CHAPTER 4

RESULTS AND DISCUSSION

For consideration on the appropriate catalyst in chemical reactions, the catalytic properties in terms of conversion and selectivity are determined. Conversion is a measurement of ability to transform reactants into products. Selectivity is a measurement of the ability of a catalyst to preferentially catalyze one of the number of possible reactions. In methanol conversion, dehydrogenation, dehydration, and decomposition can occur. The conversion and selectivity to each product are defined by the following equations :

$$\text{Conversion (\%)} = \frac{(\text{MeOH})\text{fed} - (\text{MeOH})\text{unreacted}}{(\text{MeOH})\text{fed}} \times 100$$

$$\text{Methyl Formate Selectivity (\%)} = \frac{2(\text{MF})}{(\text{MeOH})\text{reacted}} \times 100$$

$$\text{Carbon Monoxide Selectivity (\%)} = \frac{(\text{CO})}{(\text{MeOH})\text{reacted}} \times 100$$

$$\text{Carbon Dioxide Selectivity (\%)} = \frac{(\text{CO}_2)}{(\text{MeOH})\text{reacted}} \times 100$$

$$\text{Dimethyl Ether Selectivity (\%)} = \frac{2(\text{DME})}{(\text{MeOH})\text{reacted}} \times 100$$

where (MF), (CO), (CO_2) and (DME) represent the formation flow rates of methyl formate, carbon monoxide, carbon dioxide and dimethyl ether, respectively, and (MeOH) represents the flow rate of methanol in a unit of mol/min. These values were calculated from the peak area of each product obtained by means of gas chromatographic analysis.

4.1 Type of Clay Catalyst

4.1.1 Effect on catalytic activity and selectivity

The catalytic activities in methanol conversion of the three Na type of smectite clays exchanged by copper ions, namely Cu-Lapo, Cu-Sapo, and Cu-Mont have been studied. The activities and selectivities of the exchanged clay catalysts are shown in Table 4-1. Methyl formate was obviously formed on Cu-Lapo through the dehydrogenation of methanol with a high selectivity of methyl formate. The possible stoichiometric equation can be written as follow :

$$2\ CH_3OH \rightleftharpoons HCOOCH_3 + 2\ H_2 \qquad (4.1)$$

On the contrary, dehydration preferentially occured on Cu-Sapo and Cu-Mont. High selectivity to dimethyl ether was obtained and the possible stoichiometric equation can be written as follow :

$$2\ CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \qquad (4.2)$$

As shown in Table 4-1, the copper content in each catalyst was almost same. This suggests that the copper content is not the main factor causing the difference in the type of methanol conversion.

Table 4-1 Activities and selectivities of exchanged clay catalysts

Catalyst	Cu-Lapo	Cu-Sapo	Cu-Mont
Conversion (%)	12	2.5	4
Selectivity (%)			
MF	97.5	0	0
DME	0	96	100
CO	0	0	0
CO_2	2.5	4	0
Copper content (mol/g-cat.)	0.7691	0.6420	0.6335

Reaction conditions : temperature, 200°C; W/F, 300 g-cat.min/mol.
Catalysts were treated at 400°C under nitrogen atmosphere.

4.1.2 Consideration on the structure of catalysts

a. The structure of smectite

As previously mentioned in Chapter 1, smectite clay minerals are composed of silicate sheets which stacked one above the other. The layer is composed of two tetrahedral and one octahedral oxygen frame-work sheets. The oxygen atoms define upper and lower sheets of tetrahedral sites and a central sheet of octahedral sites. The structure of smectite is shown in Fig. 4-1.

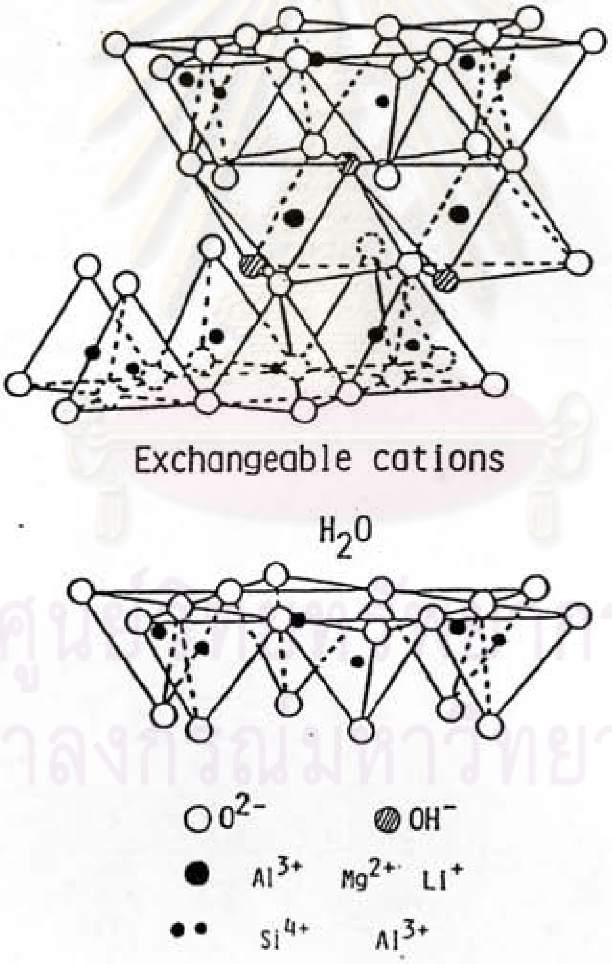


Fig. 4-1 Structure of smectite.

As shown in Fig. 4-1, silicon and sometimes aluminum normally occupy tetrahedral positions in the oxygen framework. Aluminum, magnesium, iron or lithium may occupy octahedral sites. $M^{n+}.xH_2O$ represents the interlayer exchanged cation which is easily exchangable with any desired cations, including organic, inorganic, bulky cations. Water and other polar molecules can be also intercalated into the interlayer spaces.

b. The substitution of metal ions

Considering on the chemical formula of laponite, saponite and montmorillonite, the substitution of metal ions for laponite and montmorillonite occur on octahedral sites while that of saponite occurs on tetrahedral sites as shown in Fig. 4-2. In the case of saponite, the substitution of tetrahedral Si^{4+} with Al^{3+} gives each silicate layer a localized negative charge, on the other hand, gives concentrated negative charge at the surface. In contrast, the substitution of octahedral Mg^{2+} with Li^{+} and Al^{3+} with Mg^{2+} on the layer lattice of laponite and montmorillonite give the negative charge delocalized all over the oxygen framework. The negative charge is usually compensated by Na^{+} which is easily exchanged with Cu^{2+} in catalyst preparation by means of ion exchange method. Proton liberated from hydrated copper ions also compensate the negative charge as shown in Fig. 4-3. Since the tetrahedral substitution occur on saponite as same as zeolite which is the strong acidic catalyst, suggesting that the acid sites obtained from saponite are stronger than those obtained from laponite or montmorillonite.

In this aspect, the difference in substitution is the reasonable consideration for the difference in methanol conversion between Cu-Sapo and Cu-Lapo. It is obvious to conclude that the dehydration on Cu-Sapo occured on the strong acid sites which caused by the tetrahedral substitution. For explaination of the difference in methanol conversion between Cu-Lapo and Cu-Mont which are the octahedral substitutions, the consideration in the other aspects will be done.

Montmorillonite	Saponite	Laponite
Si^{4+}	$Si^{4+} \leftarrow Al^{3+}$	Si^{4+}
$Al^{3+} \leftarrow Mg^{2+}$	Mg^{2+}	$Mg^{2+} \leftarrow Li^{+}$
Si^{4+}	$Si^{4+} \leftarrow Al^{3+}$	Si^{4+}

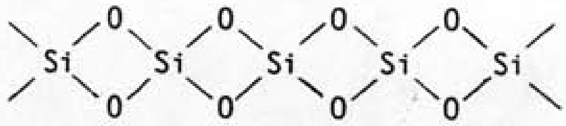
$Na_x[Al_{2-x}Mg_x](Si_4O_{10})(OH)_2.mH_2O$; Montmorillonite

$Na_x[Mg_3](Al_xSi_{4-x}O_{10})(OH)_2.mH_2O$; Saponite

$Na_x[Mg_{3-x}Li_x](Si_4O_{10})(OH)_2.mH_2O$; Laponite.

Fig. 4-2 Substitution of metal ion in layer latticed silicate clays.

Tetrahedral sheet of saponite clay.



Copper ion exchange

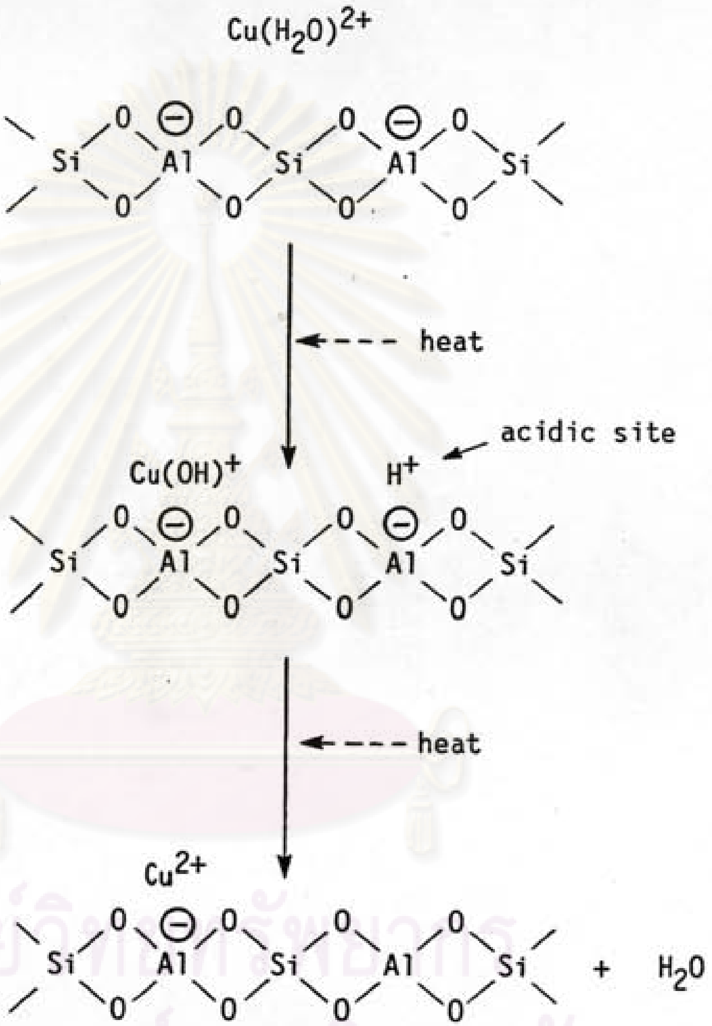


Fig. 4-3 The occurance of acidic site.

4.1.3 Consideration on electronegativity

Electronegativity (EN) is the ability that the subtance or element can attract electrons. The higher in EN, the higher in attraction force is obtained. From the substitution of metal ions in the layer of clay catalyst, the negative charges or electrons are strongly attracted by the high EN catalyst which causes the weak OH bond. When OH bond is weak, proton is easily released from the surface of catalyst leading to the strong acidic strength of catalyst. According to this concept, the EN of Laponite and Montmorillonite are compared. The calculations on the average electronegativity base on the Sanderson principle are shown in Appendix G.

From the results of calculations, the average EN of Laponite ($EN_{Lapo} = 2.50$) is lower than that of Montmorillonite ($EN_{Mont} = 2.64$). Suggesting that Cu-Mont is a stronger acidic catalyst than Cu-Lapo. From the results in Table 4-1, it can be conclude that the stronger in acidic property of Cu-Mont promoted dehydrogenation of methanol.

4.1.4 Consideration on the acidic property of catalyst

As previously quoted from the literatures, the acidity of catalyst affects on the type of reactions in methanol conversion and dehydration of methanol was promoted on the acid sites of catalyst. Thus, the acidity of these clay catalysts was studied.

a. TPD and surface area measurements

TPD measurement

Temperature programmed desorption (TPD) of ammonia was used to investigate the acidity of each catalyst. Figure 4-4 shows the ammonia-TPD spectra of Cu-Lapo, Cu-Sapo, and Cu-Mont. The spectra

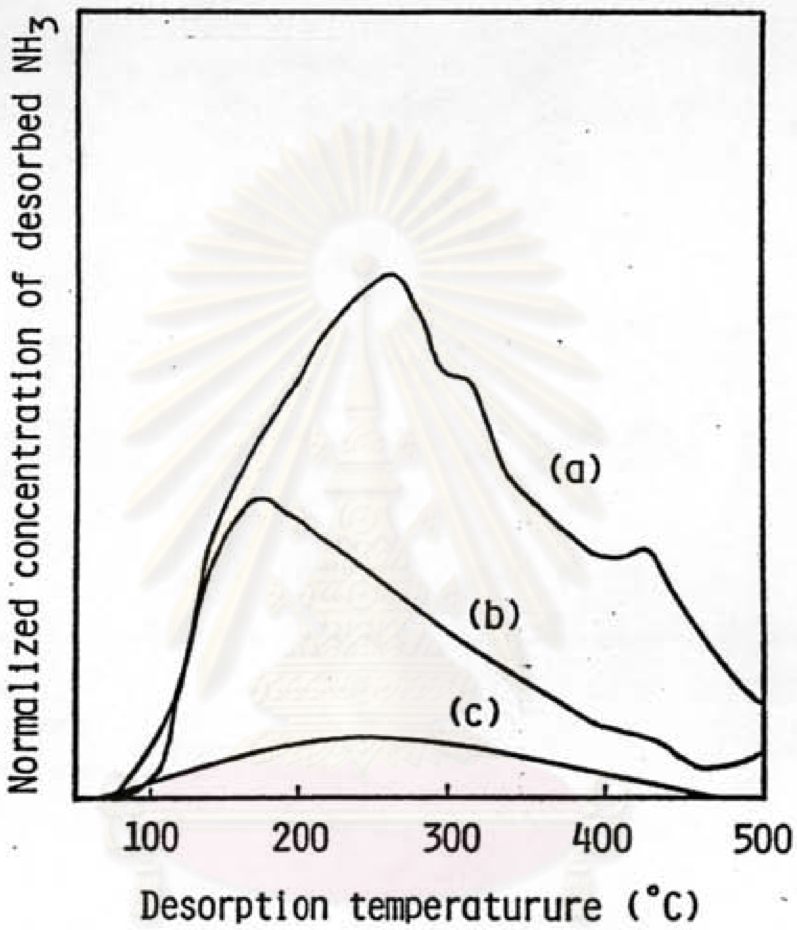


Fig. 4-4 NH_3-TPD spectra of clay catalysts : (a),Cu-Sapo; (b),Cu-Lapo; (c), Cu-Mont.

from these catalysts showed the existance of acid sites. The largest spectra is obtained from Cu-Sapo, and the smallest one is from Cu-Mont. The amount of ammonia adsorption from TPD measurements were calculated from the following equation :

$$Y = -0.0231 + 16.37977657\,X \qquad (4.3)$$

where X is weight of ammonia desorption peak (g) : paper
Y is amount of ammonia desorbed (mol x 10^{-4}).

Since 1 mole of ammonia react with 1 mole of proton as follow :

$$NH_3 + H^+ \rightleftharpoons NH_4^+ \qquad (4.4)$$

therefore the amount of desorbed ammonia represents the amount of acid sites which is shown in Table 4-2.

Surface area measurement

Surface area was determined by nitrogen adsorption isotherms using the Langmuir or BET equation calculated on the basis of dry catalyst as shown in Appendix E. The surface areas of Cu-Lapo and Cu-Sapo are considerably larger than that of Cu-Mont, reflecting the difference in the structure of each catalyst which will be study.

The results of calculation on the amount of acid sites per surface area are tabulated in the last column in Table 4-2. It is indicated that Cu-Sapo shows the largest acidity while Cu-Mont and Cu-Lapo are of lower in acidities. Consequently, it is clearly shown that the acidity of Cu-Sapo promotes the dehydration of methanol to dimethyl ether.

Table 4-2 Amount of acid sites on Copper-exchanged clay catalysts

Catalyst	Surface area a)	Amount of acid sites	
	m^2/g-cat.	mol/g-cat. b)	mol/m^2
Cu-Lapo	372.5	1.70×10^{-4}	4.51×10^{-7}
Cu-Sapo	232.8	3.42×10^{-4}	1.47×10^{-6}
Cu-Mont	80.0	0.37×10^{-4}	4.61×10^{-7}

a) on basis of dry catalyst

b) calculate from TPD measurement.

b. XRD measurement

As mentioned above, the difference in structure of each catalyst is responsible for its surface area and the size of ammonia desorption peak. X-ray diffraction measurements were done to investigate the structure of each catalyst. Figure 4-5 shows the XRD patterns of Cu-Lapo, Cu-Sapo and Cu-Mont. The sharp peak which is obtained from Cu-Mont indicates a well-ordered structure with the small interlayer space. For Cu-Lapo and Cu-Sapo, the broader peaks indicate a delaminate structure of these catalysts. The structure of well-ordered or laminated and delaminated clays are shown in Fig. 4-6.

Due to the well-ordered structure of Cu-Mont, the desorption (or adsorption) of ammonia seems to be restricted only to the outer surface of the catalyst. Thus, a small peak of ammonia desorption was obtained in TPD measurement. This explaination is also well agrees with the reason for the small surface area obtained from nitrogen adsorption measurement on Cu-Mont. In contrast, the large peak areas of ammonia desorption and high surface area for Cu-Lapo and Cu-Sapo can be explained by taking into consideration on the delaminated structure.

4.1.5 Conclusion on the effect of type of clay catalyst on methanol conversion.

For Cu-Sapo, it is obvious to conclude that the promoted dehydration is attributed to the high acidic property which is caused by the tetrahedral substitution. The difference in catalytic activities of Cu-Lapo and Cu-Mont, of which the substitution occurs on the octahedral sheet, can be explained by the calculation of the electronegativity (EN) of these catalysts. The results of average EN show that the EN of Cu-Mont is higher than that of Cu-Lapo which means Cu-Mont shows stronger in acidic strength than Cu-Lapo. The results of amount of acid sites per surface area as shown in Table 4-2 are also well agree with this conclusion. In conclusion, the acidic property of each clay catalyst is mainly responsible to the difference in catalytic activity for methanol conversion.

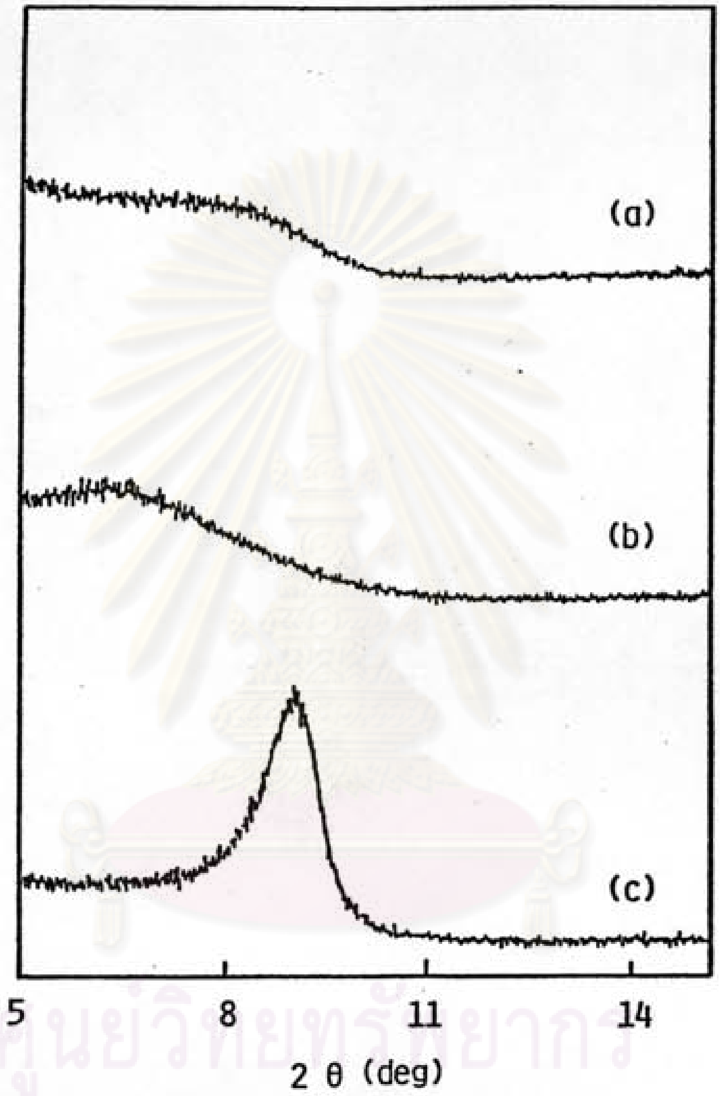


Fig. 4-5 XRD patterns of (a),Cu-Lapo; (b),Cu-Sapo; (c),Cu-Mont.

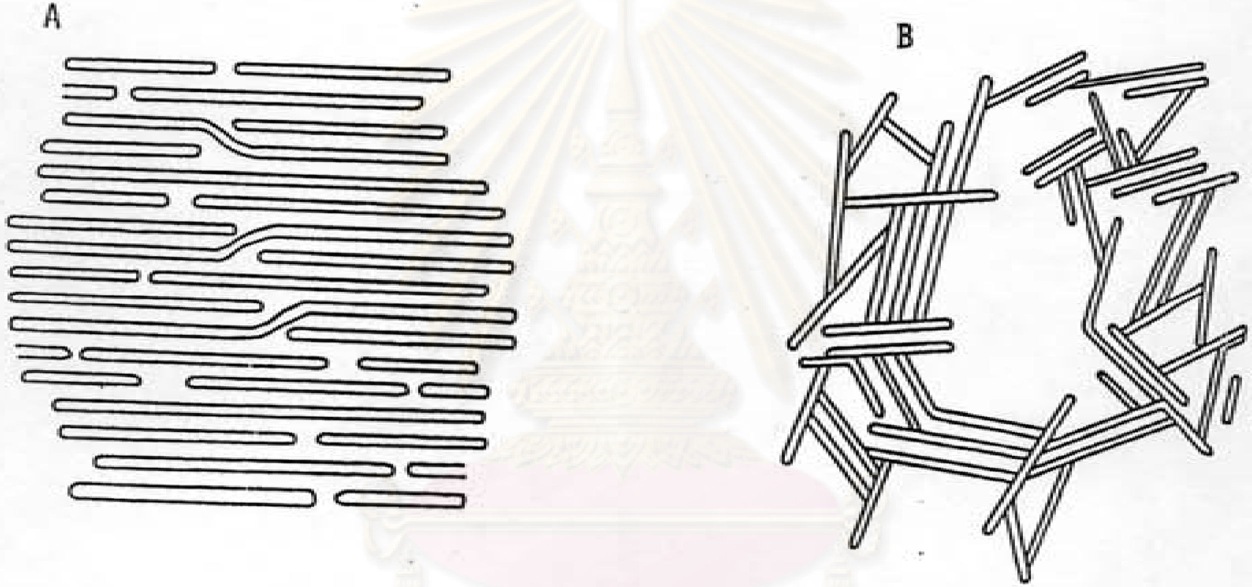


Fig. 4-6 Layer latticed aggregations of silicate clay (a),Laminated or well-ordered; (b),Delaminated

4-2. REACTION TEMPERATURE.

4.2.1 Effect on catalytic activity and selectivity

The effect of reaction temperature on the activity and selectivity of Cu-Lapo, Cu-Sapo, and Cu-Mont has been studied. The reaction temperatures were 200, 250 and 300° C. The time factor, weight of catalyst per flow rate of reactant (W/F), was fixed at 300 g-cat. min/mol. In this study, the same catalyst was used throughout each run of experiments. Therefore, preventing from catalyst deactivation which may occur, air treatment at 400 ° C for 1 h prior to the reaction at 250 and 300°C were done. For simplicity, the schematic diagram of treatment and reaction is summaraized as follows:

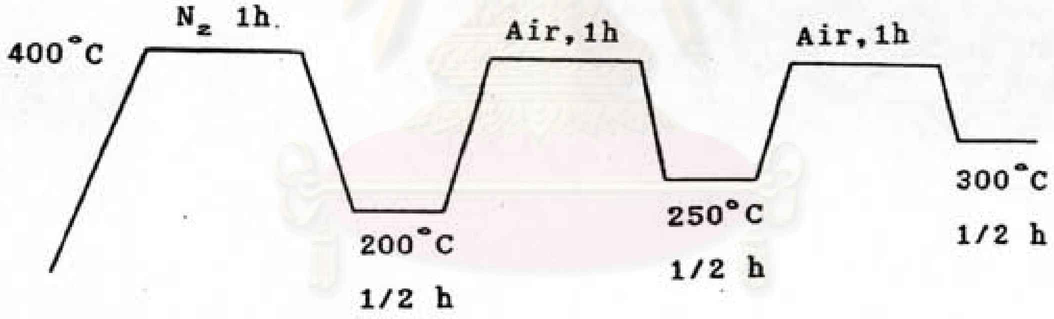


Fig. 4-7 Schematic diagram of treatment and reaction conditions.

The reaction product at 30 min of each run was collected and analyzed by means of gas chromatograph. The results are shown in Figs. 4-8, 4-9 and 4-10 for Cu-Lapo, Cu-Sapo and Cu-Mont, respectively. Dehydrogenation of methanol to methyl formate occured on Cu-Lapo, while dehydration of methanol to dimethyl ether occured on Cu-Sapo and Cu-Mont.

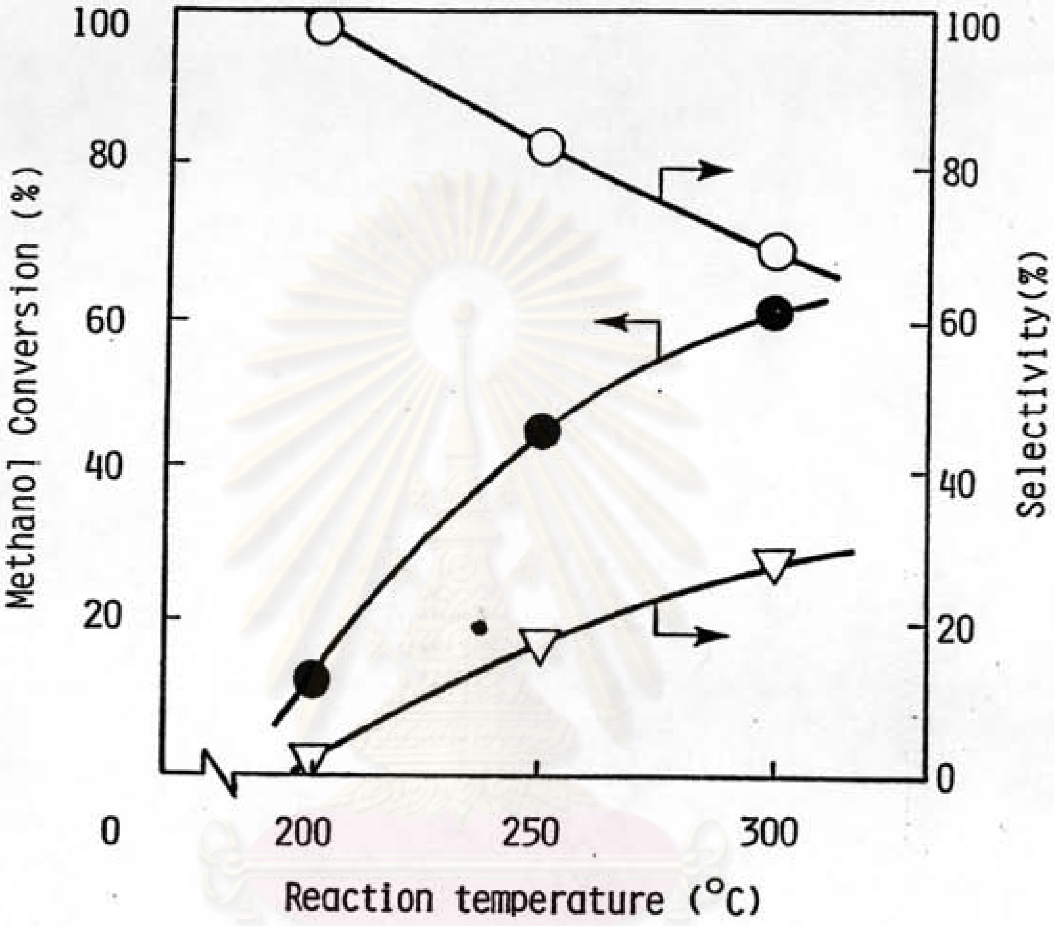


Fig. 4-8 Effect of reaction temperature on the activity and selectivity of Cu-Lapo catalyst treated at 400°C under nitrogen atmosphere:

● ,conversion of methanol; ○ ,MF selectivity;

▽ ,CO_x selectivity.

Reaction condition: W/F,300g-cat. min/mol.

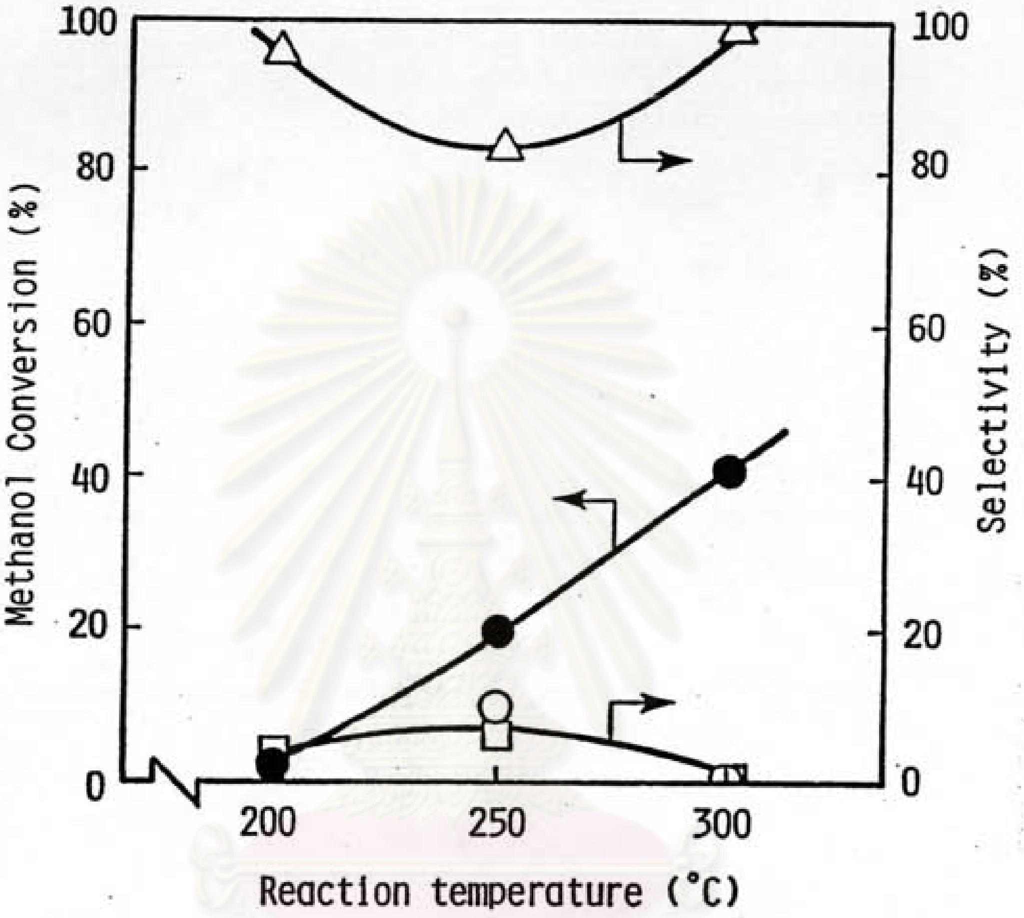


Fig. 4-9 Effect of reaction temperature on the activity and selectivity of Cu-Sapo catalyst treated at 400°C under nitrogen atmosphere:

●, conversion of methanol; ○, MF selectivity;

△, DME selectivity; □, CO_x selectivity.

Reaction condition: W/F, 300g-cat. min/mol.

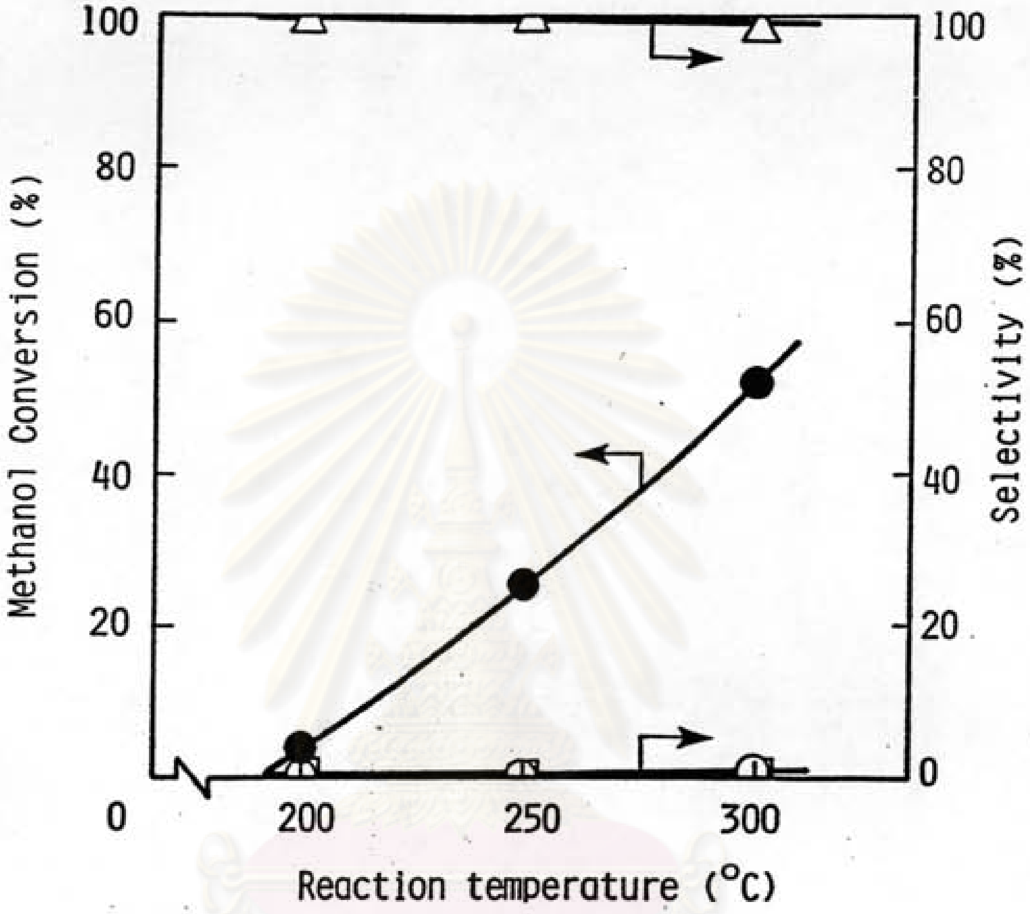


Fig.4-10 Effect of reaction temperature on the activity and selectivity of Cu-Mont catalyst treated at 400°C under nitrogen atmosphere:

●, conversion of methanol; ○, MF selectivity;

△, DME selectivity; □, CO_x selectivity.

Reaction condition: W/F, 300g-cat. min/mol.

Figure 4-8 shows the effect of reaction temperature on the activity and selectivity of Cu-Lapo catalyst. At the reaction temperature of 200°C, almost 100% of the methyl formate selectivity was obtained. With increasing reaction temperature, the methanol conversion increased while the selectivity of methyl formate decreased. And the decrease in methyl formate selectivity leads to the increase in the carbon monoxide selectivity. For this result, it is suggested that methyl formate may decompose to carbon monoxide by the high reaction temperature or by high conversion of methanol. Figures 4-9 and 4-10 show the effect of reaction temperature on the dehydration activities of Cu-Sapo and Cu-Mont. The conversion on both of these catalysts also increases with the reaction temperature while the selectivity for dimethyl ether was maintained at almost 100%. It is suggested that dimethyl ether is the main product of methanol dehydration and no side reaction occurs even at increased reaction temperatures.

4.2.2 Effect on product distributions

In the following, the product distributions at various conversion on Cu-Lapo catalyst have been studied. The time factor (W/F) was varied in the range of 100 to 2500 g-cat.min/mol. Figure 4-11 shows the relationship between the product distributions and time factor(W/F). The detected products were methyl formate, carbon monoxide and carbon dioxide which both of them abbreviated as CO_x. Unreacted methanol was also plotted to show the level of methanol conversion. The decrease of unreacted methanol means the level of methanol conversion increases with time factor. The formation of methyl formate ceased to increase with a further increase in the extent of reaction while that of CO_x (CO and CO_2) steeply increased as shown in Fig. 4-12. Methyl formate was almost a sole product up to 30 % conversion of methanol.

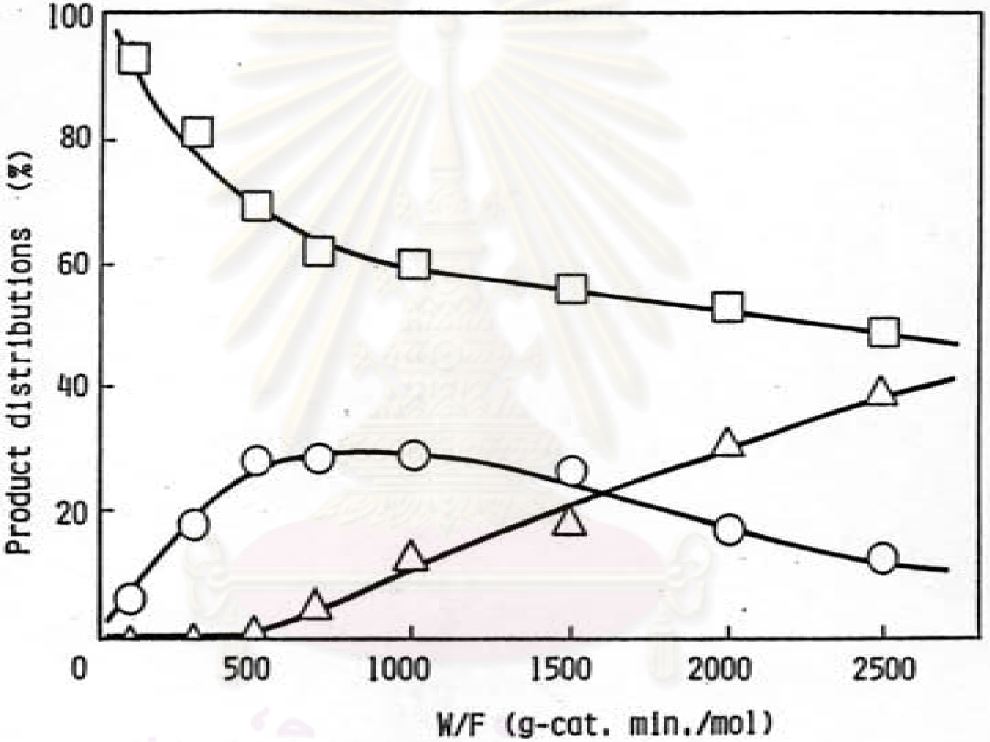


Fig. 4-11 Effect of time factor on product distribution over Cu-Lapo catalyst treated at 400^{o}C under nitrogen atmosphere: □ ,methanol; ○ ;methanol formate; △ , CO_x (CO and CO_2)
Reaction condition : temperature, 200^{o}C:

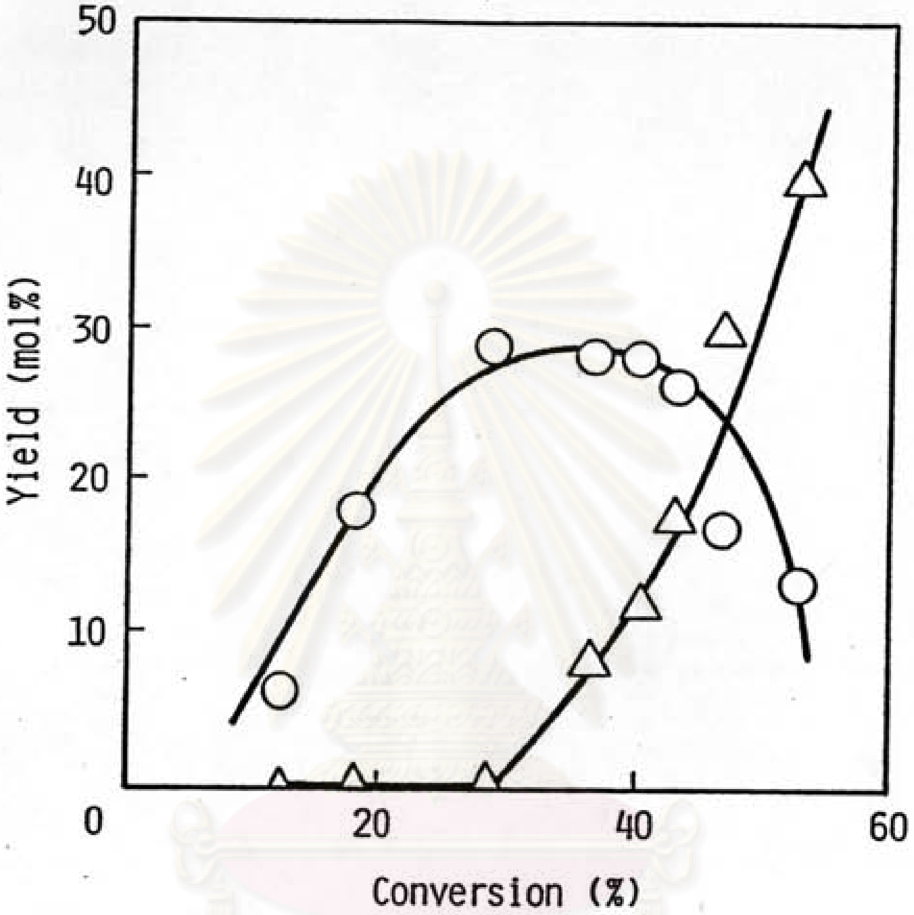


Fig.4-12 Effect of the levels of methanol conversion on yields of MF and CO_x on Cu-Lapo catalyst : ○ ,MF ; △ ,CO_x.

It can be concluded that the formation of methyl formate was limited either by reaction equilibrium or by decomposition of methyl formate to carbon monoxide as follows :

$$2\ CH_3OH \rightleftharpoons HCOOCH_3 + 2\ H_2 \qquad (4.5)$$

$$HCOOCH_3 \rightleftharpoons 2\ CO + 2\ H_2 \qquad (4.6)$$

Trace amounts of carbon dioxide were observed in the reaction products on all the catalysts. This CO_2 was probably formed due to the presence of trace qualities of water reacting as follows (Takahashi et. al., 1982)

$$HCOOCH_3 + H_2O \rightleftharpoons HCOOH + CH_3OH \qquad (4.7)$$

$$HCOOH \rightleftharpoons CO + H_2 \qquad (4.8)$$

No apparent relationship between the formation of CO_2 and disapparance of CO was observed, thereby discounting the formation of CO_2 by the water gas shift reaction is not likely to be significant.

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (4.9)$$

4.2.3 Effect on catalytic stability

In the study of stability of Cu-Lapo catalyst, the reaction was done in the long period of time. Figure 4-13 shows the variation in the level of methanol conversion and product distributions over Cu-Lapo catalyst at reaction temperature of 200 °C at W/F of 700 g-cat.min/mol where the maximum of methyl formate distribution (30% of methanol conversion) was obtained as previously shown in Fig. 4-11. In the first 30 min of reaction, the activity for the formation of methyl formate was a little bit high and it decreased to 80 % in 3 h, while the selectivity of carbon monoxide and the methanol conversion gradually increased and leveled off. After 3 h of reaction, the

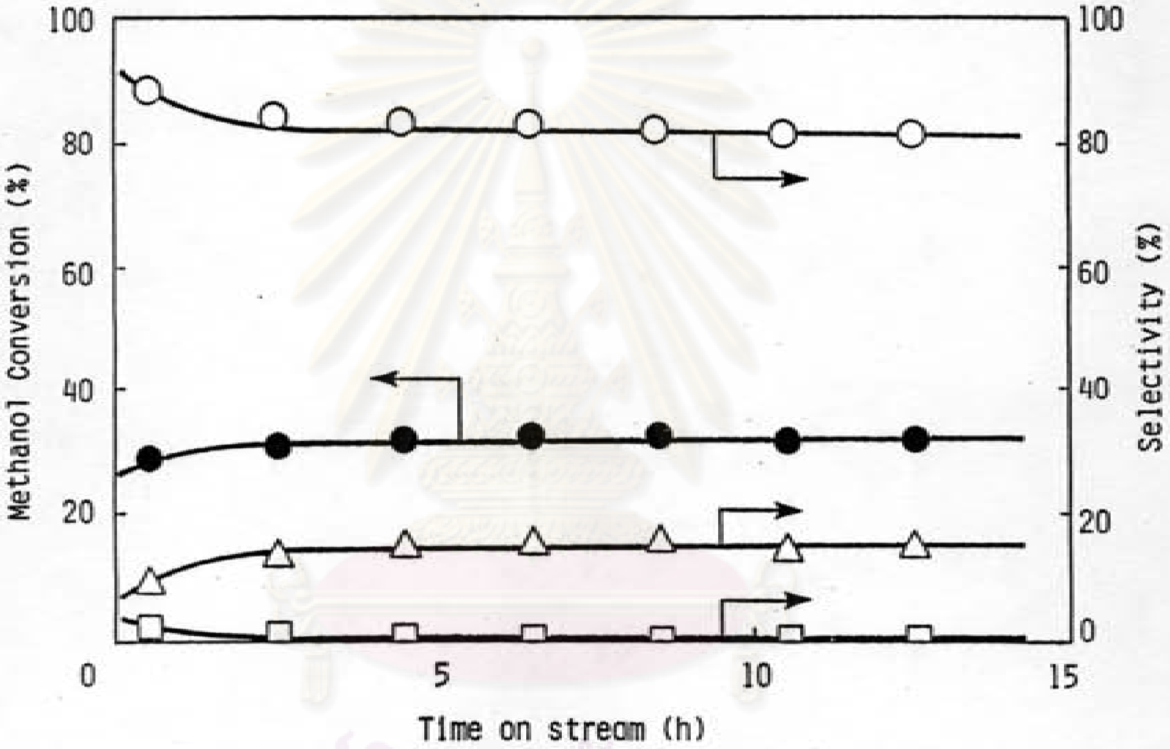


Fig.4-13 Variation in the level of methanol conversion and product distribution over Cu-Lapo catalyst treated at 400°C under nitrogen atmosphere: ● ,conversion; ○ ,MF selectivity; △ ,CO selectivity; □ ,CO_2 selectivity.

Reaction conditions:temperature,200°C;W/F,700g-cat. min/mol.

increase in time on stream had no effect on the methanol conversion and selectivities. It is indicated that no deactivation occured on Cu-Lapo at the reaction temperature of 200 °C.

Another study has been done at the reaction temperature of 300°C, as shown in Fig. 4-14. The detected products were methyl formate, carbon monoxide, carbon dioxide and dimethyl ether. Methanol conversion was initially high (80%) and dramatically decreased to 25(%) within 30 h. It is clearly indicated that deactivation dominantly occured. With decreasing methanol conversion, the selectivity for methyl formate increased while that of carbon monoxide decreased. At 30 % conversion, the selectivity to methyl formate approached 80 %, similar to the reaction at 200°C.

4.2.4 Consideration on catalytic deactivation

The catalytic deactivation occured on the Cu-Lapo catalyzed at 300°C but no deactivation was observed at the reaction temperature of 200°C. There are a number of possible reasons to explain the catalytic deactivation as follows :

a. Coke formation
b. Sintering
c. Dehydration (H_2O formation)

Coke formation

Since the catalytic deactivation occured at high reaction temperature (300°C), there is the possibility that coke may form at this high temperature. To confirm this consideration, more experiments are needed.

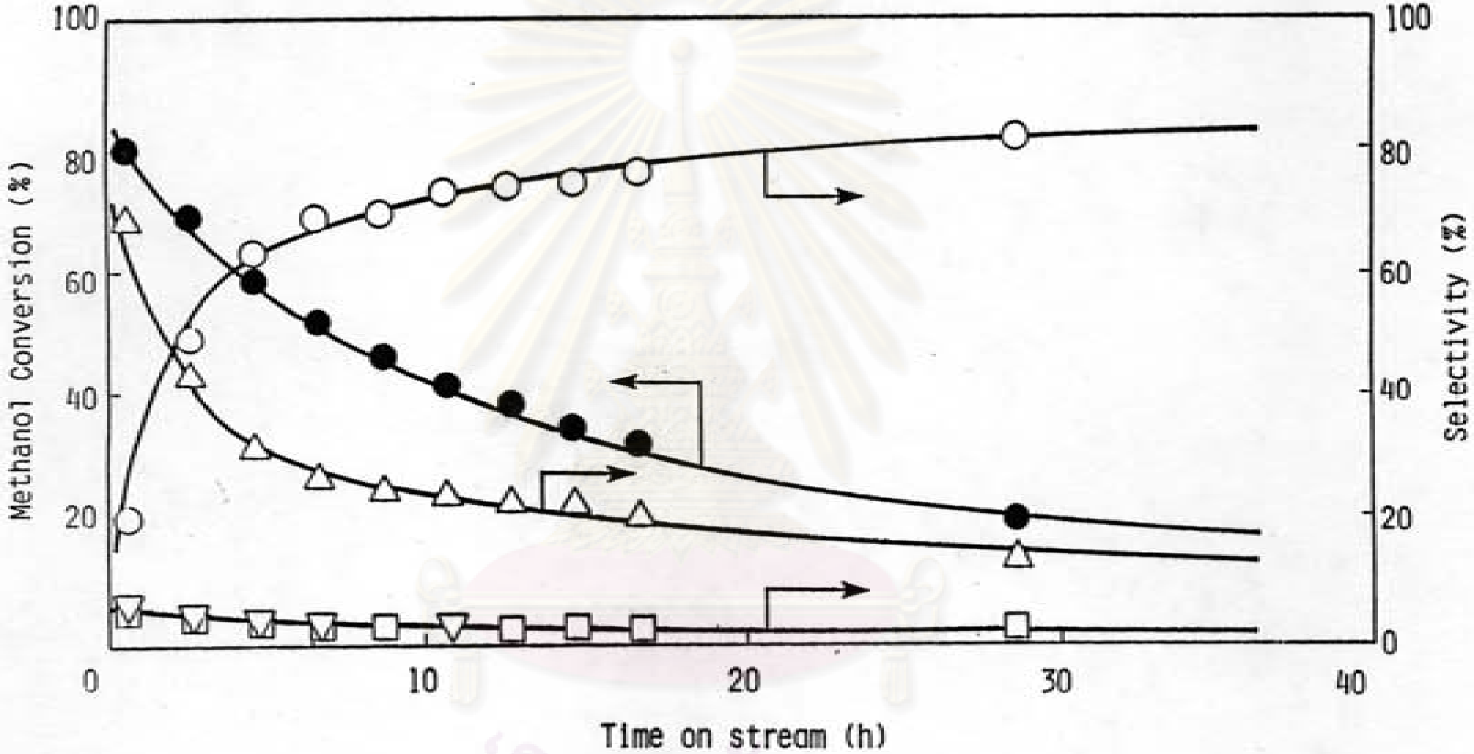


Fig.4-14 Variation in the level of methanol conversion and product distribution over Cu-Lapo catalyst treated at 400°C under nitrogen atmosphere: ●,conversion; ○, MF selectivity; △,CO selectivity; □,CO_2 selectivity; ▽,DME selectivity. Reaction conditions:temperature,300°C,W/F,700g-cat. min/mol.

Sintering

As mentioned above, the dehydrogenation occured on Cu-Lapo. In the atmosphere of H_2, the reduction of Cu^{2+} on catalyst may easily occur as follow :

$$Cu^{2+} \longrightarrow Cu^{+} \longrightarrow Cu^{0}$$

Including with high temperature, sintering of copper metal may occur easily. Since sintering is the cause of decreasing of active sites which leads to the decreasing of catalytic activity, on the other hand, deactivation. There is the possibility that sintering is the cause of deactivation.

Dehydration (H_2O formation)

As consider on Fig. 4-14, dimethyl ether was formed at high methanol conversion. Since dimethyl ether is promoted in dehydration reaction of methanol which means that H_2O is formed. In the next study, it is shown that H_2O inhibit the catalytic activity of dehydrogenation. From this consideration, it is suggested that the exist of H_2O may be one of the possible reason for catalytic deactivation.

In conclusion, the reasons of deactivation still not be confirmed yet and some more experiments are needed for the reasonable explanation.

4-3. TREATMENT TEMPERATURE.

4.3.1 Effect on catalytic activity and selectivity

In the preceding studies mentioned above, catalyst treatment was done at 400°C. In the following studies, treatments at various temperatures in the range of 300 to 500°C have been done prior to reaction at 200°C on Cu-Lapo catalyst to study the effect of reaction temperature on catalytic activity and selectivity.

As shown in Fig. 4-15, methanol increased with the treatment temperatures. Almost 100% selectivity for methyl formate was obtained by the treatment temperatures at 300 and 400°C. Figure 4-16 shows the relationship between methanol conversion and the methyl formate selectivity at various treatment temperatures. It was shown that a silimilar trend was obtained at any treatment temperature (300, 400 and 500°C), suggesting that treatment temperature didn't change the nature of active sites on the catalyst only the thermal effect on catalysts. Then the thermal gravimetric (TG) analysis was done to study the effect of temperature on catalyst.

4.3.2 Thermal Gravimetric (TG) analysis

Thermal gravimetric (TG) analysis was done to measure the weight loss of catalyst due to water desorption at various treatment temperatures. Figure 4-17 shows the TG curves of laponite and Cu-Lapo. Table 4-3 shows the amounts of H_2O desorbed from Na type and Cu type of laponite, saponite and montmorillonite. In appendix H, raw data of TG measurements of various degrees of ion exchanged are presented. It is obvious that the amount of water desorbed from Cu-Lapo is greater than from laponite suggesting that water desorbed from the copper hydrated ion[$Cu(H_2O)^{2+}$] which is obtained from the synthesis of catalyst. Since thermal treatment of catalyst is related to the desorption of water, the effect of water on the catalytic

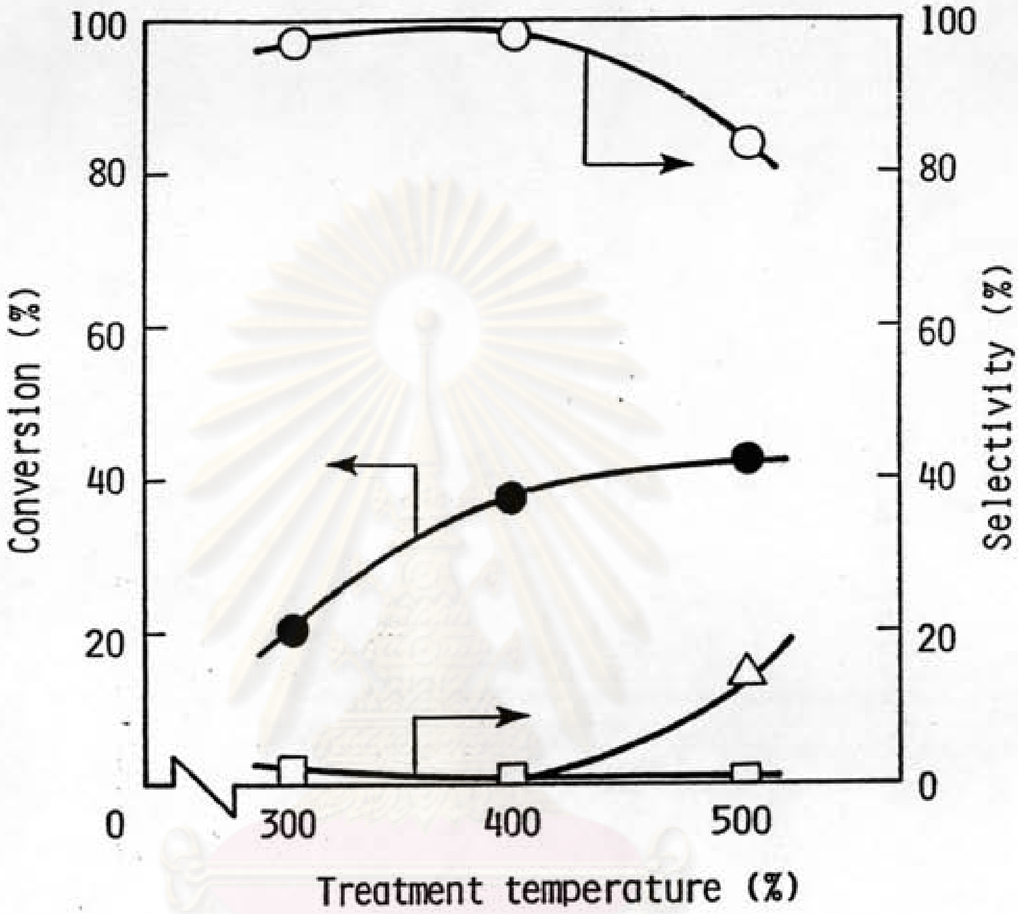


Fig.4-15 Effect of treatment temperature on the activity and selectivity of Cu-Lapo catalyst: ● ,conversion of methanol; ○ ,MF selectivity; △ ,CO selectivity; □ ,CO_2 selectivity. Reaction conditions: temperature, 200°C; W/F, 300g-cat. min/mol.

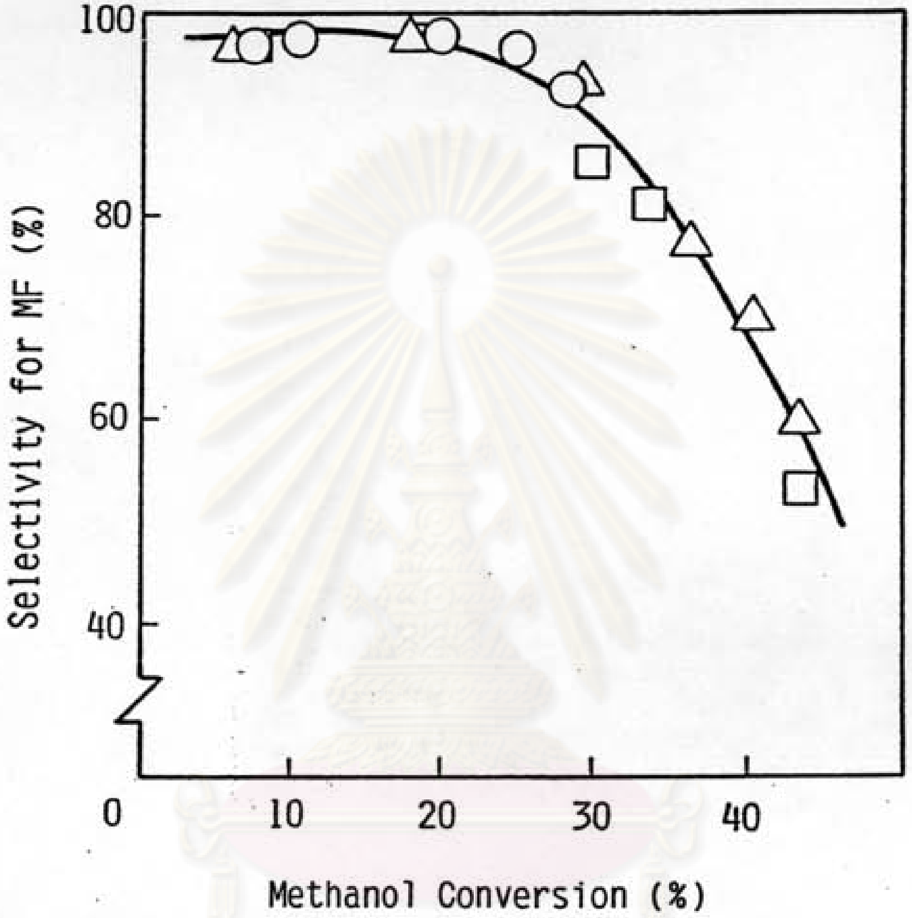


Fig. 4-16 Relationship between conversions and selectivities to methyl formate on Cu-Lapo catalyst at various treatment temperatures:
○ ,300°C; △ ,400°C; □ ,500°C
Reaction condition : temperature,200°C

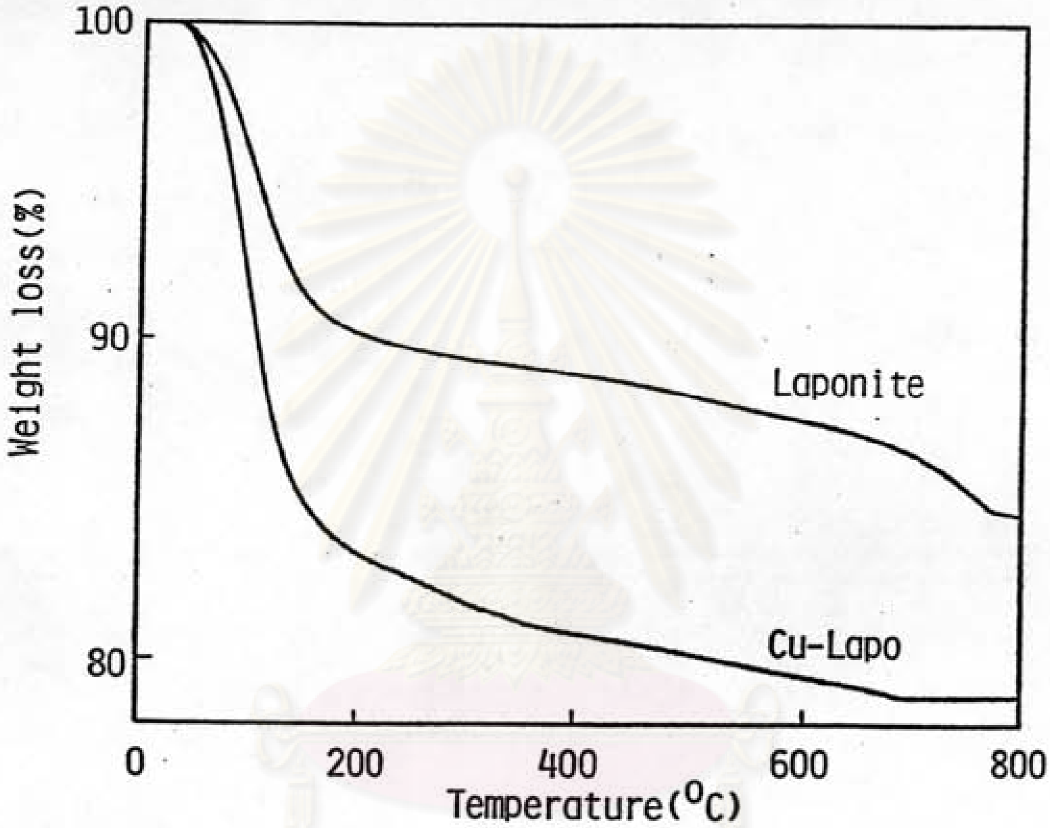


Fig. 4-17 Thermal gravimetric curves of Laponite and Cu-Lapo.

Table 4-3 Amounts of H_2O desorption from clay and clay catalysts at various treatment temperatures

Sample	Amounts of H_2O desorption at (g/g-cat.)		
	300°C	400°C	500°C
Laponite	0.1070	0.1117	0.1184
Saponite	0.0987	0.1018	0.1056
Montmorillonite	0.0629	0.0639	0.0672
Cu-Lapo	0.1831	0.1928	0.1993
Cu-Sapo	0.1852	0.1930	0.1996
Cu-Mont	0.0931	0.1048	0.1130

activity and selectivity was studied. The results are shown in Table 4-4. Methanol conversion dramatically decreased with the increase of water content even at a value of 1 mol% , and the conversion decreased from 18.1 to 2.3 %. To understand the role of water in methanol conversion, infrared (IR) spectroscopy was studied.

4.3.3 Infrared (IR) spectroscopy measurements

Infrared spectroscopy was used to investigate the effect of water on the catalysis. Methanol was adsorbed on a wafer-disc catalyst at 200°C for 30 min. After desorption of excess methanol at 200°C for 30 min, an IR measurement was done at room temperature. The obtained IR spectrum is shown in Fig. 4-18(a). Then, water was adsorbed on the catalyst at 200°C for 30 min. The excess water was desorbed at 200°C for 30 min and an IR spectrum was measured again at room temperature as shown in Fig. 4-18(b).

It is clearly shown that the IR bands for adsorbed methanol is decreased by the adsorption of water, suggested that water replaces the adsorbed methanol on the surface of catalyst. If a large amount of methanol is replaced, methanol cannot do reaction on the catalyst surface. This suggestion is well agree with the consideration on deactivation of catalyst for the reason of H_2O formation at reaction temperature of 300°C.

4.3.4 Conclusion on the effect of treatment temperature

It was clearly shown that water inhibited the catalytic activity and selectivity of Cu-Lapo in dehydrogenation of methanol. TG studied showed that a large amount of H_2O desorbed at high treatment temperature. Since treatment is the process to remove water from catalyst, the increase treatment temperature lead to the increase in catalytic activity. In conclusion, treatment is the necessary step prior to the dehydrogenation reaction.

Table 4-4 Effect of H_2O on catalytic activity and selectivity of Cu-Laponite

Content of water in methanol mol%	Conversion %	Selectivity			
		MF	DME	CO	CO_2
		%			
0.05	18.1	98.5	0	0	1.5
1.0	2.3	0	0	100	0
20.0	0	0	0	0	0

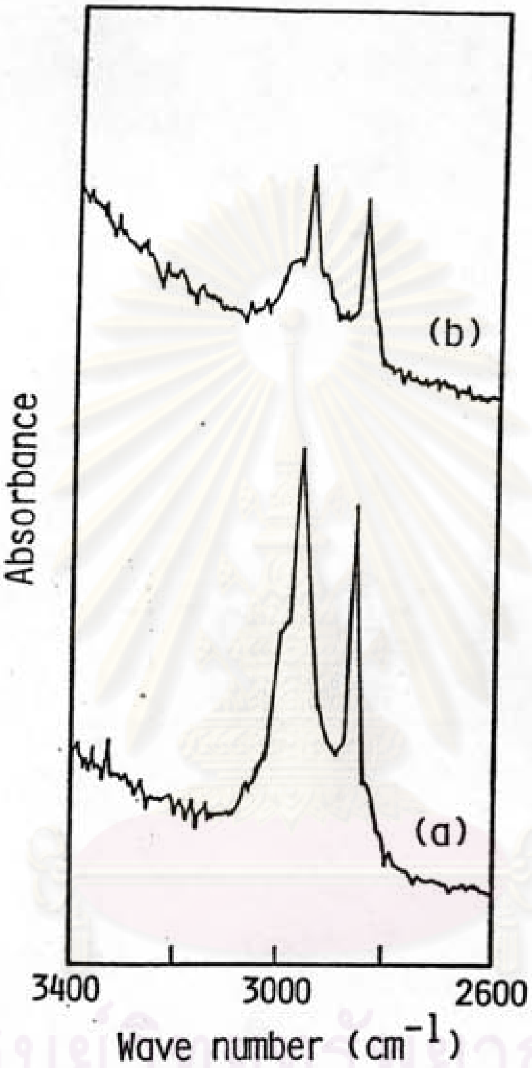


Fig. 4-18 Infrared spectra of Cu-Lapo:
(a),methanol adsorption at 200^{o}C then,
(b),H_2O adsorption at 200^{o}C

4-4. TREATMENT ATMOSPHERE.

4.4.1 Effect on catalytic activity and selectivity

The purpose of this study is to investigate the type of active sites on Cu-Lapo catalyst in dehydrogenation of methanol to methyl formate. Thermal treatment was done in the atmosphere of hydrogen, nitrogen or air at 400°C for 1 h prior to reaction at 200°C. As shown in Table 4-5, thermal treatment in the atmosphere of hydrogen and nitrogen gave the high catalytic activity, in contrast, treatment in air gave very low catalytic activity. Since the treatment in various atmosphere may effect to the oxidation state or species of copper ions, reflecting to the differences in catalytic activities. The investigation on the species of copper ion was studied.

4.4.2 Investigation on Electron Spin Resonance (ESR)

Electron spin resonance(ESR) measurements were done to investigate the presence of Cu^{2+} ions in the catalysts. Figure 4-19 shows the ESR spectra of Cu-Lapo treated under hydrogen, air or nitrogen atmosphere. Since reduction of Cu^{2+} ions occured in hydrogen atmosphere, the detected ESR spectrum of Cu^{2+} ion species gave very small peak area. In contrast, the ESR spectra of Cu-Lapo treated in air and nitrogen indicate the existance of large amount of Cu^{2+} ions. Consideration on the ESR peaks of nitrogen treatment before and after reaction, the amount of Cu^{2+} ions decreased after reaction suggesting that the reduction of Cu^{2+} ions occured due to the H_2 from the dehydrogenation reaction.

Table 4-5 Effect of treatment atmosphere on the activity and selectivity of Cu-lapo at treatment temperature of 400^{o}C and reaction temperature

Treatment atmosphere	Conversion %	Selectivity	
		MF	CO_x
H_2	20.9	98.3	1.7
N_2	32.6	82.7	17.3
Air	2.8	81.2	18.8

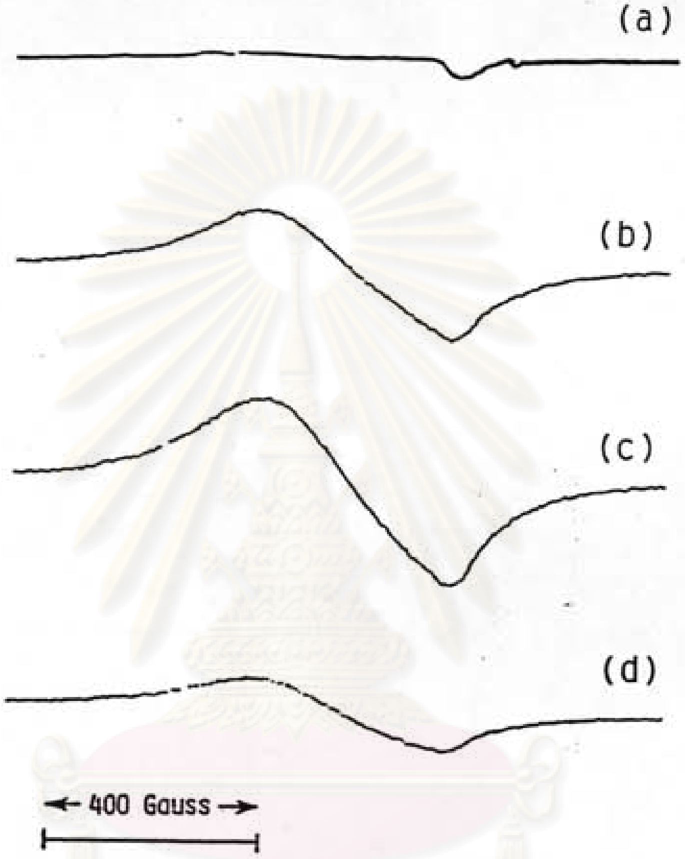


Fig. 4-19 Electron spin resonance spectra of Cu-Lapo catalyst treated under the atmosphere of: (a),hydrogen; (b),air; (c),nitrogen; and (d),used nitrogen in reaction at 200^{0}C.

The amounts of Cu^{2+} ion determined by ESR measurement are shown in Table 4-6. Large amounts of Cu^{2+} ions were detected in the catalyst which was treated in nitrogen or in air, while only trace amounts of Cu^{2+} ions can be detected on that which was treated in hydrogen due to the reduction in hydrogen atmosphere. Decrease in the amount of Cu^{2+} ion in reacted catalyst which was treated in nitrogen indicates that reduction of Cu^{2+} ions occurs during reaction.

4.4.3 Effect on catalytic stability

The results of stability studies given in Fig. 4-20 show that conversion of methanol was constant even more than 10 h of reaction, suggesting that reduced copper ions may be the active sites for methyl formate formation. In the first 2 h of reaction on the air-treated catalyst, the conversion gradually increased and then approached to the steady state. This can be explained as in the atmosphere of oxygen, the oxidation reaction occurs and CuO was obtained at the beginning of the reaction. Later the dehydrogenation is gradually increased, the reduction of Cu^{2+} ions occur which leads to the increasing of methanol conversion.

Table 4-6 Amounts of Cu^{2+} ion determined by ESR measurement

Catalyst	Treatment atmosphere	Amount of Cu^{2+} ions mmol/g-cat.
Cu-Laponite (before reaction)	N_2 /400°C	0.2812
	Air/400°C	0.1881
	H_2 /400°C	0
(after reaction)[a)]	N_2 /400°C	0.0354

a)Reaction conditions: temperature, 200°C; W/F, 700 g-cat. min/mol.

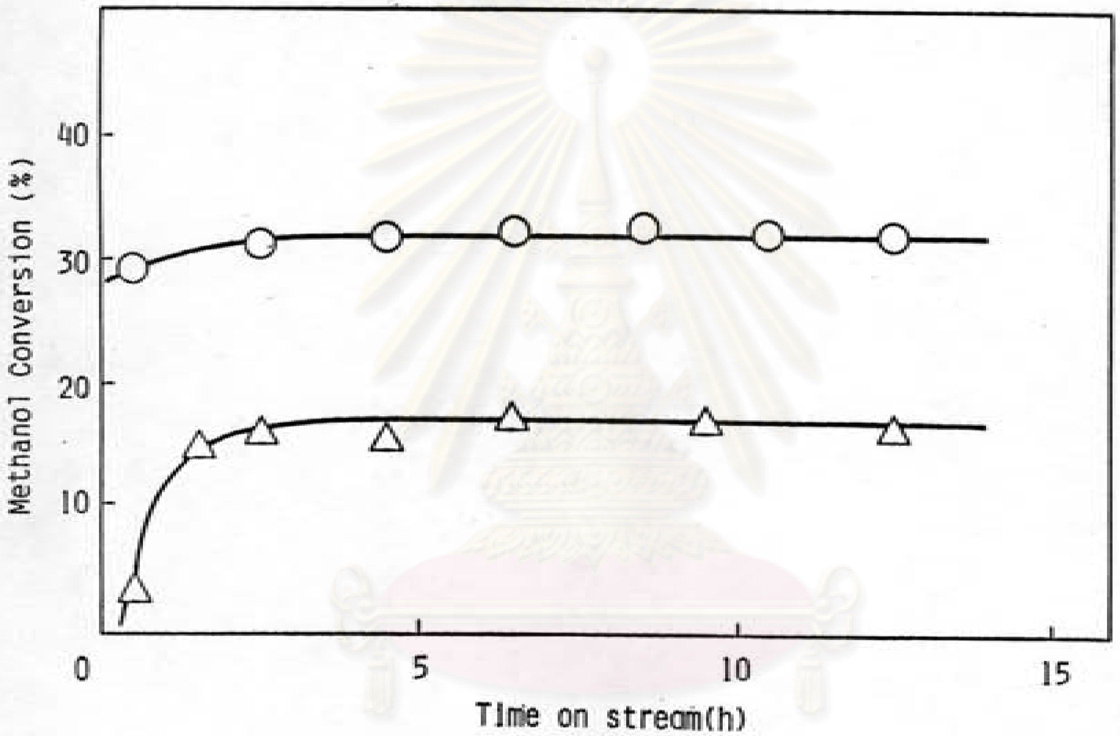


Fig. 4-20 Variation in the catalytic activities of Cu-Lapo with time on stream in the treatment atmosphere of: ,nitrogen; ,air Treatment temperature : 400°C ; Reaction temperature : 200°C.

4-5. DEGREES OF COPPER ION EXCHANGE.

4.5.1 ICP measurements

Inductivity Coupled Argon Plasma Atomic Emission Spectrophotometer (ICP) measurements were carried out to determine the amount of Cu and Na ions in the catalyst. As shown in Table 4-7 various types of Cu-Lapo catalysts have been studied. Cu-Lapo catalysts were prepared by the ion-exchange method to study the effect of degrees of copper ion exchange on the catalytic activity for dehydrogenation of methanol to methyl formate. The amount of Cu and Na ions were directly obtained from the ICP measurement, and the degrees of ion exchange was calculated on the basis of Cu^{2+} ion as equation :

$$\text{Degree of ion exchange} = \frac{2(\text{amount of Cu ion in Cu-Lapo})}{\text{amount of Na ion in laponite}} \times 100$$

Figure 4-21 shows the relationship between the amount of Cu ions introduced and the amount of Na ions removed from Cu-Lapo at various degrees of Cu ion exchange. Comparing to the ideal exchange of Cu^{2+} 1 ion with Na^{+} 2 ions, this result is well agree with the ideal line in the range of small amount of Cu^{2+} introduced. But the curve move from the ideal line at large amount of introduced Cu^{2+} ions. It is suggested that species of exchanged copper ion are more than one kind.

4.5.2 Effect on catalytic activity

The reaction was carried out on Cu-Lapo at various degrees of copper ion exchange. The effect of degrees of copper ion exchange on the catalytic activity of Cu-Lapo is shown in Fig. 4-22. It is indicated that the dehydrogenation of methanol occurred when the degrees of copper ion exchange exceeded 60 % and the conversion dramatically increased in the range of copper ion exchange from 60% to 100 % and then levelled off. Suggesting that the difference in copper species due to the difference in degrees of copper ion exchange is responsible to the difference in catalytic activity.

Table 4-7 Ion amounts of Cu and Na determined by ICP measurement

Catalyst	Ratio of Cu to clay[a)]	Amount of Ion		Degree of Ion Exchange[b)]
	mmol-Cu/g-clay	Cu	Na	%
		mmol/g-cat.		
Cu-Lapo-200	0.9462	0.7030	0.0824	121
Cu-Lapo-150	0.7096	0.6065	0.1062	104
Cu-Lapo-120	0.5677	0.5367	0.1388	92
Cu-Lapo-100	0.4731	0.3534	0.2551	61
Cu-Lapo-50	0.2365	0.2314	0.4675	40
Na-Laponite	-	-	0.9846	-

a) ratio in copper nitrate solution

b) base on Cu^{2+} ion exchanged with 2 Na^+

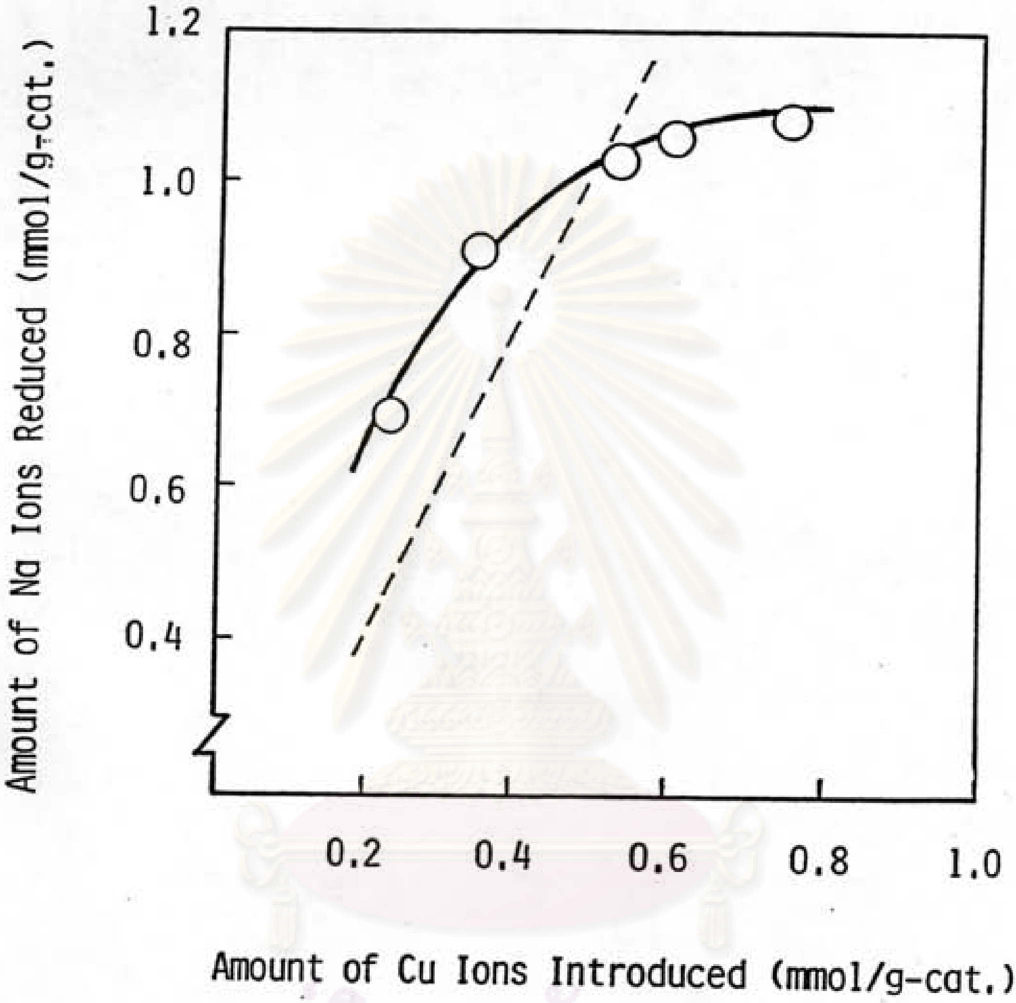


Fig. 4-21 Relationship between amount of Cu ions introduced and amount of Na ions reduced on Cu-Lapo at various degrees of copper ion exchange.

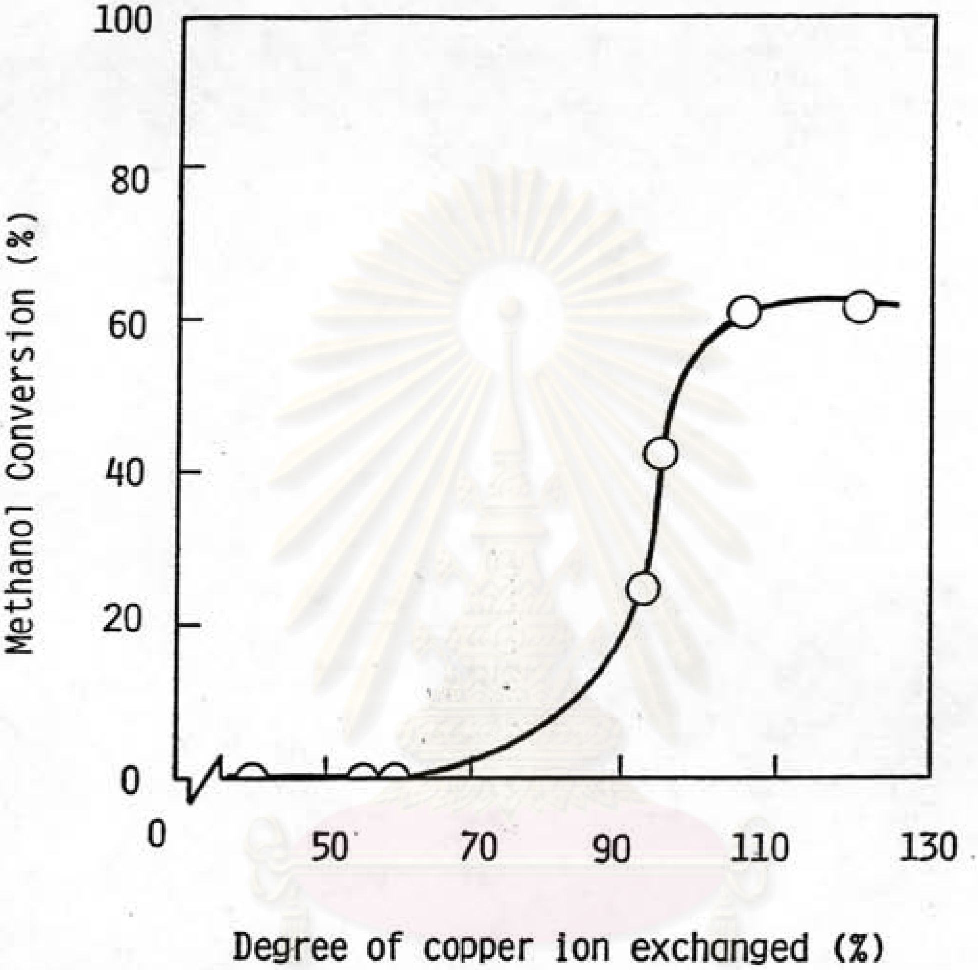


Fig. 4-22 Relationship between degrees of copper ion exchange and the catalytic activities of Cu-Lapo: treatment temperature, 400 °C ; reaction conditions: temperature, 200 °C and W/F, 700 g-cat.min/mol.