

CHAPTER 2

CATALYTIC FEATURES IN DEHYDROGENATION OF METHANOL TO METHYL FORMATE

2.1 INTRODUCTION.

Dehydrogenation of methanol to form methyl formate has been studied by a number of researchers. The efforts have been made to develop the appropriate catalyst for this reaction. This reaction was shown to be influenced by various factors, such as type of supports, metal ion exchanges, promoters, intercalation and other modification techniques. Although various aspects have been investigated, there are three features which determine predominantly the appropriate catalyst in chemical reactions: catalytic activity, selectivity, and stability. Activity indicates the reactivity of catalytic system, i.e. the rate at which reactants are transformed into products. Selectivity is the measure for ability of a catalyst to preferentially catalyze one of a number of possible reactions. Stability indicates how long a catalyst will be able to fulfil its action, on the other hand, the period of time that catalyst stills catalyze the reaction at high activity and selectivity comparable to the fresh catalyst.

The results and discussions from a number of literatures which concerning on methanol conversion especially dehydrogenation of methanol to methyl formate over various catalysts will be reviewed. At first, various type of catalytic reactions will be mentioned. Then, the effects of various factors such as types of supports, metal ion exchanges, promoters, intercalation, etc. on methanol dehydrogenation will be reviewed in the aspects of catalytic activity, selectivity and stability. Finally, investigation of the active sites of catalyst and mechanism of methyl formate formation will be studied.

2.2 METHANOL CONVERSIONS.

Possible conversions of methanol are illustrated in Fig. 2-1, which can be classified into three different reactions: dehydrogenation, dehydration, and decomposition.

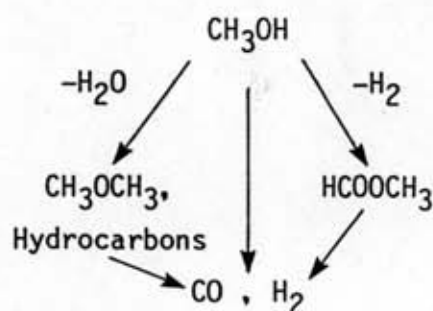


Fig. 2-1 Possible conversions of methanol.

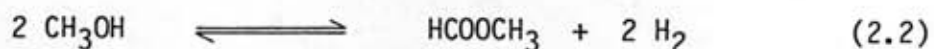
2.2.1 Dehydrogenation.

A number of researches suggested that dehydrogenation of alcohol occurred on non-acidic or basic catalysts [27]. Since methyl formate is one of the key intermediates for methanol based processes in C_1 chemistry, attention has been paid on studying and finding the appropriate catalyst for methyl formate formation via methanol dehydrogenation.

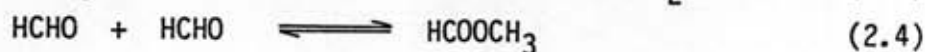
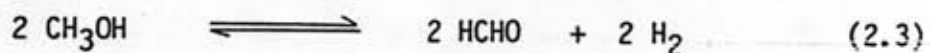
Methanol could be catalytically converted to methyl formate either by direct dehydrogenation or by oxidative dehydrogenation. A number of oxide systems are active for the latter [28] and high yields are possible since there are no thermodynamic limitations. The disadvantage is that hydrogen is eliminated as valueless water. The stoichiometric equation for oxidative dehydrogenation of methanol is :



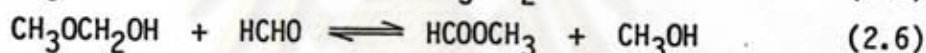
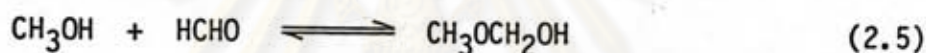
Direct dehydrogenation of which hydrogen as well as methyl formate is the main product would be an attractive industrial reaction. The stoichiometry for this reaction is :



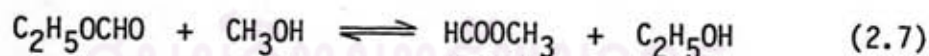
Sometimes an intermediate such as formaldehyde is formed in dehydrogenation reaction [29-33] and methyl formate is subsequently formed by dimerization of formaldehyde (The Tischenko Reaction). The reaction sequences are as follows :



Not only formaldehyde dimerization but also some other reactions yield methyl formate in the second step. Takahashi et.al.[34] concluded that, during methanol dehydrogenation, methyl formate would be similarly produced from a reaction between methanol and formaldehyde via a surface hemiacetal intermediate rather than by formaldehyde dimerization [32,33].

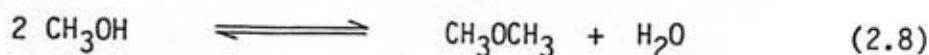


This conclusion is supported by the reaction of ethanol and formaldehyde to yield ethyl formate, not methyl formate, and no transesterification between ethyl formate and methanol to yield methyl formate and ethanol as follows :



2.2.2 Dehydration.

In methanol conversions, the dehydrogenation reaction is overwhelmed by dehydration to dimethyl ether which occurs on the acid sites of catalysts. The stoichiometry of this reaction is shown as follows :



Not only dimethyl ether but low molecular weight hydrocarbons are also produced from dehydration of methanol. Catalytic activities of Ti ion exchanged forms of layer lattice silicates were studied and novel reactions of methanol were discovered [35]. Previously, the catalytic activities of various metal ion exchanged forms of fluoro tetrasilic mica (Me-TSM's) for the conversion of methanol were investigated and it was found that Me-TSM's show characteristic activities for dehydrogenation, dehydration or decomposition of methanol [36]. It is of particular interest that Ti-TSM catalyzed the dehydration to produce dimethyl ether. This fact suggests that Ti-TSM acts as an acid catalyst distinctively. But it is not clear yet whether the interlayer Ti ions acts as acid sites or induces acidity on the silicate sheets. Accordingly, the acidity of Ti ion exchanged form of layer silicate minerals by TPD of ammonia adsorption and the catalytic activity of the minerals for the conversion of methanol were investigated.

Various clay minerals are listed in Table 1-1 [36]. TSM and Hectorite (Hect) are synthetic clay minerals. The synthesis and properties of these minerals have been studied extensively by Kitajima and Daimon [37]. Mont is a natural clay mineral.

Table 2-1 Layered silicate minerals.

Minerals	Chemical Formula
TSM (Tetrasilic Mica)	$\text{Na}[\text{Mg}_{2.5}\text{Si}_4\text{O}_{10}\text{F}_2]$
Hect (Hectorite)	$\text{Li}_{1/3}[\text{Mg}_{8/3}\text{Li}_{1/3}\text{Si}_4\text{O}_{10}\text{F}_2]$
Mont (Montmorillonite)	$\text{Na}_{1/3}[\text{Al}_{5/3}\text{Mg}_{1/3}\text{Si}_4\text{O}_{10}(\text{OH})_2]$
Mont* (Activated Clay)	Acid treated montmorillonite

The conventional ion exchange method was used in catalyst preparation. TPD spectra obtained with various catalysts are illustrated in Fig. 2-2 [35].

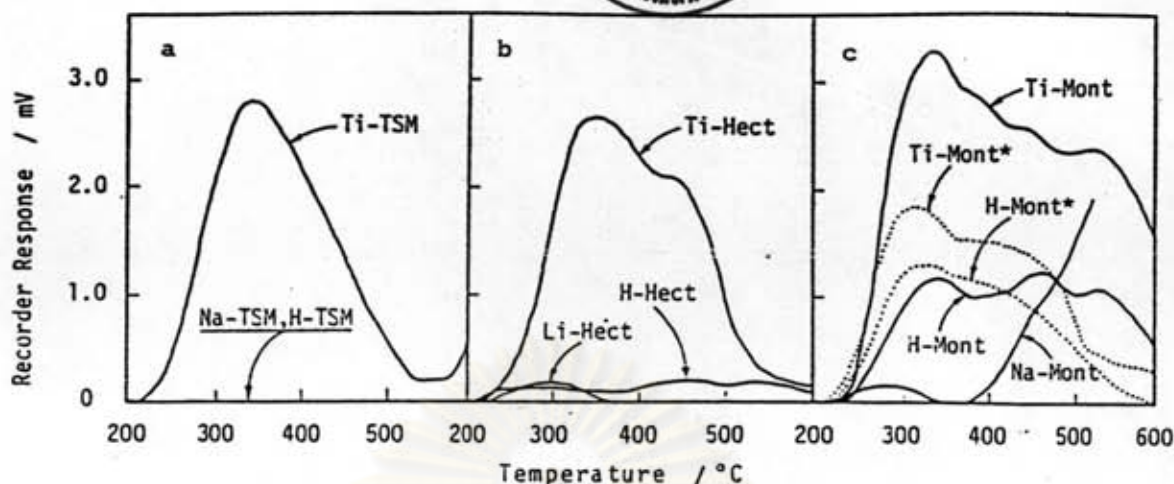


Fig. 2-2 TPD spectra of ammonia adsorbed on various layered silicate minerals.

As shown in Fig. 2-2a, ammonia desorption was not observed at all with Na-TSM and even with H-TSM. The facts strongly support the conclusion that TSM has no acid sites. On the other hand, a large desorption peak appeared at around 320°C in the TPD for Ti-TSM, suggesting that a considerable amount of acid sites was generated by exchanging the interlayer Na ions with Ti ions. In Fig. 2-2b, an amount of ammonia desorption at temperature below 350°C was increased scarcely by changing Li-Hect to H form but increased dramatically by changing it into Ti form. Fig. 2-2c shows that an acid amount on Mont increased by exchanging the interlayer Na ions with H or Ti ions. The acidity of acid treated Mont (H-Mont*) which is sometimes called activated clay is further improved by the additional treatment with Ti ions.

The results of methanol conversion are summarized in Table 2-2 [35]. No reaction took place over Na- and H-TSM and considerable activity was observed with Ti-TSM to produce dimethyl ether with a small amount of hydrocarbons. Li-Hect and Na-Mont were not active but H forms of these minerals showed fairly high activities to produce dimethyl ether. The activities of H-Mont* and H-mont did not largely

differ. As from TPD measurement, exchanging the interlayer cations with Ti ions remarkably improved the catalytic activity. The level of conversion attained more than 90% with Ti-Hect, Ti-Mont, and Ti-Mont*. Especially Ti-Mont* showed the highest activity which converted 89.5% of methanol to hydrocarbons at 350°C.

Table 2-2 Catalytic activity of various layered silicate minerals for methanol conversion.

Catalyst	300°C		350°C	
	Conv. of Methanol (%)	Conv. to Hydrocarbons (%)	Conv. of Methanol (%)	Conv. to Hydrocarbons (%)
Na-TSM	0	0	0	0
H-TSM	0	0	0	0
Ti-TSM	35.2	2.2	50.8	14.2
Li-Hect	0	0	0	0
H-Hect	11.2	0	15.1	0.6
Ti-Hect	87.3	7.2	90.4	38.0
Na-Mont	10.5	0	59.8	0
H-Mont	82.0	0	84.1	8.7
Ti-Mont	89.6	8.9	93.2	58.6
H-Mont*	90.3	3.6	92.5	5.6
Ti-Mont*	87.8	6.3	95.2	89.5

A product distribution in hydrocarbons is shown in Fig. 2-3 [35].

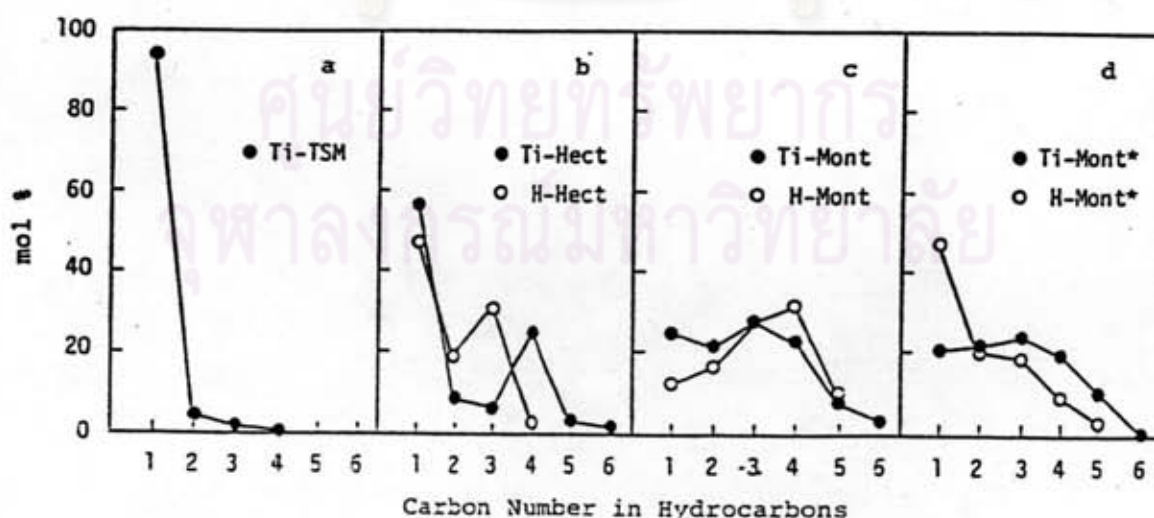


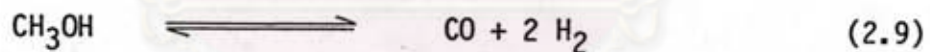
Fig. 2-3 Products distribution in hydrocarbons produced over H or Ti exchanged form of layered silicate minerals at 350°C

The hydrocarbons produced over Ti-TSM were mainly methane, suggesting that a substantial amount of carbonaceous species was accumulated on the surface. With Ti-Hect, hydrocarbons with a chain length longer than C_2 , i.e. C_2^+ , were formed in some extent but methane was still mainly produced. The facts suggest that acid sites generated on the minerals are active enough to dehydrate methanol to dimethyl ether and/or methane but do not facilitate the formation of C-C bonds by themselves. With Ti-Mont and Ti-Mont*, C_2^+ were produced considerably, while only trace amount of C_7 aliphatics or aromatics was detected. Kaeding and Butter investigated the conversion of methanol to hydrocarbons over ZSM-5 zeolite and reported that modification of the zeolite with phosphorus compounds increased yield of lower olefins which were mostly C_2 - C_4 olefins (65-75% selectivity at 80-100% conversion) and the rest were C_5 - C_6 aliphatics and aromatics [38]. It is interesting that over Ti-Mont*, methanol was selectively converted to olefins and chain growth was virtually limited at C_6 . Ti-Mont* seems to be a better catalyst than zeolitic one to yield lower olefins selectively, even though the role of Ti ions in the acid properties of Ti exchanged form of minerals and the mechanism of dehydrogenation of methanol over the catalysts are not clear yet. It is worthy to conclude that the intercalation of Ti ions greatly improved the acidity of silicate sheet minerals. The method might be applicable to modify acidity of the other minerals and useful to design solid acid catalysts.

2.2.3 Decomposition.

Decomposition reaction to form CO and H_2 can occur from methanol, methyl formate, and also from formaldehyde as illustrated in Fig. 2-4. Direct decomposition of methanol to syngas (a mixture of H_2

and CO) has been focussed as a reaction for reforming of methanol in automotive engine system and as a reaction which can readily supply syngas for C₁ chemical industry. Several types of transition metal catalysts have been investigated so far [39-47]. However, no catalyst for complete decomposition of methanol to syngas alone has never been reported: the higher the conversion of methanol, the lower the selectivity of syngas because of the formation of by-products such as methane, carbon dioxide, etc. Recently, the catalytic features of Ni-Cu/SiO₂ catalysts were studied, and 100% CO selectivity were obtained over Ni_{0.1}Cu_{0.9}/SiO₂ catalyst at a reaction temperature of 280°C during the process time of 96 h [48]. The stoichiometry of direct decomposition of methanol is shown as follows :



Besides direct dehydrogenation, methanol can be converted to carbon monoxide and hydrogen via decomposition of formaldehyde. According to the study in dehydrogenation of methanol to formaldehyde over silicalite [49], it was found that conversion and selectivity to carbon monoxide were increased with decreasing the amount of methanol injected or increasing reaction temperature. The results are illustrated in Table 2-3[49]. When an aqueous solution of formaldehyde was injected onto Na-SL (Na type silicalite) at 350°C, formaldehyde was converted into carbon monoxide and a small amount of methanol. This suggests that methanol conversion into carbon monoxide occurs via decomposition of formaldehyde.

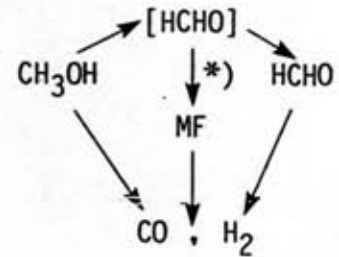


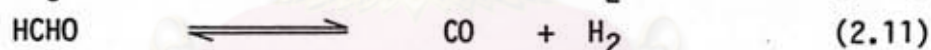
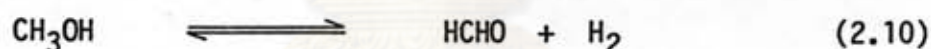
Fig.2-4. Possible products in the dehydrogenation of methanol. *) Dimerization of [HCHO]'s or reaction between [HCHO] and surface methoxide.

Table 2-3 Methanol conversion on Na-SL in a pulse microcatalytic reactor.^a

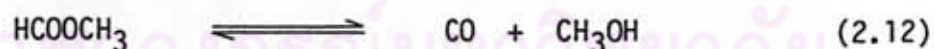
Reaction temperature/K	MeOH/ μ l	CO	Selectivity/%		Me ₂ O	Conversion of MeOH/%
			CO ₂ +CH ₄	H ₂ CO		
670	1	8	12	73	6	5
720	1	12	22	61	6	18
770	1	49	6	45	—	47
770	2	33	6	59	1	20
820	1	72	1	27	—	83
820	3	43	2	54	0.6	17

^a Reaction conditions: He carrier gas 10 ml min⁻¹; 10 mg catalyst.

The corresponding dehydrogenation of methanol to formaldehyde over copper-zinc catalysts has also been reviewed by Chono and Yamamoto (1981). This reaction has been suggested to be the first step in decomposition of methanol to carbon monoxide and hydrogen (Lawson and Thomson, 1964). The possible reaction sequences are shown as follows :



Decomposition of methyl formate to carbon monoxide proceeds via decarbonylation reaction (Higdon et.al., 1974). The stoichiometry is shown as follows :



In the formation of methyl formate via dehydrogenation of methanol, copper-based catalysts have been found to be the most active and selective (Chono and Yamamoto, 1981; Charles and Robinet, 1950). But decomposition of methyl formate to carbon monoxide is still the main problem. Accordingly, efforts have been continued to find out the effective catalyst to promote dehydrogenation to methyl formate but inhibit the decomposition.

2.3 CATALYSTS AND CATALYSIS IN DEHYDROGENATION OF METHANOL TO METHYL FORMATE.

2.3.1 The Effect of Supports.

Catalysts and catalysis of methyl formate formation will be reviewed with respect to the effects of type of supports, metal ion exchanges, and promoters on the catalytic activity, selectivity and stability. And some of the modification techniques are also investigated. Recently, methanol dehydrogenation reaction has been studied from the viewpoints of support effects of silica [51-53] and mica [54]. According to these results, the effect of supports seem to be too complicated to understand. The catalysis of various metal ion exchanged forms of zeolitic and layer silicate minerals, as supported catalysts, has been extensively studied. An appropriate support for studying the intrinsic activities of metal ions in heterogeneous catalysis will be investigated.

2.3.1.1 Characterization of supports

The acidity of various kinds of minerals as catalyst supports was investigated by means of temperature programmed desorption (TPD) of ammonia. As shown in Fig. 2-5 [55], the acidity of four kinds of layer silicate minerals were investigated. In addition, the acidity of molecular sieve 13x (Zeol) and silica gel (SiO_2) was also examined for comparison. The curves are displayed vertically for clarity. Because of large amount of NH_3 adsorption, zeolites was loaded for 1/10 of the others.

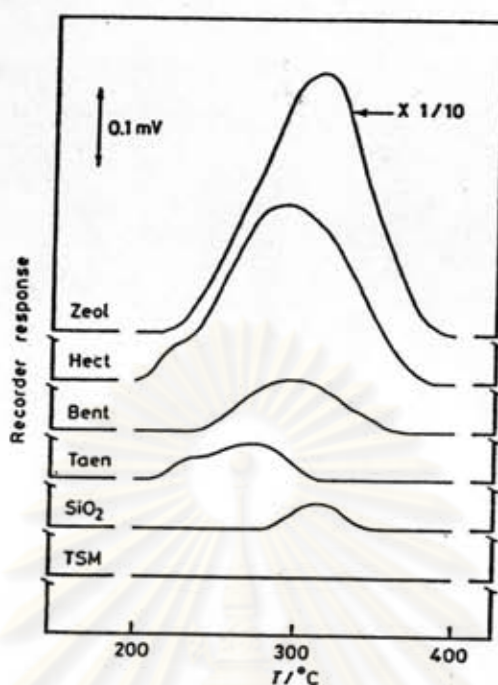


Fig. 2-5 TPD curves of ammonia desorption from various silicated clay minerals.

The chemical formula of zeolitic and layer silicate minerals are shown in Table 2-4.

Table 2-4 Zeolitic and Layered Silicate Minerals.

Minerals	Chemical Formula
<u>Synthetic minerals</u>	
Zeol (Zeolite)	
Hect (Hectorite)	$\text{Li}_{1/3}[\text{Mg}_{8/3}\text{Li}_{1/3}\text{Si}_4\text{O}_{10}\text{F}_2]$
Taen (Taeniolite)	$\text{Li}[\text{Mg}_2\text{LiSi}_4\text{O}_{10}\text{F}_2]$
TSM (Fluoro tetrasilicic mica)	$\text{Na}[\text{Mg}_{2.5}\text{Si}_4\text{O}_{10}\text{F}_2]$
Silica gel	SiO_2
<u>Natural minerals</u>	
Bent (Bentonite)	$\text{Na}_{1/3}[\text{Al}_{5/3}\text{Mg}_{1/3}\text{Si}_4\text{O}_{10}\text{F}_2]$

The TPD of ammonia was started at 200°C to eliminate the participation of weakly adsorbed ammonia and conducted up to 400°C at a heating rate of 10°C/min. Each mineral was pretreated in helium gas (20ml/min) at 400°C for 2 h. Mass spectroscopic analysis showed that no gases besides ammonia were desorbed in TPD measurements. The amount of ammonia desorbed was calculated from the peak area and the values per unit weight of each mineral are summarized in Table 2-5 [55], where the peak temperature of TPD curves and surface area are also tabulated.

Table 2-5 Amount of ammonia desorbed and peak temperature observed in TPD.

Mineral	Surface area ^a /(m ² /g)	Peak temperature /°C	Amount of ammonia desorbed	
			(μmol/g)	(nmol/m ²)
TSM	9.1	—	0	0
Taen	25.2	272	1.7	67
Bent	38.1	296	2.3	60
Hect	14.2	292	11	770
SiO ₂	347	314	0.54	1.6
Zeol	575	316	140	240

^a Brunauer-Emmett-Teller measurements with nitrogen after the sample had been evacuated at 400 °C.

The amounts of ammonia desorbed from layer silicate minerals were from 1/10 to 1/80 times smaller than that from zeolites and the peak temperatures were also lower than that of zeolite. It is suggested that there were fewer acid sites on layer lattice minerals than on zeolites and the acid strength of the minerals was weaker than that of zeolite. These observations were consistent with the acidic properties of these minerals described in some reviews [56]. The amount of ammonia desorbed from unit surface is also listed in the last column which suggested that the population of acid sites on layer silicate minerals; Taen, Bent, and Hect is comparable to that on zeolite. SiO₂ is often used as an inert carrier to prepare a supported catalyst, even though the measurement shows that SiO₂ certainly has acid sites.

No chemisorption of ammonia was detected in the TPD curve of TSM, suggesting that silicate sheets of TSM have no acid sites and are probably inactive as a catalyst. It can be concluded that TSM is a particularly appropriate support for use in the study of intrinsic activities of metal ions in heterogeneous catalysis.

2.3.1.2 Catalytic activity and selectivity

a. Fluoro tetrasilic mica (TSM)

Catalytic activities of Cu(II) ion exchanged form of layer silicate and zeolitic minerals, including TSM, have been investigated for the conversion of methanol [57]. These catalysts were prepared by the conventional ion exchanged method with Cu(II) ammine complex $[\text{Cu}(\text{NH}_3)_4]^{2+}$ solution as source of Cu(II) ions. The reaction was carried out in a fixed bed flow reactor equipped with a gas sampling valve for gas chromatographic analysis. Prior to the reaction, a catalyst was treated in nitrogen at 300°C for 2 h to decompose Cu(II) ammine complex into Cu(II) ion. The stream of reactant, mixture of methanol vapor and nitrogen was maintained at 65 ml/min for 2:5 in molar ratio.

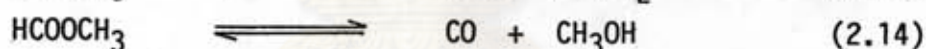
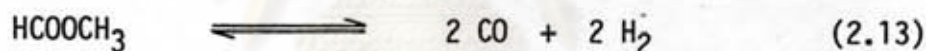
Although the layer silicate structure of TSM, Taen, Hect, and Bent are similar to each other, the catalytic activities of Cu(II) ion exchanged form of these minerals were quite different individually. The activities of various catalysts are summarized in Table 2-6 [57], where the values of selectivity to each product were calculated on methanol basis.

Table 2-6 Activities of Cu(II) ion exchanged forms of various silicate minerals.

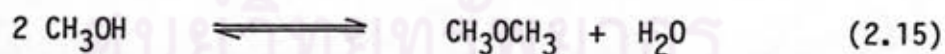
Catalyst	Conversion (%)			Selectivity (%)		
	MF	DME	CO	MF	DME	CO
	at 220 °C			at 240 °C		
Cu(II)-TSM	38	100	0	52	92*	0
Cu(II)-Hect	12	19	81	34	16	84
Cu(II)-Bent				6	27	68
Cu(II)-Zeol	18	0	100	44	0	100

MF, methyl Formate; DME, Dimethyl ether. *, CO was formed.

Cu(II)-TSM was the most active and promoted dehydrogenation of methanol to form methyl formate selectively. The value of selectivity was as high as 100% up to 50% conversion. At temperature above 240°C, the selectivity decreased and carbon monoxide was produced simultaneously, suggesting that methyl formate decomposed subsequently to carbon monoxide and hydrogen or methanol.



The activity of Cu(II)-Zeol was considerably high and promoted only dehydration to dimethyl ether (CH_3OCH_3) formation.



Over Cu(II)-Hect and Cu(II)-Bent, both dehydrogenation and dehydration proceeded. Considering that dehydrogenation of methanol readily takes place in the presence of acid catalyst, the selectivity for this reaction is greatly influenced by the acidity of silicate lattice minerals.

b. Pumice

Some more researches had been studied on the effect of supports on catalytic activity of copper-based catalysts in the dehydrogenation of methanol to methyl formate. Ai et.al.[58] studied the effect of supports on various types of compounds to ascertain whether the catalytic activity of copper would be affected by the acid-base properties of the support. The copper-based catalyst of each support was prepared by means of a conventional ion exchange technique with cupric formate as the source of copper ions. Calcination was done in a stream of air at 500°C for 3 h. Reduction of the catalyst was performed by passing the reactant gas through at 240°C for 1 h, prior to a reaction. The reaction was performed with 20 g of a catalyst bed in a steel tube reactor at atmospheric pressure in a flow apparatus. Nitrogen gas was used as carrier gas. The flow rate of nitrogen was kept constant at 400 ml/min (at 200°C) and the concentration of methanol, fed by a micro liquid-feeder, in the feed gas was 6.3 vol%. The effect of supports on the catalytic activity at 180°C is shown in Table 2-7 [58].

The supports could be classified as follows :

- (i) Acidic supports, such as γ -alumina and zeolite 13x, gave dimethyl ether exclusively.
- (ii) Weakly acidic supports, such as silica gel and α -alumina, gave CO in preference to methyl formate.
- (iii) Inert supports, such as glass bead, carborundum, porcelain, pumice, and quartz, gave methyl formate exclusively.
- (iv) Copper shavings (pure copper), showed a substantial activity for methyl formate formation, and copper supported on copper shaving showed an activity as high as copper supported on inert compounds.

Table 2-7 Effect of supports on the catalytic performance

Support ^a	Conversion of methanol /% to			
	methyl formate	CO	methyl ether	total
γ -Alumina	0.0	3	90	93
Zeolite 13X	4.8	0.0	36	41
Silica gel	9	29	0.0	35
α -Alumina	10	26	0.0	36
Glass bead	9.5	0.0	0.0	9.5
Carborundum	17.5	0.2	0.0	17.7
Porcelain ring	26	1.0	0.0	27
Pumice	24	0.2	0.0	24.2
Quartz	30	0.3	0.0	30.3
(Copper shavings) ^b	10.2	0.0	0.0	10.2
Copper shavings	24	0.1	0.0	24.1

^a0.025 mol cu/50 ml support

^bneat copper without support.

These findings indicated that acidic compounds are unsuitable as supports for the formation of methyl formate. Copper shavings was used to study whether itself can catalyze the reaction. It was found that the catalytic activity to form methyl formate is to be ascribed only to copper by itself, with support merely serving to hold the mechanical strength of catalyst.

It was also found that copper tends to flake off from support, especially when the support is nonporous compound. Pumice, originated from volcanic stones, consisting of macropores, and chemically inert was an effective and gave the best reproducibility in catalytic activity. Thus, pumice-supported copper catalyst is one of the suitable catalysts for study on catalytic performance and modification of copper catalyst.

Catalytic performance of dehydrogenation of methanol to methyl formate over pumice-supported copper catalyst have been studied in various aspects :

Product distribution

Figure 2-6 [58] shows the relationship between the change in yield of each product and reaction temperature. The only detected products were methyl formate, CO, and CO₂; formic acid and formaldehyde were not detected. Methyl formate was almost the sole product up to 30% methanol conversion. However, the formation of methyl formate ceased to increase with a further increase in the extent of reaction, while that of CO steeply increased. It can be concluded that the formation of methyl formate was limited by reaction equilibrium and by decomposition of methyl formate to CO as follows :

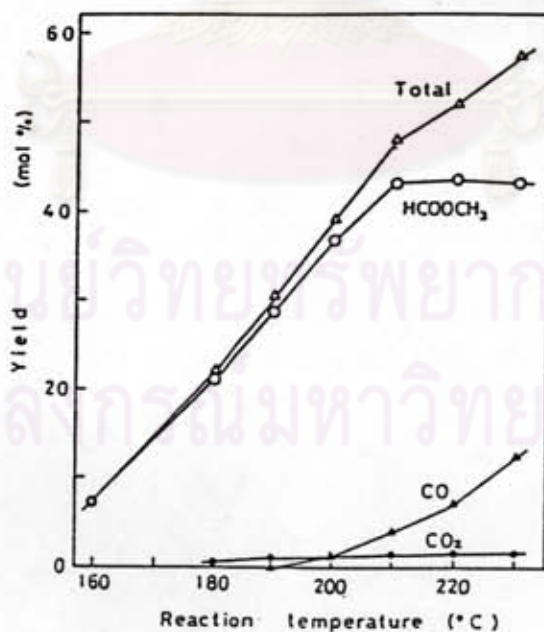
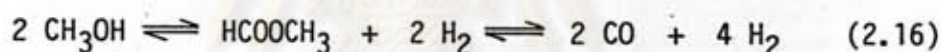


Fig. 2-6 Reaction of methanol on the pumice-supported copper catalyst.

Effect of amount of copper loading

As shown in Fig.2-7, the catalytic activity steadily increased with an increase in the amount of copper up to about 0.15 mol Cu/100 ml pumice, but the activity ceased to increase with a further increase in the amount of copper. The amount of hydrogen adsorption on each catalyst was also measured at 25°C by use of a BET apparatus to ascertain the change in copper metal surface area with an increase in the amount of copper loading. It was shown that the catalytic activity varies in the same direction as did the copper surface, suggesting that the active compound was not generated by a combination of copper and support but it was copper itself.

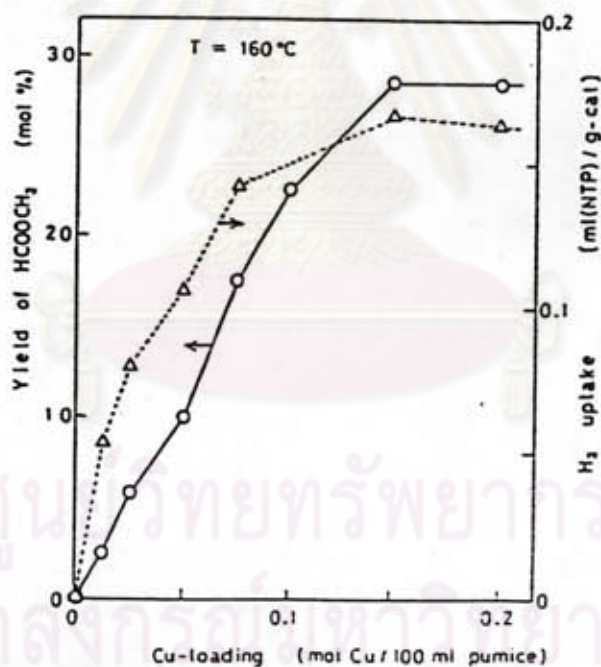


Fig. 2-7 Effect of the amount of copper loadings.

(o) yield of methyl formate at 160°C, and

(Δ) amount of hydrogen adsorbed at 25°C



Effect of methanol concentration

The effects of methanol concentration on the rate of reaction were studied. As shown in Fig. 2-8 [58], the rate of reaction was almost proportional to the square root of methanol concentration (top scale).

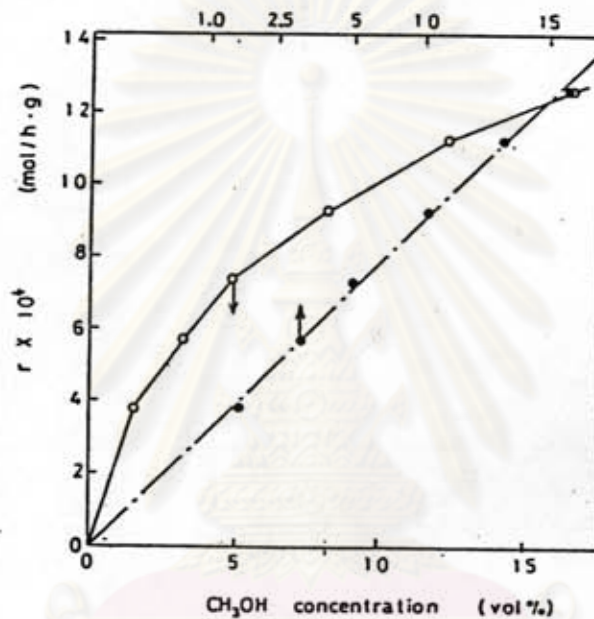


Fig. 2-8 Rate of methyl formate formation as a function of the initial concentration of methanol.

Effect of steam addition

Steam was introduced into the feed gas in the range up to 3 vol%, and its effects on the catalytic activity were examined. It was found that the catalytic activity was reduced by one-third for each 1 vol% of steam.

2.3.1.3 Catalytic stability

Catalytic stability indicates the period of time that a catalyst will be able to fulfil its action. Various types of supported copper catalysts were investigated in catalytic stability. TSM and SiO_2 which were shown by TPD curves of ammonia adsorption that no and small amounts of acid sites, respectively, were the effective supports. Figure 2-9 [57] shows the change in catalytic activities and selectivities of Cu(II)-TSM and Cu(II)-SiO_2 with reaction time. The catalytic activity of Cu(II)-SiO_2 was higher than that of Cu(II)-TSM . Therefore, the contact time was shortened to get a conversion comparable to that with Cu(II)-TSM . But the catalytic activity of Cu(II)-SiO_2 increased gradually with the reaction time. On the contrary, the selectivity to methyl formate was initially high and decreased to 80% in 5 h while the selectivity to CO increased gradually.

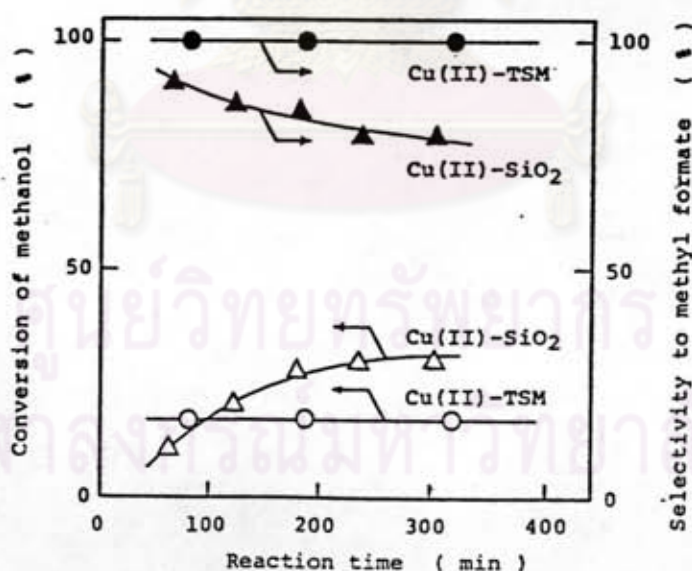


Fig. 2-9 Change in the catalytic activities with the reaction time.

Electron Spin Resonance (ESR) spectroscopy was used to explain the reason for catalytic stability in the aspect of oxidation state of

copper ions. The color of used Cu(II)-TSM was deep blue which was not so much changed compared with the blue color of fresh one. The ESR spectrum of fresh Cu(II)-TSM ($g = 2.09$) well agreed with that assigned by McBride et.al.[59] to Cu(II) ions in layer lattice silicate. The spectrum was completely reproduced on Cu(II)-TSM used in the reaction. For Cu(II)-SiO₂, the color of fresh one, which had been light blue, changed into brown after reaction. In the ESR spectra of Cu(II)-SiO₂, the signal assigned to Cu(II) ions on SiO₂ decreased stepwise in the intensity every time when the sample was exposed to methanol vapor for several seconds at 200°C. These facts suggest that Cu(II) ion on SiO₂ were reduced to Cu(0) during the reaction.

2.3.2 The effect of metal ion exchanges.

The catalytic activities of various types of metal ion exchanged form of fluoro tetrasilicic mica(Me-TSM's) were investigated for methanol conversion [60]. Since metal ions in Me-TSM are firmly held by the electrostatic force among the catalytically inactive sheets, Me-TSM is favorable to characterize the inherent activities of metal ions. The catalytic activity of various Me-TSM's were tested by means of a pulse technique. TPD curves of Na-TSM and H-TSM (Fig.2-2) showed that ammonia was not desorbed at all, on the other hand, ammonia was not chemisorbed on these catalysts. Na-TSM and H-TSM did not show any activities for methanol conversion, suggesting that the silicate sheet of TSM has no activity by itself. The catalytic activities of Me-TSM are summarized in Table 2-8 [36], where the selectivity of H₂O formation was calculated as follows :

$$\text{selectivity of H}_2\text{O formation} = \frac{\text{H}_2\text{O formed}}{\text{CH}_3\text{OH reacted}} \times 100$$

Table 2-8 Catalytic activities of metal ion exchanged form of fluoro tetra silicic mica (Me-TSM's) for the conversion of methanol. a)

(Reaction Temperature , 300°C ; Pulse Size , 0.2 μ l)

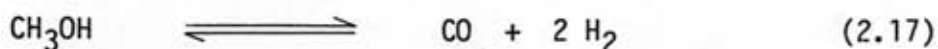
Me	Conversion of CH ₃ OH (%)	Selectivity to H ₂ O formation (%)	Products ^{b)}
Ti	44.8	69.7	<u>CH₃OCH₃</u> , CH ₄
Sn	10.7	100	} <u>CH₄</u> , C ₂ H ₄ , C ₂ H ₆
Ag	6.5	100	
Cr	9.8	68.6	
Fe	7.7	56.6	
Rh	50.3	40.1	<u>CO + H₂</u> , <u>CH₄</u> , C ₂ H ₆
Pd	72.4	7.7	} <u>CO + H₂</u> , CH ₄
Ru	64.1	6.3	
Ni ^{c)}	75.9	7.1	
Ce ^{c)}	21.6	2.5	
Ir ^{c)}	25.7	0	<u>CO + H₂</u> , CH ₄ , C ₂ H ₄ , C ₂ H ₆ , C ₃ H ₆ <u>CO + H₂</u> , CH ₄ , C ₂ H ₄

a) Mg-, Ca-, Mn-, Co-, Zn-, La-, and Th-TSM exhibited no activities.

b) The major products are indicated by underlines.

c) Reaction temperature , 400°C.

As shown in Table 2-8, Ti-TSM shows a high activity to produce dimethyl ether preferentially. Consider that dehydration of methanol over zeolites is always accompanied by the formation of dimethyl ether. Thus, Ti-TSM is likely to act as an acid catalyst. These facts lead to the idea that the catalytic ability of acidic layered silicate minerals could be improved by exchanging interlayer cations with Ti ions, as mentioned above. The selectivity of H₂O was higher than 50% on some Me-TSM's and even the value of 100% was attained with Sn- and Ag-TSM, suggesting that dehydrogenation occurred as shown in Fig. 2-1. The reaction products besides H₂O mostly consisted of CH₄, on Sn-, Ag-, Cr-, and Ag-TSM, suggesting that considerable accumulation of carbonaceous deposited over these catalysts. The catalytic activities of Rh-, Pd-, Ru-, and Ni-TSM were much higher than those of Me-TSM described above, but the formation of CO and H₂ were rather predominant over these catalysts. Supplemental studies with a flow reaction system revealed more clearly that CH₃OH was selectively decomposed to CO and H₂ over all of these catalysts as follows :



And subsequent methanation reaction fairly took place over Rh-TSM. The high activity of Pd-, Ru-, and Ni-TSM for selective decomposition of CH_3OH is attractive, because this reaction can make CO and H_2 which can be transported in the form of CH_3OH .

Cu-TSM was one of the most active catalysts and exclusively catalyzed dehydrogenation to form HCOOCH_3 among reactions shown in Fig. 1-1. In the studies with a flow reaction system, the selectivity for HCOOCH_3 formation was kept at 100% up to 50% conversion of methanol.

As mentioned above, it can be concluded that copper is particularly appropriate one among various types of metal ions as a preferential catalyst for dehydrogenation of methanol to methyl formate formation.

2.3.3 The effect of promoters.

Even though produced copper catalyst was found to be an effective catalyst to form methyl formate through dehydrogenation of methanol, but in some cases reduction of catalytic activity or decomposition of methyl formate to carbon monoxide occurred. The reduction of activity may result from interaction between catalyst and support, or sintering of copper metals on the surface of support. Decomposition may occur by decarbonylation of methyl formate (eq.2-12), by formation of intermediate formaldehyde (eq.2-10,11), or by direct decomposition of methanol (eq.2-9).

Addition of a suitable promoter is one of the modification techniques to promote the catalytic activity, selectivity, or stability. There are a number of researches studied on the

modification of copper catalysts in various ways of approach. The effects of promoter have been studied in details over various kinds of supported catalysts.

2.3.3.1 Metal oxides

As mentioned above, pumice-supported copper was one of the effective catalysts for dehydrogenation of methanol to methyl formate. The modifications of copper catalyst by using various types of metal oxide promoter have been studied on this catalyst. Two ways of approach were investigated to make clear whether the acid-base properties of the promoter affect the catalytic performance.

1. In the first approach, a series of binary copper catalysts containing an equal atomic amount of oxides (M/Cu atomic ratio = 1, where M represents an element corresponding to the oxide) have been investigated and compared in their catalytic performances.

2. In the second approach, the effects of the amount of metal oxides on methyl formate formation have been investigated.

a. Effect of types of promoter

According to the classification of metal oxides in terms of their acid-base properties [61], the catalytic performance in methanol conversion and yield of methyl formate over copper catalysts supported on various types of metal oxides are shown in Table 2-9 [58]. The reaction temperature required to achieve a given conversion acts as an index of the relative activity of each catalyst.

Table 2-9 Catalytic performance of M/Cu = 1 catalysts a)

Additive M_nO_m	Reaction temp. /C	Conv. of CH_3OH /%	Yield of $HCOOCH_3$ /mol%	Maximum yield of $HCOOCH_3$ /mol%
None	180	22	20.3	44
Li_2O	180	50	47.5	50
Na_2O	180	45	38.4	40
K_2O	180	33	30	35
Rb_2O	200	19	12	(12)
Cs_2O	200	8	1	(1)
BeO	160	47	35	37
MgO	160	45	40	40
CaO	160	47	40	40
SrO	160	41	38	40
BaO	160	41	37	39
Cr_2O_3	160	48	37	39
ZrO_2	180	31	28	50
MnO	180	40	37	46
ZnO	180	43	41	44
SiO_2	180	52	44	44
Fe_2O_3	180	20	14	(14)
CoO	180	22	8	(8)
NiO	180	19	0	(0)
Bi_2O_3	200	8	1	(2)
PbO	200	4	0	(0)
Ag_2O	200	0	0	0
SnO_2	200	3	2	(2)
TiO_2	200	2	1	(1)
V_2O_5	200	0	0	0
WO_3	200	0	0	0
MoO_3	200	0	0	0
P_2O_5	200	0	0	0
B_2O_3	200	0	0	0

^a0.5 mol Cu + 0.5 mol M/100 ml pumice.

From Table 2-9, it may be summarized as follows :

1. Alkali metal oxides : oxides of Li, Na, and K increase the activity. But with an increase in the atomic number of the metal, the activity decreases.

2. Alkaline earth metal oxides : all of them increase the activity to a great extent.

3. Cr₂O₃ : it increases the activity to the same extent as do alkaline earth metal oxides.

4. Amphoteric oxides : oxides which can be solved in both acid and base solvents, such as oxides of Zr, Zn, Mn, and Si, they increase the activity to a certain extent.

5. Reducible oxides : such as oxides of Fe, Co, Ni, Pb, Bi, and Ag, they inhibit the activity. These oxides might be reduced to metals by methanol during the reduction of catalyst. It may be assumed that alloy is formed by the combination of copper and a metal additive, which results in eliminating the catalytic action of copper.

Because yield of methyl formate is limited both by thermodynamical equilibrium and by consecutive reactions, the maximum yield of methyl formate is compared by a measurement of selectivity. It is shown that catalysts containing basic or amphoteric oxides show good selectivities to methyl formate, while catalysts containing acidic or reducible oxides are unsuitable for methyl formate productions.

b. Effect of the amount of additive

As the second approach to the study of modification of a catalyst, the effects of the amount of each oxide were investigated.

1. Alkali metal oxides. The activity increases markedly with the addition of a small amount (1 atom%) of alkali metal oxides. With a further addition, the activity passes through a maximum and then decreases as shown in Fig 2-10 [58]. A clear correlation between the properties of metal oxides added and their promotive effects is 'the higher the atomic number of metal, the less amount of oxide is needed to attain the maximum value of activity'.

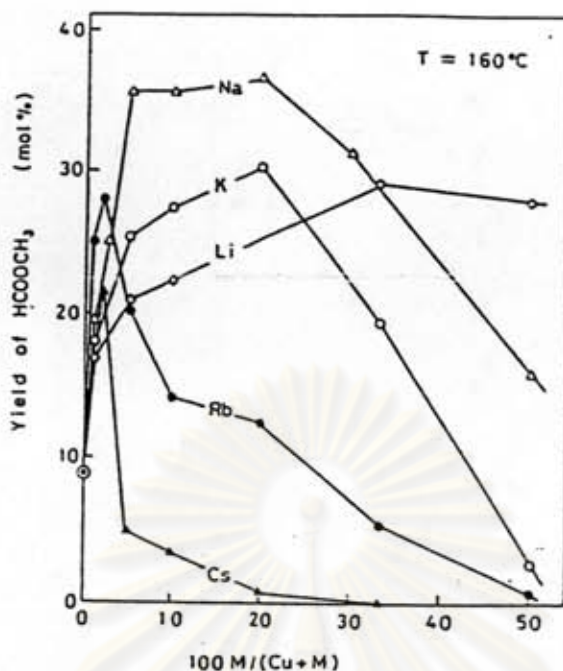


Fig. 2-10 Effect of the amount of alkali metal oxides.

2. Alkaline earth metal oxides. With an increase in the amount of oxide, the activity first increases and then levels as shown in Fig. 2-11 [58]. A clear correlation between the properties of these metal oxides and their promotive effects on activity is 'the higher the atomic number of metal, the more steeply the activity increases'.

3. Amphoteric oxides. The promotive effects of such oxides as Cr, Zr, Mn, Zn, and Si are remarkable especially in the cases of Cr and Zr oxides as shown in Fig. 2-12 [58].

4. Acidic oxides. As shown in Fig. 2-13 [58], strongly acidic oxidee such as oxides of V, W, Mo, and P act as strong poisons for copper catalyst, even in amount of less than 1 atom% (Fig. 2-13a). Weakly acidic oxides such as Sn, Ti, and B, the effects are relatively small at small amount, but the activity falls markedly with the addition of large amount of these oxides (Fig. 2-13b).

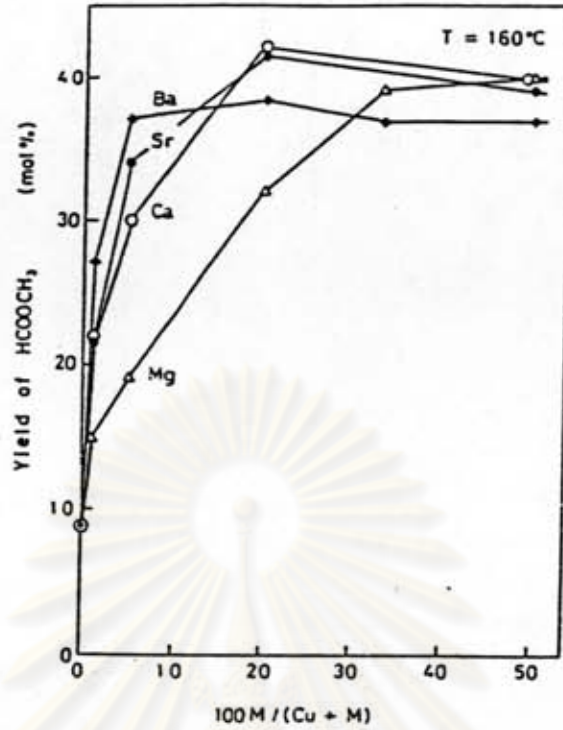


Fig. 2-11 Effect of the amount of alkaline earth metal oxides.

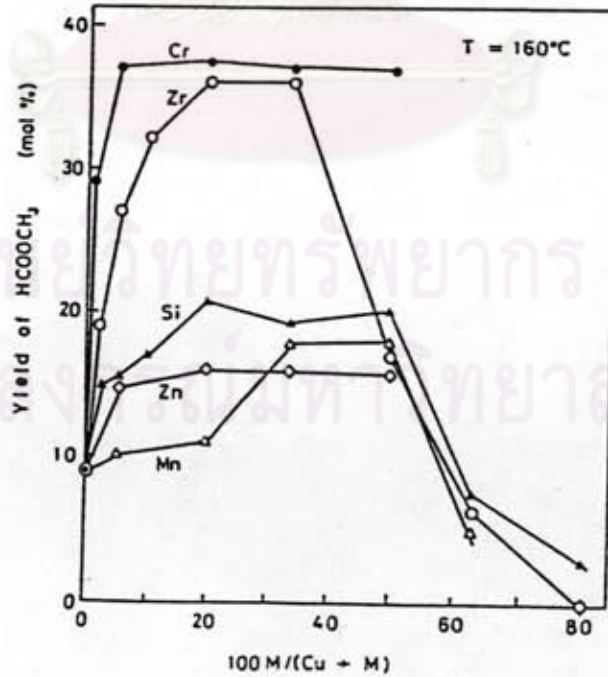


Fig. 2-12 Effect of the amount of amphoteric oxides.

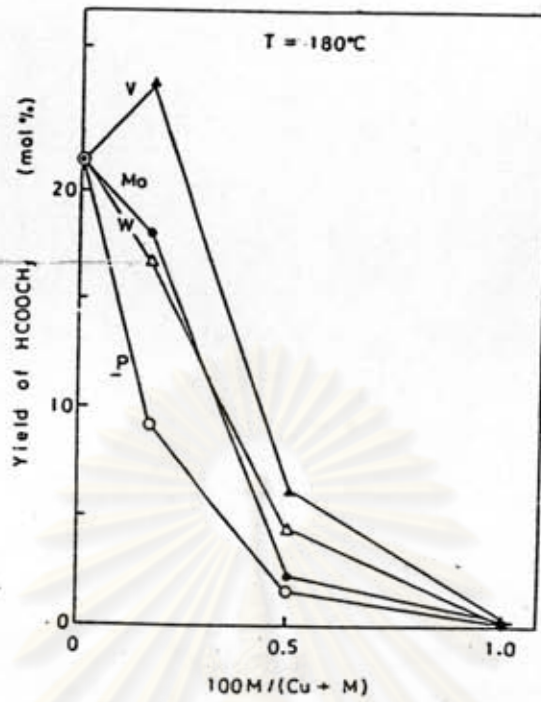


Fig. 2-13a Effect of amount of strongly acidic oxides.

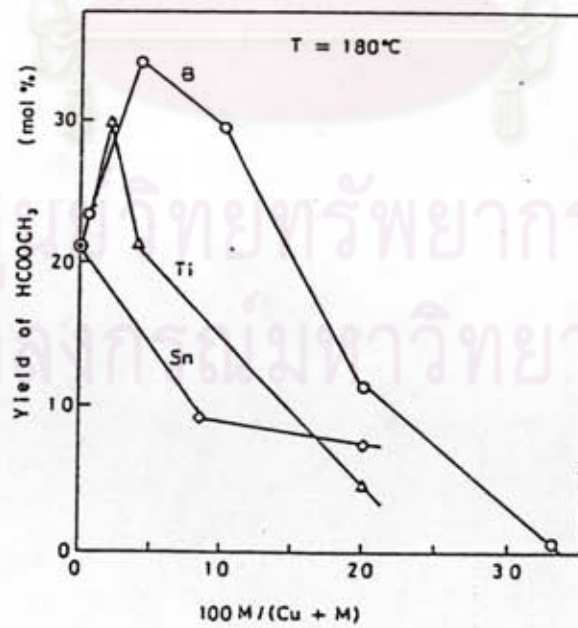


Fig. 2-13b Effect of the amount of weakly acidic oxides.

As mentioned above, it is clearly indicated that the activity of a copper catalyst is strongly influenced by the acid-base property of additives. The addition of a proper amount of basic oxides enhances the catalytic activity, although the optimum amount of each oxide is related to its basic property. In contrast, the addition of strongly acidic oxides harms the activity. The best results for the production of methyl formate were obtained with the addition of weakly basic and amphoteric oxides. The presence of an acidic property, to a very weak extent, seems to be favorable in promoting the reaction. Possibly, the weakly acid sites play a role in enhancing the affinity of a catalyst for methanol. These results suggest that the balance between acid-base property is an important factor for catalytic activity of a metal catalyst.

2.3.3.2 Chromium oxide

SiO_2 is often used as an inert carrier to prepare a supported catalyst, even though the TPD measurement of ammonia adsorption showed that SiO_2 certainly has acid sites, as shown above in Fig 2-5. Copper supported on SiO_2 has been used as an active catalyst for dehydrogenation of alcohols, particularly of ethanol, in the earlier works. It has been reported that the presence of chromia in catalyst composition improves the activity and life of catalyst in the dehydrogenation of ethanol [62,63]. For methanol dehydrogenation, supported copper catalysts as well as copper chromate catalysts have been studied by some researchers. The development of a catalyst with a high degree of dispersion of copper using fine textured Cr_2O_3 and SiO_2 as spacer and support, respectively, has been reviewed as follows. Several catalysts have been examined in order to determine the role of the components in the system of $\text{Cu}:\text{Cr}_2\text{O}_3:\text{SiO}_2$. Finally, some more modifications in catalyst compositions have also been examined.

It was found that very high and sustained activity could be

achieved by the method adopted for preparation of catalysts. A copper catalyst was prepared by impregnating silica hydrogel with the active component in solution, instead of the incipient wetness method which is commonly used for the preparation of supported catalyst, followed by drying and decomposition at a low temperature. Silica hydrogel possesses silica particles in the form of tiny globules which form a skeleton filled with water. When mixed with a soluble salt solution of active components and other ingredients, a high degree of dispersion of these components in the gel mass is achieved. When the mass is dried and decomposed, the active component is kept divided by the tiny silica particles which in addition provide a high surface area. The final mass is thus designed to effectively protect the active metal from sintering when catalyst is used over a prolonged period at relatively high temperatures. When chromia, obtained from ammonium dichromate, was incorporated along with copper in solution form, additional protection was provided to the active copper by the Cr_2O_3 formed in the final catalyst. It was proved that this procedure yielded a very active catalyst for dehydrogenation of ethanol to acetaldehyde [63]. The preparative method for copper chromite followed the procedure recommended by Braure [64].

a. Catalyst characterization

Various types of catalyst were characterized for surface areas by means of nitrogen adsorption at -196°C , using a classical volumetric adsorption apparatus. Pore volumes and pore size distributions were evaluated from the adsorption-desorption isotherms, using the conventional technique. In addition, X-ray diffraction (XRD), scanning electron microscopy (SEM) and temperature programmed reduction (TPR) studies of the catalysts were carried out for a better understanding in the nature of catalysts. The catalyst characterization is shown in Table 2-10 [60].

Table 2-10 Characterization of catalysts

Catalyst	Constituents and mass ratios	BET surface area (m ² /g)				Pore volume (V _p × 10 ⁴ cm ³ g ⁻¹)	
		Fresh	Reduced	Used	S _p *	Fresh	Used
1. Silica gel (Xerogel)	SiO ₂	747	—	—	223.92	231.75	—
2. A	Cu (Reduced CuO)	32.4	7.4	2.2	26.67	38.83	13.1
3. B	Cu:SiO ₂ 34.0:66.0	189.4	86.4	34.3	73.04**	138.85**	52.73
4. C	Cu:Cr ₂ O ₃ :SiO ₂ 33.5:32.0:34.5	142.6	148.44	135.5	121.53**	165.75**	148.45
5. D	Cu:Ni:Cr ₂ O ₃ :SiO ₂	118.2	121.56	120.65	116.76**	157.23**	150.31
6. Copper chromite	CuCr ₂ O ₄	26.5	—	5.9	—	—	—

*S_p: Cumulative surface area from pore size distribution.

**Reduced.

b. Performance of various catalysts

The reaction was carried out in a flow reactor over a fixed bed of 14–16 mesh size of catalysts at atmospheric pressure. The reaction products were collected in a series of condensers and analyzed by IR spectrometry. The effect of the continuous use of catalysts on their performances is shown in Fig. 2-14 [60], where activity represented by fraction of methanol converted is plotted against time on stream.

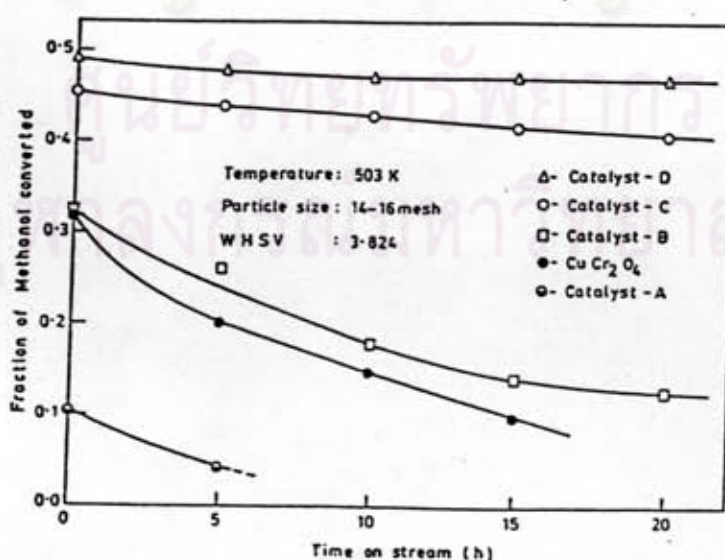


Fig. 2-14 Performance of the catalysts in dehydrogenation of methanol

Depending on the catalyst constituents and composition, a large variation in activity is obtained. In comparison of catalysts A (pure Cu) and B (Cu:SiO₂), it can be concluded that silica support promotes high activity and stability. The activity of catalyst A (pure CuO) and copper chromite decreased very rapidly. It could be the results from agglomeration and sintering of small copper crystallites leading to the decrease of active surface area (Table 2-10). Prasad et.al.[62] concluded by XRD and SEM studies that crystalline growth is the primary cause of the decrease in activity. The rapid decrease in the activity could also result from the decrease in pore volumes (Table 2-10) and an alteration of nature of the active surface at elevated temperatures during reduction. With catalyst C (Cu:Cr₂O₃:SiO₂) and catalyst D (Cu:Ni:Cr₂O₃:SiO₂), high activity and stability were attained because of the presence of chromia and nickel in the catalyst compositions.

c. Role of chromia

Sintering of copper crystallites can be prevented by the presence of another component acts as an spacer between them which could reduce the sintering tendency of copper. Therefore, chromia has been used as a phase which possibly acts as a textural promoter forming a barrier phase between the copper crystallites. Catalyst C, in which chromia was incorporated, appeared higher and more stable on the activity compared to catalyst B (Cu:SiO₂). In addition, the method by which the catalyst has been prepared gave the opportunity for the excellent distribution of the chromia and copper phases since the solution of chromia and copper complex was first mixed before impregnating the silica gel. Some more researches have also been shown that the presence of chromia in catalysts provided long-life catalysts in dehydrogenation of ethanol [62,63,65]. Prasad et.al.[62] have reported that the presence of chromia also increased the copper metal surface area which was responsible for the catalytic activity.

d. Role of nickel

Nickel promoted catalyst (catalyst D) was more active for dehydrogenation of methanol. The activity was kept steadily at above 92 % of the initial value and showed no tendency for change even after 50 h of reaction. However, it was found that catalyst containing more than 1.25% Ni promoted decarbonylation of methyl formate (eq.2.18) as shown in Fig. 2-15 [61].

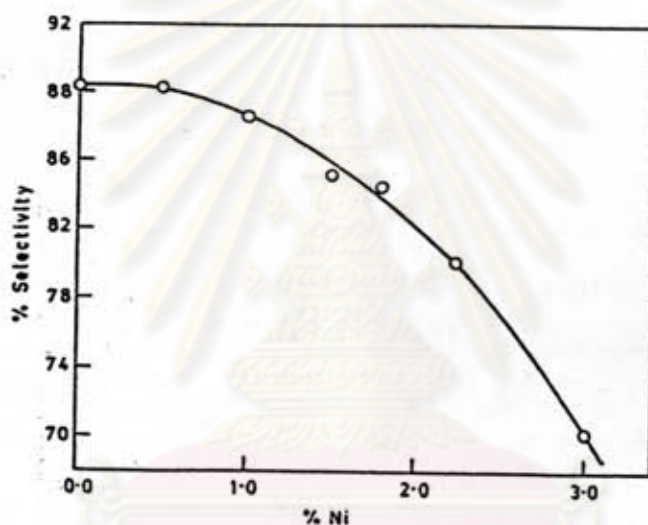
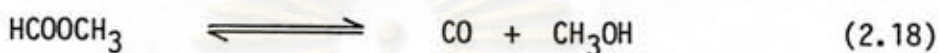


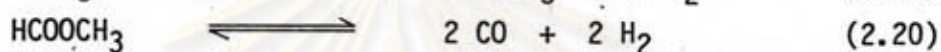
Fig. 2-15 Effect of nickel on selectivity for methyl formate.

In conclusion, silica is one of the most popular supports for active copper catalysts for dehydrogenation of methanol to methyl formate. A copper catalyst, prepared by mixing the active component in solution with silica hydrogel followed by drying and decomposition at low temperatures, showed a high degree of dispersion of copper, resulting in high activity at low temperatures and high resistance to deactivation. The presence of chromium oxide in these catalysts greatly improved the performance of copper catalysts by prolonging the life and increasing the activity of catalysts. Chromia acts as a spacer between copper crystallites inhibiting the sintering process while silica helps in exposing a larger surface area.



2.3.4 Intercalation.

Cu-TSM exclusively catalyzed the dehydrogenation of methanol to methyl formate. The selectivity was kept at 100% up to 50% conversion. The selectivity gradually decreased with raising reaction temperature, while the formation of CO and H₂ increased simultaneously, suggesting that the subsequent decomposition of methyl formate took place as shown in the stoichiometric equations as follows:



Recently, Shabtai et.al.[66] and Yamanaka and Brindley [67] reported that bulky compound intercalated into a layer mineral acted as a pillar to expand the interlayer distance and to increase the surface area dramatically. On heating at moderate temperature, however, the interlamellar molecules decompose and the interlayer structure collapses. The use of inorganic polyoxycations to provide pillared clays has been investigated to improve the thermal stability. Most of the intercalated clays by the polyoxycations have been prepared by the reaction of Na⁺ type of smectite clay with a solution of the polyoxycation. In general, the reaction proceeds by a direct ion exchange of surface Na⁺ cation in the native clay by polyoxycation. Na⁺ type in aqueous suspension are swelled with the thickness ranging from one to a few silicate layers. Therefore, most of Na⁺ cations are easily replaced by pillar species. Exchanged polyoxycations are immobilized in the interlamellar space by calcination, resulting in formation of a highly porous product, called pillared interlayer clay (PILC). Figure 2-16 demonstrates a schematic representation of a PILC synthesis.

Thus, effect of intercalation on catalytic activity was investigated. Al_n-TSM was prepared in the same way as the other

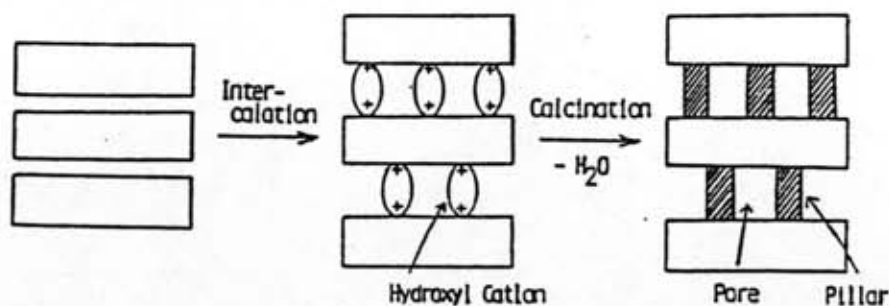


Fig. 2-16 Synthesis of pillared interlayer clay (PILC).

Me-TSM's but with the solution of oligomeric cations of aluminum hydroxide (Al_n). Cu- Al_n -TSM was obtained by two step exchanges, firstly with Al_n and secondary with Cu ions. The catalytic activities of catalysts are shown in Table 2-11 [36], where the value of selectivity was calculated on methanol basis and the same amount of Cu was loaded on each catalyst. The activity of Cu- Al_n -TSM was much higher than that of Cu-TSM: the conversion was the same as that of Cu-TSM at a higher temperature by 100°C. Furthermore, the selectivity of Cu- Al_n -TSM was as high as that of Cu-TSM. This high activity of Cu- Al_n -TSM seemed not to originate in the intercalated Al_n species, because Al_n -TSM was also active for the conversion of methanol but gave only dehydration products. The high activity of Cu- Al_n -TSM was due to an increase in the effective surface of active sites by the pillar effect of intercalated Al_n .

Table 2-11 Catalytic Activities of Cu-TSM and Effect of Intercalated Aluminium Hydroxide (Al_n).

Catalyst	Reaction Temperature (°C)	Conversion of CH_3OH (%)	Selectivity	
			to $HCOOCH_3$ (%)	to CH_3OCH_3 (%)
Cu-TSM	300	53.0	67.5	0
	350	72.1	58.0	0
	400	82.1	31.8	0
Cu- Al_n -TSM	250	71.1	76.1	0
	300	84.1	64.8	2.2
Al_n -TSM	300	29.2	0	100
	350	39.5	0	100

Pulse Size, 1.0 μ l

The nature of active sites of copper catalysts for methanol dehydrogenation has been investigated by means of x-ray diffraction (XRD), thermal gravimetric analysis (TGA), and selective extraction of copper oxide. The distribution of copper on the catalyst surface has been determined by the measurements of total and metal surface area. Considerable work has been done in determining the nature of active sites, the distribution of copper, and the reasons for catalyst deactivation on copper chromite catalysts which are active for a number of reactions as well as dehydrogenation of methanol to methyl formate. X-ray diffraction [68] and magnetic studies [69] have shown that prior to reduction, copper chromite catalysts consist of intimate mixtures of copper oxide (CuO) and copper chromite (CuCr_2O_4). Adkins [70] first suggested that divalent copper was the active species in high pressure (200 atm) dehydrogenation of esters and ketones, and deactivation was caused by reduction to the monovalent and metallic states. Stroup [68] proposed that after reduction, the catalyst consisted of copper metal and cuprous chromite ($\text{Cu}_2\text{Cr}_2\text{O}_4$). Rabes and Schneck [71] believed that cuprous chromite was formed initially and that further reduction at high pressure produced highly dispersed copper metal on chromia (Cr_2O_3). It has been shown that copper metal is an active site for methanol dehydrogenation, the unreduced catalyst does not catalyze the reaction and pretreatment in pure hydrogen at 220°C is necessary for activation of these catalysts being in agreement with the results of TGA.

According to the importance of nature of active catalysts, characterizations of the compositions, total and metal surface areas, X-ray powder diffraction, thermal gravimetric analysis and selective extraction of copper oxide to investigate the nature of the active catalyst have been reviewed. Furthermore, the effects of various oxidation states of copper on methanol dehydrogenation have been investigated.

2.4.1 Compositions

The compositions of catalysts have been determined by atomic absorption spectroscopy of acid-digested solutions. The amounts of total copper and the other metals have been determined by using solutions obtained by use of a 60/10/30 volumetric mixture of HF/HClO₄/HNO₃. The copper presented as copper oxide was measured by washing the catalyst with a hot 32 wt% solution of HCl which Cu(II) was retained in the filtrate [70].

2.4.2 Surface Area

The catalyst in which copper metal is an active site, total (BET or Langmuir) and copper metal surface areas of reduced catalyst have been determined from N₂ adsorption at -196°C and reaction with nitrous oxide (N₂O) at 90°C, respectively.

2.4.3 X-Ray Diffraction (XRD)

X-ray powder diffraction studies have been carried out using a Rigaku Geiger-flex diffractometer. Silicon powder was used as a reference for determining crystallite sizes by the X-ray line broadening. Reduced catalysts were coated with colloid ions to prevent oxidation prior to examination. Small copper crystallite sizes, as well as high copper surface areas, are indicative of a relatively high degree of dispersion for an easily sintered metal. X-ray diffraction is also used to identify different components of unreduced and reduced catalysts using lines with angles in the range of $10^\circ < 2\theta < 70^\circ$. XRD studies of reduced catalysts showed that peaks corresponding to CuO had been lost and peaks corresponding to copper had emerged as shown in Fig. 2-17 [72]. The intense maxima prior to reduction(a) are obtained at $2\theta = 35.6$ (CuO, CuCr₂O₄),

38.9 (CuO) and 37.6 (CuCr_2O_4). After leaching with HCl (b) the contribution of CuCr_2O_4 is more evident. On reduction(c), identification is very poor and broad maximum at $2\theta = 36.3$ emerges indicating the presence of cuprous chromite, $\text{Cu}_2\text{Cr}_2\text{O}_4$. Although the maxima are poorly defined and overlapped throughout the spectra, a significant transition from cupric, Cu(II) , to cuprous, Cu(I) , phase have clearly taken place.

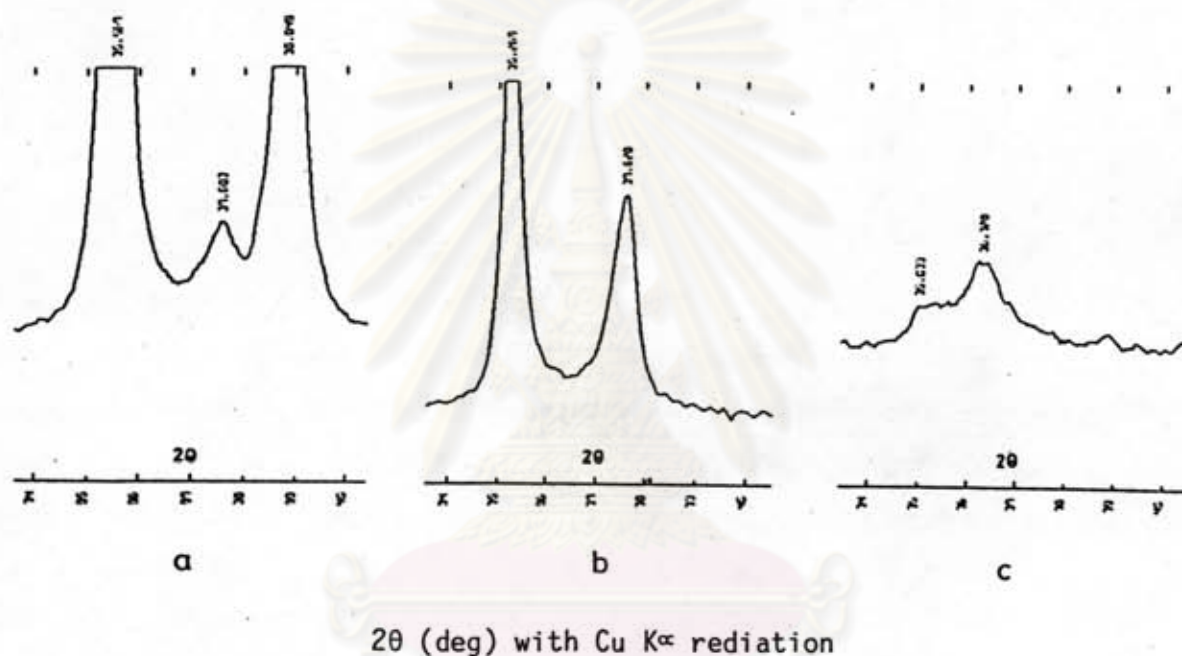


Fig. 2-17 X-ray diffraction patterns of unreduced, leached, and reduced over copper chromite catalyst.

2.4.4 Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis has been carried out in atmospheres of pure nitrogen and pure hydrogen using a Du Pont Series 99 Thermal Analyser. A temperature range of $50\text{--}650^\circ\text{C}$ was used with a heating rate of $10^\circ\text{C}/\text{min}$. For example, TGA of copper chromite catalysts, the weight loss curves obtained by heating catalysts in hydrogen to 650°C are shown in Fig. 2-18 [72]. Two distinct stages

of weight loss curves, a sharp loss between 200 and 250°C and a slower loss up to 550°C, can be identified. The first stage is attributed to rapid and complete reduction of CuO to Cu and the second stage to complete reduction of chromite to Cu, each involving the loss of one oxygen atom per atom of copper.

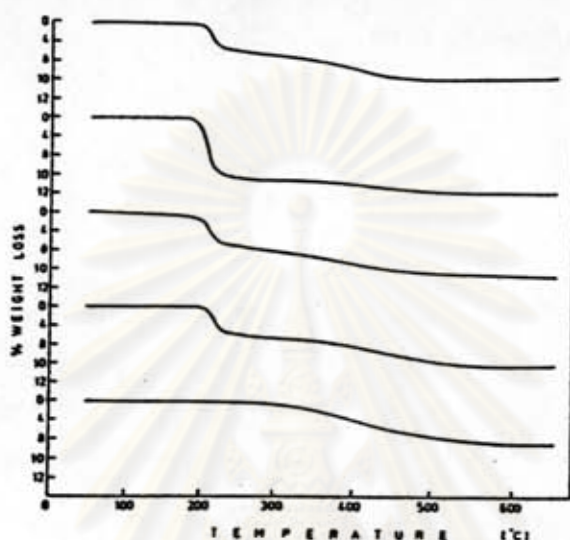


Fig. 2-18 Thermal Gravimetric Analysis in hydrogen atmosphere of various copper chromite catalysts showing the weight loss due to copper reduction.

Regarding the copper supported on fluoro tetrasilicic mica (Cu-TSM) which is a particularly appropriate catalyst in methanol dehydrogenation to form methyl formate, the nature of the active sites has been investigated. The catalytic activities of various oxidation state of copper, Cu(II)-, Cu(I)-, and Cu(0), supported on TSM have been examined. Electron spin resonance (ESR) has been used to characterized the nature of active sites or the oxidation state of copper. Table 2-12 [73] shows activities of various catalysts for dehydrogenation of methanol, where the values of selectivity were calculated on methanol basis. Cu(II)-TSM shows high selectivity for methyl formate at temperatures below 240°C (run 1,2). ESR studies showed that Cu(II) ions on Cu(II)-TSM were not reduced at all during

Table 2-12 Activities of coppers in the various oxidation states for the dehydrogenation of methanol.

Run No	Catalyst	Temperature / °C	Conversion / %	Selectivity / %		
				HCOOCH ₃	CO	H ₂ CO
1	Cu(II)-TSM	220	21.1	100	0	0
2		240	44.8	100	0	0
3		400	11.0	6.7	13.3	80.0
4	Cu(I)-TSM	220	1.1	100	0	0
5		240	4.3	100	0	0
6	Cu(0)-TSM	240	1.6	0	0	100
7		300	2.0	0	0	100
8		400	6.1	0	0	100
9	Cu(0)/SiO ₂	400	36.9	0	54.3	45.6
10		240	1.8	50.0	tr	50.0
11		300	7.1	45.0	6.5	48.6

the reaction. At higher temperatures, the catalytic activity and selectivity to methyl formate formation decreased with time on stream, while formaldehyde and carbon monoxide were formed (run 3). The decline in catalytic activity is caused by the reduction of Cu(II) ions during the reaction. The ESR spectra of fresh and used catalysts showed only a small decrease in intensity of the signal assigned on Cu(II) ions, suggesting that only a part of Cu(II) ions, which might be located near outer surface of Cu(II)-TSM and effective for catalysis, are reduced during the reaction.

The catalytic activity of Cu(I)-TSM was much lower than that of Cu(II)-TSM and methyl formate was produced selectively (runs 4,5). The ESR spectrum for Cu(I)-TSM showed a weak signal due to Cu(II)-TSM which suggested that the activity was promoted by Cu(II)-TSM and Cu(I)-TSM had no activity. Furthermore, the catalytic activity of Cu(0)-TSM was investigated as shown in Fig. 2-19 [73]. The conversion of methanol decreased with reaction time and leveled off, while the selectivity to formaldehyde increased and attained a value of 100%. At the initial period of reaction, a small amount of methyl formate was formed due to the presence of trace amount of Cu(II) ions. In X-ray diffraction pattern with the reduced catalyst, broad and small

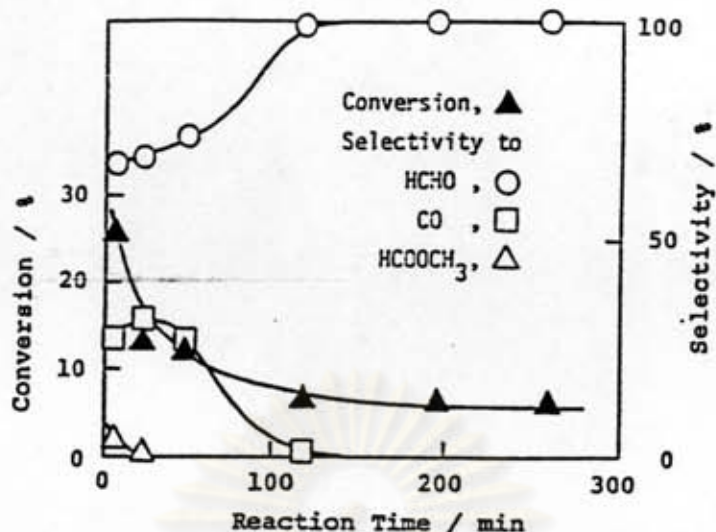


Fig. 2-19 Change in the activity and the selectivity during the final reduction at 400°C to obtain Cu(0)-TSM.

peaks of metallic copper were observed, suggesting that Cu(0) ions promote the formaldehyde formation selectively as shown in Fig. 2-19 and Table 2-12.

It is clearly shown that the selectivity in dehydrogenation of methanol over copper catalysts widely varies depending on the oxidation state of copper as summarized in Fig. 2-20. Cu(II) ion and Cu(0) selectively catalyze dehydrogenation to form methyl formate and formaldehyde, respectively, while Cu(I) ion is inactive for methanol conversion.

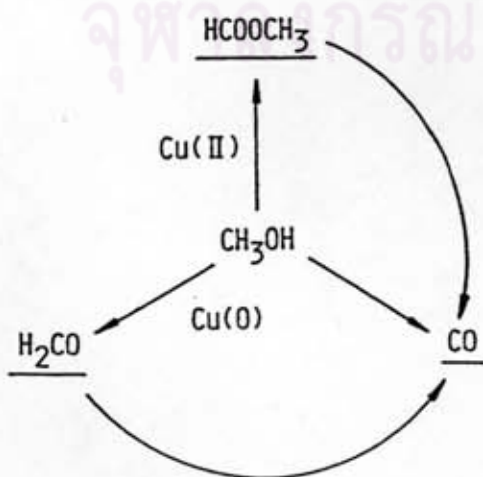
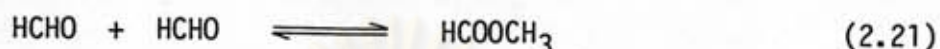


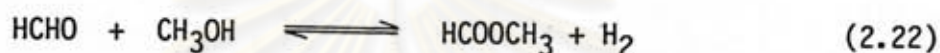
Fig. 2-20 Difference in the selectivity of methanol dehydrogenation over Cu(II) ion and Cu(0).

2.5 MECHANISM OF METHYL FORMATE FORMATION.

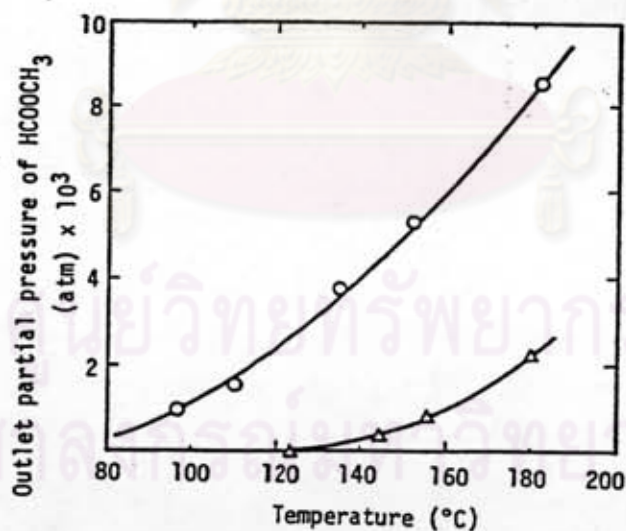
Although formaldehyde which is primarily formed by dehydrogenation of methanol is considered to be an intermediate species of methyl formate formation, it is still controversial whether methyl formate is produced primarily through the bimolecular reaction of formaldehyde (The Tischenko Reaction) :



or the reaction between formaldehyde and methanol [74] :



The mechanisms of methyl formate formation have been investigated, using a deuterium labeling technique, in the reaction between formaldehyde and methanol as well as dehydrogenation of methanol over copper-silica and support-free copper catalysts.



- (-Δ-) : The reaction was carried out with formaldehyde alone. Inlet partial pressure : $P_{\text{HCHO}} = 0.011$ atm.
 (-o-) : The reaction was carried out with the formaldehyde-methanol mixture. Inlet partial pressure : $P_{\text{HCHO}} = 0.011$ atm and $P_{\text{CH}_3\text{OH}} = 0.12$ atm.

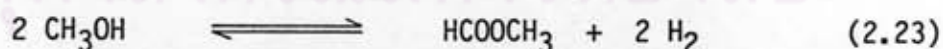
Fig. 2-21 Methyl formate formation versus temperature.

When formaldehyde alone or the mixture of formaldehyde and methanol was admitted in a nitrogen stream over copper-silica catalyst, methyl formate was formed. Figure 2-21 shows the outlet partial pressure of methyl formate formed at various temperatures. The ratio of the amount of formaldehyde consumed to that of methyl formate formed at various reaction temperatures is shown in Table 2-13 [75].

Table 2-13 The ratio of formaldehyde consumed to methyl formate formed at steady state for the reaction of formaldehyde and methanol.

Temperature (°C)	100	116	135	150	180
$\frac{\text{HCHO consumed}}{\text{HCOOCH}_3 \text{ formed}}$	1.9	2.0	1.9	1.6	1.2

The ratio obtained approached two at reaction temperature below 135°C which led to the idea that one molecule of methyl formate was formed by consumption of two molecules of formaldehyde even in the presence of methanol at these temperatures. The formations of by-products such as hydrogen, carbon monoxide, carbon dioxide, and the consumption of methanol were practically negligible under these conditions. On the other hand, the situation is complicated at higher temperatures where methanol was consumed and hydrogen was formed favorably. It is likely that methanol admitted with formaldehyde was dehydrogenated by the following reaction:



In fact, when methanol alone was admitted over the catalyst, no reaction occurred at 135°C while at temperatures above 160°C dehydrogenation was found to be appreciable. In these respects, the ratio (HCHO consumed/ HCOOCH₃ formed) decreased with increasing reaction temperatures.

For the investigation of reaction mechanism, isotopic studies have been done with formaldehyde- d_0 (HCHO) and methanol- d_3 (CD_3OH) at reaction temperature of 130°C at which no dehydrogenation of methanol occurred. The mass spectra of methyl formate formed are shown in Fig. 2-21 [75] where an intense peak due to the parent species is seen at $m/e = 63$, indicating that methyl formate- d_3 (HCOOCD_3) was predominantly formed.

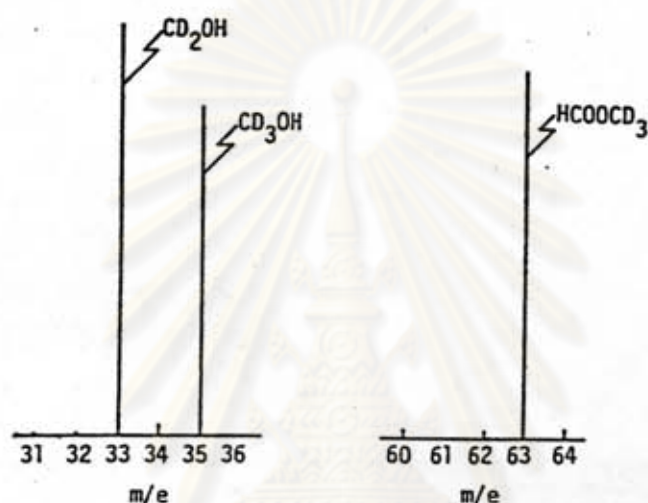
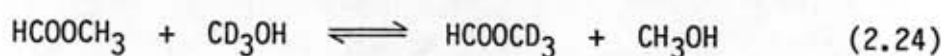


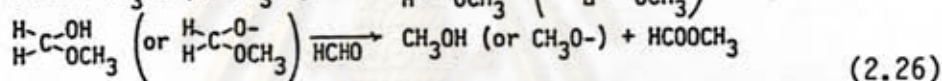
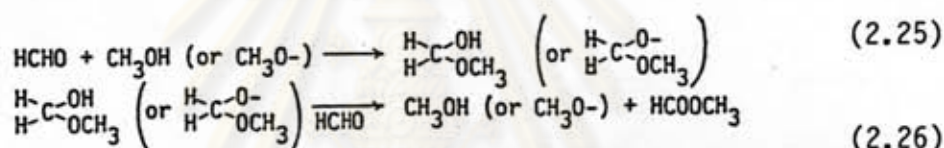
Fig. 2-22 Mass spectra of methyl formate formed by the reaction between formaldehyde- d_0 and methanol- d_3 CD_3OH . Temperature : 130°C . Inlet partial pressures : $P_{\text{HCHO}} = 0.011$ atm. $P_{\text{CD}_3\text{OH}} = 0.017$ atm.

Due to the selective reaction between formyl hydrogen and methoxy group of methyl formate and the elimination of a hydrogen atom in methyl group of CH_3OH [76], intense peaks of CD_3OH and CD_2OH were seen at $m/e = 35$ and 33 , respectively. Since it would be probable that methyl formate- d_0 (HCOOCH_3) was initially formed by bimolecular reaction (2.21) and transformed to HCOOCD_3 by the exchange reaction :

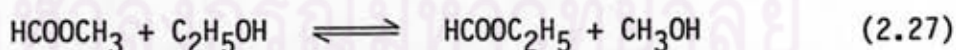


When the reaction was carried out between methanol- d_4 (CD_3OD) and formaldehyde- d_0 (HCHO), methyl formate- d_3 (HCOOCD_3) was also

formed predominantly. No bimolecular reaction (2.21) was involved and methyl formate was formed primarily through the reaction between methanol and formaldehyde. In this case, a hydrogen of formaldehyde molecule was kept as formyl hydrogen in methyl formate molecule. When hydrogen was admitted with the mixture of formaldehyde and methanol, it was found that methyl formate formation was unaffected by the presence of hydrogen. No hydrogen was consumed and no methanol was formed in any addition amount. This indicated that no hydrogenation of formaldehyde occurred in the case of methyl formate formation. In these respects, it was most likely that when formaldehyde reacted with methanol, hemiacetal and hemiacetal-like species were primarily formed and hydrogen transfer occurred between either of the latter species or formaldehyde as



When the latter step proceeded at a greater rate than the former step, one molecule of methyl formate was formed by consumption of two molecules of formaldehyde although methanol participates in the reaction. In consistent with these reaction routes, when ethanol was admitted with formaldehyde, ethyl formate and methanol were formed but the formation of methyl formate was practically negligible. It was also confirmed that the following reaction (2.27) did not occur.



As for methyl formate formation by dehydrogenation of methanol, the reaction was extremely slow compared to that between methanol and formaldehyde. As has been concluded by Miyazaki and Yasumori[32], the formation should be controlled by dehydrogenation of methanol to formaldehyde. When dehydrogenation was carried out at 180°C, methyl formate-d₄ (DCOCD₃) was formed exclusively and no

hydroxyl hydrogen was involved in the reaction to yield methyl formate.

When the reaction was carried out with a mixture of CD_3OH and CH_3OH , the product methyl formate showed peaks at $m/e = 64, 63, 61,$ and 60 in the mass spectra, indicating that methyl formate $-d_4, -d_3, -d_1$ and $-d_0$ ($\text{DCOOCd}_4, \text{HCOOCd}_3, \text{DCOOCH}_3$ and HCOOCH_3) were formed as shown in Fig. 2-23. The formation rates of d_3- and d_0- species were found three or five times greater than those of d_4- and d_1- species. As compared with the above reviews, methanol was first dehydrogenation to formaldehyde and the latter species transformed to methyl formate through the equations (2.25) and (2.26). The same results were obtained for the reaction over support-free copper catalyst. It was confirmed that the reaction occurred over copper surface as shown in Fig. 2-24.

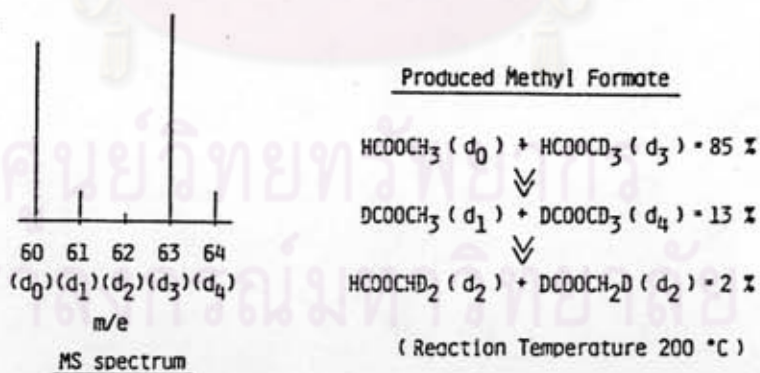


Fig. 2-23 Isotopic distribution in methyl formate produced from the mixture of CH_3OH and CD_3OD (1:1 in molar ratio)

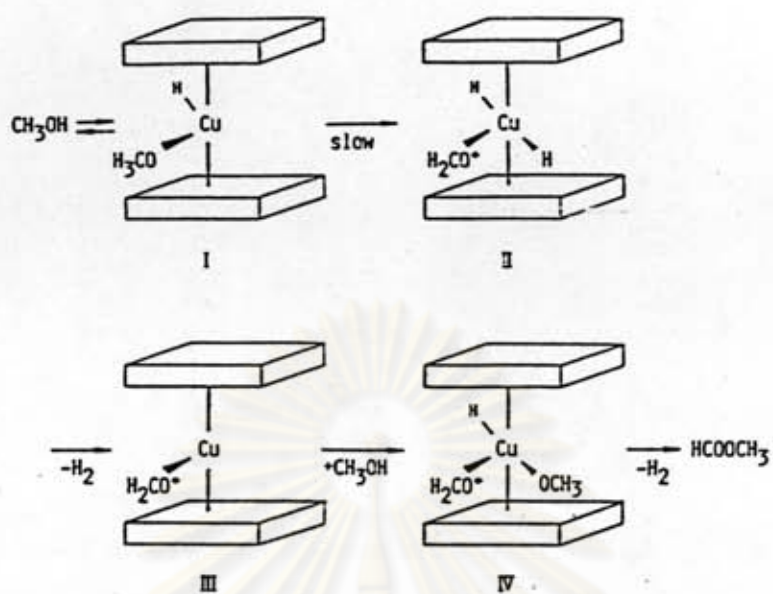
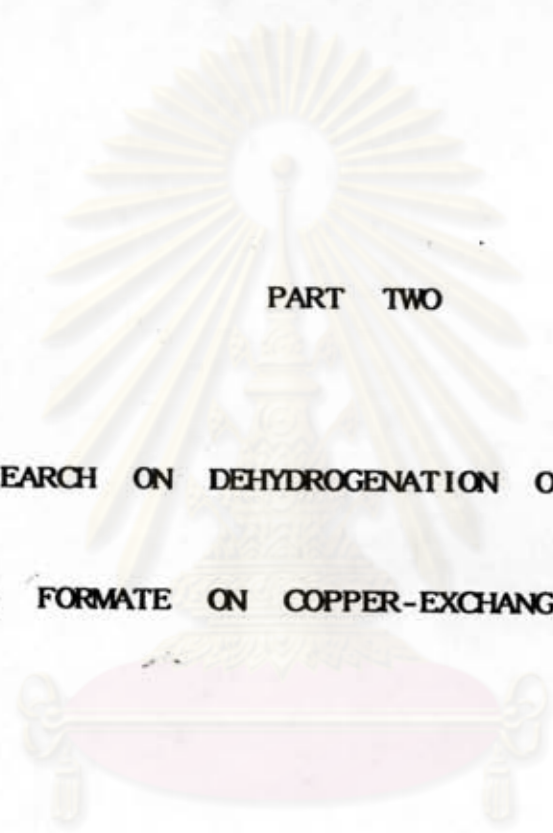


Fig. 2-24 Mechanism for methyl formate formation.

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PART TWO

RESEARCH ON DEHYDROGENATION OF METHANOL
TO METHYL FORMATE ON COPPER-EXCHANGED CLAY CATALYSTS.

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