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# The Production of Methyl Formate by the Vapor-Phase Oxidation of Methanol

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Methanol is oxidized to methyl formate, but not to formaldehyde, over $SnO_2$–$MoO_3$ catalysts. Tests of various binary-oxide catalysts indicated that the best results for both activity and selectivity were obtained with the Sn/Mo atomic ratio = 7/3 catalyst. It was proposed that methyl formate is formed via formaldehyde as follows: $2\ CH_3OH \rightarrow 2\ HCHO \rightarrow HCOOCH_3$. It was concluded that the possession of both acidic and basic properties is required to catalyze the reaction.

## INTRODUCTION

It is well known that methanol is oxidized selectively to formaldehyde in the presence of a large excess of air with $MoO_3$- and $V_2O_5$-based catalysts (*1–8*) and that formaldehyde is, in practice, manufactured by methanol oxidation over $Fe_2O_3$–$MoO_3$-based catalysts. In a previous report (*9*), we have proposed, as a general rule, that formaldehyde can be obtained only from such acidic oxides as $MoO_3$, $WO_3$, $V_2O_5$, and $U_3O_8$, but not from oxides which are more basic than $TiO_2$, e.g., $TiO_2$, $SnO_2$, $Fe_2O_3$, $Bi_2O_3$, ZnO, and $Co_3O_4$ (*10*), and that a clear correlation always exists between the catalytic activity for formaldehyde formation and the acidity (number of acidic sites) in the cases of many $MoO_3$- and $V_2O_5$-containing catalysts. Interestingly, it was also found that a significant amount of methanol is oxidized to formic acid, methyl formate, and CO and water over the $SnO_2$–$MoO_3$ catalysts.

From a survey of the patent literature, Chono and Yamomoto (*11*) recently stated that three methods have been presented for the production of methyl formate, which can be converted to such useful chemicals as acetic acid and *N,N*-dimethylformamide: (i) the dehydrogenation of methanol (in the absence of oxygen) over CuO-based catalysts, giving a yield of 40 to 50% with a selectivity of 85 to 90%; (ii) the dimerization of formaldehyde (Tischenko reaction) over Cu, PbO, or $Fe_2O_3$, and (iii) the carbonylation of methanol with CO.

It is very interesting that methyl formate can be obtained directly from a contact oxidation of methanol. In this study, we focused our attention on the formation of methyl formate and attempted to clarify the effects of catalysts and of reaction variables, since no information about this oxidation reaction has been reported.

## EXPERIMENTAL

The catalysts used in this study were various $MoO_3$- and $SnO_2$-containing binary oxides. They were the same as those used in our previous works (*9, 12–14*) and so the acid–base properties of some of them have already been determined.

The vapor-phase oxidation of methanol was carried out in a conventional continuous-flow system. The reactor and the experimental procedures were almost the same as those employed in the previous work (*9*), but the reactions were conducted under milder conditions—that is, at a lower temperature, a much lower oxygen concentration, and a lower flow rate of oxygen–nitrogen mixed gas.

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## RESULTS

### *Comparison of the Performances of Various Catalysts*

Various $MoO_3$- or $SnO_2$-containing binary-oxide catalysts were tested for the ability to form methyl formate from methanol. The amount of catalyst used was 20 g, and the feed rates of the reactants were: $CH_3OH = 6.3 \times 10^{-2}$ mol/hr, $O_2 = 4.0 \times 10^{-2}$ mol/hr, and $N_2 = 91 \times 10^{-2}$ mol/hr. The results are listed in Table 1. The reaction temperature required to achieve the conversion shown in the third column represents the relative oxidation activity of each catalyst.

The results may be summarized as follows:

(i) The $SnO_2$–$MoO_3$ catalysts, notably the Sn/Mo atomic ratio = 7/3 catalyst, are much more active than the other catalysts.

(ii) Over the $SnO_2$–$MoO_3$ and $SnO_2$–$WO_3$ catalysts, the main product is methyl formate, not formaldehyde.

(iii) The Sn/Mo = 7/3 catalyst shows a high selectivity to methyl formate of 90 mol% at the methanol conversion of 72%.

(iv) The main product is formaldehyde over the other $MoO_3$-containing catalysts. The V/Mo = 9/1 and Fe/Mo = 3/7 catalysts show a high selectivity to formaldehyde of from 90 to 95 mol%.

(v) The second best catalyst for the production of methyl formate is the Sn/W = 8/2 catalyst, though here the oxidation activity is much lower than in the case of the Sn/Mo = 7/3 catalyst.

(vi) As the main degradation product, $CO_2$ is formed over the Ti/Mo = 8/2 catalyst, but CO is formed over the other catalysts.

### *Effect of the $SnO_2$–$MoO_3$ Composition on the Methanol Oxidation*

Six catalysts of different Sn/Mo compositions were tested for both activity and selectivity. The charge rates of methanol, ox-

TABLE 1

Oxidation of Methanol with Various Catalysts[a]

| Catalyst (atom ratio) | Reaction temp. (°C) | $CH_3OH$ conv. (%) | Selectivity (mol%) to | | | | |
|---|---|---|---|---|---|---|---|
| | | | $HCOOCH_3$ | HCHO | HCOOH | CO | $CO_2$ |
| V–Mo (9–1) | 240 | 54 | 7 | 91 | 1 | 1 | 0 |
| | 250 | 80 | 7 | 85 | 3 | 4 | 1 |
| Fe–Mo (8–2) | 228 | 71 | 20 | 72 | 4 | 3 | 1 |
| | 235 | 84 | 17 | 69 | 5 | 8 | 1 |
| Fe–Mo (3–7) | 300 | 57 | 3 | 95 | 0 | 2 | 0 |
| Ti–Mo (8–2) | 260 | 24 | 7 | 74 | 0 | 2 | 17 |
| | 280 | 42 | 4 | 57 | 0 | 9 | 30 |
| Ti–Mo (2–8) | 220 | 26 | 31 | 65 | 0 | 3 | 1 |
| | 230 | 37 | 27 | 65 | 1 | 6 | 1 |
| Sn–Mo (7–3) | 150 | 34 | 92 | 8 | 0 | 0 | 0 |
| | 160 | 72 | 90 | 5 | 3 | 1 | 1 |
| Sn–Mo (4–6) | 190 | 33 | 57 | 24 | 0 | 15 | 4 |
| Sn–W (8–2) | 275 | 39 | 73 | 4 | 0 | 18 | 5 |
| Sn–P (9–1) | 305 | 54 | 25 | 29 | 0 | 36 | 10 |

[a] Catalyst = 20 g; feed gas: $CH_3OH = 6.3 \times 10^{-2}$ mol/hr, $O_2 = 4.0 \times 10^{-2}$ mol/hr, $N_2 = 91 \times 10^{-2}$ mol/hr.

ygen, and nitrogen were the same as those indicated above. The rate of methanol oxidation to form methyl formate at 160°C is plotted as a function of the composition in Fig. 1. The pure $SnO_2$ is completely inactive for the oxidation; with an increase in the $MoO_3$ content, the activity increases at first, passes through a maximum at the Mo/(Sn + Mo) atomic ratio of 0.3, and then sharply decreases.

It may not be proper to compare the selectivities obtained either at a fixed temperature or at a fixed methanol conversion, because the selectivity is affected by both the conversion and the temperature. Therefore, the selectivity is plotted as a function of the conversion, and the temperature corresponding to the selectivity and conversion is also described (Fig. 2).

It was found that the best results for the selectivity, as well as for the activity, are obtained with the Sn/Mo = 7/3 catalyst. The one-pass yield of methyl formate reaches from 65 to 70 mol% at around 160°C under the present reaction conditions. However, it should be noted that when the conversion attains a certain level, depending on the reaction conditions, almost all of the methanol is suddenly consumed to form CO (55 mol%), methyl formate (25 mol%), formic acid (14 mol%), formaldehyde (3 mol%), and $CO_2$ (3 mol%), accompanied by a large heat evolution, and that once this side reaction occurs, the reaction cannot be controlled by the temperature. Special care is, therefore, required in the elevation of the reaction temperature.

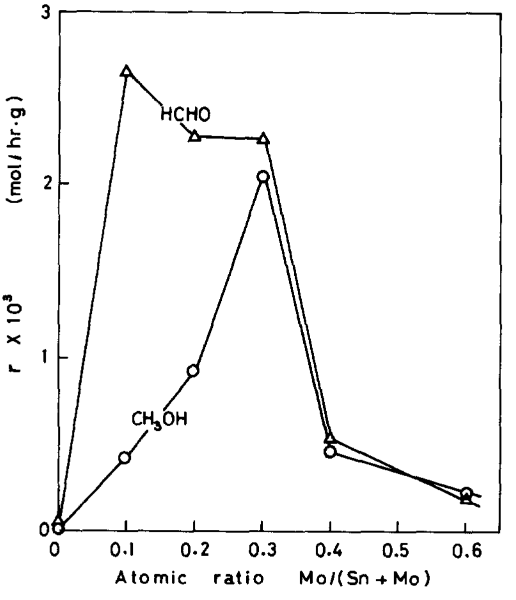

FIG. 1. Effect of catalyst composition on the catalytic activity. (○) Rate of methyl formate formation from methanol at 160°C; (△) rate of methyl formate formation from formaldehyde at 120°C.

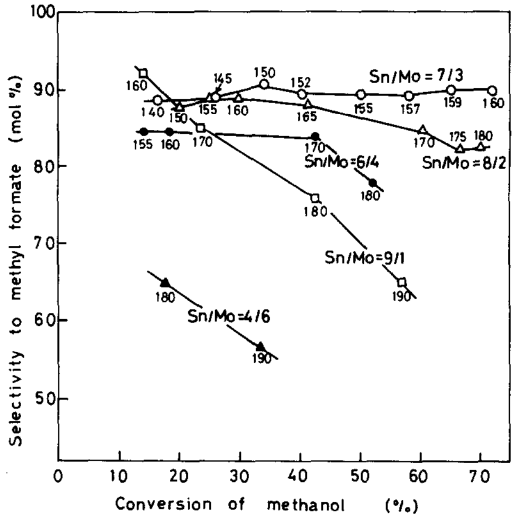

FIG. 2. Selectivity of $SnO_2$–$MoO_3$ catalysts to methyl formate as a function of the methanol conversion. Numeral denotes the reaction temperature.

### *Catalytic Property of the Sn/Mo = 7/3 Catalyst*

When the methanol conversion is low, methyl formate and formaldehyde are almost the sole products. Therefore, it seemed that it would be interesting to check the catalytic activity for the reactions of the two compounds, too.

Methanol, formaldehyde, and methyl formate were passed over the Sn/Mo = 7/3 catalyst (20 g) at fixed charge rates of oxygen and nitrogen of $4.0 \times 10^{-2}$ and $91 \times 10^{-2}$ mol/hr, respectively. The charge rates of methanol, formaldehyde, and methyl formate were $6.3 \times 10^{-2}$, $7.5 \times 10^{-2}$, and $4.1 \times 10^{-2}$ mol/hr, respectively. Formaldehyde was charged as about a 33 wt% aqueous

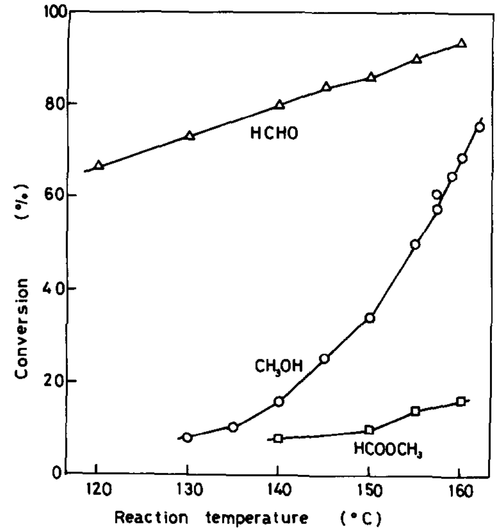

FIG. 3. Conversion as a function of the reaction temperature. Catalyst: Sn/Mo = 7/3.

solution. The overall conversions of the three compounds are plotted as a function of the reaction temperature in Fig. 3. It was found that formaldehyde is much more reactive, and methyl formate is much less reactive, than methanol over the catalyst.

The product distributions in the oxidation of methanol, the reaction of formaldehyde, and the reaction of methyl formate are shown in Figs. 4 and 5 and Table 2, respectively.

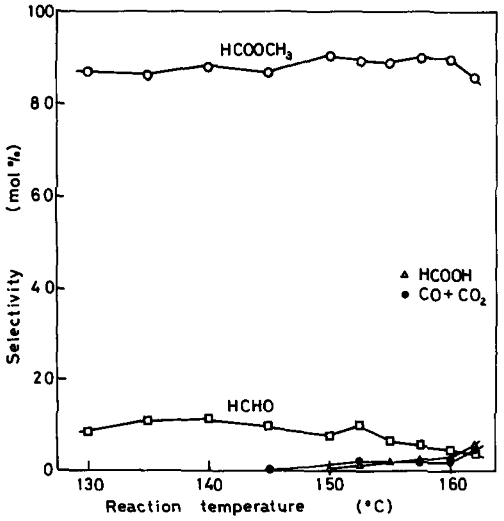

FIG. 4. Selectivity in the oxidation of methanol as a function of the reaction temperature. Catalyst: Sn/Mo = 7/3.

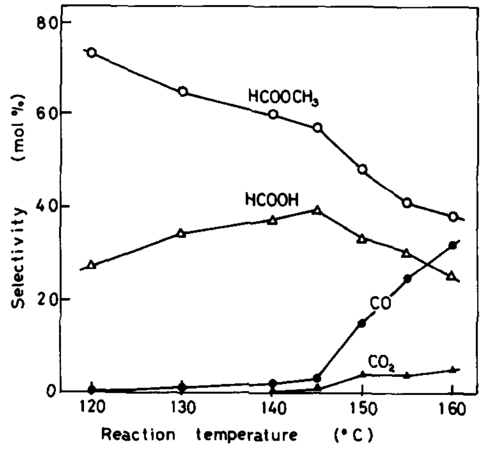

FIG. 5. Selectivity in the reaction of formaldehyde as a function of the reaction temperature. Catalyst: Sn/Mo = 7/3.

The results may be summarized as follows:

(i) The selectivity to methyl formate in the oxidation of methanol remains almost constant at 90 mol% under the present reaction conditions.

(ii) The selectivity to formaldehyde is about 10 mol% when the temperature is low and the conversion is low, and it decreases with an increase in the temperature.

(iii) The selectivities to formic acid, CO, and $CO_2$ are negligibly small when the temperature is low and the conversion is low,

TABLE 2

Reaction of Methyl Formate over the Sn/Mo = 7/3 Catalyst[a]

| Reaction temp. (°C) | $HCOOCH_3$ conv. (%) | Selectivity (mol%) to | | | |
|---|---|---|---|---|---|
| | | HCHO | HCOOH | CO | $CO_2$ |
| 140 | 8 | 12 | 71 | 13 | 4 |
| 150 | 10 | 11 | 53 | 30 | 6 |
| 155 | 14 | 11 | 47 | 36 | 6 |
| 160 | 16 | 11 | 44 | 39 | 6 |
| 165 | 20 | 10 | 37 | 45 | 8 |
| 170 | 24 | 9 | 30 | 53 | 8 |
| 175 | 35 | 7 | 22 | 62 | 9 |
| 180 | 45 | 6 | 15 | 69 | 10 |

[a] Catalyst = 20 g; feed gas: $HCOOCH_3 = 4.1 \times 10^{-2}$ mol/hr, $O_2 = 4.0 \times 10^{-2}$ mol/hr, $N_2 = 91 \times 10^{-2}$ mol/hr.

but they increase with an increase in the temperature.

(iv) The selectivity to methyl formate from formaldehyde is much lower than that from methanol, and it decreases with an increase in the temperature and the formaldehyde conversion.

(v) The selectivity to formic acid from formaldehyde is markedly higher than that from methanol, and it seems to pass through a maximum as the temperature increases.

(vi) The main product in the reaction of methyl formate is formic acid when the temperature is low and the conversion is low, and the selectivity to CO increases at the expense of a decrease in that to formic acid as the temperature increases.

### *Effect of the $SnO_2$–$MoO_3$ Composition on the Activity for the Dimerization of Formaldehyde*

The effect of the $SnO_2$–$MoO_3$ composition on the activity for the dimerization of formaldehyde to methyl formate (Tischenko reaction), 2 HCHO → $HCOOCH_3$, was studied under these conditions: $T$ = 120°C, catalyst = 10 g, formaldehyde–oxygen–nitrogen = $7.5 \times 10^{-2}$–$4.0 \times 10^{-2}$–1.88 mol/hr. The rate of methyl formate formation from formaldehyde is plotted in Fig. 1, together with the rate from methanol at 160°C.

The pure $SnO_2$ catalyst is scarcely active at all, but the activity sharply increases with an increase in the $MoO_3$ content, passes through a maximum at about Mo/(Sn + Mo) = 0.1, and then decreases.

### *Effects of Reaction Variables*

In order to ascertain the characteristic feature of the reaction from methanol or formaldehyde to methyl formate over the Sn/Mo = 7/3 catalyst, the effects of the reaction variables were studied.

*Effect of oxygen concentration.* The oxidation of methanol was carried out by changing the initial oxygen concentration from 1.3 to 6.0 vol%, while fixing the other conditions as: $T$ = 145°C, methanol = 3.4 vol%, and charge rate of nitrogen = 1.88 mol (about 45 liters at 20°C)/hr. The rate of methyl formate formation, as calculated from the low-level conversion (about 10%), was then compared. As may be seen in Fig. 6, the rate is completely independent of the oxygen concentration.

*Effect of methanol concentration.* The reaction was carried out by changing the initial methanol concentration from 1.25 to 9.0 vol%, while fixing the other conditions as: $T$ = 145°C, oxygen = 6.0 vol%, and charge rate of nitrogen = 1.88 mol/hr. The rate is plotted in Fig. 7. When the methanol concentration is low (less than 3 vol%), the rate increases with an increase in the methanol concentration, but with a further increase in the concentration, it remains the same.

*Effect of steam addition to feed gas.* The effect of steam on the methanol oxidation was tested by adding steam into the feed gas in the range of 0 to 10 vol%. The reaction conditions were: $T$ = 150°C, methanol–oxygen = 3.4–2.25 vol%, and charge rate of nitrogen = 1.88 mol/hr. As may be seen in Fig. 8, the rate decreases markedly with an increase in the concentration of steam.

*Effect of formaldehyde concentration.* The dimerization of formaldehyde was carried out by changing the initial formalde-

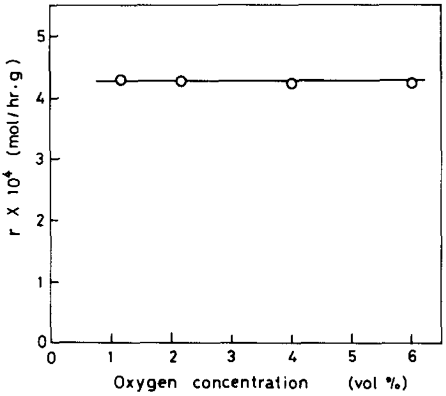

FIG. 6. Effect of oxygen concentration on the rate of methanol oxidation. Catalyst: Sn/Mo = 7/3; $T$ = 145°C; methanol = 3.4 vol%.

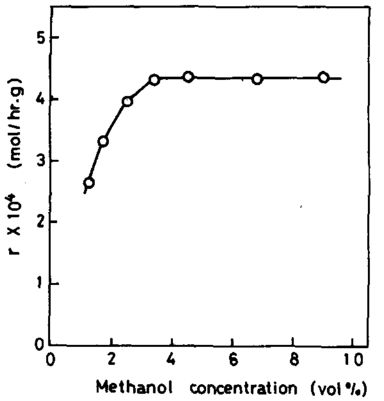

FIG. 7. Effect of methanol concentration on the rate of methanol oxidation. Catalyst: Sn/Mo = 7/3; $T$ = 145°C; oxygen = 6.0 vol%.

hyde concentration from 1.2 to 5.7 vol% (the steam/formaldehyde molar ratio was about 3.3), while fixing the other conditions as: $T$ = 130°C, catalyst = 8 g, and charge rate of air = 2.0 mol/hr. As may be seen in Fig. 9, the rate is proportional to the concentration, when the concentration is less than 3 vol%.

*Effect of methanol charge rate on the conversion and selectivity.* As is shown in Fig. 7, the rate of methanol oxidation is not affected by the methanol concentration when the concentration is more than 3 vol%. It can, therefore, be predicted that the higher the methanol charge rate (or the methanol concentration), the lower the fraction of methanol which will be converted at a fixed temperature and, as a result, the higher the temperature which will be required to achieve a fixed level of conversion. To check this thesis, the effect of the charge rate of methanol on the conversion and selectivity was studied (Table 3). It is evident that the methanol conversion varies depending on the methanol charge rate or the methanol concentration. However, the effect on the selectivity seems to be small.

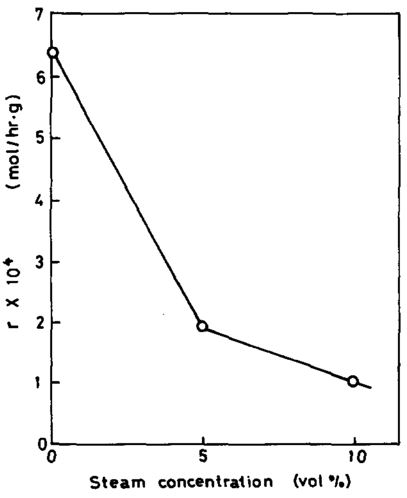

FIG. 8. Effect of steam addition to the feed gas on the rate of methanol oxidation. Catalyst: Sn/Mo = 7/3; $T$ = 150°C; methanol–oxygen = 3.4–2.25 vol%.

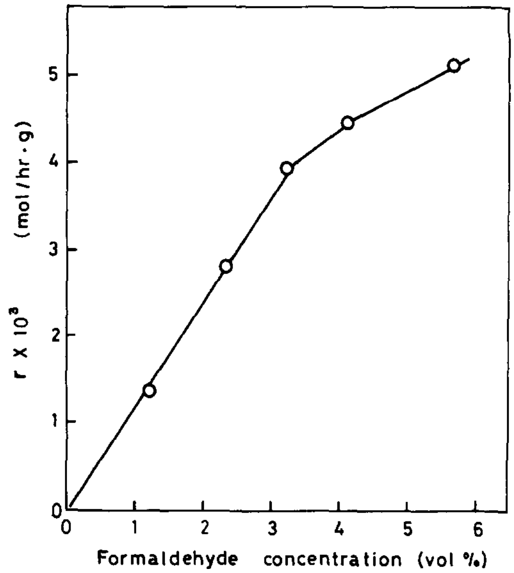

FIG. 9. Effect of formaldehyde concentration on the rate of formaldehyde dimerization. Catalyst: Sn/Mo = 7/3; $T$ = 130°C; charge of air = 2.0 mol/hr.

## DISCUSSION

Because the formation of formic acid is very small at a low level of methanol conversion, because it increases with an increase in the conversion, much as the formation of CO and $CO_2$ does (Fig. 4), and because much more formic acid is formed in the reactions of formaldehyde and methyl formate (Fig. 5 and Table 2), it seems unlikely that methyl formate is

TABLE 3

Effect of Methanol Concentration on the Conversion and Selectivity[a]

| $CH_3OH$ | | Reaction temp. (°C) | $CH_3OH$ conv. (%) | Selectivity (mol%) to | | | | |
|---|---|---|---|---|---|---|---|---|
| Charge (mol/hr) | Concn. (vol%) | | | $HCOOCH_3$ | HCHO | HCOOH | CO | $CO_2$ |
| $4.2 \times 10^{-2}$ | 4.4 | 160 | 76 | 91 | 4 | 2 | 2 | 1 |
| | | 162 | 83 | 90 | 4 | 3 | 2 | 1 |
| | | 164 | 89 | 89 | 4 | 3 | 3 | 1 |
| | | 166 | 94 | 84 | 4 | 5 | 4 | 1 |
| $8.4 \times 10^{-2}$ | 8.1 | 160 | 50 | 93 | 5 | 1 | 1 | 0 |
| | | 162 | 55 | 92 | 5 | 2 | 1 | 0 |
| | | 164 | 68 | 91 | 5 | 2 | 1 | 1 |
| | | 168 | 73 | 88 | 5 | 4 | 2 | 1 |
| | | 170 | 85 | 70 | 5 | 4 | 15 | 6 |
| $12.6 \times 10^{-2}$ | 11.7 | 172 | 68 | 88 | 5 | 3 | 3 | 1 |

[a] Catalyst (Sn/Mo = 7/3) = 20 g; charge: $O_2 = 4.0 \times 10^{-2}$ mol/hr, $N_2 = 91 \times 10^{-2}$ mol/hr.

formed via formic acid, as is shown in Eq. (1):

$$2\ CH_3OH \rightarrow HCHO + CH_3OH \rightarrow HCOOH + CH_3OH \rightarrow HCOOOH_3. \quad (1)$$

From the variation in the selectivity to formic acid shown in Figs. 4 and 5 and Table 2, it is likely that formic acid is formed from methyl formate and then decomposed to CO, as follows:

$$HCOOCH_3 \rightarrow 2\ HCOOH \rightarrow 2\ CO. \quad (2)$$

On the other hand, the findings that formaldehyde is dimerized selectively to methyl formate and that, moreover, the rate of this reaction is much more rapid than that of the methanol oxidation over the $SnO_2$–$MoO_3$ catalysts, suggest that methyl formate is formed via formaldehyde, as is shown in Eq. (3).

$$2\ CH_3OH \rightarrow 2\ HCHO \rightarrow HCOOCH_3. \quad (3)$$

However, a question arises as to the possibility of another route, such as the reaction of methanol with formaldehyde to form methyl formate, as is shown in Eq. (4).

$$2\ CH_3OH \rightarrow HCHO + CH_3OH \rightarrow HCOOCH_3. \quad (4)$$

To answer this question, a couple of tests were carried out. In the first test, a mixture of formaldehyde (aqueous solution) and methanol was passed over the Sn/Mo = 7/3 catalyst (12 g) with charge rates of HCHO = $7.5 \times 10^{-2}$ mol/hr and $CH_3OH = 4.1 \times 10^{-2}$ mol/hr. In the second, only formaldehyde ($7.5 \times 10^{-2}$ mol/hr) was passed. Other reaction conditions were the same: oxygen–nitrogen = $4.0 \times 10^{-2}$–1.88 mol/hr. The results of the two tests are compared in Fig. 10, where the runs with methanol are shown with open symbols and solid lines, and the runs without methanol are given with solid symbols and broken lines.

The results may be summarized as follows:

(i) The formation of methyl formate at lower temperatures is little affected by the presence of methanol.

(ii) A large amount of methylal is formed at lower temperatures according to Eq. (5), but the amount decreases more markedly than that of formaldehyde at temperatures above 140°C.

$$HCHO + 2\ CH_3OH \rightarrow CH_3OCH_2OCH_3 + H_2O. \quad (5)$$

(iii) The presence of methanol suppresses

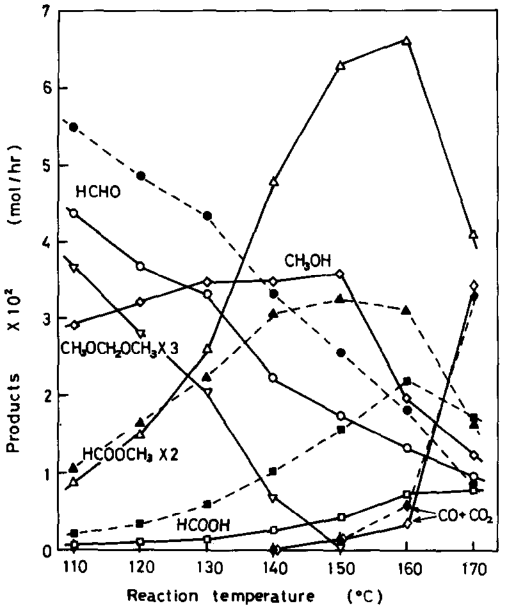

FIG. 10. Effect of methanol on the reaction of formaldehyde over Sn/Mo = 7/3 catalyst. Runs with methanol: open symbols and solid lines; runs without methanol: solid symbols and broken lines.

markedly the formation of formic acid from formaldehyde and, as a result, enhances the selectivity to methyl formate.

Then, methylal was also passed over the catalyst with the charge rate of 2.8 mol/hr (charge rate of carbon atom corresponds to 8.4 mol/hr). Other reaction conditions were the same as those used in the foregoing tests: catalyst = 12 g and oxygen–nitrogen = $4.0 \times 10^{-2}$–1.88 mol/hr. As may be seen in Fig. 11, the formation of methyl formate from methylal is lower than that from formaldehyde, indicating that in the reaction of methylal, methyl formate is formed from formaldehyde and methanol which are formed by decomposition of methylal.

In view of these findings, it is concluded that methyl formate is formed by the dimerization of formaldehyde. It is noticeable that the side reaction, i.e., the formation of formic acid from formaldehyde, is suppressed by the presence of methanol.

The $SnO_2$–$MoO_3$ catalysts with a low Mo content (Sn/Mo > 1/2) show a much higher catalytic activity for the dimerization of formaldehyde than for the reaction of methanol (Figs. 1 and 3). Since the rate of the dimerization is almost proportional to the formaldehyde concentration (Fig. 9), the amount of formaldehyde, which is determined by the balance between the rate of the formation and that of the dimerization, remains very small. The rate of methyl formate formation is practically limited by the first step, i.e., the oxidation of methanol to formaldehyde, which is itself controlled by the acidic function of the catalyst (*9*).

The acidity obtained from the amount of pyridine required to poison the isomerization activity for 1-butene at 160°C and the basicity obtained from the amount of $CO_2$ irreversibly adsorbed at 20°C, which were measured in our previous study (*12*), are shown as a function of the $SnO_2$–$MoO_3$ composition in Fig. 12. The catalytic activities for both dehydration and dehydrogenation of 2-propanol, which were measured as indices of the acidic and basic properties of the catalysts in our earlier study (*13*), are also shown in Fig. 12. The activity for the oxidation of methanol to methyl formate (Fig. 1) varies in the same fashion as the

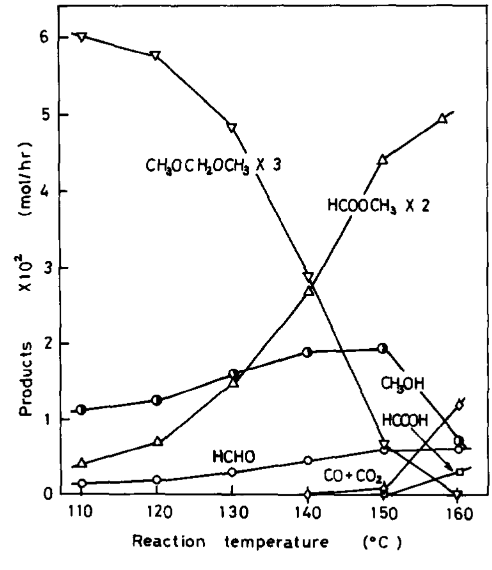

FIG. 11. Reaction of methylal over Sn/Mo = 7/3 catalyst. Catalyst = 12 g; charge: methylal–oxygen–nitrogen = $2.8 \times 10^{-2}$–$4 \times 10^{-2}$–1.88 mol/hr.

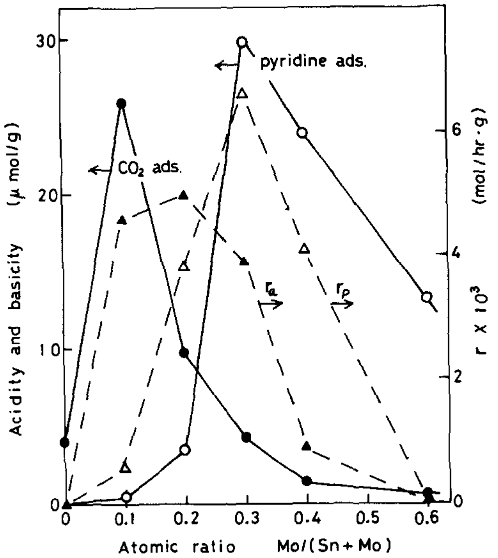

FIG. 12. Acidic and basic properties as a function of the $SnO_2$–$MoO_3$ composition. (○) Amount of pyridine required to poison the isomerization activity for 1-butene; (●) amount of $CO_2$ irreversibly adsorbed at 20°C; (△) activity for dehydration of 2-propanol at 140°C and 1.65 mol% 2-propanol in air: $r_p$; (▲) activity for dehydrogenation of 2-propanol at 140°C and 1.65 mol% 2-propanol in air: $r_a$.

acidity and the activity for 2-propanol dehydration, suggesting that the oxidation of methanol is controlled by the acidic function of the catalyst.

It is reasonable to consider that the catalysts showing a high selectivity to formaldehyde in the oxidation of methanol (for example, the V/Mo = 9/1 and Fe/Mo = 3/7 catalysts), are poor in catalytic function for the dimerization of formaldehyde to methyl formate. It may be seen in Table 1 that the catalysts with a lower $MoO_3$ content show a higher selectivity to methyl formate and a lower selectivity to formaldehyde, except for the $TiO_2$–$MoO_3$ catalysts, suggesting that the catalytic activity for the second step, i.e., the dimerization of formaldehyde (Tischenko reaction), is connected with the basic property of the catalyst.

The activity for the dimerization of formaldehyde (Fig. 1) varies in the same fashion as the basicity and the activity for the dehydrogenation of 2-propanol, which is ascribable to both the acidic and basic functions of a catalyst (*12*, *13*). This finding also supports the view that the basic property of a catalyst plays an important role in the dimerization activity. It should also be noted that some of the catalysts claimed in the patent literature to be useful for the dimerization consist of basic oxides (*11*).

However, it should be borne in mind that methanol is oxidized to $CO_2$ and water by the action of basic sites (*9*). For example, a great deal of methanol is oxidized to $CO_2$ and water at a relatively high temperature (280°C) over the Ti/Mo = 8/2 catalyst. Possibly the catalyst is deficient in acidic property and, as a result, is deficient in activity for formaldehyde formation, and possibly the total oxidation due to basic sites becomes considerable under severe conditions.

We are, therefore, led to the conclusion that the possession of an eminent function as both acid and base is required for a catalyst of methyl formate formation from methanol. It is, naturally, not easy to possess two opposite properties on the surface. We believe at present that the $SnO_2$–$MoO_3$ catalysts are the most likely to satisfy this requirement.

It should be noted that the $SnO_2$–$MoO_3$ catalysts, notably the Sn/Mo = 7/3 catalyst (*13*), give the best results for acetone formation from propylene; which was first found by Buiten (*15*). Therefore, it seems that the requirement for a catalyst is the same for both acetone formation from propylene and methyl formate formation from methanol.

It has still remained unresolved why a great deal of methanol is suddenly converted to by-products above a certain level of methanol conversion. Further detailed studies are necessary to answer the question.

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