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CHEMICAL KINETICS AND CATALYSIS

Effect of the Nature of the Catalyst on Catalytic Activity and Selectivity in the Formaldehyde Hydrogenation

A. L. Tarasov[a],*
[a]Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia
*e-mail: atarasov@ioc.ac.ru

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Abstract—The effect the nature of the carrier and supported metal on the activity and selectivity of the catalyst in the reaction of formaldehyde hydrogenation to methanol is studied. The formation of such oxygenates as ethanol, formic acid, and diethyl formal is observed. It is found that ethanol forms on Fe-containing alloyed catalyst, while formic acid forms on the catalysts containing Au. Thermodynamic calculations are performed for a series of side reactions that confirm the formation of the resulting oxygenates.

Keywords: formaldehyde, methanol, ethanol, formic acid, hydrogenation
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INTRODUCTION

Supported catalysts are widely used to obtain valuable products [1–6], while physicochemical studies of the nature of active phases allows us to improve the activity and selectivity of catalysts and replace their expensive components [7–11]. Formaldehyde is a multi-tonnage product, so the design of new, more effective means of its synthesis using nanosize and hybrid materials as catalysts [12–14] is highly required. The subsequent synthesis of valuable products from formaldehyde is a most important problem, but its production is the key step. Formaldehyde is currently produced in industry in two ways [15]. A silver or copper catalyst and a rich mixture of methanol and air are used in the first classic variant, where waste gases are 18–20% hydrogen and less than 1% oxygen, along with small amounts of methane and carbon oxides. In the second way, where oxide catalysts (e.g., Fe and Mo oxides) are employed, poor mixtures of methanol and air are used. Waste gases then contain unreacted oxygen and virtually no hydrogen. Nonoxidative methanol dehydrogenation on zinc-copper catalysts at 600°C has yet to be thoroughly developed, but it is promising because it allows water-free formaldehyde to be produced.

The catalytic formaldehyde (FA) hydrogenation reaction remains virtually unstudied. Industrial practice shows that the hydrogenation of higher aldehydes (e.g., butanal and pentanal) is of more interest. The most promising catalysts of these processes are mixed copper–zinc–chromium oxides [16]. In contrast, different reactions involving FA, i.e., production of phenol–formaldehyde resins and other valuable organic products are now being widely studied, along with adsorption and catalytic methods of removing FA from gas discharges [17, 18]. However, the FA hydrogenation itself is of particular interest, from the viewpoint of both forming other valuable oxygenates (e.g., ethanol, formic acid, and diethyl formal) and understanding FA's role in numerous reactions with the participation of carbon oxides and H_2. The main product of FA hydrogenation is methanol. The authors of [19] investigated the effect the nature of supports, VIII group metals, and different alkaline promoters have on the selectivity of methanol formation in FA hydrogenation.

However, the reactions providing other oxygenates from FA are also known. For example, scientists from the Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, have developed a new way of preparing formic acid via the catalytic oxidation of formaldehyde with atmospheric oxygen in the gas phase. A key component of this processing is a vanadium–titanium oxide catalyst that shows high selectivity in the temperature range of 110–140°C [20]. Microbiological FA conversion to methanol and formic acid catalyzed by a highly active enzyme, dismutase [21], is also known.

The aim of this work was to determine the dependence of product distribution of the formaldehyde hydrogenation reaction on the nature of the carrier and supported metal for the catalysts, which are most promising in the reactions of carbon oxides. To explain the results of our catalytic experiments, thermodynamic calculations of equilibrium concentrations of products and reactants are performed for the side reactions giving different oxygenates in FA hydrogenation.

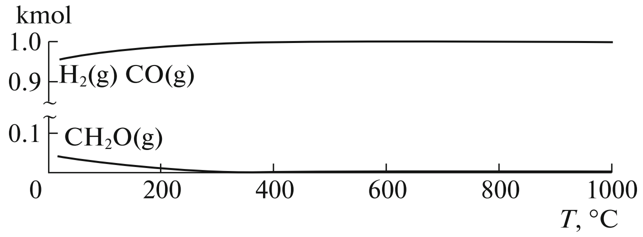

Fig. 1. Thermodynamic equilibrium concentrations of products and reactants in the reaction $CO + H_2 = CH_2O$ at 100 atm.

EXPERIMENTAL

Catalysts and Their Preparation

For our investigations, we selected a number of the catalysts which are most promising in carbon oxides hydrogenation.

Fe–K Alloyed

Conventional catalyst for the Fischer–Tropsch (F–T) process was prepared by alloying iron oxide (magnetite) with chemical promoter K_2O and structural promoters MgO and Al_2O_3 in an electric-arc furnace at 1650°C. The specific surface measured via BET method was 95 m^2/g.

CuO–ZnO–Al$_2$O$_3$

Industrial methanol synthesis catalyst (C-79-7GL, Süd Chemie) with the composition 56% CuO, 32% ZnO, and 12% Al_2O_3 was used. The specific surface of the catalyst was 160 m^2/g.

2% Au/S–ZrO$_2$

Industrial catalyst of the water-shift reaction (Chevron Co.), produced according to the procedure in [22]. The specific surface is 140 m^2/g.

2% Au/Al$_2$O$_3$

Gold nanoparticles were supported on the surface of γ-Al_2O_3 microspheres (IKT-02-6M, produced by AO Katalizator). The specific surface are of the catalyst was 138 m^2/g. The catalyst was prepared according to the procedure described in [23] using $HAuCl_4$ as gold precursor by precipitation with NaOH until pH 7.0. The obtained suspension was agitated for 1 h at 70°C. The resulting catalyst precursor was collected by filtration, washed with distilled water, dried in air for 24 h, and calcined at 300°C under an inert atmosphere for 3 h.

Catalytic Testing

A mixture of hydrogen and formaldehyde at atmospheric pressure was fed into a flow reactor in the form of a quartz tube 7 mm in diameter. A saturator was positioned upstream of the reactor, charged with paraformaldehyde, and heated to 170°C. H_2 was then fed through it at a rate of 10 mL/min. The catalyst charge was 1 cm^3. The molar ratio was $H_2/CH_2O = 5/1$. A trap cooled to −10°C was placed at the reactor's outlet to condense the liquid products. The gas at the trap output was analyzed on a 3700 model chromatograph (NPO Granat) equipped with two columns packed HayeSep-Q (H_2 + CO, CH_4, CO_2, C_2) and 5A molecular sieves (H_2, CH_4, CO). Liquid products were analyzed on the same chromatograph equipped with a flame-ionization detector, using an SE-30 capillary column (50 m) in the isothermal mode at 65°C. The carrier gas was helium.

Thermodynamic Calculations

Thermodynamic calculations of the equilibrium concentrations of the reactants and products in different direct and accompanied reactions were performed using the HSC-4 computer program designed by Haldor Topsøe company.

RESULTS AND DISCUSSION

Table 1 presents the results from formaldehyde (FA) catalytic conversion in mixtures with hydrogen on the investigated catalysts.

It should be noted that on all of the investigated catalysts, the main reaction was formaldehyde decomposition to carbon oxides (CO and CO_2). The selectivity toward carbon oxides was quite high (50–80%). This agrees with our thermodynamic calculations of the equilibrium concentrations presented in Fig. 1 for the products and reactants in the reversible reaction $CO + H_2 = CH_2O$.

It is clear from Fig. 1 that even at an elevated pressure (100 atm), the equilibrium of the reaction was strongly shifted toward CO formation. The equilibrium concentration of formaldehyde was no higher than 2%. Additional calculations showed that at atmospheric pressure within the investigated range of temperatures, it is generally measured in hundredths and thousandths of a fraction of a percent, and the reaction of the formation FA in that of CO_2 hydrogenationis not thermodynamically favorable. We may therefore conclude that formaldehyde cannot be considered an intermediate compound in the reaction of methanol synthesis from synthesis gas containing CO and CO_2. This is important for understanding the mechanism of reactions with the participation of CO, CO_2, and hydrogen.

Table 1. Results from formaldehyde conversion in the hydrogenation at atmospheric pressure at the molar ratio $H_2/CH_2O = 5/1$ and GHSV of 720 h^{-1}

Catalyst	T, °C	K_{CH_2O}, %	Conversion, mol %				CO/CO_2	Distribution of oxygenates, mol %			
			$CO + CO_2$	CH_4	C_2–C_4	oxygenates		methanol	formic acid	ethanol	diethyl formal
Fe–K-Alloyed	260	66.1	50.8	–	Traces	15.3	6.1	–	–	62.2	37.8
	310	80.2	60.4	3.1	0.6	16.1	7.3	–	–	85.0	15.0
	360	99.8	69.8	10.0	1.8	18.2	8.2	–	–	97.8	2.2
CuO–ZnO–Al_2O_3	180	100	66.1	8.5	–	25.4	2.6	100	–	–	–
	220	100	72.6	9.3	–	18.1	3.5	100	–	–	–
	260	100	80.8	10.1	–	9.1	4.8	100	–	–	–
2% Au/S-ZrO_2	180	100	45.1	2.0	–	52.9	4.2	10.1	80.9	9.0	Traces
	220	100	56.3	7.1	–	36.6	5.2	13.3	55.2	24.5	7.0
	260	100	64.4	15.4	0.5	19.7	7.0	15.8	58.1	23.0	3.1
	360	100	60.1	21.7	2.2	16.0	9.5	10.1	74.2	14.8	0.9
2% Au/Al_2O_3	180	90.6	55.6	Traces	–	35.0	2.0	62.1	29.9	5.1	2.9
	220	97.8	69.4	5.7	–	22.7	2.4	67.0	19.4	11.8	1.8
	260	100	61.4	12.8	0.2	25.6	2.8	40.5	34.5	24.0	1.0
	360	100	53.2	21.4	0.8	24.6	3.1	26.3	42.8	30.1	0.8

Along with the carbon oxides in the reaction products, we observed the formation of different oxygenates such as methanol, ethanol, formic acid, diethyl formal (DEF) on all the investigated catalysts. The selectivity of their formation depended largely on the nature of the catalyst (Table 1). It is obvious from Table 1 that the reaction on the Fe–K alloyed catalyst resulted in the preferential formation of ethanol and diethyl formal—the product of FA and ethanol condensation. The yield of ethanol grew with temperature, while the yield of DEF fell. At elevated reaction temperatures (higher than 310°C), small amounts of different C_1–C_4 gaseous hydrocarbons also formed, including the C_2–C_4 olefins that are precursors of high-molecular paraffins and olefins in F–T synthesis.

Thermodynamic calculations of the equilibrium concentrations of products and reactants in reaction $CH_2O + H_2 = C_2H_5OH + H_2O$ confirmed the formation of ethanol from FA. In the investigated range of temperatures (180–360°C), the thermodynamics of this reaction favored the complete conversion of FA to ethanol.

Along with the main reaction of FA decomposition to form carbon oxides, the reaction on the CuO–ZnO–Al_2O_3 catalyst yielded methanol and methane. Total conversion took place in the investigated range of temperatures from 180 to 260°C. The yield of methanol fell with temperature, corresponding to patterns known from the literature for the methanol synthesis from CO and H_2 (though in our case, methanol formed via the FA hydrogenation reaction). Note that this tendency was characteristic of all the catalysts studied for methanol synthesis, as the results presented in Fig. 2 show.

It is strange that fairly high selectivity toward methane (25%) was observed for the CuO–ZnO–Al_2O_3 catalyst at a fairly low temperature (180°C), as this is not characteristic of catalysts for methanol synthesis. As noted earlier, however, FA cannot be an intermediate in synthesizing methanol from CO and H_2, and in our case, methane apparently formed through the hydrogenation of FA itself, not during the hydrogena-

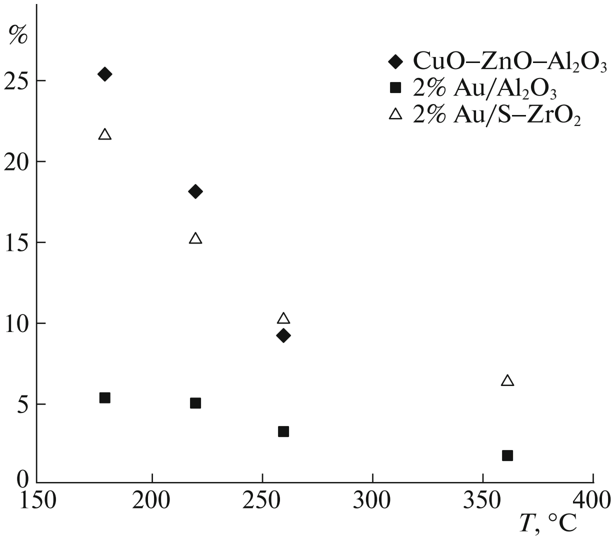

Fig. 2. Dependences of the methanol yield on temperature on different catalysts.

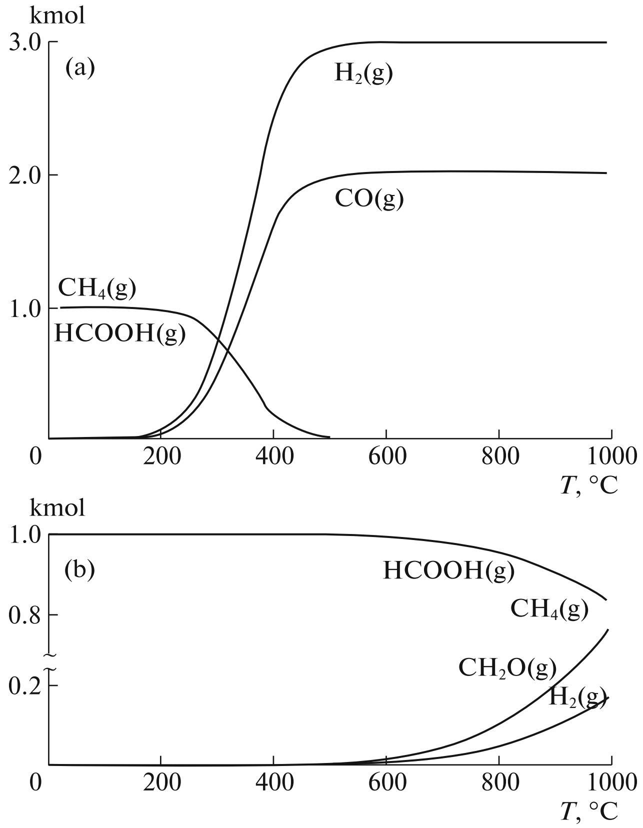

Fig. 3. Thermodynamic equilibrium concentrations of products and reactants in reactions (a) $2CO + 3H_2 = HCOOH + CH_4$ and (b) $CH_2O + H_2 = HCOOH + CH_4$ at 1 atm.

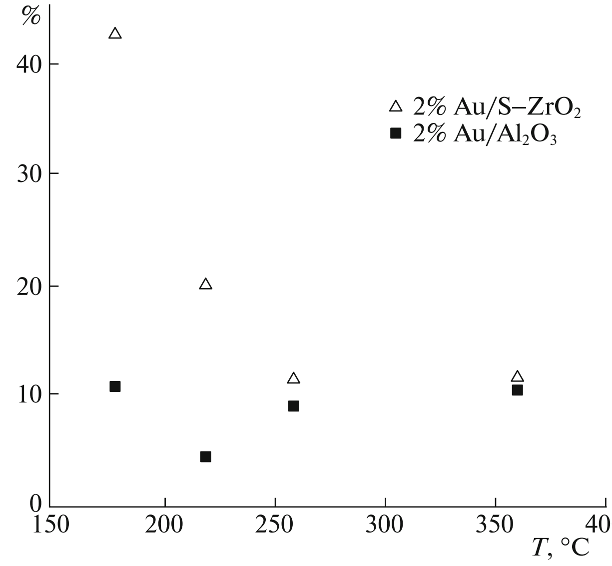

Fig. 4. Dependence of the formic acid yield on temperature on different catalysts.

tion of carbon oxides that form intensely in the process. This is important for understand mechanisms of side reactions.

The investigated gold-containing 2% Au/S-ZrO_2 and 2% Au/Al_2O_3 catalysts catalyzed the reaction of formic acid formation with high selectivity along with FA decomposition to form carbon oxides and alcohols (methanol and ethanol). Note especially that nothing is known about the formation of formic acid during FA hydrogenation. According to [15], FA in the hydrogenation reaction first converts to methanol, and then to methane. Note too that the synthesis of formic acid from carbon oxides according to reactions $CO_2 + H_2 = HCOOH$ and $CO + H_2O = HCOOH$ is not thermodynamically favorable because the equilibrium in these reactions is strongly shifted to the left. Our thermodynamic calculations show that on the other hand, formic acid can easily form in the hydrogenation of both FA (Fig. 3b) and the carbon oxide (Fig. 3a) that forms during FA decomposition (Table 1). In both cases, however, methane must surely present in reaction products.

The calculated data (Fig. 3) show clearly that in the range of temperatures selected for our experiments (180–360°C), the formation of formic acid preferentially occurs during FA hydrogenation, not in the hydrogenation of the CO that forms during FA decomposition. The data in Fig. 3 agree with the experimental results we obtained for Au-containing catalysts. We can see from Table 1 that along with formic acid, the products of the reaction on the 2% Au/S–ZrO_2 and 2% Au/Al_2O_3 catalysts contained comparable amounts of methane throughout the investigated range of temperatures (180–360°C). Figure 4 presents the dependences for the yield of formic acid on the temperature of the reaction on different Au catalysts.

It is clear that the yield of formic acid on the 2% Au/S–ZrO_2 catalyst was very high (43%) at a moderate temperature (180°C). The yield of acid on the 2% Au/Al_2O_3 sample the investigated range of temperatures was much lower (around 10%). It is seen that the yield of formic acid on the 2% Au/S–ZrO_2 sample fell sharply when the temperature was raised to 260°C, and then stabilized at the level of 10%. The sharp drop in the yield agrees with the calculated data presented in Fig. 3, from which we can see that at a temperatures higher than 200°C the equilibrium of the reaction is shifted towards formic acid decomposition with formation of CO and H_2. Note too that this decomposition is catalyzed by acid catalysts (e.g., phosphomolybdic acid supported on silica gel [24]), and such supports as sulfated zirconia in 2% Au/S–ZrO_2 have pronounced acidity [25].

The results presented in Table 1 also show that in addition to formic acid, ethanol forms on both gold-containing and Fe–K alloyed catalysts. Figure 5 shows the dependence of the ethanol yield on the tempera-

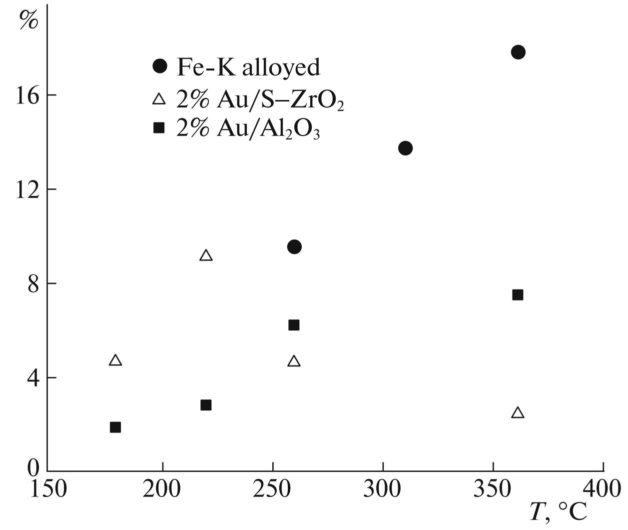

Fig. 5. Dependence of the ethanol yield on temperature on different catalysts.

ture of the reaction for two Au-containing and Fe–K alloyed catalysts.

As is seen from Fig. 5, the yield of ethanol on the Fe–K alloyed catalyst tends toward stable growth along with temperature, and this agrees with our thermodynamic calculations. On Au-containing catalysts supported on different carriers, this tendency ends abruptly at temperatures higher than 250°C. C_2–C_4 hydrocarbons (including ethylene) appeared in the reaction products at 260 and 360°C, clearly indicating the reaction of ethanol dehydration to form ethylene. This was obviously associated with the pronounced acidity of the carriers that were used (2% Au/S–ZrO_2 and 2% Au/Al_2O_3), which agrees with the findings in [25]. In our case, this was most pronounced for the 2% Au/S–ZrO_2 catalyst.

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