Catalytic Decomposition of Methyl Formate in the Presence of Transition Metal Complexes, Phosphine Ligands and Water

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Abstract—The catalytic decomposition of methyl formate into gaseous components in the presence of transition metal complexes, phosphine ligands, and water has been studied. It has been shown that in the presence of monometallic and bimetallic Rh/Ru catalysts, methyl formate can be converted to gas mixtures with high hydrogen content. These mixtures are suitable for use in hydroformylation, hydroaminomethylation, and hydroformylation—acetalization reactions; therefore, methyl formate may be thought of as being an alternative source of synthesis gas in oxo processes.

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The attention of researchers is currently attracted to the use of alternative sources of synthesis gas, such as methyl formate (MF), formaldehyde, and formic acid, for the implementation of various processes involving carbon monoxide [1-3]. It is known that the catalytic decomposition of MF in the presence of water (a variety of the water-gas shift reaction) leads to the formation of a gas mixture, the main components of which are carbon monoxide and hydrogen. Owing to the availability and relatively low cost of MF, this material is promising for a more common use as a feedstock for petroleum chemistry. The use of MF for the implementation of hydroformylation reactions and hydroformylation-acetalization and hydroaminomethylation tandem reactions is based on the possibility of converting it to carbon monoxide and, under certain conditions, a mixture of carbon monoxide, carbon dioxide, and hydrogen (Fig. 1).

The aim of this study is to analyze the composition of the gas mixture formed during the MF decomposition as a function of process conditions, namely, the catalyst composition, the presence of ligands, and the amount of water in the reaction mixture.

EXPERIMENTAL

Methyl formate; the phosphine ligands $P(Cy)_3$, PPh_3 , $P(OPh)_3$, Xantphos, and TPPTS; and diethylamine HNEt₂ and triethylamine NEt₃ (Sigma-Aldrich) were used as received. Solvents were prepared in accordance with standard procedures. The studied transition metal complexes were synthesized as described in the literature: $Rh(acac)(CO)_2$ [4], $Ru_3(CO)_{12}$, [5], $Rh(cod)_2BF_4$ [6], and $Co(acac)_3$ [7].

Gas-liquid chromatography analysis was conducted on an HP-6990 chromatograph equipped with a flame ionization detector and a 50-m-long capillary column coated with the SE-30 phase using temperature programming and helium as the carrier gas.

Infrared spectra of the complexes were recorded on a Nicolet IR200 FTIR spectrometer in the range of $300-4000 \text{ cm}^{-1}$. The samples were pelletized in potassium bromide (2%).

Gas chromatography analysis was conducted on a Chrom-5 chromatograph equipped with a thermal conductivity detector and a 3-m-long packed column coated with the Porapak-Q phase at a temperature of 25°C using argon as the carrier gas.

General Procedure for Methyl Formate Decomposition

The decomposition was run in a 7-mL steel autoclave in a temperature range of 130–200°C. The autoclave was charged with 2.0 mL (32 mmol) of MF and required amounts of a metal (iron, manganese, nickel, cobalt, ruthenium, rhodium, palladium) complex, a donor ligand (PPh₃, PCy₃, HNEt₂, Xanthos, TPPTS), and water in amounts of 0.0156–0.025, 0.16–0.4, and 1.6–2.8 mmol, respectively. After that, the autoclave was closed and heated to a required temperature. Reaction was run with constant stirring for a



Fig. 1. Hydroformylation and tandem reactions based on hydroformylation using MF as an alternative source of synthesis gas.

given time (2 h). After that, the autoclave was cooled to room temperature, and the composition of the resulting gas mixture was determined by gas chromatography. Gases were sampled using a non-return water valve. The liquid phase was analyzed using an internal standard (ethanol).

RESULTS AND DISCUSSION

It is known that the following processes can occur during the thermal decomposition of MF ($100-200^{\circ}$ C) [8-10]:

$$\text{HCOOCH}_3 \to \text{CO}_2 + \text{CH}_4, \tag{1}$$

 $HCOOCH_3 \rightarrow CO + CH_3OH,$ (2)

$$\text{HCOOCH}_3 \rightarrow \text{CO} + 2\text{H}_2.$$
 (3)

Decomposition via route (1) is thermodynamically most favorable; however, this version is of the least interest for the implementation of other reactions. The most thoroughly studied process is decomposition to carbon monoxide and methyl alcohol (route (2)), i.e., decarbonylation that occurs in the presence of catalysts based on transition metal compounds [11–15]. The catalytic decomposition of MF in the presence of water (a variety of the water-gas shift reaction) leads to the formation of a gas mixture, the main components of which are carbon monoxide and hydrogen (3). The presence of water in the reaction system ensures the occurrence of the following stages of decomposition of the ester [16]:

$$HCOOCH_3 \rightarrow CO + CH_3OH, \qquad (2)$$

$$CO+H_2O \to CO_2 + H_2, \tag{4}$$

$$HCOOCH_3 + H_2O \rightarrow HCOOH + CH_3OH,$$
 (5)

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$$\text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2. \tag{6}$$

The first stage is the MF decarbonylation; it can be catalyzed by both metal complexes and bases (e.g., amines). Hydrogen generation in the system can occur through the water-gas shift reaction, which is catalyzed, in particular, by ruthenium complexes with donor phosphine ligands. The presence of hydrogen is required for the implementation of the above reactions; therefore, it is relevant to study the MF decomposition under various conditions, particularly in the presence of reactants and catalysts that are intended to be used in hydroformylation (primarily, phosphorus ligands and metal complexes).

In this study, the catalyst system components and their ratios were varied to determine the MF conversion, the pressure in the reactor, and the hydrogen content in the resulting gas mixture.

It was found that the fraction of hydrogen in the mixtures varies from 45 to 90% depending on the nature of the metal and the amount of water added (Table 1). Thus, for the ruthenium complexes, the fraction of hydrogen increases from 15 to 54% at a slight level of excess water and approaches 81% with high water content. A decrease in the water content, conversely, leads to a decrease in the hydrogen content to 46% (Table 1, entries 1–3). The activity of the rhodium and cobalt complexes in decomposition is significantly lower; however, in this case, the amount of produced hydrogen is also significant. For the cobalt complexes, at high water content, this value is as high as 90% (entries 5, 6).

The data suggest that the hydrogen generation process involves not only carbon monoxide, but also the produced methanol. It should be noted that the formation of methanol owing to the occurrence of steam-

No.	Catalyst	[HCOOCH ₃]/[H ₂ O]	Pressure at T_{room} , MPa	MF conversion, %	$\rm H_2$ content, %
1	Ru ₃ (CO) ₁₂	2.28	1.0	8	81
2	Ru ₃ (CO) ₁₂	11	3.0	21	54
3	Ru ₃ (CO) ₁₂	20	1.0	8	46
4	$Rh(acac)(CO)_2$	11	<0.5	12	46
5*	Co(acac) ₃	2.85	<0.5	2	90
6	Co(acac) ₃	2.85	<0.5	2	90

Table 1. Methyl formate decomposition in the presence of transition metal complexes and salts without the addition of ligands at different MF/water ratios

Experimental conditions: MF, 2.0 mL (0.032 mol); $Ru_3(CO)_{12}$, 0.016 mmol; $Rh(acac)(CO)_2$, 0.004 mmol; $Co(acac)_3$, 0.06 mmol; 180°C; and 2 h. *T = 200°C.

to-water conversion under relatively mild conditions has long been known. According to [17], the reaction

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$$

is characterized by a negative change in the free energy (-30 kJ/mol), unlike the conventional dehydrogenation of methanol. This reaction is catalyzed by both rhodium and ruthenium complexes; at temperatures above 150°C, the hydrogen formation rates are fairly high. In addition, at high temperatures, methanol dehydrogenation can also take place; however, in the absence of ligands, it typically occurs at a relatively low rate [18]. It should also be noted that these reactions still cannot provide an explanation to the fact that the hydrogen content in the mixture is more than 66%; to obtain this value, one mole of carbon dioxide should be bound by one mole of hydrogen.

The kinetics of MF conversion at different temperatures was also studied. According to the data in Fig. 2, decomposition occurs at a high rate both in the absence of water and in the presence of small amounts of water. In this case, the maximum pressure is achieved even within 60–70 min. In addition, an increase in the catalyst content leads to an increase in the total yield of gaseous products; however, the rate of pressure rise slightly decreases. This finding is apparently attributed to the fact that an increase in the catalyst content provides the presence of several MF decomposition routes. An increase in temperature from 180 to 200°C leads to an abrupt increase in both the reaction rate and the final pressure in the system, which increases almost by 25%.

The addition of water leads to a decrease in the total rate; at an MF/water ratio of 11, the pressure increases more slowly than it does at MF/water = 20. In the latter case, the shape of the kinetic curve resembles the shape of the curves recorded in the absence of water, whereas in the second case, the time dependence of pressure is an almost rectilinear; that is, it indicates the occurrence of a zeroth-order reaction.

Apparently, in this case, an increase in the amount of water can cause a change in the general MF decom-

position route. Decarbonylation is not the first stage any longer; the first stage is the MF hydrolysis to methanol and formic acid:

$CH_3OC(O)H + H_2O \rightleftharpoons HCOOH + CH_3OH.$

Formic acid undergoes decomposition to hydrogen and carbon dioxide in the presence of ruthenium catalysts and to water and carbon monoxide under the action of temperature. Thus, the water-gas shift reaction largely occurs via the formic acid dehydrogenation:



In addition, it can be directly catalyzed by ruthenium complexes without the formation of formic acid. There exist process schemes involving the formation of Ru–H compounds and the proton abstraction from water. It should be noted that, according to the published data, both mononuclear and polynuclear ruthenium complexes can be involved in the reaction via several routes; this feature significantly complicates the process mechanism [19–21].

The effect of a number of parameters on the cobaltcatalyzed decomposition of MF was also studied (Table 2).

An increase in the catalyst concentration leads to an increase in the MF conversion and a slight decrease in the fraction of hydrogen, although the hydrogen content is significantly higher than the fraction of 66% characteristic of ordinary stoichiometry. This finding indicates the occurrence of carbon binding to nongaseous compounds containing several oxygen atoms per carbon atom. A decrease in the amount of water leads to an increase in the hydrogen content; a simultaneous decrease in the catalyst concentration leads to a decrease in the conversion and the fraction of hydrogen.

It should be noted that with an increase in the reaction time, the fraction of hydrogen in the final mixture



Fig. 2. Time dependence of the pressure of the gas mixture during methyl formate decomposition under different conditions (0.032 mol of MF).

slightly decreased; this finding suggests the following: on one hand, hydrogen undergoes a reaction to form nongaseous products; on the other hand, the evolution of carbon monoxide and carbon dioxide increases and this process is not accompanied by the water-gas shift reaction because of a significant decrease in the water concentration in the system. This trend is observed at various catalyst concentrations (Table 3); it is much more pronounced with an increase in the catalyst concentration.

It can be assumed that the decrease in the hydrogen content is associated with the formation of a larger fraction of carbonyl complexes of cobalt in the system over time. In fact, the use of cobalt nitrate as a source of the metal leads to the formation of 45% of hydrogen in the system, while the use of cobalt carbonyl provides an increase in the MF conversion and the presence of 20% of hydrogen in the gas mixture. Modification of the proposed catalyst systems for MF decomposition was conducted by adding a number of ligands. The choice of the ligands was based on the different electron-donating abilities of these systems and the different degrees of steric hindrances. Data on the MF decomposition without water admixture in the presence of the rhodium and ruthenium complexes are shown in Table 4.

It should be noted that the addition of ligands has a negligible effect on the amount of hydrogen produced. In addition, the MF conversion is low, except for the case of the rhodium complex with phosphine exhibiting a high electron-donating ability—tricyclohexyl-phosphine—taken in a significant excess; this complex was highly active. In addition, this complex provided the highest proportion of hydrogen (35%). Taking into account the absence of water, the most probable reaction in this case is methanol dehydrogenation to formaldehyde; in addition, the reaction apparently pro-

[HCOOCH ₃]/[H ₂ O]	[HCOOCH ₃]/[metal]	MF conversion, %	H_2 content, %
2.85	2280	1	90
2.85	1140	2	90
2.85	760	5	89
2.85	570	10	85
2.85	450	11	70
3.8	450	10	90
5.7	450	10	90
3.8	760	4	65

Table 2. Methyl formate decomposition in the presence of cobalt acetylacetonate

Experimental conditions: MF, 2.0 mL (0.032 mol); 200°C; and 2 h.

[HCOOCH ₃]/[H ₂ O]	[HCOOCH ₃]/[metal]	Time, h	H ₂ content, %
2.85	1140	2	90
2.85	1140	3	80
2.85	760	2	89
2.85	760	4	71
2.85	760	6	61

 Table 3. Methyl formate decomposition in the presence of cobalt acetylacetonate

Experimental conditions: MF, 2.0 mL (0.032 mol); 200°C.

ceeds to a significant extent. At least 30% of the total amount of methanol undergoes dehydrogenation, which is followed by the decarbonylation of the resulting formaldehyde. These data are confirmed by published data on methanol dehydrogenation catalyzed by rhodium complexes under heating.

With a decrease in the MF/water ratio (Table 5), a significant increase in the pressure of the final gas mixture is observed; a decrease in the ratio from 11 to 5.5 leads to an abrupt pressure jump in the system and, accordingly, a multiple increase in the MF conversion.

It should be noted that with an increase in the amount of water, the proportion of hydrogen in the gas mixture also abruptly increases. At a ratio of 5.5, the hydrogen content corresponds to the equilibrium amount for MF decomposition and the formation of a carbon dioxide-hydrogen mixture, whereas at a ratio close to unity, the system contains 86% of hydrogen. Analysis of the liquid phase for methyl alcohol shows that the final pressure in the system corresponding to the total amount of this substance should be almost 2 times higher. This finding confirms our hypothesis that, during the reaction, a portion of the formed carbon dioxide is bound to form nongaseous compounds that are soluble in water and/or methanol. An increase in the amount of water contributes to this process. As a consequence, an abrupt increase in the amount of hydrogen in the system—up to 86%—is observed, while the fraction of carbon monoxide is not high.

Data on the effect of excess ligand on the MF decomposition process are shown in Table 6. An increase in the ligand/metal ratio from 10 to 20 leads to a slight decrease in activity, particularly with an increase in the fraction of water in the system. At the same time, the fraction of hydrogen significantly decreases. During reaction at a ligand/metal ratio of 10, the fraction of hydrogen was 75%, whereas during reaction with the doubled amount of the ligand, the hydrogen content was as low as 55%. Apparently, at a large level of excess phosphine, both the water-gas shift reaction and the methanol dehydrogenation reaction are suppressed. As a consequence, the decrease in the pressure and MF conversion is not extremely abrupt and the fraction of hydrogen, even at a large amount of water, is not high. In this case, a portion of the gas is carbon monoxide, rather than carbon dioxide.

Interesting data were obtained in studying the dependence of conversion and hydrogen content in the system on the nature of the ligand used (Table 7).

It should be noted that the complexes with phosphorus-containing ligands exhibited high activity. Complexes with amines were significantly less active in MF decomposition. It is worth noting that the bidentate ligand of the XANTHOS type exhibits relatively high activity; it provides a relatively high MF conversion at a fairly high hydrogen content in the mixture.

Data on the use of the rhodium complexes in the MF decomposition reaction in the presence of water additives are shown in Table 8.

For further research, it was of particular interest to study the MF decomposition in a mixed system containing both a rhodium complex and a ruthenium complex (Table 9). It should primarily be noted that the system containing the two metals and tricyclohexylphosphine is significantly more active than similar monometallic catalysts. A synergistic effect is observed with an increase in the MF conversion to 38% versus 19 and 30% provided by the pure rhodium

No.	Catalyst	Ligand	[L]/[metal]	Pressure at T_{room} , MPa	MF conversion, %	H_2 content, %
1	$\operatorname{Ru}_3(\operatorname{CO})_{12}$	PCy ₃	10.00	<0.5	3	<1
2	$\operatorname{Ru}_3(\operatorname{CO})_{12}$	PPh ₃	10.00	<0.5	0.3	2
3	$\operatorname{Ru}_3(\operatorname{CO})_{12}$	HNEt ₂	10.00	<0.5	1	12
4	$Rh(acac)(CO)_2$	PCy ₃	40.00	10.0	70	35
5	Rh(acac)(CO) ₂	PPh ₃	40.00	<0.5	1	24
6	Rh(acac)(CO) ₂	HNEt ₂	40.00	<0.5	1	<5

Table 4. Methyl formate decomposition with the addition of ligands in an anhydrous medium

Experimental conditions: MF, 2.0 mL (0.032 mol); $Ru_3(CO)_{12}$, 0.016 mmol; $Rh(acac)(CO)_2$, 0.004 mmol; ligand, 0.16 mmol; 180°C; and 2 h.

[HCOOCH ₃]/[H ₂ O]	Pressure at T_{room} , MPa	MF conversion, %	H_2 content, %
11.00	—	4	47
5.50	2.0	18	50
2.75	4.0	28	75
1.00	7.0	48	86

Table 5. Methyl formate decomposition in the presence of ruthenium complexes with triphenylphosphine as a function of the MF/water ratio

Experimental conditions: MF, 2.0 mL (0.032 mol); Ru₃(CO)₁₂, 0.016 mmol; PPh₃, 0.16 mmol; 180°C; and 2 h.

Table 6. Methyl formate decomposition in the presence of ruthenium complexes with triphenylphosphine as a function of the ligand/metal ratio

[L]/[metal]	[HCOOCH ₃]/[H ₂ O]	Pressure at T_{room} , MPa	MF conversion, %	H_2 content, %
10.00	11.00	<0.5	4	47
20.00	11.00	<0.5	4	34
10.00	2.75	4.0	28	75
20.00	2.75	3.0	21	55

Experimental conditions: MF, 2.0 mL (0.032 mol); Ru₃(CO)₁₂, 0.016 mmol; 180°C; and 2 h.

and pure ruthenium systems, respectively. In this case, the hydrogen content in the mixture is as low as 13% (about 50% for the monometallic systems under similar conditions). This fact means that the system contains a fairly high amount of carbon monoxide, which is favorable for the occurrence of the hydroformylation reaction.

In the case of using sulfonated triphenylphosphine, which is a water-soluble ligand, the MF conversion is relatively high and the amount of hydrogen in the system is significant. In this case, owing to the high water solubility of the ligand, the rhodium and ruthenium complexes are present almost completely in the aqueous phase; this feature provides an abrupt increase in the rates of reactions involving water and the binding of carbon dioxide in an aqueous medium. At an MF/water ratio of 2.75, the amount of produced hydrogen in the gas mixture is more than 90%, whereas for the phosphine complexes, it does not exceed 75% at the same ratio; at a ratio of 5.5, the fraction of hydrogen is 75%; for the triphenylphosphine—ruthenium system, it is 50%.

Data on the MF decomposition in a mixed system in the presence of the triphenylphosphine ligand are shown in Table 10. As in the case of the ruthenium systems, an increase in the proportion of water leads to an increase in the hydrogen content in the gaseous products and an increase in the MF conversion.

It is also significant that unlike the case of the ruthenium system, an increase in the amount of the ligand does not lead to a decrease in the hydrogen selectivity and the MF conversion. Conversely, the conversion increases almost by a factor of 1.5, while the fraction of hydrogen in the system remains high. Apparently, this fact is attributed to the establishment of a system of equilibria between the phosphine com-

Ligand	[L]/[metal]	[HCOOCH ₃]/[H ₂ O]	MF conversion, %	H_2 content, %
PPh ₃	10.00	2.75	28	75
PPh ₃	10.00	11.00	4	47
PCy ₃	10.00	2.75	30	70
PCy ₃	10.00	11.00	25	38
P(OPh) ₃	10.00	2.75	40	87
XANTPHOS	2.00	2.75	32	77
HNEt ₂	10.00	11.00	4	62
NEt ₃	10.00	11.00	7	26

Table 7. Methyl formate decomposition in the presence of various ruthenium complexes

Experimental conditions: MF, 2.0 mL (0.032 mol); Ru₃(CO)₁₂, 0.016 mmol; 180°C; and 2 h.

No.	Ligand	[L]/[metal]	[HCOOCH ₃]/[H ₂ O]	Pressure at T_{room} , MPa	MF conversion, %	H_2 content, %
1*	PCy ₃	40.00	11.00	2.5	19	50
2*	PPh ₃	40.00	11.00	<0.5	5	45
3*	NEt ₃	40.00	11.00	2.0	17	44
4*	PPh ₃	40.00	2.75	3.5	24	76
	HNEt ₂ (P/N=3)					

Table 8. Methyl formate decomposition catalyzed by rhodium complexes in the presence of water

Experimental conditions: MF, 2.0 mL (0.032 mol); * Rh(acac)(CO)₂, 0.004 mmol; ** [RhL₂]BF₄, 0.01 mmol; 180°C; and 2 h.

Table 9. Methyl formate decomposition in the presence of the $Ru_3(CO)_{12}-Rh(acac)(CO)_2$ bimetallic catalyst system

Ligand	[HCOOCH ₃]/[H ₂ O]	Pressure at T_{room} , MPa	MF conversion, %	H_2 content, %
PCy ₃	11.00	5.0	35	13
PPh ₃	11.00	<0.5	1	20
TPPTS	5.50	2.0	17	75
TPPTS	2.75	4.0	28	92
P(OPh) ₃	2.75	4.5	32	85
$PPh_3 + HNEt_2$	2.75	4.8	34	75

Experimental conditions: MF, 2.0 mL (0.032 mol); $Ru_3(CO)_{12}$, 0.016 mmol; $Rh(acac)(CO)_2$, 0.004 mmol; PPh_3 , 0.16 mmol; $P(OPh)_3$, 0.16 mmol; HNEt₂, 0.48 mmol; TPPTS, 0.2 mmol; 180°C; and 2 h.

Table 10. Methyl formate decomposition in the triphenylphosphine $-Ru_3(CO)_{12}-Rh(acac)(CO)_2$ mixed system

Ligand	[HCOOCH ₃]/[H ₂ O]	Pressure at T_{room} , MPa	MF conversion, %	H_2 content, %
PPh ₃	11.00	<0.5	1	20
PPh ₃	5.50	2.0	17	55
PPh ₃	2.75	3.0	21	77
PPh ₃ *	2.75	4.5	32	77

Experimental conditions: MF, 2.0 mL (0.032 mol); $Ru_3(CO)_{12}$, 0.016 mmol; $Rh(acac)(CO)_2$, 0.004 mmol; PPh₃, 0.16 mmol; and * PPh₃, 0.32 mmol.

plexes of rhodium and ruthenium in the system and the difference in the activity and selectivity of these complexes in MF decomposition: the rhodium complexes, for the most part, are responsible for hydrogen selectivity, while the ruthenium component of the system is largely responsible for the decomposition rate.

CONCLUSIONS

The experimental data obtained in this study suggest that along with the MF decomposition to methanol and carbon monoxide and the water-gas shift reaction, a number of processes occur that significantly complicate the decomposition and make it possible to control the composition of the gaseous mixture. In continuation of this research, we are going to explore the possibility of using methyl formate as an alternative source of synthesis gas for running the hydroformylation, hydroformylation-acetalization, and hydroaminomethylation reactions.

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