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The Reaction of Formaldehyde on Various Metal Oxide Catalysts

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Formaldehyde was passed over various single and binary oxide catalysts in an oxidizing atmosphere. The primary products were methyl formate and formic acid, while, by the consecutive reactions of these products, methanol, CO, and CO_2 were formed. The MoO_3- and V_2O_5-based oxides are relatively inactive for the reaction of formaldehyde. Methanol is not obtained with V_2O_5- and MoO_3-containing catalysts. An enhanced yield of formic acid is obtained with V_2O_5-based catalysts. The best result for the formation of methyl formate is obtained with the Sn/W = 67/33 (atomic ratio) catalyst, which shows a very low activity for the oxidation of methanol. The second-best result is obtained with the Sn/Mo = 70/30 catalyst. When the catalysts are a little more basic—for example, pure SnO_2, SnO_2–K_2O, pure Al_2O_3, Al_2O_3–K_2O, pure Fe_2O_3, Fe_2O_3–K_2O, and TiO_2–K_2O, the methyl formate reacting with formaldehyde tends to decompose to methanol and CO_2. On the other hand, when the catalysts are a little more acidic—for example, TiO_2–WO_3 and TiO_2–P_2O_5, the methyl formate tends to decompose to methanol and CO.

INTRODUCTION

It is well known that methanol is oxidized selectively to formaldehyde with many MoO_3- and V_2O_5-based catalysts. However, we showed in a preceding paper (*1*) that methanol is oxidized selectively to methyl formate with the Sn/Mo = 70/30 (atomic ratio) catalyst and that this catalytic function is attributable to the possession of both the acidic and the basic properties required to catalyze the dimerization of formaldehyde (Tischenko reaction).

In practice, methyl formate is manufactured by the dimerization of formaldehyde over Cu, PbO, or Fe_2O_3 catalysts in the absence of oxygen (*2*). However, no scientific report on the catalytic action of metal oxides for this reaction has yet been published. As for the Tischenko reaction of benzaldehyde, Tanabe and Saito (*3*) have reported that a Lewis acid site and a basic site play important roles as active sites in the case of a heterogeneous reaction.

In this study, we focused our attention on the reaction of formaldehyde and attempted to clarify the catalytic action of metal oxides for this reaction. Because many oxides of transition metals are reduced by formaldehyde during the reaction and, as a result, lose their catalytic action the present study was carried out mainly in an oxidizing atmosphere, though the participation of oxygen in the reaction is not desirable.

EXPERIMENTAL

Reaction procedures. The reaction of formaldehyde was carried out with a conventional continuous-flow system. The reactor and the experimental procedures were almost the same as those employed in a earlier work (*4*). Oxygen–nitrogen mixed gases were fed in from the top of the reactor and an about 33 wt% formaldehyde aqueous solution was introduced into a preheating section of the reactor by means of an infusion syringe pump. The feed rates of reactants were formaldehyde–oxygen–nitrogen–steam = 7.5×10^{-2}–4.0×10^{-2}–91×10^{-2}–25×10^{-2} mole per hour, and the amount of catalyst used was 15 g, unless otherwise indicated. The effluent gas from the reactor was led successively into four chilled water-scrubbers to recover the wa-

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ter soluble compounds. At the end of 1 hr, the contents of the water-scrubbers were collected (300 ml). The reaction products were analyzed by gas chromatographs. The gaseous products were intermittently analyzed by a 6-m column of propylene carbonate (CO_2 and dimethyl ether) and a 1-m column of molecular sieve 13X (CO). The aqueous products were sampled by use of a microsyringe and analyzed by a 2-m column of PEG 20M kept at 100°C (dimethyl ether, methylal, methyl formate, and methanol) and a 1-m column of AT-1200 + H_3PO_4 kept at 130°C (acids). The formic acid was also analyzed by titration with 0.1 *N* NaOH. The formaldehyde was analyzed by means of iodometry (*5*).

Catalysts. The catalysts used in the study were various single and binary oxides. Many of them were the same as those used in our previous works (*4, 6–8*); they were supported on natural pumice and calcinated in air or oxygen at 500°C.

RESULTS

SnO_2-*Based Oxides*

Preliminary catalyst-screening tests revealed that interesting results are obtained with SnO_2-, Fe_2O_3-, TiO_2-, Al_2O_3-, and V_2O_5-based oxides. The reaction of formaldehyde was studied in detail with these oxides. The reaction conditions were fixed as presented in the Experimental section. First of all, the SnO_2-based oxides were dealt with.

The change in the yield of each product with an increase in the extent of reaction, a change attributable to the elevation of the reaction temperature, was studied. The main products were methyl formate, formic acid, methanol, CO, and CO_2; the amounts of methylal and ether were less than 1 mol% under the conditions used here. The results obtained in the case of a pure SnO_2 catalyst are shown in Fig. 1. Formic acid is formed in parallel with methyl formate, though the amount of the former is much smaller than that of the latter. Both products pass through a maximum at a formaldehyde conversion of about 50%. With a further increase in the extent of the reaction, the formation of methanol, CO_2, and CO rapidly increases at the expense of a decrease in the amounts of methyl formate and formic acid. It is clear that methanol and carbon oxides are formed by the consecutive degradation of methyl formate and formic acid. The selectivity to methyl formate is about 70 mol%, and the formation of carbon oxides is small, when the extent of the reaction is less than 40%. However, because of the consecutive reaction, the yield of methyl formate cannot exceed 33 mol%.

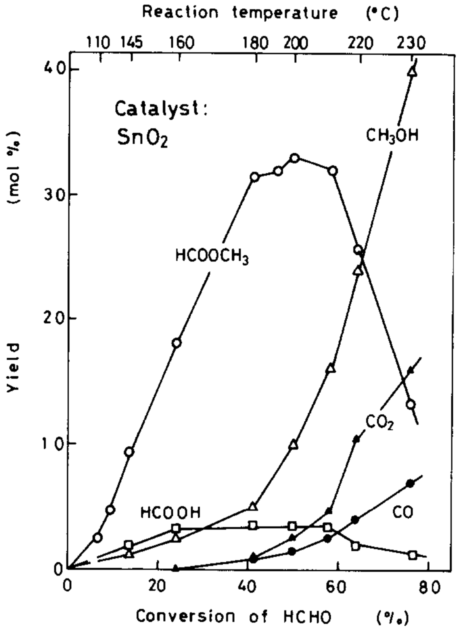
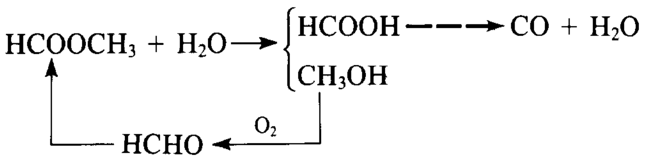


FIG. 1. Reaction of formaldehyde on the SnO_2 catalyst.

Figure 2 shows the profile of the reaction products in the case of the Sn/W = 67/33 (atomic ratio) catalyst. With the addition of WO_3 to SnO_2, the activity strongly increases and the formation of formic acid and the consecutive degradation of methyl formate and formic acid are markedly suppressed. The selectivity to methyl formate is about 80 mol% up to the formaldehyde conversion of 70%. The yield of methyl formate attains 57 mol%.

MoO_3 was then added to SnO_2 in the place of WO_3 (Fig. 3). The overall activity of the Sn/Mo = 70/30 catalyst is almost the same as that of the Sn/W = 67/33 catalyst, but the product distribution is not the same. The formation of methanol was not observed. The amounts of methylal and ether were negligibly small. Possibly, the methanol producted is immediately oxidized to formaldehyde. The shape of the formic acid curve indicates that a part of the formic acid is formed by the consecutive decomposition of methyl formate as follows:



$$HCOOCH_3 + H_2O \longrightarrow \begin{cases} HCOOH \longrightarrow CO + H_2O \\ CH_3OH \end{cases} \qquad CH_3OH \xrightarrow{O_2} HCHO \longrightarrow HCOOCH_3 \quad (1)$$

The initial selectivity to formic acid is also higher than that of the Sn/W = 67/33 catalyst.

Then, the effect of V_2O_5 addition was studied (Fig. 4). The Sn/V = 60/40 catalyst shows an activity a little lower than that of the Sn/W = 67/33 and Sn/Mo = 70/30 catalysts. The formation of formic acid is enhanced from the initial stage of the reaction, and a remarkable amount of CO_2 is formed, even in a low range of conversion, 20%. The yield of methyl formate cannot exceed 23 mol%. The formation of methanol is not observed, much as in the case of the Sn/Mo = 70/30 catalyst.

TiO_2-Based Oxides

As an example of TiO_2-based oxides, the

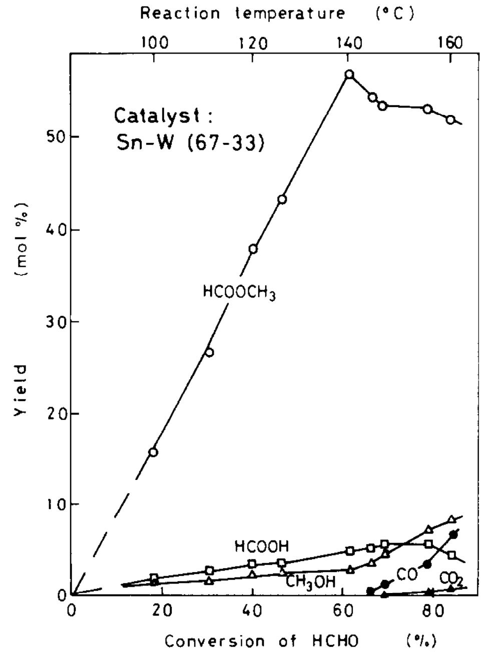


FIG. 2. Reaction of formaldehyde on the Sn/W = 67/33 catalyst.

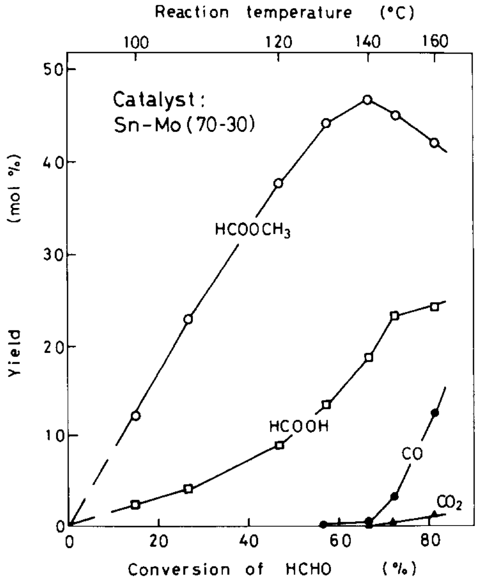


FIG. 3. Reaction of formaldehyde on the Sn/Mo = 70/30 catalyst.

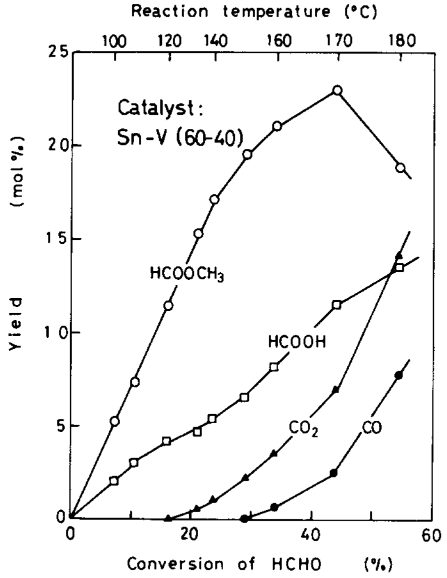


FIG. 4. Reaction of formaldehyde on the Sn/V = 60/40 catalyst.

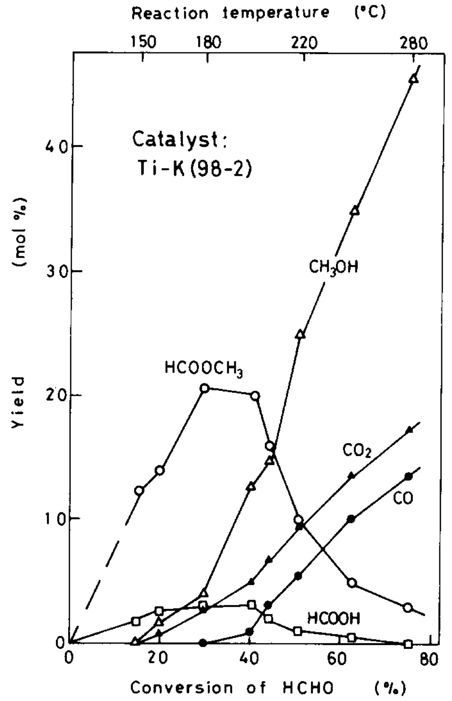


FIG. 5. Reaction of formaldehyde on the Ti/K = 98/2 catalyst.

Ti/K = 98/2 catalyst was chosen (Fig. 5). When the extent of the reaction is low, methyl formate and formic acid are the sole products, and the amount of formic acid is much lower than that of methyl formate, much as in the cases of the SnO_2-based oxides. However, the consecutive reaction of methyl formate and formic acid is much more significant with the TiO_2–K_2O catalyst than with the SnO_2-based catalysts.

Al_2O_3-Based Oxides

Pure Al_2O_3 was studied, as an example of Al_2O_3-based oxides (Fig. 6). The results indicate that methanol and CO_2 are formed by the consecutive reaction of methyl formate.

V_2O_5-Based Oxides

As an example of V_2O_5-based oxides, the V/Ti = 90/10 catalyst was studied (Fig. 7). Methyl formate and formic acid are the sole products when the extent of the reaction is low, while CO and CO_2 are formed by the consecutive decomposition of methyl formate and formic acid. It should be noted that the formation of formic acid is greater than that of methyl formate. No methanol was obtained, just as in the cases of other V_2O_5- or MoO_3-containing catalysts (Figs. 3 and 4).

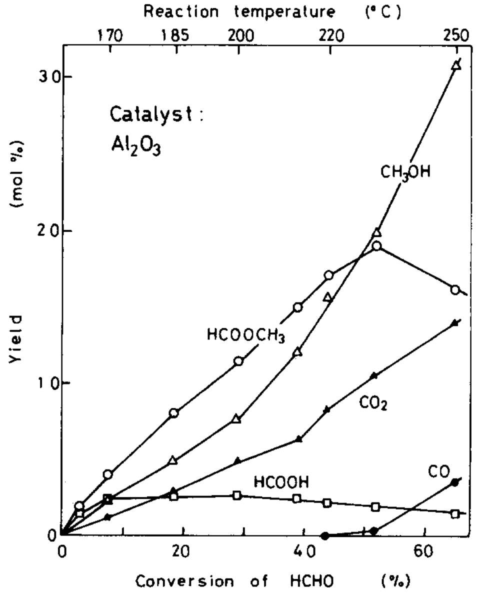


FIG. 6. Reaction of formaldehyde on the Al_2O_3 catalyst.

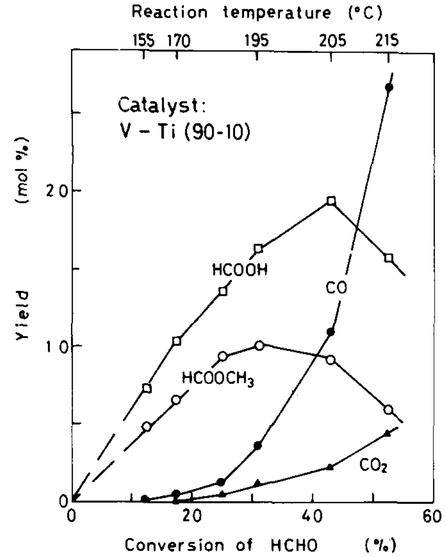


FIG. 7. Reaction of formaldehyde on the V/Ti = 90/10 catalyst.

Reaction of Methyl Formate

It is evident from the results described above that the primary products in the reaction of formaldehyde are methyl formate and formic acid, irrespective of the difference in catalyst. The reaction of formic acid over various metal oxides has already studied (*7*); formic acid is decomposed to CO on acidic oxides and to CO_2 on basic oxides.

Therefore, it seems necessary to clarify the reaction of methyl formate over different metal oxides. The reaction of formaldehyde was conducted in the presence of steam, because it is very hard to charge quantitatively a water-free formaldehyde in the case of a flow reaction system. For this reason, the reaction of methyl formate was studied in the presence of steam.

First, the decomposition of methyl formate was performed with the pure SnO_2 and Al_2O_3 and Ti/K = 98/2 oxide catalysts. The reaction conditions were methyl formate–oxygen–nitrogen–steam = 4.1×10^{-2}–4.0×10^{-2}–91×10^{-2}–25×10^{-2} mole per hour, catalyst = 15 g. The results are shown on the left-hand side of Figs. 8 to 10.

The formation of CO_2 is much lower than that of CO, and the amount of CO is almost equal to the amount of methanol, indicating that methyl formate is decomposed to methanol and formic acid, and that the formic acid is then decomposed to CO, for example,

$$HCOOCH_3 + H_2O \rightarrow \begin{cases} HCOOH \rightarrow CO + H_2O \\ CH_3OH \end{cases} \qquad (2)$$

However, this finding is not consistent with the results obtained in the reaction of formaldehyde (Figs. 1, 5, and 6); that is, CO_2 rather than CO is formed in the reaction of formaldehyde.

Next, formaldehyde was charged together with methyl formate. The charge rates were methyl formate–formaldehyde–oxygen–nitrogen–steam = 3.4×10^{-2}–7.5×10^{-2}–4.0×10^{-2}–91×10^{-2}–25×10^{-2} mole per hour. The results are shown on the right-hand side of Figs. 8 to 10. With addition of formaldehyde, the formation of methanol and CO_2 increases, while that of CO decreases, except for the case of the Ti/K = 98/2 catalyst.

Methanol obtained from a reaction other than that shown by Eq. (2) can be estimated from the difference between the formations of methanol and CO. It should be noted that this value is about twice that of the CO_2 formation. This finding is in conformity with the stoichiometry for the following reaction:

$$HCOOCH_3 + HCHO + H_2O \rightarrow 2CH_3OH + CO_2 \qquad (3)$$

Thus, it is considered that, in the presence

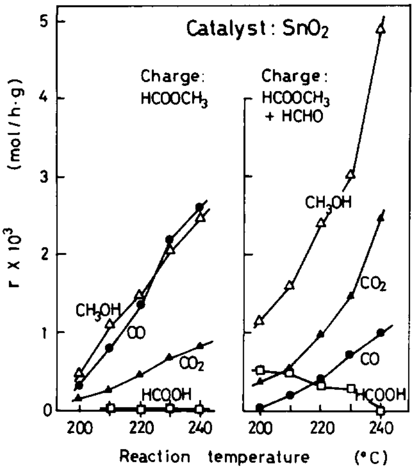


FIG. 8. Decomposition of methyl formate on the SnO_2 catalyst. Left-hand side, in the absence of formaldehyde; right-hand side, in the presence of formaldehyde.

of formaldehyde, methyl formate is decomposed according to Eq. (3) as well as according to Eq. (2).

On the other hand, in the case of catalysts containing V_2O_5 or MoO_3, methanol is not obtained because of the quick oxidation of methanol. However, the mode of methyl-formate decomposition may be estimated from the amounts of CO_2 and CO, though a part of the CO and CO_2 is formed from formic acid. For example, in the case of the Sn/V = 60/40 catalyst (Fig. 4), methyl formate is decomposed mainly by Eq. (3), while in the cases of the V/Ti = 90/10 and Sn/Mo = 70/30 catalysts (Figs. 7 and 3), methyl formate is decomposed by Eq. (2).

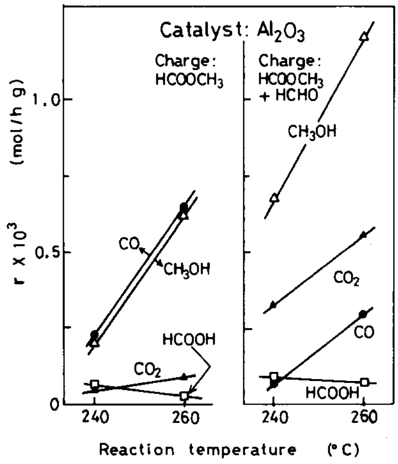


FIG. 9. Decomposition of methyl formate on the Al_2O_3 catalyst. Left-hand side, in the absence of formaldehyde; right-hand side, in the presence of formaldehyde.

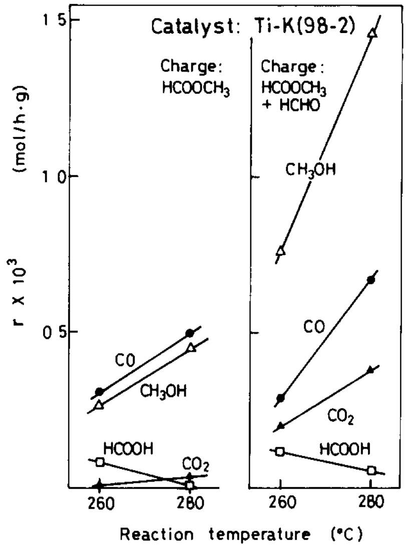


FIG. 10. Decomposition of methyl formate on the Ti/K = 98/2 catalyst. Left-hand side, in the absence of formaldehyde; right-hand side, in the presence of formaldehyde.

Comparison of the Catalyst Performances of Various Oxides

Since little information has been reported about the reaction of formaldehyde, it seemed necessary to make a character sketch of the catalyst activity. Therefore, a series of experiments was carried out using various kinds of single and binary metal-oxide catalysts. The reaction conditions were fixed as presented in the Experimental section. The main products were methyl formate, formic acid, methanol, CO, and CO_2; the amounts of methylal and ether were less than 3 mol%. The results are listed in Tables 1 and 2, according to the classification of the metal oxide in view of both the acid–base and oxidizing function (9). As an index of relative activities of each catalyst, the reaction temperature required

TABLE 1

Catalytic Activity of Metal Oxides for Reaction of Formaldehyde (I)

Catalyst (atomic ratio)		Temperature (°C)	Conversion (mol%) of HCHO to					
			MF[a]	FA[b]	MeOH[c]	CO	CO_2	Total
W		300	0.3	0.0	1.5	2.1	0.8	4.7
W–V	90–10	300	0.6	0.0	0.0	5.3	0.6	6.5
W–P	90–10	300	0.0	0.0	0.0	12.5	1.2	13.7
W–K	90–10	300	0.4	0.0	3.0	2.4	0.8	7.6
W–Ni	90–10	300	0.0	0.0	3.0	8.0	1.1	12.1
W–Ti	90–10	230	8.0	1.3	4.3	5.0	0.5	19.1
W–Fe	90–10	230	5.1	0.9	3.0	10.0	0.1	19.1
W–Sn	90–10	200	19.8	3.5	3.0	1.0	0.2	27.5
Mo		300	0.1	0.3	0.0	0.0	0.4	0.8
Mo–K	90–10	300	0.1	0.0	0.0	0.2	0.3	0.6
Mo–Ni	90–10	300	1.0	0.0	0.0	2.3	0.4	3.7
Mo–Fe	90–10	300	0.6	0.2	0.0	2.2	0.2	3.7
Mo–Co	90–10	300	0.0	0.4	0.0	3.0	0.6	4.0
Mo–Bi	90–10	300	0.0	0.1	0.0	0.4	6.5	7.0
Mo–V	90–10	300	0.0	0.7	0.0	10.0	0.7	11.4
Mo–P	90–10	300	2.5	0.0	0.0	10.0	0.4	12.7
Mo–Ti	90–10	270	2.8	1.3	0.0	11.3	0.6	16.0
Mo–Sn	90–10	220	11.1	6.5	0.0	6.5	1.6	25.7
V		260	3.4	4.5	0.0	12.7	1.7	22.3
V–Mo	90–10	260	1.4	2.1	0.0	13.0	0.4	16.9
V–K	90–10	260	2.8	5.9	0.0	12.5	5.3	26.5
V–Fe	90–10	230	4.0	4.1	0.0	6.3	0.3	14.7
V–Ni	90–10	230	6.6	6.3	0.0	5.5	1.1	19.5
V–Sn	90–10	230	6.8	9.8	0.0	2.5	2.1	21.2
V–Ti	90–10	200	12.0	19.0	0.0	3.5	1.6	36.1
U		300	5.7	1.6	1.5	0.9	2.7	12.4
U–Mo	90–10	300	4.0	1.2	3.0	1.9	1.7	11.8
U–K	90–10	300	6.3	1.0	6.0	0.6	5.1	19.0
Al		225	19.8	2.2	18.	0.4	9.2	49.6
Al–Mo	90–10	225	2.8	1.4	4.	0.3	1.5	10.0
Al–K	90–10	225	12.8	2.2	15.	0.0	8.5	38.2
Zn		275	0.6	2.2	1.0	0.0	1.8	5.6
Zn–Mo	90–10	275	0.8	2.7	4.	0.0	1.8	9.3
Zn–K	90–10	275	0.3	2.0	0.0	0.0	2.4	4.7

[a] MF = methyl formate.

[b] FA = formic acid.

[c] MeOH = methanol.

to achieve an appropriate conversion of formaldehyde is shown in the third column.

The results may be summarized as follows:

(i) The catalysts based on an acidic oxide, such as WO_3, MoO_3, V_2O_5, and U_3O_8, are relatively inactive for the reaction of formaldehyde, indicating that these catalysts are effective for the formation of formaldehyde from methanol.

(ii) The addition of a small amount of SnO_2 or TiO_2, and sometimes also Fe_2O_3 and NiO, to an acidic oxide markedly increases the catalytic activity. This leads us

TABLE 2

Catalytic Activity of Metal Oxides for Reaction of Formaldehyde (II)

Catalyst (atomic ratio)		Temperature (°C)	Conversion (mol%) of HCHO to					
			MF[a]	FA[b]	MeOH[c]	CO	CO_2	Total
Sn		180	31.5	3.8	5.4	0.3	1.7	42.7
Sn–Mo	70–30	150	48.5	13.0	0.0	4.0	0.5	66.0
Sn–V	90–10	180	17.0	3.3	0.0	1.2	6.2	27.7
	80–20	180	18.3	3.3	0.0	1.2	6.3	29.1
	60–40	180	8.0	3.5	0.0	31.	27.	69.5
	60–40	160	21.	8.0	0.0	3.5	0.8	33.3
Sn–W	90–10	180	32.4	4.4	4.	8.0	1.4	50.2
	70–30	180	47.	4.0	8.	10.0	2.1	71.1
	50–50	180	38.	4.4	6.	6.	1.1	55.5
	30–70	180	25.5	3.4	4.	7.	1.1	41.0
Sn–P	90–10	220	8.6	3.2	0.0	1.5	0.4	13.7
Sn–K	90–10	220	7.7	1.0	17.0	0.1	10.6	36.4
Ti		275	10.	1.1	23.	20.	6.1	70.2
Ti–Mo	90–10	275	3.4	1.0	3.	5.5	5.2	18.1
Ti–W	93– 7	275	2.9	0.0	34.	19.4	10.3	66.6
Ti–P	96– 4	275	1.1	0.0	44.	32.	7.8	84.9
Ti–K	94– 6	275	5.4	0.0	33.	2.4	22.0	62.8
Ti–V	90–10	210	13.1	14.5	0.0	17.0	14.2	58.8
Fe		260	21.4	7.0	14.0	1.5	5.1	56.0
Fe–Mo	98– 2	260	15.2	6.0	0.0	10.	1.8	33.0
Fe–P	98– 2	260	23.4	4.3	22.	6.5	6.3	62.4
Fe–K	99– 1	260	30.0	4.4	13.	1.5	4.1	53.0
Fe–W	90–10	230	24.3	3.4	9.	7.5	2.3	46.5
Fe–V	98– 2	210	22.7	5.8	0.0	1.7	6.5	36.7
Bi		200	4.3	1.0	0.0	0.0	7.3	12.6
Bi–Mo	90–10	200	5.4	1.1	1.0	0.0	2.8	10.3
	50–50	250	3.4	1.7	0.0	0.0	2.1	7.2
Bi–K	90–10	200	1.3	0.4	0.0	0.0	8.7	10.4
Cu		180	0.6	1.8	0.0	0.0	15.3	17.7
Cu–Mo	90–10	225	4.3	2.3	0.0	0.0	6.9	13.5
Mn		240	6.6	2.0	3.0	0.0	7.3	18.9
Cr		250	0.6	0.2	3.0	0.0	3.8	7.6
Mg		275	0.3	0.0	0.0	0.0	3.0	3.3

[a] MF = methyl formate.

[b] FA = formic acid.

[c] MeOH = methanol.

to estimate that the basic property is effectively fortified by these additives, without a serious loss in the acidic properties.

(iii) For the production of methyl formate, SnO_2-based catalysts, notably SnO_2–WO_3 and SnO_2–MoO_3, are the most favorable. The next best are Fe_2O_3- and Al_2O_3-based catalysts.

(iv) The formation of methanol is the largest in the case of TiO_2-based catalysts. In the cases of Fe_2O_3- and Al_2O_3-based catalysts also, a large amount of methanol is formed.

(v) The formation of methanol is very small when the catalyst contains either V_2O_5 or MoO_3. This may be understood in terms of the high catalytic activity of these oxides for the oxidation of methanol (4).

(vi) Considerable formic acid is formed in the case of V_2O_5-based catalysts.

(vii) The formation of formic acid is relatively low when considerable methanol is formed. This may be due to the fact that the formation of formic acid by oxidation of formaldehyde is suppressed by the presence of methanol (*1*).

(viii) As for the degradation products, CO is mainly formed with acidic oxides, while CO_2 is formed with basic oxides, and both CO and CO_2 are formed with the intermediate oxides. This finding is in conformity with the results obtained in the case of the decomposition of formic acid (*7*).

(ix) Bi_2O_3- and CuO-based oxides show a high activity, but the main product is CO_2. Also, no favorable results can be expected from ZnO-, MnO_2-, Cr_2O_3-, MgO-, and K_2O-based oxides.

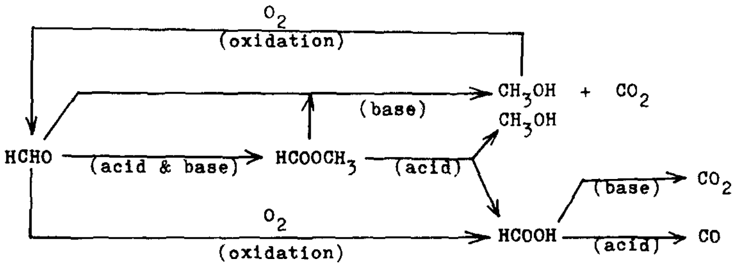
DISCUSSION

Let us now study the decomposition of methyl formate, which is closely related to the yield of methyl formate. As may be seen in Tables 1 and 2, pure Al_2O_3, Al_2O_3–K_2O, pure SnO_2, SnO_2–K_2O, TiO_2–K_2O, pure Fe_2O_3, and Fe_2O_3–K_2O give considerable amounts of both methanol and CO_2, indicating that these oxides are fairly active for the reaction of Eq. (3). Naturally, these oxides are not satisfactory as catalysts for the formation of methyl formate. It should be noted that these oxides are a little too basic, though both acidic and basic properties are required for the dimerization of formaldehyde to methyl formate (*1, 3*).

On the other hand, in the cases of the SnO_2–WO_3, SnO_2–MoO_3, SnO_2–P_2O_5, pure TiO_2, TiO_2–WO_3, TiO_2–P_2O_5, Fe_2O_3–MoO_3, Fe_2O_3–P_2O_5, and Fe_2O_3–WO_3 catalysts, methyl formate is decomposed by the reaction of Eq. (2) rather than by the reaction of Eq. (3). It is therefore considered that the reaction of Eq. (3) is promoted by basic sites; for this reason, the catalytic activity for this reaction is suppressed by the addition of acidic compounds, such as WO_3, MoO_3, and P_2O_5. It should be also noted that pure TiO_2 is more acidic than pure SnO_2 and Fe_2O_3 (*6, 7, 9*). However, in the cases of the TiO_2–WO_3 and TiO_2–P_2O_5 catalysts, the formation of methyl formate is very low; the main products are methanol and CO. It is also considered that when the catalysts are too acidic and are lacking in the basic property the activity for the reaction of Eq. (2), which is promoted by acidic sites, becomes more noticeable than the activity for the dimerization of formaldehyde to methyl formate.

We would like to consider that the best results for the formation of methyl formate are obtained with the SnO_2–WO_3 and SnO_2–MoO_3 catalysts, because they possess both acidic and basic properties in just the manner proper to promote the dimerization.

The SnO_2–WO_3 catalyst is much less active than the SnO_2–MoO_3 catalyst for the formation of methyl formate from methanol, for the SnO_2–WO_3 catalyst is lacking in oxidizing function (*1*). This lack of oxidizing function is beneficial for avoiding the side reaction; that is, the oxidation of formaldehyde to formic acid. It is concluded



that the most favorable catalyst for the formation of methyl formate from formaldehyde is the SnO_2–WO_3 catalyst.

For the moment, we believe that the following sequence of reactions best represents what is occurring during the process.

Amphoteric oxides, such as Al_2O_3-, SnO_2-, TiO_2-, and Fe_2O_3-based oxides, may be classified in view of the catalytic action for the formation of methyl formate as follows

(1) Oxides with oxidation activity (V- or Mo-containing oxides); oxidation of HCHO to HCOOH decreases the yield of $HCOOCH_3$.

(2) Oxides with low oxidation activity:

- (a) Oxides deficient in acidic property (Al, Al–K, Sn, Sn–K, Ti–K, Fe, Fe–K); the reaction of Eq. (3) decreases the yield of $HCOOCH_3$.
- (b) Oxides deficient in basic property (Sn–P, Ti, T–W, Ti–P); the reaction of Eq. (2) decreases the yield of $HCOOCH_3$.
- (c) Oxide proper in both acid and base (Sn–W).

In succeeding papers, we will describe the reaction of formaldehyde in the absence of oxygen.

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