content was increased, so, the formation of gaseous olefins was favored. Ethanol dilution (water content = 4%, 15%, 30% wt) ; the yield of products obtained hardly vary when the water content in feed increasing, but its influence on the catalyst activity. Temperature (300, 350, 400, 450, 500°C) ; the maximum yield in liquid aromatic hydrocarbons was 450°C. Pressure (0.05-20 atm) ; the effect of higher pressure was to increase paraffin and aromatic amounts, decreasing olefins.

Selim, et. al.(11) studied the influence of the composition, the calcination temperature, and the reaction temperature on the activity and selectivity of chromia-alumina catalysts in isopropanol conversion. Isopropanol  $2 \times 10^{-3}$  ml were injected into a micro-reactor containing 0.2 g of catalyst, and the reaction products were then transferred directly by an inert-carrier gas (nitrogen at 40 ml/min) to a gas-liquid chromatograph. The results obtained for the conversion of isopropanol to propylene increased with a gradual increase in the reaction temperature from 220 to 340°C. Pure alumina catalysts thermally treated at 400°C or 600°C exhibit more or less the same activity and selectivity towards isopropanol conversion, yielding mainly propylene as a result of the dehydration reaction. For, chromia-alumina catalyst containing 25% chromia are more active as dehydrogenation catalysts than those containing 75% chromia which tend to catalyze mainly the dehydration of isopropanol.

Itoh, et. al.(12) described the effect of cation exchange on the product distribution in the conversion of methanol to hydrocarbons. Alkali cation - (Li, Na, K, Rb), Ca-, and La- exchanged mordenites were prepared by the following methods : H - mordenite was used as the starting material for all catalysts. HM was partially ion-exchanged with an aqueous solution of an appropriate acetate. The exchanged zeolites were washed with deionated water and



dried at 378 K. These catalysts were calcined at 673 K in a flow of O<sub>2</sub> to remove acetate ions. The conversion of methanol was 100% on all of the catalysts. The hydrocarbon products contained the C<sub>1</sub> - C<sub>6</sub> paraffins and olefins, and the A<sub>6</sub> - A<sub>12</sub> aromatics, which were the same on all of the cation exchanged catalysts as those on the HM catalyst, although the product distribution was changed. By alkali ion-exchange, the yields of C<sub>2</sub> - C<sub>3</sub> products decreased, while those of C<sub>4</sub> and aromatics increased. Ca - and La - cations had the same effect but to a lesser degree. Moreover, the olefins/paraffins ratio increased on the alkali ion-exchanged catalysts with increasing atomic number, while it decreased on the Ca and La exchanged catalysts. Thus, it was considered that the product distribution can be controlled by cation exchange.

Ahmed, I., et. al. (13) investigated physicochemical and catalytic properties of silica-alumina gels (Al<sub>2</sub>O<sub>3</sub> Content = 0-100 mol%). The present investigation was an attempt at elucidation wheater the concerted mechanism was operative in dehydration of alcohols over aluminosilicates. Catalytic activity : isopropanol undergoed only dehydration over catalysts studied. The mole conversion of alcohol greatly depended the reaction temperature and the catalyst used. The comparison of the reaction results with the data on the surface acidity and basicity leaded to the conclusion that both basic and acid sites were needed to dehydrate



isopropanol. It was inferred that acid and basic sites coexisting on a silica-alumina surface in adequate ratio and exhibiting proper strengths were simultaneously involved in dehydration of alcohol to give an olefin.

Yue and Birk (14) studied the dehydration of ethanol over Laporte type 13x zeolite in fluidised bed reactor. Products of reaction were mainly ethylene, diethyl ether, and water as a co-product of both at operating condition, Reactor Pressure = 101 kN/m<sup>2</sup>, T = 598 K, static bed height = 0.75 m.. Modelling of fluidised reactors were the CSTR model, Kato and Wen model, and Peter et al model. The experimental results for the dehydration reaction in a fluidised bed showed that only the distributor region of the bed was effectively utilised. The reactor could be treated as a CSTR with no more than 15% of the bed being effective. When a more complex model, such as that of Peter et al., was applied, the effective region was less than 10%. The ineffecient utilization of the upper region of the reactor may be attributed to, bubble channelling, gas bypassing, and gas-solid interphase transfer limitation. Ceckiewicz (15) studied the reaction of methanol on T-type Zeolites at T = 400°C in a flow reactor. The result demonstrate the influence of decationization and dealumination of zeolites on catalytic lifetimes. The rate of deactivation at high temperatures depended mainly on the degree of cation exchange for protons and the

percentage of amorphous material in the samples. The shortest lifetime was observed for HT-zeolite, which contained the highest amount of amorphous material and the highest degree of ion-exchange. To improve the catalytic stability of HT/77 and reduce coking, Ni- and Pt-exchanged zeolites were used. The deactivation of Pt-HT was much slower than that of HT but only paraffinic hydrocarbons were produced. The result illustrated the increasing ease of olefin formation with increasing degree of ion exchange in decationized zeolite T.

Chang and Bell (16) studied about the conversion of alcohols and/or ethers to hydrocarbons. The invention concerns the conversion of lower organic alcohols and ethers in a molten salt bath catalyst under such conditions as to minimize coke formation, but maintain a significant conversion of reactant to hydrocarbons, particularly a conjunct mixture of hydrocarbons. The molten salt bath comprises  $ZnCl_2$ , but may contain < 50 mole % KCl. The conversion takes place at 570-750°F. The H<sub>2</sub> is cofed with the organic reactant. The proportion of H<sub>2</sub> to reactant is ~ 10 : 1 on a molar basis, preferably 2 : (0.5-1). The H<sub>2</sub> is provided under a partial pressure ~ 15-1500 psig and in amount of 0-3600 ft<sup>3</sup>/lb mole of feed.

Thomke, Kurt (17) said that the common mechanism for ethanol on  $BPO_4$ , for 2-propanol on  $Ca_3(PO_4)_2$ , and for 2-methyl-2-propanol on  $Sm_2O_3$  is the OH group and the



$\alpha$  -  $\beta$  proton are split off simultaneously. This can be explained by a decrease of the strength of the C - OH bond caused by  $\alpha$  - Me substitution on the one hand and by an increase of basicity of the catalyst on the other hand.

Jacob, P.A. (18) said about active sites in zeolites. Isopropanol and butanol were dehydrated over alkali cation-exchanged zeolites X and Y. The first reaction was carried out in a differential continuous flow reactor, the second one in a recirculation reactor, using deuterated alcohols. From isopropanol, propylene and diisopropyl ether are formed as dehydration products. The kinetic data can be fitted to a Langmuir - Hinshelwood equation where the reaction rate is showed by the desorption of H<sub>2</sub>O. The inter - and intramolecular dehydrations are parallel reactions catalyzed by weak OH groups. The selectivity is determined by the concentration and acidity of these groups.

Rodewald, P.G. (19) said that the C<sub>1</sub> - C<sub>4</sub> alcohols and C<sub>1</sub> - C<sub>4</sub> alkyl ethers were converted to hydrocarbons rich in ethylene and propylene by contacting them at 250°F - 600°F, 0.2-30 atm, and a LHSV of 0.1-50 hr<sup>-1</sup> with a ZSM-5 crystalline zeolite catalyst containing 0.2-30 wt. 70 added amorphous SiO<sub>2</sub>. Thus, Methanol passed at 300°F and 1.25 LHSV over 1 g. silica-loaded HZSM-5 zeolite containing 5 wt. % added silica was 29% converted to a hydrocarbon mixture containing 20% ethylene and 14% propylene.



Chen, N.Y. (20) studied about the conversion of oxygenated compounds. A process for exothermic vapor phase reactions of methanol or other low-boiling alcohols and their derivatives to form gasoline boiling hydrocarbons was accomplished by using crystalline zeolite catalysts in the presence of an inert material to distribute the exothermic heat.

Penick, J.E. et al. (21) found that the methanol produced by conversion of coal or natural gas is converted to LPG and high-octane gasoline by a proprietary process that uses a shape-selective zeolite catalyst. The chemistry and reaction engineering of the process and the result obtained in a fluid-bed pilot unit are described.

Winnick, C.N. (22) studied about the catalytic dehydration of alcohols. A silylated dehydration catalyst, formed by contacting a high surface area ( $>15$   $m^2/g$ ) alumina with  $>1$  organic silylating agent at high temperature, has improved catalytic activity in the dehydration of alcohols to ethylene and propylene. Thus, 0.125 inch alumina spheres were dried 16 hr. at  $150^\circ C$  and 20 hr. at  $500^\circ C$ , contacted with 1.4 ml/hr.  $(CH_3)_3SiCl$ , and vaporized into 20l. of Nitrogen at  $315^\circ C$  for 6 hr to give a silylated dehydration catalyst. Ethanol (29 ml/hr) was vaporized into 10 l/h of  $N_2$  and passed over 25 ml. catalyst at  $350^\circ C$ . The effluent gas contained 24 wt. % ethylene, compared with 19 wt. % ethylene when an

oven-dried, non-silylated catalyst was used.

Parera, J.M. (23) studied about the poisoning of acidic catalysts. Dehydration of alcohols was studied over silica-alumina catalysts poisoned by NaOH and various nitrogen bases. Model studies indicate that the poison transforms the catalyst surface into one with a weaker acid strength distribution.

Ezzo, E.M. (24) has researched about the conversion of alcohols on alumina. The dehydration kinetics of ethanol, isopropanol, and tert-butanol were determined over 5 types of  $Al_2O_3$  calcined at different temperatures. All of the dehydrations involve a polymolecular catalytic complex.

Wu, Y. et al. (25) said that alcohols are dehydrated over  $\gamma$ -alumina pretreated with base ; yields are increased by using a diluent inert gas. Thus,  $(CH_3)_2CHCH_2CH_2OH$  vapor mixed with nitrogen is dehydrated over  $\gamma$ -alumina to  $(CH_3)_2CHCH=CH_2$  with 93.4% conversion, compared to 78.2% without nitrogen.

Rudham, R. and Stockwell, A. (26) studied about the effects of temperature, exchange and base poisoning on isopropanol dehydration on HY Zeolites. Both propene and dipropyl ether are formed at a single Broensted acid site.



Skundric, B. and Spanic, M. (27) said that the rate constants for isopropanol dehydration over X zeolites containing  $Mn^{2+}$ ,  $Ni^{2+}$ , or  $Co^{2+}$  are larger than those for the reaction over NaX zeolites. With the latter the reaction is first-order. First-order kinetics was not obeyed with the transition metal modified zeolites. However, the dehydration of mixtures containing 30%  $H_2O$  obeyed first-order kinetics.

Haag, W.O., et al. (28) said that the conversion of MeOH to hydrocarbons with zeolite ZSM-5 as catalyst provides a novel route to gasoline as well as to olefins and aromatic as chemical raw materials. The reaction is acid-catalyzed and involves alkylation of olefins and aromatics as major MeOH conversion steps, accompanied by olefin isomerization, polymerization/cracking, cyclization and aromatization via H-transfer. Shape-selective control of the aromatics produced results from the use of the medium pore size zeolite ZSM-5. The true kinetic paths are often disguised by diffusion/desorption effects.  $C_2H_4$  is most likely the first olefinic hydrocarbon formed.

Parris, D. et al. (29) studied about the catalytic conversion of hydrocarbons. In relation to production of olefins and gasoline, dimethyl ether, methanol, or ethanol in He was passed over an amorphous aluminosilicate at 300-382°C, 145 KPa, and mass hourly space velocity 0.2-1.8. Dimethyl ether was converted to give ethylene



2.1-13.0, propylene 7.5-17.3, butylene 3.1-38.2, C<sub>1</sub> - C<sub>4</sub> saturated hydrocarbons 15.2-41.0, and C<sub>5</sub>+ hydrocarbons 23.4-59.2 mass %. A similar series of experiments was carried out at 336-418°C and 145 KPa.

Romero, S. et al. (30) studied about the kinetic behavior of silica-alumina catalysts in the dehydration of alcohols. The dehydration kinetics of butanol or 2-ethylhexanol over SiO<sub>2</sub> - Al<sub>2</sub>O<sub>3</sub> catalysts were related to the catalyst chemical properties (total acidity, acid strength distribution, and Al<sub>2</sub>O<sub>3</sub> content) and physical properties (specific surface area and pore volume) as a function of catalyst preparation. The initial activity and degree of deactivation are related to the amount of Al<sub>2</sub>O<sub>3</sub> in the catalyst and the molecular size of the alcohols.

Ball, W.J. and Stewart, D.G. (31) researched about the crystalline aluminosilicate catalysts and their use. A process is described for the production of a catalyst based on a crystalline aluminosilicate having a silica to alumina molar ratio > 12 : 1 by mixing a source of silica, source of alumina, a source of alkali metal, water, and a source of ammonium ions in defined proportions, crystallizing the mixture, recovering the crystalline aluminosilicate, cation exchanging and/or impregnating the recovered crystalline aluminosilicate, and finally calcining, wherein either the recovered crystalline

aluminosilicate or the cation exchanged aluminosilicated or the impregnated aluminosilicate is washed with a solution containing either an organic base, a carboxylic acid, an alcohol, a glycol, a phenol, or an ester. The washing treatment result in a reduction in the rate of declined in catalytic activity in reactions such as the conversion of aliphatic to aromatic hydrocarbons.

Murakami, et al (32) studied about the roles of acid property and pore structure of various zeolites in conversion of methanol to hydrocarbons. The acidity of ion-exchanged, dealuminated and ZSM-5 zeolites was examined by  $\text{NH}_3$  adsorption-desorption. The product distribution of MeDH conversion on various zeolites was mainly attributed to the acidity. For example, on zeolites with few strong acid sites, the major products were propylene, butene, and  $\text{C}_5$ . As the number of strong acid sites increased, the selectivities to these hydrocarbons decreased and the selectivities to  $\text{C}_2\text{H}_4$ , alkanes, and aromatics increased. Further increase in acid sites lead to a decrease in the aromatic production because of coke formation. The pore structure of the zeolites determined the molecular sites of the largest hydrocarbons producted.

Inui, T. and Takegami, Y. (33) described about the modified zeolite catalyst for olefin synthesis from methanol. Preparation of ZSM-34 zeolites was modified for



the purpose of obtaining an active catalyst for the preparation of C<sub>2</sub> - C<sub>4</sub> olefins from MeOH, while increasing selectivity, catalyst life, and decreasing catalyst crystallization time. Catalysts prepared 200°C for 2 hr) in the presence of organic bases had an order of activity of choline chloride < choline < (CH<sub>3</sub>)<sub>4</sub>NOH.

Balkishnan, I. et al. (34) studied that ethanol was passed through ZSM zeolite at 450°C to give 63% C<sub>4</sub> - aliphatics and 37% liquid products. The liquid fraction contained 88% C<sub>6</sub>H<sub>6</sub>, toluene, xylene, 6% C<sub>5</sub> - C<sub>8</sub> aliphatics, and 6% C<sub>9</sub> and C<sub>10</sub> aromatics. The product distribution for ethanol and methanol conversion was highly temperature dependent.

Fremuth, D.R. et al. (35) said about the converting methanol into gasoline over a ZSM-5 type catalyst. The risk of a temperature increase in the catalyst bed by entry of undiluted MeOH diminished by recycle of hot diluent gas flow over liquid MeOH to evaporate it and by feeding the MeOH vapor-recycle gas mixture to the catalyst.

Santilli, D.S. and Zones, S.I. (36) said about the selective conversion of methanol to low-molecular-weight olefins over high silica SSZ-13 zeolite. The high silica zeolite SSZ-13 catalyzed the conversion of MeOH to olefins. MeOH conversion over this catalyst at 800°C gave 88% C<sub>2</sub> - C<sub>4</sub> products containing 93% olefins. the catalyst



was also used for cracking of n-hexane and of 3-methylpentane.

Moravek, V. and Kraus, M. (37) studied about the perturbation of steady-state catalytic dehydration of alcohols by pulses of water and other substances. The dynamic behavior of systems consisting of 2-propanol or tert-butanol and of a solid dehydration catalyst was studied by pulses of the alcohols, water, nitrogen or CO<sub>2</sub> introduced onto the fresh catalyst surface in a stream of nitrogen or onto the working surface. The catalysts used were alumina, alumina modified by fluoride, sulfate or Na ions, thoria, silica-alumina, phosphotungstic acid and a sulfonated styrene-divinylbenzene copolymer. The positions and shapes of the response curves allowed the distinction between catalysts operating by formation of alkoxides or protonated alcohols as surface intermediates in the transformation of the alcohols into alkenes.

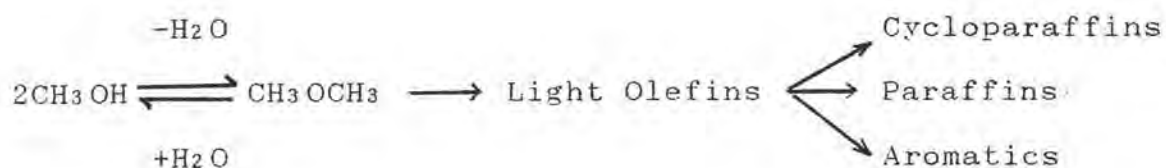
Bilbao, J. et al (38) investigated about the coke deposition on silica-alumina catalysts in dehydration reactions. Structural and kinetic aspect were studied of deactivation by coke deposition. The reactions studied are dimerization of acetaldehyde to crotonaldehyde, dehydration of 1-BuOH and dehydration of 2-ethylhexanol. Relations between the catalysts properties and the coke deposition are established from the differences among the physical properties and surface acidity of the fresh catalysts and from the study of their evolution with time.



Vinek, H. et al (39) prepared the NaHX zeolites and amorphous  $\text{SiO}_2/\text{Al}_2\text{O}_3$  oxides and compared for their catalytic activity in the dehydration of BuOH and  $(\text{C}_2\text{H}_5)_2\text{CH}(\text{CH}_3)\text{OH}$ ,  $\text{CH}_3\text{OH}$  conversion and 1-butene isomerization. The activity for dehydration (formation of butene and dimethyl ether) was highest for amorphous 67.1%  $\text{SiO}_2$  and was significantly lower for NaHX zeolite and for amorphous 92.3%  $\text{SiO}_2$ . This suggests a maximum of the total number of acid sites per surface area with amorphous 67.1%  $\text{SiO}_2$ . The C : C - bond isomerization proceeded much faster over amorphous 67.1-92.3%  $\text{SiO}_2$  than over NaHX zeolites, indicating significantly higher acid strength for the former. The similar activities of amorphous 67.1-92.3%  $\text{SiO}_2$  for 1-butene isomerization suggest similar densities and strengths of the strong acid sites.

## 2.2 Reaction Mechanism for Methanol Conversion to Light Olefins (40), (41)

The reaction path for the conversion of methanol to hydrocarbons has been shown to involve a sequence of steps which can be summarized as follows





The catalyst, with both acidic and basic centers, is a synthetic zeolite with a small crystal density, which is a measure of the number, dimension, and stability of the pores. The methanol conversion occurs in two steps, i.e., the conversion to ether and the formation of hydrocarbons.

### 2.2.1 The Etherification Reaction.

The dehydration of methanol occurs even at low temperatures (150-200°C). The formation of dimethyl ether (DME) is reversible and fast enough to reach equilibrium immediately. In a primary step the catalyst surface is completely methoxylated, so that each surface -OH group is replaced by a stable -OCH<sub>3</sub> group. Afterward, these -OCH<sub>3</sub> groups should be able to react with the methanol molecules, which are filling in the structural cavities of the catalyst.

### 2.2.2 The Formation of Light Olefins

The formation of light olefins from methanol and DME is the limiting step of the process. At high temperatures (more than 240°C) reactions take place with formation of a carbene. The carbenoid species may be formed by decomposition of the methoxylated surface due to the high temperature

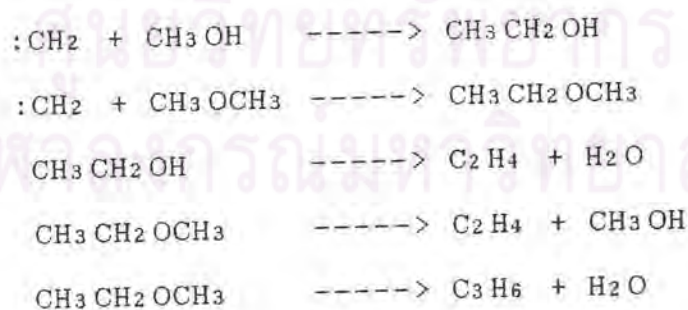




where it is not necessarily meant to imply the existence of a free carbene. The decomposition of methanol and DME into carbene was found to be first order with respect to the oxygenated compounds (42)

### The Carbene Reactions

The carbene is a "hot" radical with excess energy ; in any particular system many possible reactions of carbene occur with closely similar probabilities, the rates being insensitive to the small differences in activation energy. The attack of carbene on methanol-DME is an insertion into a C-H bond, forming higher alcohols or ethers, which, once formed, are rapidly converted into corresponding olefins. This is suggested by the failure to detect more than trace quantities of higher oxygenates in the products.



Chang et al.(43) reported an increasing selectivity for propene upon lowering the pressure of methanol in experiments on methanol conversion. Since methanol is first converted to DME and water, because of the

hydrophobic character of the zeolite, the concentration of water in the pores will be lowered to a greater extent than the concentration of DME. But the DME conversion to propene, in opposition with the DME conversion to ethene, does not imply water; therefore the propene selectivity should increase.

The attack of carbene on ethene gives rise to two products: propene by an insertion into a C-H bond, and cyclopropane by addition to the double bond. The cyclopropane has all the energy carried by the "hot" diradical and the ethene; this is considerably more than the activation energy for the isomerization of cyclopropane to propene; see into Figure 2.1

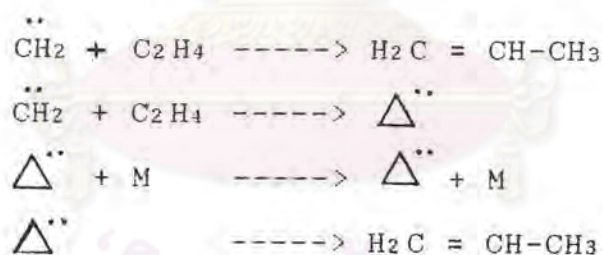


Figure 2.1 The carbene attack on ethene.

Although the relative rate of addition to the double bond compared with insertion into a C-H bond is large (22.7 : 1), owing to the high rate of isomerization of cyclopropane, only the propene formation is taken into account. For the attack of carbene on propene and butene is described in the same terms. Carbene inserts



considerably more rapidly into tertiary C-H bonds than with secondary C-H bonds, and more rapidly with the latter C-H bonds than into primary C-H bonds. The branched isomer will be prevailing ; see into Figure 2.2

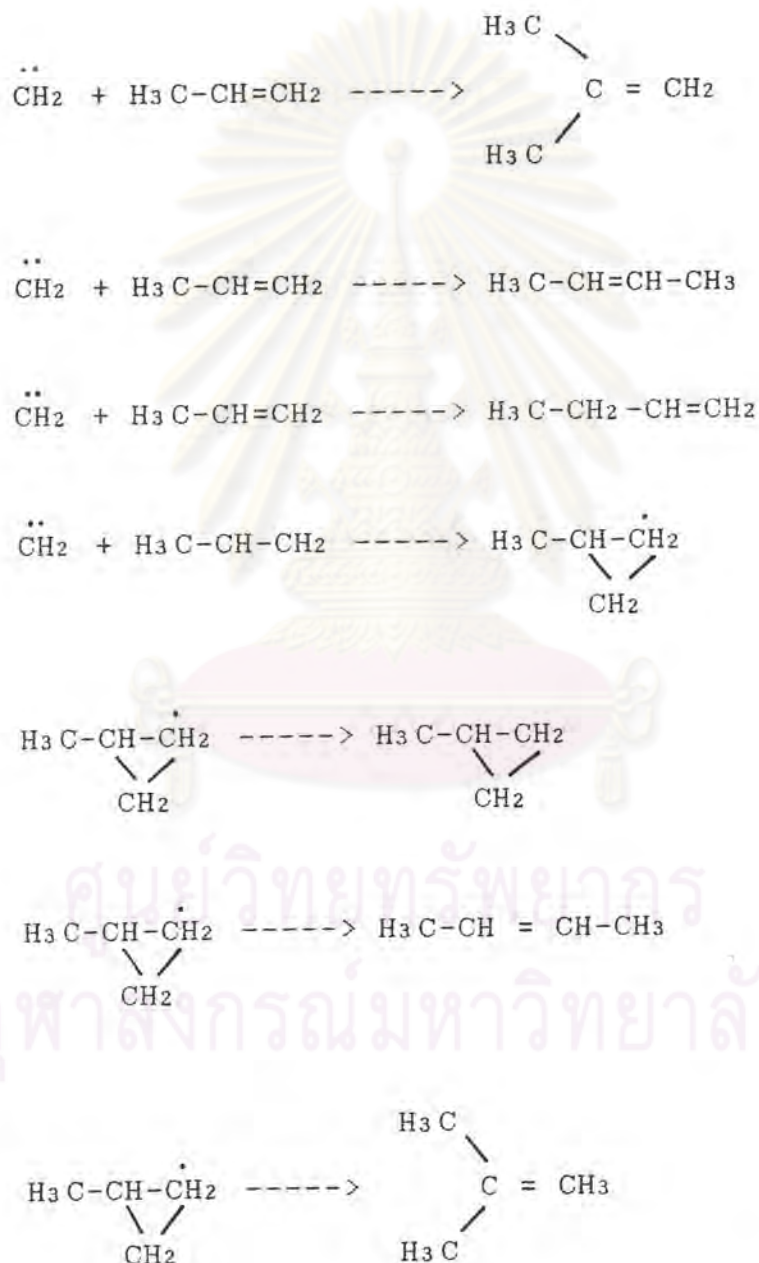
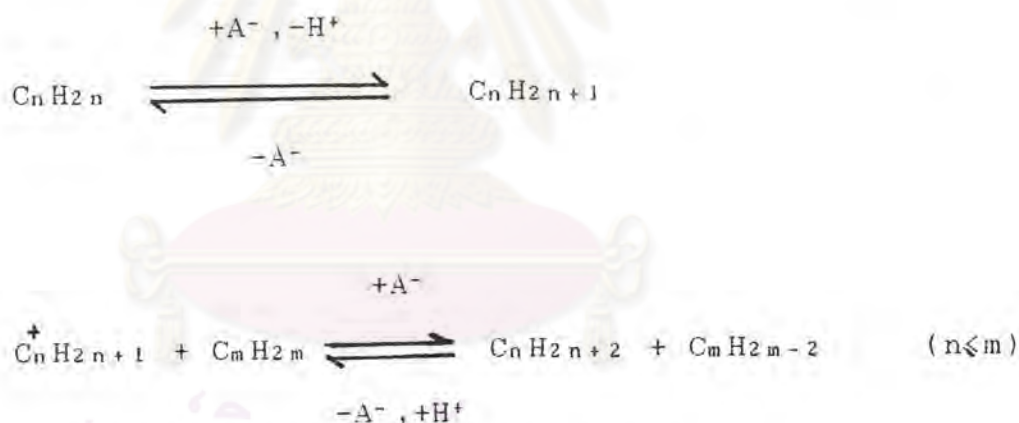


Figure 2.2 The carbene attack on propene

The attack of carbene on hydrogen is an insertion into an H-H bond, more rapid than into a C-H bond, giving rise to methane.

### 2.2.3 The Conversion of Olefins into Paraffins

The conversion of olefins into paraffins is first order with respect to olefins. The catalyst, with its cages and channels, appears as a solid, crystalline structure in which high electrostatic gradients prevail favoring and stabilizing the carbenium ions.



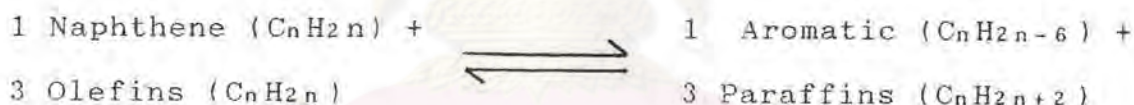
The proposed mechanism involves as a slow stage the appearance of the protonate species, due to the acid character of the catalyst. The attack of this intermediate on the olefins is rapid and the whole process will have first-order kinetics. The olefins reactivity depends on the structure ethene being the least active one. The transfer of proton in the conversion of olefins into paraffins is preferentially from higher olefins to



lower olefins. Fleckenstein et al. (44) detected paraffin formation only when the catalyst had an acidic character.

#### 2.2.4 The Conversion of Olefins to Aromatic Compounds (45)

It has been well established that C<sub>2</sub> - C<sub>4</sub> olefins could act as precursors of aromatic compounds. Reaction pathways are essentially analogous to those describing conjunct polymerization, that is, the conversion of olefins (by oligomerization and/or cyclization) into naphthenes and the dehydrogenation of naphthenes into aromatics by hydrogen transfer reactions of the type :



This scheme predicts a stoichiometric paraffinic/aromatic ratio of 3, which is effectively observed in a normally run MTG conversion.

Figure 2.3 schematizes the aromatization pathway of olefins, using propylene as a model reactant. UV-spectroscopy allows the identification of the carbocations intermediates and shows that cyclopentenyl carbocations are first formed. Cyclohexenyl species, aromatics, and (Poly) alkylaromatics then appear successively.

Haag et al. (46) have shown that the distribution of aromatic compounds resulted from the combination of two factors : the methanol alkylation of lower aromatics which is very effective at low methanol conversion and diffusion limitations (product selectivity) which stem from the comparable sizes of the zeolite pores and of the methyларomatics.

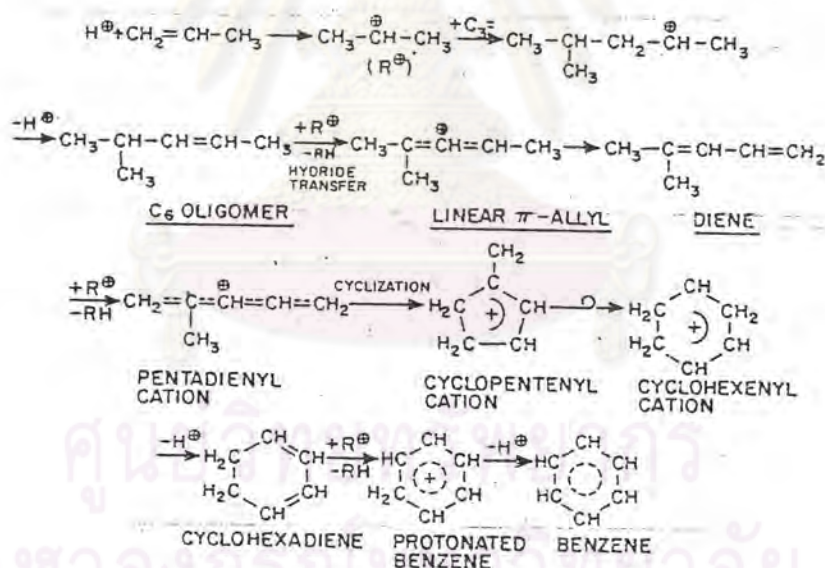


Figure 2.3 Typical intermediates in the conversion of olefins to naphthenes and aromatics

At above part, mechanism of the reaction concluded in Table 2.6 involves intermediate species, such as carbene, carbenium ions, dienes and cyclo-dienes. Implicitly, through reaction, the trimethyloxonium ion is involved. (47)

Table 2.6 The chemical reactions for MTHC (47)

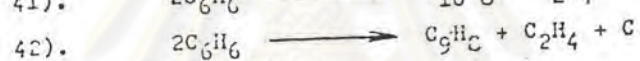
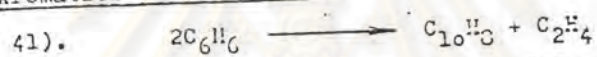
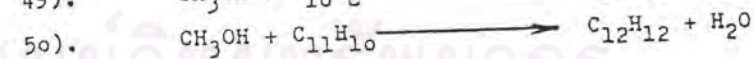
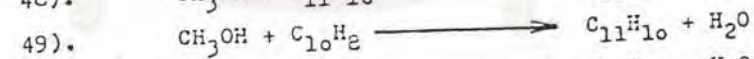
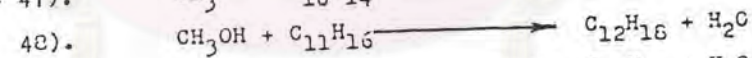
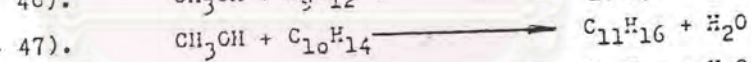
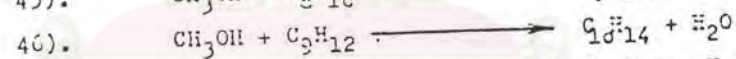
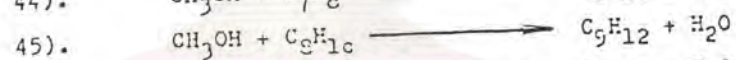
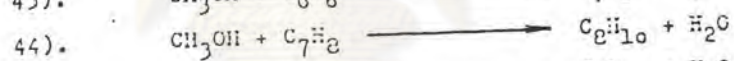
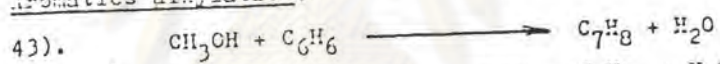
A kinetic model for methanol conversion to hydrocarbons

Table 2. The chemical reactions

<p>I). Methanol reactions:</p> <p>1). <math>CH_3OH \longrightarrow CO + 2H_2</math></p> <p>2). <math>2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O</math></p> <p>3). <math>CH_3OCH_3 \longrightarrow 2:CH_2 + H_2O</math></p> <p>II). Light olefins formation from carbene and oxygenates:</p> <p>4). <math>:CH_2 + CH_3OH \longrightarrow C_2H_4 + H_2O</math></p> <p>5). <math>:CH_2 + CH_3OCH_3 \longrightarrow C_2H_4 + CH_3OH</math></p> <p>6). <math>:CH_2 + CH_3OCH_3 \longrightarrow C_3H_6 + H_2O</math></p> <p>III). Higher olefins formation from carbene and light olefins:</p> <p>7). <math>:CH_2 + C_2H_4 \longrightarrow C_3H_6</math></p> <p>8). <math>:CH_2 + C_3H_6 \longrightarrow C_4H_8</math></p> <p>9). <math>:CH_2 + C_4H_8 \longrightarrow C_5H_{10}</math></p> <p>10). <math>:CH_2 + C_5H_{10} \longrightarrow C_6H_{12}</math></p> <p>11). <math>:CH_2 + C_6H_{12} \longrightarrow C_7H_{14}</math></p> <p>IV). Methane formation from carbene and hydrogen:</p> <p>12). <math>:CH_2 + H_2 \longrightarrow CH_4</math></p> <p>V). Carbenium ions formation from olefins:</p> <p>13). <math>C_2H_4 \xrightleftharpoons{+A^+H^+} C_2H_5^+</math></p> <p>14). <math>C_3H_6 \xrightleftharpoons{+A^+H^+} C_3H_7^+</math></p> <p>15). <math>C_4H_8 \xrightleftharpoons{+A^+H^+} C_4H_9^+</math></p> <p>16). <math>C_5H_{10} \xrightleftharpoons{+A^+H^+} C_5H_{11}^+</math></p> <p>VI). Carbenium ions attack on light olefins giving higher olefins (oligomerization)</p> <p>17). <math>C_3H_7^+ + C_3H_6 \xrightleftharpoons{+A^-} C_6H_{12}</math></p> <p>18). <math>C_4H_9^+ + C_3H_6 \xrightleftharpoons{+A^-} C_6H_{12}</math></p> <p>19). <math>C_4H_9^+ + C_3H_6 \xrightleftharpoons{+A^-} C_7H_{14}</math></p> <p>20). <math>C_5H_{11}^+ + C_3H_6 \xrightleftharpoons{+A^-} C_7H_{14}</math></p> <p>VII). Carbenium ions attack on higher olefins giving paraffins and dienes:</p> <p>21). <math>C_4H_9^+ + C_4H_8 \xrightleftharpoons{+A^-} C_2H_4 + C_6H_{10}</math></p> <p>22). <math>C_4H_9^+ + C_4H_8 \xrightleftharpoons{+A^-} C_2H_4 + C_7H_{12}</math></p>	<p>23). <math>C_3H_7^+ + C_6H_{12} \xrightleftharpoons{+A^-} C_3H_6 + C_6H_{10}</math></p> <p>24). <math>C_3H_7^+ + C_7H_{14} \xrightleftharpoons{+A^-} C_3H_6 + C_7H_{12}</math></p> <p>25). <math>C_4H_9^+ + C_6H_{12} \xrightleftharpoons{+A^-} C_4H_{10} + C_6H_{10}</math></p> <p>26). <math>C_4H_9^+ + C_7H_{14} \xrightleftharpoons{+A^-} C_4H_{10} + C_7H_{12}</math></p> <p>27). <math>C_5H_{11}^+ + C_6H_{12} \xrightleftharpoons{+A^-} C_5H_{12} + C_6H_{10}</math></p> <p>28). <math>C_5H_{11}^+ + C_7H_{14} \xrightleftharpoons{+A^-} C_5H_{12} + C_7H_{12}</math></p> <p>VIII). Carbenium ions attack on dienes giving paraffins and cyclo-dienes:</p> <p>29). <math>C_3H_7^+ + C_6H_{10} \xrightleftharpoons{+A^-} C_6H_8 + C_3H_8</math></p> <p>30). <math>C_3H_7^+ + C_7H_{12} \xrightleftharpoons{+A^-} C_7H_{10} + C_3H_8</math></p> <p>31). <math>C_4H_9^+ + C_6H_{10} \xrightleftharpoons{+A^-} C_6H_8 + C_4H_{10}</math></p> <p>32). <math>C_4H_9^+ + C_7H_{12} \xrightleftharpoons{+A^-} C_7H_{10} + C_4H_{10}</math></p> <p>33). <math>C_5H_{11}^+ + C_6H_{10} \xrightleftharpoons{+A^-} C_6H_8 + C_5H_{12}</math></p> <p>34). <math>C_5H_{11}^+ + C_7H_{12} \xrightleftharpoons{+A^-} C_7H_{10} + C_5H_{12}</math></p> <p>IX). Carbenium ions attack on cyclo-dienes giving paraffins and olefins:</p> <p>35). <math>C_3H_7^+ + C_6H_8 \xrightleftharpoons{+A^-} C_6H_6 + C_3H_8</math></p> <p>36). <math>C_3H_7^+ + C_7H_{10} \xrightleftharpoons{+A^-} C_7H_8 + C_3H_8</math></p> <p>37). <math>C_4H_9^+ + C_6H_8 \xrightleftharpoons{+A^-} C_6H_6 + C_4H_{10}</math></p> <p>38). <math>C_4H_9^+ + C_7H_{10} \xrightleftharpoons{+A^-} C_7H_8 + C_4H_{10}</math></p> <p>39). <math>C_5H_{11}^+ + C_6H_8 \xrightleftharpoons{+A^-} C_6H_6 + C_5H_{12}</math></p> <p>40). <math>C_5H_{11}^+ + C_7H_{10} \xrightleftharpoons{+A^-} C_7H_8 + C_5H_{12}</math></p>
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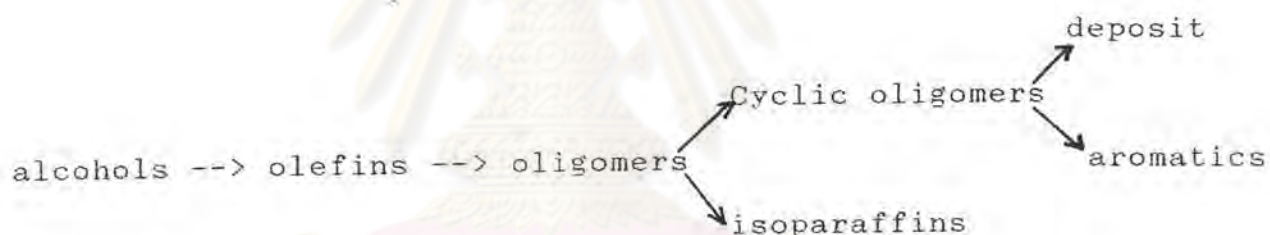


Table 2.6 (Continued)

X). Aromatics condensation:XI). Aromatics alkylation:XII). Paraffins demethanization:

### 2.3 Hydrocarbon Manufacture from Alcohols (48)

Since the development of the process of conversion of methanol into hydrocarbons by Mobil a few years ago, the mechanism of the transformations of alcohols on zeolite catalysts has been studied extensively. One of the striking features of the chain of these consecutive transformation is that practically the same product distribution is observed for all  $C_1$  to  $C_8$  alcohols, which indicates that a common reaction path must be followed.



So, hydrocarbon formation over the new zeolites is not limited to methanol. A wide variety of hetero-organic compounds can be efficiently transformed to hydrocarbons. In this chapter we describe the conversion of alcohols over the new zeolites. (48)

Typical hydrocarbon distributions from alcohol conversion are shown in Table 2.7 for three representative alcohols : methanol, t-butanol, and 1-heptanol. The data were obtained at 371°C, 1 LHSV, and atmospheric pressure. Under these conditions, water elimination is essentially complete. The three hydrocarbon product distributions are

strikingly similar, suggesting a common reaction pathway. As noted previously, the distribution is shape selective. Essentially no hydrocarbons above C<sub>11</sub> are produced.(2)

Table 2.7 Zeolite - catalyzed hydrocarbon formation (2)

Reactant:	Methanol	<i>t</i> -Butanol	1-Heptanol
Reaction conditions			
<i>T</i> (°C)	371	371	371
LHSV (hr <sup>-1</sup> )	1.0	1.0	0.7
Conversion (%)	100.0	100.0	99.9
Hydrocarbon distribution (wt%)			
Methane	1.0	0.1	0.0
Ethane	0.6	0.7	0.3
Ethylene	0.5	0.5	<0.1
Propane	16.2	18.8	16.4
Propylene	1.0	1.1	0.2
<i>i</i> -Butane	18.7	18.4	19.3
<i>n</i> -Butane	5.6	8.6	11.0
Butenes	1.3	0.7	<0.1
<i>i</i> -Pentane	7.8	6.2	8.7
<i>n</i> -Pentane	1.3	1.4	1.5
Pentenes	0.5	0.2	0.1
C <sub>6</sub> <sup>+</sup> aliphatics	4.3	7.6	3.0
Benzene	1.7	3.3	3.4
Toluene	10.5	11.6	14.3
Ethylbenzene	0.8	1.3	1.2
Xylenes	17.2	12.4	11.6
C <sub>9</sub> Aromatics	7.5	6.1	5.3
C <sub>10</sub> Aromatics	3.3	0.4	2.9
C <sub>11</sub> <sup>+</sup> Aromatics	0.2	0.6	0.6

The stoichiometric yields of hydrocarbon and water from methanol are 44 and 56% by weight, respectively. Such yields are observed in methanol conversion with the class of zeolites used and referred to above. In contrast, the normal end products of methanol dehydration are dimethyl ether and water, since unlike higher alkanols, methanol cannot form an alkene via simple *p*-elimination. Under certain conditions, however, small amounts of hydrocarbon products have been observed



during catalytic dehydration. Light Hydrocarbons have been detected in the product of methanol dehydration over cation exchanged faujasites and H-mordenite

Drake, C.A. (49) studied about specialty olefin production. A new technology has been developed that provides high conversion and high yield of 3-methyl-1-butene by controlling reaction conditions.

The dehydration of alcohols to give olefins is one of the oldest catalytic reactions known and has been studied extensively. Elimination of water to give an olefin is generally agreed to occur by a concerted mechanism involving both acidic and basic catalyst sites. (in Figure 2.4)

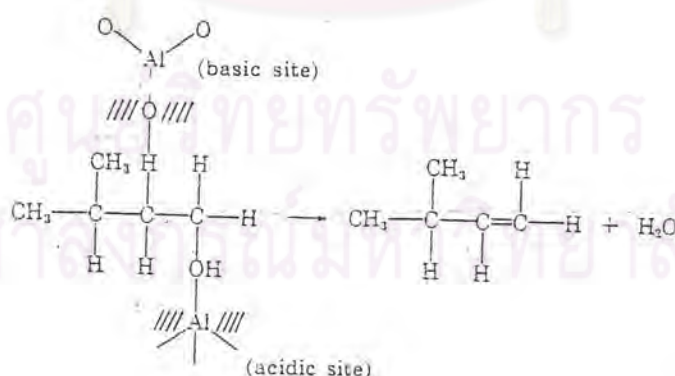


Figure 2.4 The dehydration of alcohols mechanism involving both acidic and basic sites (49)

The dehydration of a high purity 3-methyl-1-butanol (99% pure obtained via oxochemistry) over a variety of readily available high surface area aluminas proceeded to completion, but the selectivity to 3-methyl-1-butene was only about 80% with the other product either rearranged olefins or the ether corresponding to the starting alcohol. These products are : shown in Figure 2.5

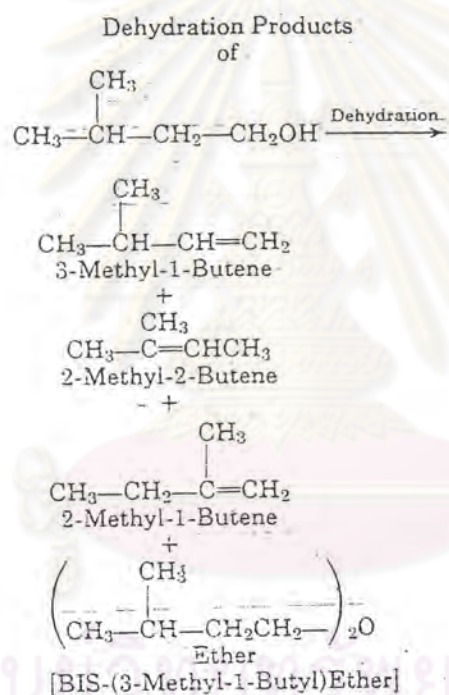


Figure 2.5 The dehydration of high purity 3-methyl-1-butanol. (49)

Since the rearranged olefins and ether were formed by acid catalysis, tests were made to determine if the addition of small amounts of base to the alumina would remove some of the acid sites and raise the selectivity

Equipment used in the pilot plant for 3-methyl-1-butene synthesis is shown in Figure 2.6. The basic elements consisted of : an alcohol feed tank, feed pump, preheater, reactor, product cooler, phase separator, crude 3-methyl-1-butene make tank, and tank for the column kettle bottoms.

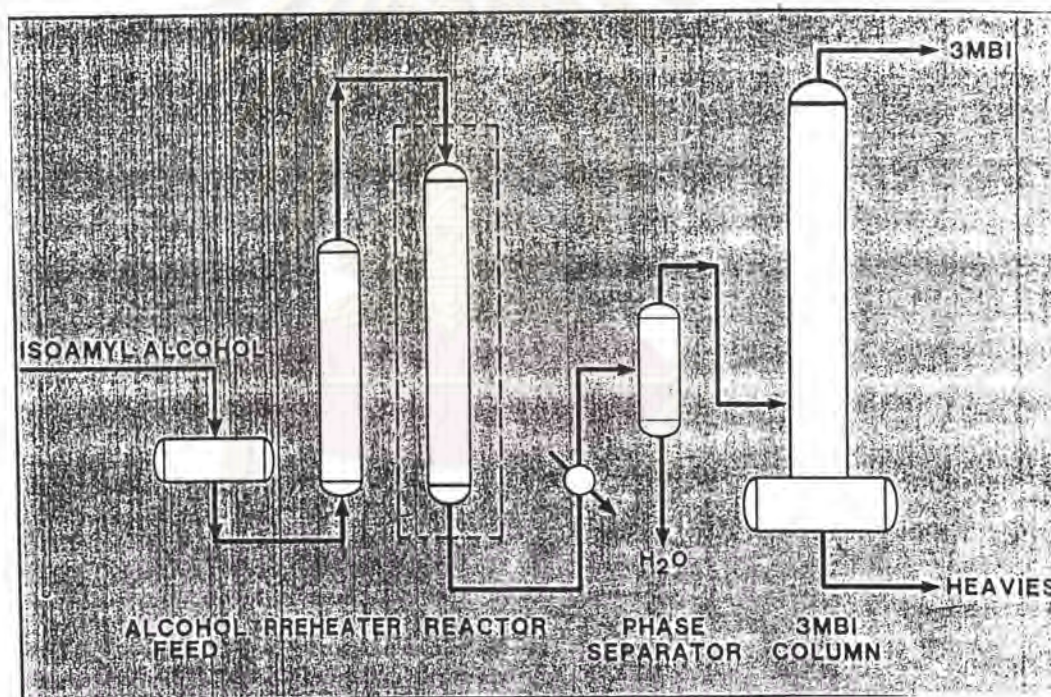


Figure 2.6 Process of 3-methyl-1-butene (49)



In the fixed-bed MTG process, removal of reaction heat is accomplished by dividing the overall reaction (and reactor system) into two steps and by light-gas recycle, as shown in Figure 2.7. Crude methanol is vaporized and heated to reaction temperature (315°C) by exchange with reactor effluent. It is then passed into a dehydration reactor, where it is partially dehydrated to form an equilibrium mixture of methanol, DME, and Water. The dehydration catalyst is a Mobil proprietary catalyst which is different from the ZSM-5 catalyst. Because this reaction is controlled by chemical equilibrium, excessive temperatures cannot be attained and the reactor system is inherently stable. About 20 percent of the heat of reaction is liberated in this first step.

The equilibrium mixture of methanol, DME, and water is then mixed with recycle gas and passed into conversion reactors which contain the ZSM-5 catalyst. The function of the recycle gas is to limit the temperature rise in the conversion reactor to less than 60°C. Without this heat sink, the temperature rise could be much greater. In the conversion reactors the methanol and DME are converted to gasoline range hydrocarbons and water.

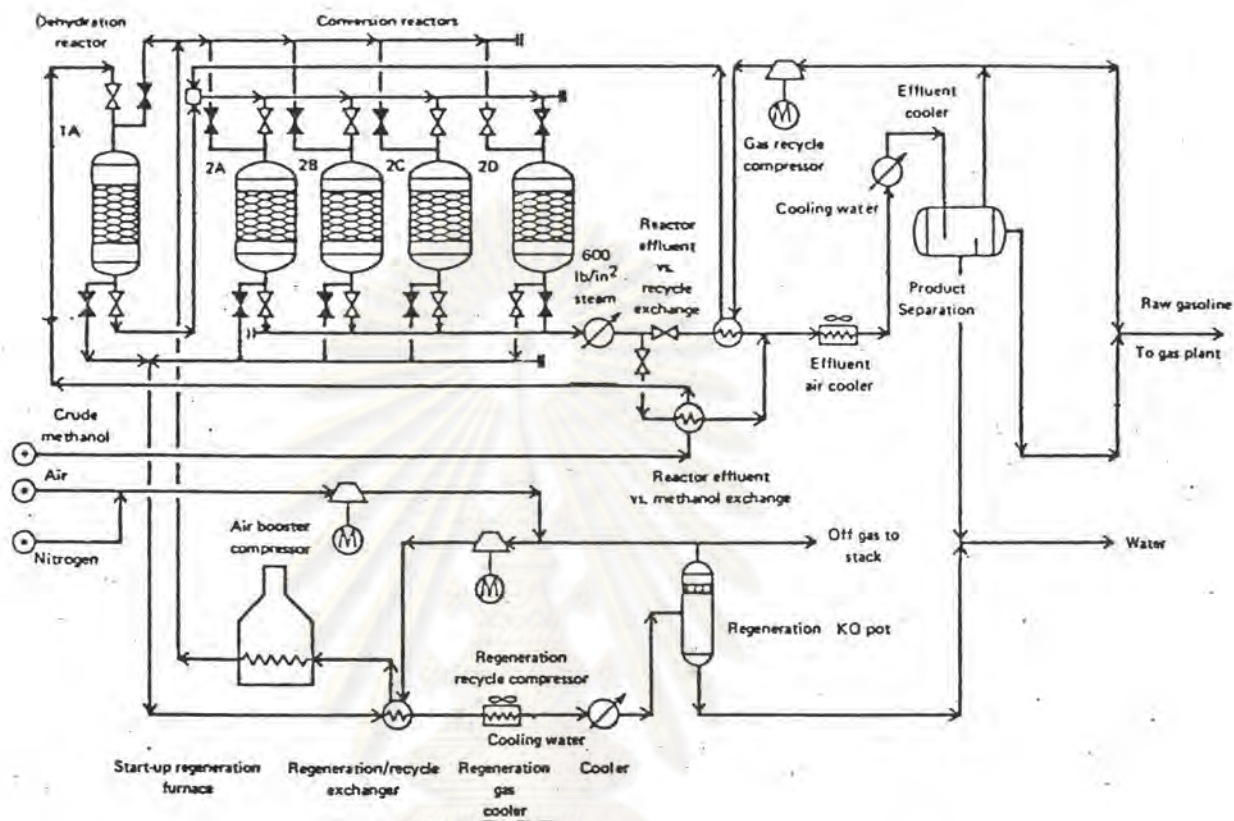


Figure 2.7 Typical flow diagram of fixed-bed MTG reaction section (50)

In a commercial system there would be multiple conversion reactors in parallel, as shown in Figure 2.7. The product leaving the conversion reactors are cooled by steam generation by heat exchange with recycle gas, and

finally by air and/or water cooling to a temperature of about 38°C. The product is then separated into three phases : (1) a liquid hydrocarbon phase from which gasoline and LPG are recovered, (2) a gas phase which is mostly recycled to the conversion reactor, and (3) an aqueous phase which will be treated to remove trace oxygenates or recycled to the synthesis-gas production step. The aqueous phase contains very little methanol and DME, since essentially complete conversion of these compounds occurs over the ZSM-5 catalyst.(50)

The fluid-bed MTG process is shown schematically in Figure 2.8. Crude methanol feed, which may contain variable amounts of water, is vaporized, superheated to the range of 175 to 260°C, and charged into the dense fluid-bed reactor. Typical reactor operating conditions are shown in Table 2.8. The fluid-bed catalyst is a Mobil proprietary ZSM-5 catalyst with physical properties similar to those of commercial fluid catalytic-cracking (FCC) catalyst. In a single pass through the reactor, virtually complete methanol conversion is achieved.



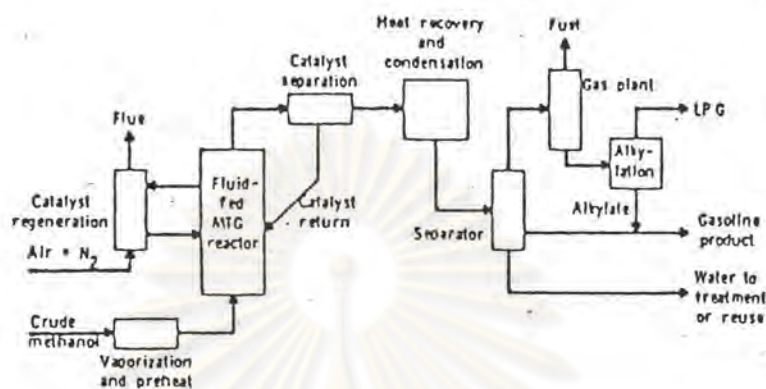


Figure 2.8 Fluid-bed MTG process (50)

After catalyst disengagement, the effluent stream is collected and separated into hydrocarbon and aqueous products. The hydrocarbons are sent through fractionation columns to yield C<sub>5</sub>+ gasoline, C<sub>3</sub> and C<sub>4</sub> streams, and a C<sub>2</sub> - stream. Typical yields from the reactor are also shown in Table 2.8. The C<sub>5</sub>+ gasoline fraction is 60 percent by weight of the hydrocarbon products. However, the C<sub>3</sub> - C<sub>4</sub> fraction contains significant quantities of isobutane, propane, and butenes. By means of the well-known alkylation process, these components are easily converted to additional gasoline. (50)

Table 2.8 Yields from methanol in a 4-bbl/day fluid-bed unit. (50)

Average bed temperature, °C	413
Pressure, kPa	275
Space velocity (WHSV)*	1.0
Yields, wt % of methanol charged	
Methanol + DME	0.2
Hydrocarbons	43.5
Water	56.0
CO, CO <sub>2</sub>	0.1
Coke, other	0.2
Total	100.0
Hydrocarbon product, wt %	
Light gas (C <sub>1</sub> + C <sub>2</sub> )	5.6
Propane	5.9
Propylene	5.0
Isobutane	14.5
<i>n</i> -Butane	1.7
Butenes	7.3
C <sub>5</sub> + gasoline	60.0
Total	100.0
Gasoline (including alkylate)†	88.0

\*Weight hourly space velocity, wt feedstock/(wt catalyst) (hour).

†Reid vapor pressure (RVP) is 9 lb/in<sup>2</sup> (62 kPa); unleaded research octane number (R + O) is 96.

## 2.4 Change of Product Distribution

A new and simple catalytic process for the conversion of methanol to hydrocarbons and water is recently announced by Mobil. The hydrocarbons produced in this process are olefin, aliphatic, and aromatic. Hydrocarbon formation over the Zeolites is not limited to methanol. A wide variety of hetero-organic compounds can be efficiently transformed to hydrocarbons. (describe in the past section)

In this section we describe the factors, which give effect to the product distribution. These factors can be concluded to the type of reactants, the operating condition of system, and the properties of zeolites.

### 2.4.1 Effect of Reactant (2)

The reactions of O-compounds over the new zeolites can be most generally characterized as, dehydration or decarboxylation with shape-selective transformation leading to hydrocarbons having a narrow distribution of molecular weights.

The data presented in Table 2.9 are representative survey of the conversion of various compounds and provide an indication of the scope of the reaction.



Table 2.9 The conversion of O-compounds to hydrocarbon (2)

Reactant:	Methanol	<i>t</i> -Butanol	1-Heptanol	Methanethiol	Propanal	Methylal
Reaction conditions						
<i>T</i> (°C)	371	371	371	482	371	371
LHSV (hr <sup>-1</sup> )	1.0	1.0	0.7	1.0	1.0	1.0
Conversion (%)	100.0	100.0	99.9	99.9 <sup>a</sup>	99.9	100.0 <sup>b</sup>
Hydrocarbon distribution (wt%)						
Methane	1.0	0.1	0.0	6.6	0.8	1.5
Ethane	0.6	0.7	0.3	8.3	0.4	0.7
Ethylene	0.5	0.5	<0.1	6.7	0.4	0.3
Propane	16.2	18.8	16.4	15.3	7.3	16.4
Propylene	1.0	1.1	0.2	1.3	0.6	0.9
<i>i</i> -Butane	18.7	18.4	19.3	9.0	4.6	15.1
<i>n</i> -Butane	5.6	8.6	11.0	3.1	3.0	5.8
Butenes	1.3	0.7	<0.1	0.2	0.3	0.9
<i>i</i> -Pentane	7.8	6.2	8.7	1.2	1.8	5.8
<i>n</i> -Pentane	1.3	1.4	1.5	<0.1	0.6	1.0
Pentenes	0.5	0.2	0.1	<0.1	0.2	0.2
C <sub>6</sub> <sup>+</sup> aliphatics	4.3	7.6	3.0	0.1	1.3	3.2
Benzene	1.7	3.3	3.4	0.2	4.1	1.1
Toluene	10.5	11.6	14.3	1.3	23.7	7.9
Ethylbenzene	0.8	1.3	1.2	<0.1	2.6	0.7
Xylenes	17.2	12.4	11.6	8.9	26.4	20.5
C <sub>9</sub> Aromatics	7.5	6.1	5.3	27.0	18.6	12.4
C <sub>10</sub> Aromatics	3.3	0.4	2.9	9.5	3.7	5.4
C <sub>11</sub> <sup>+</sup> Aromatics	0.2	0.6	0.6	1.3	0.6	0.2

Typical hydrocarbon distributions from alcohol conversion are shown in Table 2.9 (Examples 1-3) for three representative alcohols : methanol, *t*-butanol, and 1-heptanol. The data were obtained at 371°C, LHSV = 1 hr<sup>-1</sup>, and atmospheric pressure. Under these conditions, water elimination is essentially complete. The three hydrocarbon product distributions are strikingly similar, suggesting a common reaction pathway. As noted

previously, the distribution is shape-selective. Essentially no hydrocarbons above  $C_{11}$  are produced. Isoparaffins predominate, as do isoolefins, though the latter have not been detailed. Aromatics are mostly methyl-substituted. Included for comparison in Table 2.9 are data from a sulfur analogue, methanethiol (Example 4). The reaction temperature for methanethiol, converted with greater difficulty was at  $482^{\circ}\text{C}$ . At this temperature and  $\text{LHSV} = 1 \text{ hr}^{-1}$ , desulfurization was partial, with 27.2% of the feed carbon converted to dimethylsulfide. The overall hydrocarbon distribution is quite similar to the previous, with the main difference being that more light gas was produced, a result of the higher severity. Furthermore, the aromatics appear to peak at  $C_9$ , rather than  $C_8$ , as observed with alcohol feeds.

The conversion of propanal and methylal, a formaldehyde derivative, is shown also in Table 2.9. Propanal is efficiently converted to hydrocarbons, with higher selectivity to aromatic than the alcohols. Methylal gives a product similar to that obtained from the alcohols. However, some dissociation to  $\text{CO}$  and  $\text{CO}_2$  is evident.

#### 2.4.2 Effect of Operating Condition

Operating condition of this process can be subdivided in three case, which are the effect of space velocity or the effect of contact time, the effect of temperature, and the effect of pressure.



Effect of space Velocity (2) (Contact time) :

Table 2.10 shows the effect of contact times over three orders of magnitude on the product distribution in methanol conversion. The results at the lowest contact time ( $LHSV = 1080 \text{ hr}^{-1}$ ) show that the product contains substantial amounts of dimethylether (DME) formed by the reversible dehydration of methanol. Solely on the basis of these data, the ether-forming reaction might be regarded as either sequential in or only parallel to the major reaction steps leading to hydrocarbons.

However, DME is found (without the addition of water required to form methanol) to give essentially the same product distribution as methanol. Thus the conversion of methanol to DME may desirably be a first step in the overall sequence of the conversion of methanol to hydrocarbons.

The hydrocarbon distribution for the run at the lowest conversion (9.1% at  $LHSV = 1080 \text{ hr}^{-1}$ ) shows that 78% of the primary hydrocarbon product is  $C_2$  to  $C_4$  olefins. The interesting question of the mechanism of olefin formation from methanol is discussed has been in the past section. The olefins formed then undergo condensations and rearrangements leading finally to the aromatic product slate shown in the last column ( $LHSV = 1 \text{ hr}^{-1}$ ) of Table 2.10



Table 2.10 Effect of space velocity on methanol conversion (2)

LHSV [vol of liquid methanol/ (vol of catalyst/hr)]	1080	108	1
Product distribution (wt%)			
Water	8.9	33.0	56.0
Methanol	67.4	21.4	0.0
Dimethyl ether	23.5	31.0	0.0
Hydrocarbons	0.2	14.6	44.0
Conversion (MeOH + MeOMe) (wt%)			
	9.1	47.5	100.0
Hydrocarbon distribution (wt%)			
Methane	1.5	1.1	1.1
Ethane	—	0.1	0.6
Ethylene	18.1	12.4	0.5
Propane	2.0	2.5	16.2
Propylene	48.2	26.7	1.0
<i>i</i> -Butane	13.8	6.5	18.7
<i>n</i> -Butane	—	1.3	5.6
Butenes	11.9	15.8	1.3
C <sub>5</sub> + Aliphatics	4.4	27.0	14.0
Aromatics	—	6.6	41.1

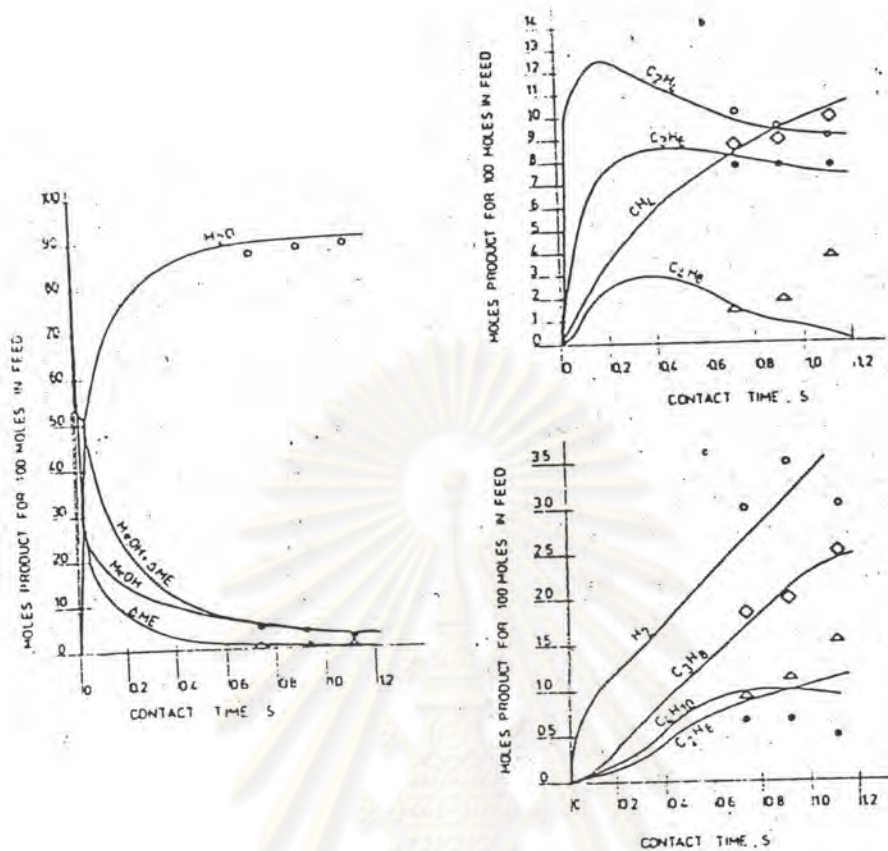


Figure 2.9 The major products distribution for the pure methanol conversion (40)

In Figure 2.9 the major products distribution is presented for the case of pure methanol, as a function of the contact time. It shows that methanol conversion increased with increased contact time but the olefin selectivity decreased.

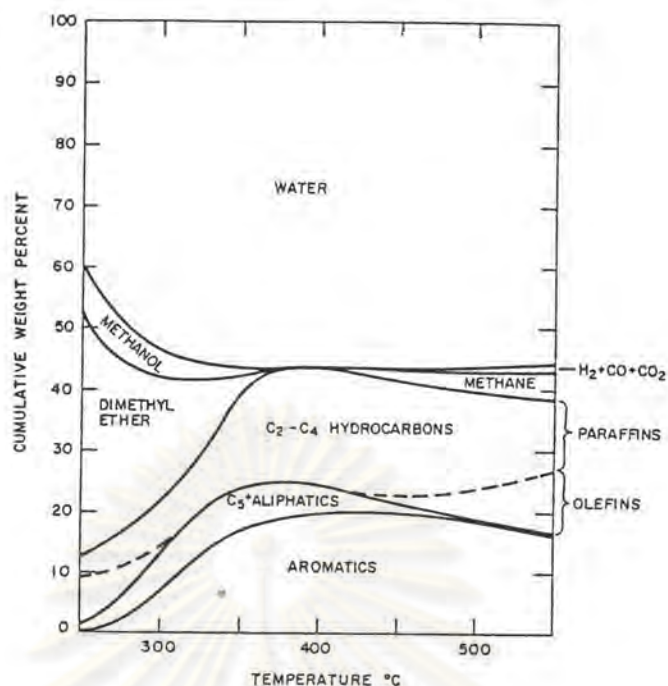


Figure 2.10 Zeolite-catalyzed methanol conversion ;  
yield structure VS temperature (2)

Effect of Temperature (2) : The effect of temperature on product distribution is summarized in Figure 2.10. These data were obtained at moderately low space velocity (LHSV = 0.6-0.7 hr<sup>-1</sup>), and span a range of 260-538°C. At 260°C, the main reaction is the dehydration of methanol to DME. The hydrocarbons formed are predominantly C<sub>2</sub> - C<sub>5</sub> olefins. The conversion of methanol/DME approaches completion between 340 and 375°C, with the formation of substantial amounts of aromatics. With further increase in temperature, only second-order changes in product distribution are evident. Light olefins and methane begin to rise as a result of secondary cracking reactions. Above about 500°C, the decomposition of methanol to H<sub>2</sub> and CO becomes measurable. The sequence



of events is formally identical to the reaction path previously defined through variation of contact time at a constant temperature.

Effect of Pressure (10) : The hydrocarbons produced in the ethanol conversion were grouped in four fractions ; gaseous paraffins (methane, ethane, propane, and butanes), GP ; gaseous olefins (ethylene, propylene, and butenes), GO ; nonaromatic liquid hydrocarbons ( $C_5 - C_8$ ), NA ; and aromatic liquid hydrocarbons (up to ten carbon atoms), AR.

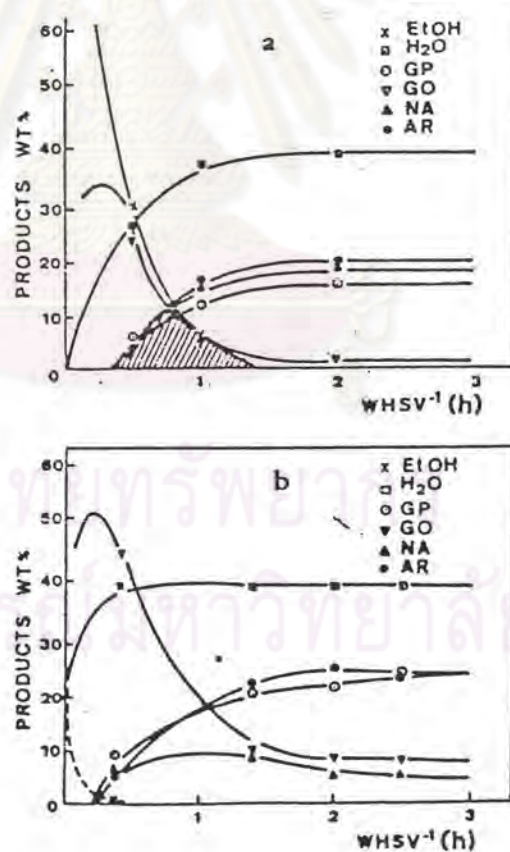


Figure 2.11 Effect of pressure on ethanol conversion (10)

The yields obtained for the four hydrocarbon fractions VS space time at pressures of 0.5, and 20 atm

quoted above are plotted in Figure 2.11. As the pressure increases, the overlapping of the conversion curves of ethanol and ethylene with the hydrocarbon formation curves shows that ethanol dehydration becomes more difficult. Likewise, the effect of higher pressure is to increase paraffin and aromatic amounts, decreasing olefins until they practically disappear.

The effect of pressure on the product distribution is summarized in Figure 2.12. It can be seen that the liquid hydrocarbon yield increases with pressure, reaching 70 wt % at 20 atm, simultaneously increasing its paraffinic nature.

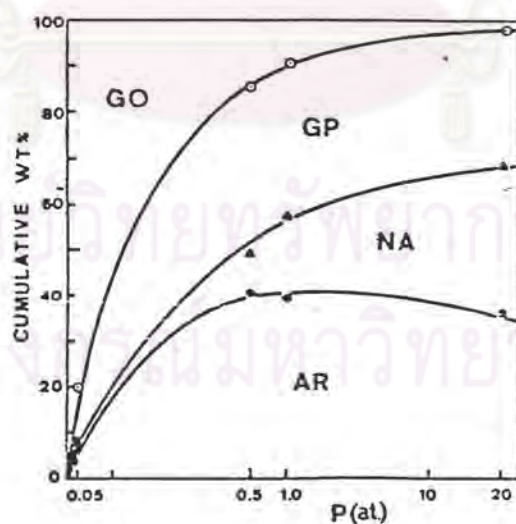


Figure 2.12 Effect of pressure on hydrocarbon distribution (10)

### 2.4.3 Effect of Property of Zeolite

The effect of zeolite can be subdivided in two case. They are the effect of Si/Al charged ratio, and influence of pore aperture. The details are shown below :

Effect of Si/Al charged Ratio (5) : In figure 2.13 and figure 2.14 show that the Si/Al atomic ratio were varied from 2.5 to 12.5 keeping Al constant. SEM photographs of typical examples of formed crystals and their catalytic activities and BET surface areas versus Si/Al charged ratio are shown in Figure 2.13 and 2.14, respectively. In the 6.5-11.5 range of Si/Al charged atomic ratios, methanol was converted completely to hydrocarbons with a high olefin selectivity and there was no formation of DME. Within the 6.5-11.5 ratio range, when the ratio was low, formation of propylene by the resultant catalysts was predominant ; when the ratio was high, formation of ethylene was predominant. On either side of the 6.5-11.5 range of Si/Al charged ratios, the catalytic activity for hydrocarbon formation decreased dramatically, and only DME and small amounts of methane were formed. BET surface areas of catalysts with various Si/Al charged ratios were consistent with both catalytic activity for hydrocarbon formation and the degree of crystallization.

Effect of Pore Size (45) : Synthesis of light olefins from methanol by using new type zeolites.



However, improvements in the catalyst's properties in this respect will be important for establishing its potential usefulness.



Figure 2.13 Variation of formed crystals for Si/Al charged ratios (5)

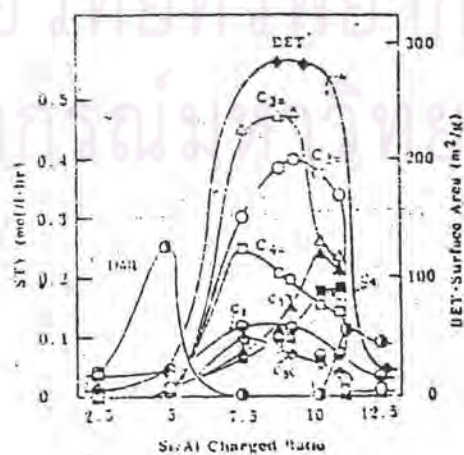


Figure 2.14 Effect of Si/Al charged ratio (5)

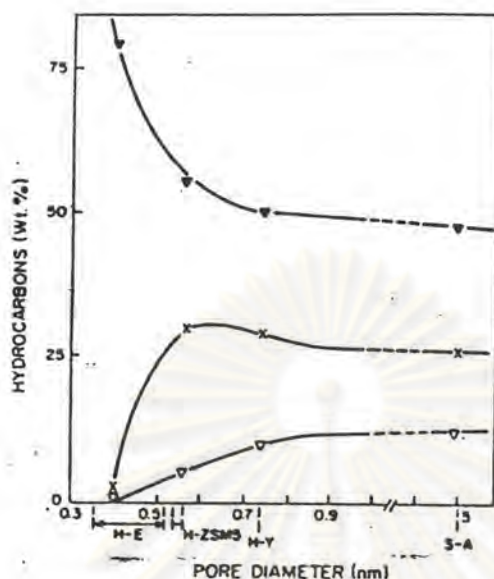


Figure 2.15 Influence of pore aperture on the distribution of hydrocarbon products (51)

The selectivity to the formation of light olefins is also determined by the structure of the zeolite used as catalyst, in particular its pore size.

Cormerais et al. (51) have investigated the conversion of methanol/DME over H-erionite, HZSM-5 and H-Y zeolites. They found that smaller pore sizes led to higher yields in ethylene and propylene while the formation of isobutane and C<sup>+</sup><sub>5</sub> hydrocarbons was strongly reduced as illustrated in Figure 2.15.