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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

Full Text

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LIQUID-PHASE OXIDATION OF CARBON MONOXIDE

Recently a large number of works have appeared $^{(1-7)}$ devoted to the oxidation of olefins to aldehydes and ketones in the liquid phase. The catalysts of these processes are acidic solutions of salts of platinum-group metals and copper. The process of olefin oxidation proceeds through the formation of complexes with halide salts of platinum-group metals of the Zeise-salt type, which in the second stage decompose into zerovalent palladium and an aldehyde. Halide salts of divalent copper are used for the oxidation of zerovalent palladium.

There is a certain analogy in the properties of carbon monoxide and ethylene —primarily their great tendency toward complex formation as a consequence of the presence of multiple bonds. There are almost no literature data on the liquid-phase oxidation of carbon monoxide $^{(8,9)}$.

Fig. 1. Effect of temperature on the depth of oxidation of carbon monoxide. CO concentration 0.5%, $V = 220$ l/h.
1—20°, 2—40°, 3—60°

Fig. 2. Dependence of the depth of oxidation on the partial pressure of carbon monoxide at 40°, $V = 220$ l/h. CO concentration: 1—0.3%, 2—0.5%, 3—1%, 4—1.75

We studied the oxidation of small concentrations (0.3-2%) of carbon monoxide in the liquid phase in a flow system at 20, 40, and 60°. The main component of the apparatus is a reactor 58-60 cm high and 3.5 cm in internal diameter, equipped with a jacket for thermostating and a device for measuring the potential of the system. A catalytic solution was poured into the reactor, which had a porous glass filter in the lower part; through this solution a gas containing from 0.3 to 2% carbon monoxide was bubbled, while the flow rate was varied from 150 to 300 l/h. The composition of the gas leaving the reaction zone was analyzed on an automatic GIPT-7 instrument with accuracy to the second decimal place. At the first stage, in the reactions of carbon monoxide oxidation, catalysts used for obtaining aldehydes and ketones were investigated $^{(1-4)}$. The experiments showed that in the presence of palladium chloride and copper chloride, with variation of the hydrochloric-acid concentration from 0.02 to 0.1 N, the depth of oxidation of carbon monoxide does not exceed, in the optimal case, 12% at a temperature of 20°. Raising the temperature

to 40° decreases the oxidation of carbon monoxide to 6%. A. A. Grinberg (10) showed for Zeise salts that the stability of the complexes $K_2[\mathrm{PdX}_4]$ depends to a considerable degree on the nature of the ligand and increases in the series $\mathrm{Cl}^- < \mathrm{Br}^- < \mathrm{J}^-$. The activity of the complexes in exchange reactions also depends on their stability and, consequently, on the nature of the ligand entering the inner sphere.

In this connection, we studied the effect of bromide and iodide ions on the activity of the catalyst. Introduction of the bromide ion increases the extent of oxidation of carbon monoxide from 12 to 20%. In this case the extent of oxidation of carbon monoxide changes almost not at all with increasing temperature. The iodide ion almost completely suppresses the activity of the catalyst.

Special studies showed that the maximum extent of oxidation of carbon monoxide (35%) for this catalyst is observed at the ratio $[\mathrm{Pd}^{2+}] : [\mathrm{Cu}^{2+}] = 0.22$ and $[\mathrm{Cl}^-] : [\mathrm{Br}^-] = 0.2$. The results obtained make it possible to suggest that the increase in the extent of oxidation of carbon monoxide from 12 to 35% is associated with the formation of more active palladium complexes of mixed composition $[\mathrm{PdCl_3Br}]^{2-}$ or $[\mathrm{PdCl_2Br_2}]^{2-}$, in which the chlorine ion located in the trans position relative to bromine can readily be replaced by a molecule of carbon monoxide (11). Table 1 presents the dependence of the catalyst activity on the hydrochloric acid concentration.

Table 1

Effect of hydrochloric acid concentration on the oxidation of carbon monoxide (0.5%)
Flow rate 220 l/h

Experimental temperature, °C	HCl concentration, g-eqv/l	$[\mathrm{Pd}^{2+}]/[\mathrm{Cu}^{2+}]$	$[\mathrm{Cl}^-]$, g/l	$[\mathrm{Br}^-]$, g/l	Oxidation of carbon monoxide, %
20	0.066	0.22	5.8	20.6	14
40	0.066	0.22	5.8	20.6	12
20	0.04	0.22	4.88	20.6	16
40	0.04	0.22	4.88	20.6	14
20	0.02	0.22	4.17	20.6	35
40	0.02	0.22	4.17	20.6	25

Experimental temperature, °C	HCl concentration, g-eqv/l	$[Pd^{2+}]/[Cu^{2+}]$	$[Cl^{-}]$, g/l	$[Br^{-}]$, g/l	Oxidation of carbon monoxide, %
20	0.01	0.22	3.81	20.6	30
40	0.01	0.22	3.81	20.6	18
20	0.005	0.22	3.64	20.6	28
40	0.005	0.22	3.64	20.6	18
20	0.005	0.22	3.64	20.6	29
40	0.005	0.22	3.46	20.6	18

It follows from Table 1 that the maximum oxidation of carbon monoxide corresponds to $0.02\,N$ HCl and that a change in the concentration of hydrochloric acid rather sharply lowers the activity of the catalyst.

K. I. Matveev, A. M. Osipov et al. (4) found that the process of oxidation of $Cu^{+} \rightarrow Cu^{2+}$ is facilitated in the presence of oxygen-containing ligands owing to the formation of copper complexes. In this connection, we investigated the effect of additions of acetate ion on the activity of the catalyst. Addition of acetate ion led to a twofold increase in the extent of oxidation of carbon monoxide, to 50% at 20° (Fig. 1). When the temperature is raised to 40°, the extent of oxidation of carbon monoxide increases to 55%; however, a further rise in temperature to 60° leads to a sharp decrease in the activity of the catalyst (Figs. 1, 3).

Fig. 3. Effect of the pH of the medium on the process of oxidation of carbon monoxide (0.5%) at 20°, $V = 220$ l/h. 1 –water, 2 –$0.02\,N$ HCl, 3 –$0.06\,N$ CH_3COOH, 4 –$0.005\,N$ KOH

Figure 2 presents the dependence of the extent of oxidation on the partial pressure of carbon monoxide. As the carbon monoxide content in the initial gas is increased from 0.3 to 1.75%, the extent of oxidation increases by a factor of 2. A change in the pH of the medium also affects the activity of the catalyst (Fig. 3). On going from acidic to weakly alkaline solutions, the extent of oxidation increases from 20 to 70%. The low activity of the catalyst in

in acidic solutions, is possibly associated with the destruction of copper acetate complexes. It follows from the experimental data that copper acetate complexes are not only the oxidant for the reaction $Pd^{0} \rightarrow Pd^{2+}$, but also participate directly in the oxidation reaction of carbon monoxide. Prolonged tests showed that the activity of the catalyst does not decrease during 5-6 hours of operation without regeneration. The preservation of catalyst activity is associated with the establishment of a constant mobile equilibrium between the oxidized and reduced forms of the catalytic solution, which can be monitored by measuring the potential of the system. The activity of the catalyst is completely restored when air is blown through for 1-2 hours.

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