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Kinetics and Mechanisms of the Catalytic Reactions of Formaldehyde with Copper Oxides and a Copper Ion Complex in Aqueous Alkali

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Abstract—The kinetics of the autocatalytic reactions of formaldehyde with copper(II) and copper(I) oxides and with the Cu^{2+} ion of the copper EDTA complex, as well as formaldehyde disproportionation in the presence of copper metal, have been investigated in aqueous solutions of sodium hydroxide. Two likely reaction mechanisms are presented. The difference between these mechanisms does not alter the observed kinetics of the processes, whose rate is determined by their first, slow step, namely, the oxidation of the methylene glycol anion adsorbed on the copper surface into formic acid. In the slow step of the first mechanism, a hydride ion is abstracted from the methylene glycol anion and is transferred to copper. In the slow step of the second mechanism, the methylene glycol anion undergoes anodic oxidation, releasing a hydrogen atom and an electron. In the rapid steps of the first mechanism, the hydride ion undergoes anodic oxidation to hydrogen, the copper compound undergoes cathodic reduction to copper metal, and, simultaneously, the electron and hydrogen are transferred to a nonionized formaldehyde molecule to yield methanol. Mathematical models are suggested for the reactions. The effective rate constants and activation energies of the slow steps of the reactions have been determined. The effective rate constants of the noncatalytic reduction reactions of the copper compounds and the ratios of the rates of the rapid hydrogen and methanol formation reactions have been estimated.

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The reduction of the Cu^{2+} ion with formaldehyde has long been known and is now widely used in the deposition of copper coatings onto various materials. Copper hydroxide precipitation in this process is ruled out by introducing ligands capable of binding the Cu^{2+} ion, such as the disodium salt of ethylenediaminetetraacetic acid. The data available on the kinetics and mechanism of this reaction [1–3] are controversial and do not cover the range of conditions in which copper precipitates from the reaction system. We failed to find any information on the kinetics and mechanism of the reaction of formaldehyde with copper oxides. We have found only patents concerning the use of copper [4, 5], copper oxalate [6, 7], copper(II) hydroxide and oxide [8, 9], and copper(I) oxide [8, 10] in pentaerythritol synthesis for preventing the formation of by-products from formaldehyde. There is no information about the kinetics and mechanism of formaldehyde disproportionation in the presence of copper. This imposes a limit on the understanding of the above reactions and on their applications, including the purification of polyols. Here, we attempt to make up for part of this lack of information.

EXPERIMENTAL

The chemicals used in this work were formalin containing 37 wt % formaldehyde and 10 wt % methanol, sodium hydroxide, and a number of copper compounds. Copper(II) oxide was obtained by reacting sodium hydroxide with copper(II) acetate; copper(I) oxide, by reacting glucose with copper sulfate in the presence of sodium hydroxide; the copper EDTA complex, by the reaction between the disodium salt of ethylenediaminetetraacetic acid and copper sulfate. Reaction mixtures containing formaldehyde condensation products were also used.

Appropriate amounts of an aqueous solution of sodium hydroxide and formalin were placed in a temperature-controlled glass flask with a magnetic stirrer, and a copper compound was then added. The reaction temperature was maintained with an accuracy of ±0.5°C.

The reactions were conducted under stirring such that a decrease or an increase in stirring intensity exerted no effect on their rate. The initial reaction conditions were as follows: formaldehyde concentration, 0.5–3.6 mol/l; sodium hydroxide concentration, 0.35–2.5 mol/l; reactant molar ratio, 1 : 1 to 1 : 0.4; copper ion complex concentration, 0.05–0.17 mol/l; copper oxide weight, 0.5–3.1 g; volume of the reacting solution, 0.05–0.9 l; the temperature ranges for the reactions involving copper(II) oxide, copper(I) oxide, and the copper ion complex were 3–18, 5–30, and 13–40°C, respectively.

The reaction mixture was sampled during the reactions. Each sample was poured into a flask containing a known, excess amount of 0.1 N hydrochloric acid, and the mixture was titrated with 0.1 N sodium hydroxide in the presence of phenolphthalein to determine the sodium hydroxide concentration in the initial sample. Next, the formaldehyde concentration was determined. To do this, a prescribed amount of an aqueous solution of hydroxylamine hydrochloride was added to the solution in the flask, and the resulting solution was titrated with a 0.1 N alkali in the presence of bromophenol blue.

The amount of released hydrogen was determined as the volume of water displaced by the gas from the vessel connected with the flask. In calculations, we took into account that Cu^{2+} reduction to copper metal is not accompanied by Cu^{+} accumulation [11], used the material balance data presented below, and assumed that the amount of the resulting copper is equimolar to the amount of released hydrogen. The amount of copper that was formed upon the completion of the reaction was also determined gravimetrically. The amounts of copper oxides, copper ion complex, and methanol during the reactions were determined using material balance equations.

The current concentrations of hydroxide ions (C_{OH^-}) and methylene glycol anions ($C_{CH_2(OH)O^-}$) were calculated using Eqs. (1) and (2), which were derived from the ion equilibrium and material balance equations for the methylene glycol anionization reaction with the electroneutrality of the solution taken into account [12]:

$$C_{OH^-} = \frac{-[1 + 6(C_{CH_2O} - C_{NaOH})] + \sqrt{[1 + 6(C_{CH_2O} - C_{NaOH})]^2 + 24C_{NaOH}}}{12}, \quad (1)$$

$$C_{CH_2(OH)O^-} = C_{CH_2O}\frac{6C_{OH^-}}{1 + 6C_{OH^-}}, \quad (2)$$

where C_{NaOH} and C_{CH_2O} are the sodium hydroxide and formaldehyde concentrations in the reacting solution.

RESULTS AND DISCUSSION

An analysis of the material balances for the reactions of formaldehyde with copper(II) oxide, copper(I) oxide, and the copper ion complex in aqueous sodium hydroxide (table) shows that the reduction of the copper compounds to copper metal is accompanied by formaldehyde oxidation to formic acid, hydrogen evolution, formaldehyde reduction to methanol, and formaldehyde condensation.

The formation of an additional amount of hydrogen, which exerts no significant effect on the kinetics of the reactions examined, is unlikely to be due to the reduction of the initial copper compounds, because, as follows from the data presented in the table, approximately the same amount of hydrogen forms in the presence of Cu. The causes of the formation of this extra amount of hydrogen will not be considered here.

It is difficult to understand a priory whether the formaldehyde condensation products are weaker or stronger reductants than formaldehyde, even though glucose is known to be capable of reducing Cu^{2+} only to Cu^{+}. Our experimental data demonstrate that these products, like formaldehyde, reduce the copper compounds and undergo disproportionation in alkaline solution in the presence of copper. However, these reactions proceed very slowly and show themselves only after the complete disappearance of formaldehyde (Figs. 1, 2). Replacement of water with a solution containing formaldehyde condensation products [13] does not change the induction period or the kinetics of the reactions examined.

As is clear from Figs. 1–3, the reduction reactions of copper(II) oxide, copper(I) oxide, and the Cu^{2+} ion are autocatalytic. These reactions, as well as formaldehyde oxidation and reduction (disproportionation), are catalyzed by copper metal, which results from slow reaction steps during the induction period:

$$CuO + 2CH_2(OH)O^- \longrightarrow Cu + 2HCOO^- + H_2 + H_2O, \quad (I)$$

$$Cu_2O + 2CH_2(OH)O^- \longrightarrow 2Cu + 2HCOO^- + H_2 + H_2O, \quad (II)$$

$$Cu^{2+} + 2CH_2(OH)O^- \longrightarrow Cu + 2HCOO^- + H_2 + 2H^+. \quad (III)$$

Copper metal crystallizes on the surface of oxide particles or, when the copper ion complex is used, in the bulk of the reacting solution.

The length of the induction period under fixed initial reaction conditions is not always the same. This is most likely due to the uncontrolled effects of various factors on copper crystallization. For example, the reduction of the copper ion in the complex in the presence of a copper "seed" occurs without any induction period. The reaction kinetics after the induction period (in the absence of a "seed") is the same as in the reaction without an induction period (in the presence

Material balances for the reactions

Volume of the reaction mixture, l	Amounts of components in the reaction mixture, mmol								Δn_{CH_2O}	Δn_{H_2}	$\frac{n_{H_2}}{n_{CH_3OH}}$
	before reaction			after reaction							
	CuR	CH_2O	NaOH	CH_2O	NaOH	H_2	HCOONa	CH_3OH			
Reaction with CuO											
0.2	6.3	384.0	184.0	7.0	29.0	6.7	155.0	141.6	80.4	0.4	0.047
0.2	12.7	364.0	232.0	0.0	58.0	13.3	174.0	147.4	42.6	0.6	0.090
0.2	12.6	752.0	372.0	0.0	41.0	13.1	331.0	304.8	116.2	0.5	0.043
0.4	12.5	1733.0	354.0	851.0	15.0	13.3	339.0	312.4	230.6	0.8	0.043
0.4	12.5	1703.0	356.0	890.0	52.0	13.2	304.0	277.6	231.4	0.7	0.048
0.2	25.0	388.0	194.0	70.0	45.0	25.6	149.0	97.8	71.2	0.6	0.262
0.2	25.1	720.0	459.0	20.0	127.0	28.0	332.0	276.0	92.0	2.9	0.101
0.2	37.5	376.0	194.0	0.0	6.0	34.4	188.0	119.2	68.8	3.1	0.289
Reaction with Cu^{2+}											
0.2	8.5	418.0	266.0	112.0	119.0	8.9	147.0	192.2	29.8	0.4	0.046
0.2	16.0	376.0	248.0	0.0	69.0	16.6	179.0	145.8	51.2	0.6	0.113
0.2	16.0	746.0	510.0	187.0	246.0	17.1	264.0	229.8	65.2	1.1	0.074
0.2	33.0	380.0	235.0	70.0	56.0	35.3	179.0	108.6	22.4	2.0	0.320
Reaction with Cu_2O											
0.4	12.2	850.0	630.0	0.0	240.0	12.7	390.0	364.6	95.4	0.5	0.035
0.8	25.0	1600.0	1240.0	0.0	584.0	26.1	656.0	603.8	340.2	1.1	0.043
Reaction with Cu from CuO											
0.2	1*	356.0	180.0	2.0	24.0	0.5	156.0	155.0	43.0	–	–
0.4	1*	707.0	359.0	35.0	73.0	0.7	286.0	284.6	101.4	–	–
0.4	1*	1550.0	352.0	683.0	15.0	0.7	337.0	335.6	194.4	–	–
0.2	2*	362.0	182.0	51.0	52.0	1.6	130.0	126.8	54.2	–	–
0.2	3*	309.0	165.0	75.0	71.0	2.9	94.0	88.2	51.8	–	–
Reaction with Cu from Cu^{2+}											
0.2	1*	372.0	278.0	0.0	109.0	0.6	169.0	167.8	35.2	–	–
0.2	3*	418.0	270.0	115.0	140.0	2.8	130.0	124.4	48.6	–	–
Reaction with Cu from Cu_2O											
0.2	1*	756.0	432.0	13.0	116.0	0.5	316.0	315.0	125.0	–	–

* Amount of Cu, g.

of a “seed”). The induction period shortens with an increasing weight of the copper compound, methylene glycol anion concentration, or temperature.

The explanation of the catalytic action of copper presented in earlier publications [2, 3] is based on the quantum mechanical theory of charge transfer in polar media: electron transfer will require less energy if the reductant and the ion of the oxidizer are localized near the metallic surface, not in the bulk of the solution. Calculations demonstrated that the adsorption of a methylene glycol anion or hydride ion on the copper surface is accompanied by almost complete transfer of one electron. This is evidence that electron transfer to the oxidizer is more likely mediated by the conducting metallic surface; that is, an electrochemical mechanism takes place.

Several Cu^{2+} reduction mechanisms have been considered in the literature [1–3].

According to the electrochemical mechanism, two independent electrode reactions occur on the copper surface. One is the anodic oxidation of formaldehyde,

$$\begin{gathered} 2HCHO + 4OH^- \\ \longrightarrow 2HCOO^- + 2H_2O + H_2 + 2e^-, \end{gathered} \tag{IV}$$

and the other is cathodic Cu^{2+} reduction. The released electrons are transferred via the copper surface to the Cu^{2+} ions, reducing them to copper metal.

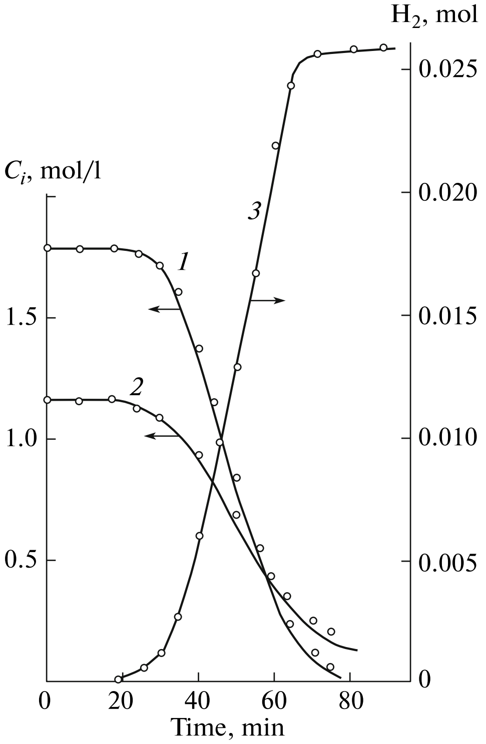

Fig. 1. Copper(II) oxide reduction kinetics: (*1*) formaldehyde, (*2*) sodium hydroxide, and (*3*) hydrogen. The points represent experimental data, and the curves represent calculated data. Reaction conditions: 5°C, 2 g of CuO, $k = 6 \times 10^{-14}\,\mathrm{l\,g^{-1}\,min^{-1}}$, $V = 0.2$ l.

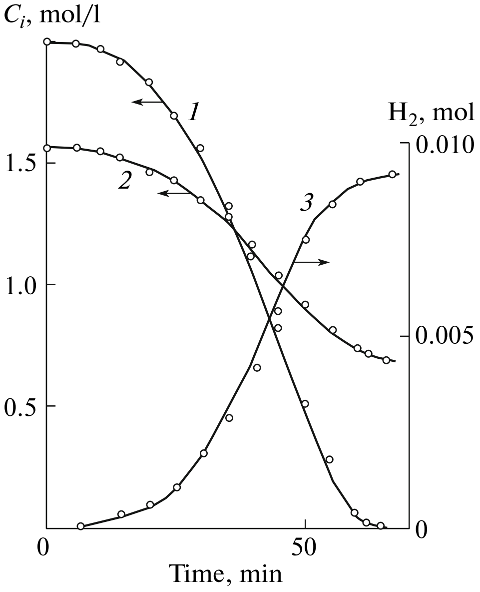

Fig. 2. Copper(I) oxide reduction kinetics: (*1*) formaldehyde, (*2*) sodium hydroxide, and (*3*) hydrogen. The points represent experimental data, and the curves represent calculated data. Reaction conditions: 25°C, 1.24 g of Cu_2O, $k = 3 \times 10^{-6}\,\mathrm{l\,g^{-1}\,min^{-1}}$, $V = 0.8$ l.

According to the chemical mechanism, formaldehyde dehydrogenation takes place on the copper surface to yield hydrogen molecules or atoms or hydride ions, which act as electron donors for the Cu^{2+} ions. It is not impossible that the copper ion complex and formaldehyde interact directly through electron transfer from the latter to the former.

Under the given experimental conditions, the reduction rates of the copper oxides and the copper ion after the induction period depend on the initial amounts of the compounds, on the extent of their reduction to copper metal, on the reaction temperature, and on pH.

Formaldehyde disproportionation uncomplicated by the reduction of copper compounds was observed in the presence of copper metal that had resulted from the reduction of copper(II) or copper(I) oxide or the copper ion in the complex.

The effect of the other reactions on the kinetics is insignificant, and it can be taken into account. Sodium hydroxide consumption in the Cannizzaro reaction is given by the equation

$$\frac{dC_{\mathrm{NaOH}}}{dt} = k_5 C_{\mathrm{CH_2(OH)O^-}} C_{\mathrm{CH_2O}}, \qquad (3)$$

where $k_5 = (2.9 \pm 0.2) \times 10^{14} e^{-\frac{99045}{8.314T}}\,\mathrm{mol\,l^{-1}\,min^{-1}}$ is the rate constant of this reaction. The consumption of NaOH in the reaction accompanied by hydrogen evolution can be estimated as the amount of gas released.

According to experimental data, sodium hydroxide consumption at a constant amount of copper depends on the methylene glycol anion concentration and temperature and is independent of the formaldehyde concentration. At a fixed temperature, the NaOH disappearance rate is similar to a typical adsorption isotherm and is described by the equation

$$-\frac{dn_{\mathrm{NaOH}}}{dt} = k_r S_{1,0} k_{\mathrm{ads}} C^n_{\mathrm{CH_2(OH)O^-}} \qquad (4)$$
$$= k_r S_{\mathrm{sp1},0} m_{0,\mathrm{Cu}} k_{\mathrm{ads}} C^n_{\mathrm{CH_2(OH)O^-}} = k_{1,0} m_{0,\mathrm{Cu}} C^n_{\mathrm{CH_2(OH)O^-}},$$

where k_r is the formaldehyde oxidation rate constant, $S_{1,0}$ is the total surface area of copper, $k_{\mathrm{ads}} C^n_{\mathrm{CH_2(OH)O^-}}$ is the methylene glycol anion concentration on the copper surface (here, the adsorption equilibrium is described in terms of Freundlich's adsorption isotherm equation and n is the empirical exponent), $S_{\mathrm{sp1},0}$ is the specific surface area of copper, $m_{0,\mathrm{Cu}}$ is the weight of copper, and $k_{1,0} = k_r S_{\mathrm{sp1},0} k_{\mathrm{ads}}$ is the effective rate constant of formaldehyde oxidation; the subscript 0 means that the given quantity refers to then point in time at which the formation of a copper layer on the particle surface is complete.

The experimental data suggest that formaldehyde disproportionation in the presence of copper metal

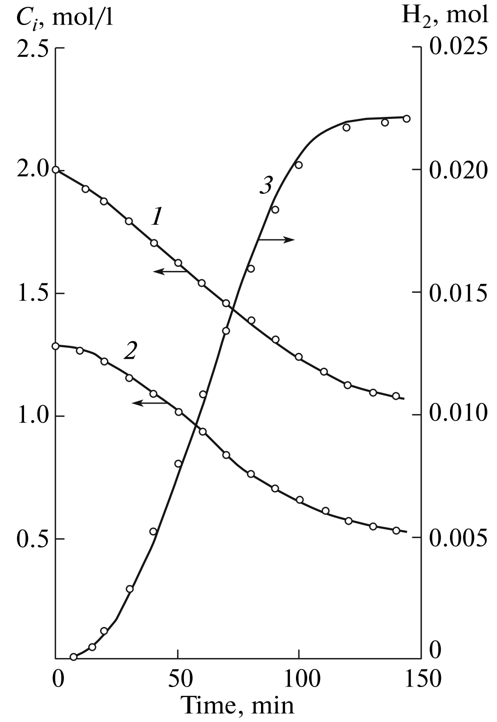

Fig. 3. Reduction kinetics of Cu^{2+} in the complex: (*1*) formaldehyde, (*2*) sodium hydroxide, and (*3*) hydrogen. The points represent experimental data, and the curves represent calculated data. Reaction conditions: 25°C, initial copper ion complex concentration of 0.11 mol/l, $k = 7 \times 10^{-5}$ l g^{-1} min^{-1}, $V = 0.2$ l.

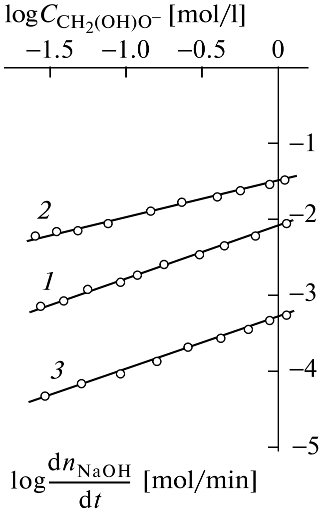

Fig. 4. Determination of $k_{1,0}$ and n from Eq. (4) for the reactions on (*1*) copper from copper(II) oxide at 5°C, (*2*) copper from copper(I) oxide at 25°C, and (*3*) copper from the copper ion complex at 25°C. The initial formaldehyde and sodium hydroxide concentrations are 2.0 and 1.6 mol/l, respectively; the copper content is 1 g.

takes place in steps. We think that the most likely mechanism is that whose first, slow step is the loss of a hydride ion by the methylene glycol anion adsorbed on the copper surface:

$$CH_2(OH)O^- \xrightarrow{k_1} HCOOH + H^-. \qquad (V)$$

This hydride ion stays on the copper surface and reacts with nonionized formaldehyde to yield methanol (second, rapid step):

$$H^- + CH_2O \xrightarrow{k_2} H_3CO^-. \qquad (VI)$$

Also possible is the mechanism whose first, slow step is the anodic oxidation of the methylene glycol anion adsorbed on the copper surface. In this process, the anion loses a hydrogen atom and an electron:

$$CH_2(OH)O^- \longrightarrow HCOOH + H + e. \qquad (VII)$$

In the second, rapid step, the hydrogen and electron interact with nonionized formaldehyde to yield methanol:

$$CH_2O + H + e \longrightarrow H_2COO^-. \qquad (VIII)$$

The difference between these mechanisms does not alter the observed reaction kinetics.

Clearly, the formaldehyde disproportionation mechanism in the presence of copper differs from the Cannizzaro mechanism, in which the hydride ion is transferred directly from the methylene glycol anion to nonionized formaldehyde and the rate equation is second-order with respect to the formaldehyde concentration [14].

For an ion strength of 1.2–1.5 and an ion activity of 0.72–0.75 in the solution [15], we determined the numerical values of the coefficient n and constant $k_{1,0}$ (Fig. 4). If copper forms from copper(II) oxide, then, at $n = 0.7$ $k_{1,0} = (1.94 \pm 0.3) \times 10^{12} e^{-\frac{76490}{8.314T}}$; if copper forms from copper(I) oxide, then, at $n = 0.5$ $k_{1,0} = (5.1 \pm 0.7) \times 10^{11} e^{-\frac{75200}{8.314T}}$; if copper forms from the copper ion complex, then, at $n = 0.67$ $k_{1,0} = (2.95 \pm 0.5) \times 10^{6} e^{-\frac{55946}{8.314T}}$.

The difference between the $k_{1,0}$ values is evidence that the three copper specimens differ in catalytic activity. It is possible that this difference arises from the difference between the crystal structures of the specimens. Note that the copper specimens obtained by Cu^{2+} ion reduction with formaldehyde and zinc show nearly the same catalytic activity. According to gravimetric data, the copper specimens obtained from copper(I) oxide and from the copper ion complex are almost free of impurities, while the impurity content of copper from copper(II) oxide is as high as 5 wt %. The impurities were not identified.

In the interaction of formaldehyde with the copper compounds, formaldehyde disproportionation is accompanied by the reduction of these compounds to copper metal with hydrogen evolution. Again, two mechanisms are possible here. In the first mechanism, the first, slow step is methylene glycol anion dehydrogenation into formic acid with hydride ion transfer to copper (reaction (V)), which is followed by the rapid anodic oxidation of the hydride ion into hydrogen with electron transfer through metallic copper to the copper compound:

$$H^- \xrightarrow{k_{3,1}} H + e. \tag{IX}$$

In the second mechanism, the first, slow step is the anodic oxidation of the methylene glycol anion into formic acid with hydrogen abstraction and electron transfer to copper:

$$CH_2(OH)O^- \longrightarrow HCOO^- + H + e. \tag{X}$$

In both cases, the reaction ends with the rapid cathodic reduction of the copper compound to copper metal:

$$CuO + 2e + H_2O \xrightarrow{k_{3,2}} Cu + 2OH^-, \tag{XI}$$

$$Cu_2O + 2e + H_2O \xrightarrow{k_{3,2}} 2Cu + 2OH^-, \tag{XII}$$

$$Cu^{2+} + 2e \xrightarrow{k_{3,2}} Cu. \tag{XIII}$$

The difference between these mechanisms does not alter the observed reaction kinetics.

The way the ratio of the resulting amounts of hydrogen and methanol varies with the ratio of the initial amount of the copper compound to the initial formaldehyde concentration (table) suggests that hydrogen and methanol form via parallel reactions and that the common initial reactant for these products is either the hydride ion or the methylene glycol anion. From experimental data alone, it is rather difficult to conclude whether this is actually the case because the surface area of the resulting copper varies during the reaction. For this reason, it is pertinent to use a mathematical model in further investigation.

Under the assumption that the reactions in question have a common slow step described by the rate equation

$$-\frac{dn_{NaOH}}{dt} = 2\frac{dn_{H_2}}{dt} + \frac{dn_{CH_3OH}}{dt}, \tag{5}$$

the oxide reduction model should include, along with Eqs. (1) and (2), the following equations:

$$-\frac{dC_{NaOH}}{dt} = \left(kC^l_{CH_2(OH)O^-}S + k_1C^n_{CH_2(OH)O^-}S_1\right)\frac{1}{V}, \tag{6}$$

$$\frac{dC_{CH_3OH}}{dt} = \left(k_1C^n_{CH_2(OH)O^-}S_1\frac{1}{1+\dfrac{2k_3S_2}{k_2C^n_{CH_2O}S_1}}\right)\frac{1}{V}, \tag{7}$$

$$\frac{dn_{H_2}}{dt} = \frac{dC_{CH_3OH}}{dt}\frac{k_3S_2}{k_2C^n_{CH_2O}S_1}V, \tag{8}$$

$$\frac{dn_{Cu}}{dt} = kC^l_{CH_2(OH)O^-}S + \frac{dn_{H_2}}{dt}, \tag{9}$$

$$-\frac{dn_{CuO}}{dt} = \frac{dn_{Cu}}{dt} \text{ or } -\frac{dn_{Cu_2O}}{dt} = 0.5\frac{dn_{Cu}}{dt}, \tag{10}$$

$$-\frac{dC_{CH_2O}}{dt} = 2.4\left(\frac{dn_{H_2}}{dt}\frac{1}{V} + \frac{dC_{CH_3OH}}{dt}\right). \tag{11}$$

The parameter l in Eqs. (6) and (9) is the empirical exponent in the Freundlich equation for adsorption on the surface of the oxides.

In the case of the reduction of the copper ion complex, the model should include, apart from Eqs. (1) and (2), the following equations:

$$-\frac{dC_{NaOH}}{dt} = k_5C_{CH_2(OH)O^-}C_{CH_2O} + \left(k_1C^n_{CH_2(OH)O^-}S_1\right)\frac{1}{V}, \tag{12}$$

$$\frac{dC_{CH_3OH}}{dt} = \left(k_1C^n_{CH_2(OH)O^-}S_1\frac{1}{1+\dfrac{2k_3C_{Cu}}{k_2C_{CH_2O}}}\right)\frac{1}{V} + k_5C_{CH_2(OH)O^-}C_{CH_2O}, \tag{13}$$

$$\frac{dn_{H_2}}{dt} = \frac{dC_{CH_3OH}}{dt}\frac{k_3C_{Cu^{2+}}}{k_2C_{CH_2O}}V, \tag{14}$$

$$\frac{dn_{Cu}}{dt} = kC_{CH_2(OH)O^-}C_{Cu^{2+}}V + \frac{dn_{H_2}}{dt}, \tag{15}$$

$$-\frac{dn_{Cu^{2+}}}{dt} = \frac{dn_{Cu}}{dt}, \tag{16}$$

$$-\frac{dC_{CH_2O}}{dt} = 2.4\left(\frac{dn_{H_2}}{dt}\frac{1}{V} + \frac{dC_{CH_3OH}}{dt}\right). \tag{17}$$

In Eqs. (6)–(17), C_{CH_2O}, C_{CH_3OH}, and $C_{Cu^{2+}}$ are, respectively, the formaldehyde, methanol, and copper ion complex concentrations in the reacting solution; k, k_1, k_2, and k_3 are the effective rate constants of the reaction between copper oxide or the copper ion and the methylene glycol anion, methylene glycol anion oxidation, formaldehyde reduction, and copper compound reduction, respectively; S, S_1, and S_2 are the areas of contact between copper oxide and the reacting solution, between copper and the reacting solution, and between copper and copper oxide, respectively; and V is the volume of the reacting solution.

Note that these models disregard the reaction yielding the additional amount of hydrogen, which, according to the data presented in the table, does not exert any insignificant effect on the reaction kinetics. In addition, the models do not include the formaldehyde condensation reaction, and formaldehyde disappearance due to this reaction is taken into account by introducing an empirical coefficient in Eqs (11) and (17).

Because the surface areas of the solid reactants were unknown, they were replaced by the weights of these reactants:

$$kS = S_{sp}km,\ k_1S_1 = S_{sp1}k_1m_{Cu},\ \frac{k_3S_2}{k_2S_1} = K_{sp}K_{3,2}\frac{m_2}{m_{Cu}}, \tag{18}$$

where m, m_{Cu}, and m_2 are the weights of copper oxide, copper, and solid phase, respectively (m_2 determines the copper/copper oxide contact area); S_{sp} and S_{sp1} are the specific copper oxide/reacting solution and copper/reacting solution contact areas, respectively; K_{sp} is the ratio of the copper/copper oxide and copper/reacting solution specific contact areas; and $K_{3,2} = k_3/k_2$. Obviously,

$$\frac{\mathrm{d}m_{\text{Cu}}}{\mathrm{d}t} = 64\frac{\mathrm{d}n_{\text{Cu}}}{\mathrm{d}t},\quad \frac{\mathrm{d}m_{\text{CuO}}}{\mathrm{d}t} = 80\frac{\mathrm{d}n_{\text{CuO}}}{\mathrm{d}t},\quad \frac{\mathrm{d}m_{\text{Cu}_2\text{O}}}{\mathrm{d}t} = 144\frac{\mathrm{d}n_{\text{Cu}_2\text{O}}}{\mathrm{d}t}, \tag{19}$$

where m_{CuO} and $m_{\text{Cu}_2\text{O}}$ are the weights of copper(II) oxide and copper(I) oxide.

As was noted above, the copper contact areas vary continually during the reaction. We did not find any models or methods for taking into account these variations, so we had to carry out additional investigations.

According to experimental data, the variation of the specific copper/reacting solution contact area is described by the equation

$$k_1S_{\text{sp1}} = k_{10}x^{-p}, \tag{20}$$

where x is the conversion of the copper compound and p is 0.33 ± 0.02 for the copper oxides and 0.37 ± 0.04 for the copper ion complex.

This character of specific contact area variation for the copper oxide reduction reactions can be explained by assuming that the oxide particles are identical spheres and that the copper particles forming in these spheres are identical hemispheres. For the reactions involving the copper ion complex, it should be assumed that the reduction of the copper ions yields identical spherical particles. Under these assumptions,

$$k_1S_{\text{sp1}} = k_{1,0}\frac{\mathrm{S}_1m_{0,\,\text{Cu}}}{\mathrm{S}_{1,\,0}m_{\text{Cu}}} = Ak_{1,\,0}\frac{R_0}{R} = A_1k_{1,\,0}\left(\frac{N}{N_0}\right)^{0.33}\left(\frac{m_{0,\,\text{Cu}}}{m_{\text{Cu}}}\right)^{0.33} = A_2k_{1,\,0}\left(\frac{N}{N_0}\right)^{0.33}\left(\frac{x_0}{x}\right)^{0.33}, \tag{21}$$

where A_1, A_2, and A_3 are correction factors; R and R_0 are the copper particle radii during the reaction and after the completion of copper layer formation, respectively; N and N_0 are the numbers copper particles in the initial oxide particle during the reaction and after the completion of copper layer formation, respectively; and x_0 is the oxide-to-copper conversion upon the completion of copper layer formation.

The observed approximate constancy of the $A_2\left(\frac{N}{N_0}\right)^{0.33} \approx 1$ value is explained by the marked difference between the rates of the noncatalytic and catalytic reactions and by the low probability of the appearance of new crystallization centers after the formation of the copper particles.

As compared to the reduction rate of the copper oxides, the rate of the limiting step of the reduction of the copper ion in the complex is described by a more complicated equation:

$$\frac{\mathrm{d}C_{\text{NaOH}}}{\mathrm{d}t} = k_5C_{\text{CH}_2\text{(OH)O}^-}C_{\text{CH}_2\text{O}} + \left[k_{1,0}x^{-p}\left(1 + KC^q_{\text{Cu}^{2+}}\right)C^n_{\text{CH}_2\text{(OH)O}^-}m_{\text{Cu}}\right]\frac{1}{V}. \tag{22}$$

This is likely due to the effect of the complex on the adsorption equilibrium. According to experimental data, the empirical coefficients in Eq. (22) are as follows: $q = 0.5$ and $K = 4.4 \pm 0.5$ (25°C).

The specific copper/oxide contact area also varies during the reaction. According to experimental data, at $x \le 0.6$ $\frac{k_3S_2}{k_2S_1} = K_{\text{sp}}K_{3,2}$; at $x \ge 0.6$ $\frac{k_3S_2}{k_2S_1} = K_{\text{sp}}K_{3,2}\frac{m}{m_{\text{Cu}}}$. For copper(II) oxide, $K_{3,2} = 0.014 \pm 0.001$; for copper(I) oxide, $K_{3,2} = 0.0075 \pm 0.0005$; that is, the latter is less reactive than CuO. At $x \le 0.6$ $K_{\text{sp}} = 2$; at $x \ge 0.6$,

$$K_{\text{sp}} = A_3x(1-x)^{-0.33}. \tag{23}$$

For copper(II) oxide, $A_3 = 2.95$; for copper(I) oxide, $A_3 = 3.28$.

The character of this dependence can be explained by assuming that, at $x \ge 0.6$, the oxide particles turn into identical bilayer spheres. In this case, taking into account the volume and the surface area of the oxide, which is the core of the particle, and the surface area of copper, which is in contact with the reacting solution, we can write the following equation:

$$K_{\text{sp}} = \frac{\mathrm{S}_2m_{\text{Cu}}}{\mathrm{S}_{1,0}m} = A_4\frac{r^2}{R_0^2}\frac{x}{1-x} = A_5\left(\frac{\rho_{\text{Cu}}}{\rho_{\text{ox}}}\frac{m}{m_{0,\,\text{Cu}}}\right)^{0.66}\frac{x}{1-x} = A_3x(1-x)^{-0.33}, \tag{24}$$

where A_3, A_4, and A_5 are correction factors; ρ_{Cu} and ρ_{ox} are the copper and oxide densities; and r is the radius of the particle core.

According to experimental data, for the reaction involving the copper ion complex, $K_{3,2} = 71.4 \pm 5$.

Systems of differential equations were solved by numerical integration, setting the initial amount of copper ("seed") so that it corresponded to a conversion value of 0.01 (end of the induction period). Next, the effective rate constants of the noncatalytic reactions were estimated under the assumption that $l = n$. A comparison between the calculated and experimental data and the corresponding estimates of the rate constants of the noncatalytic reductions of the copper compounds are presented in Figs. 1–3.

The above assumptions and reaction mechanisms provide an explanation for the experimental data reported here.

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