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CATALYSIS

Effect of Iodine-Containing Promoter on the Catalytic Activity of Silver in the Course of Ethylene Glycol Oxidation

V. S. Shmotin, A. S. Knyazev, A. I. Titkov, A. N. Salanov, O. V. Vodyankina, and L. N. Kurina

Tomsk State University, Tomsk, Russia
Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, Russia

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Abstract—Surface morphology and catalytic properties of electrolytic silver crystals in partial oxidation of ethylene glycol into glyoxal were studied.

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Glyoxal is widely used in industry for preparing high-quality paper, films, adhesives, various polycondensates, and pharmaceuticals [1]. Being the nearest analog of formaldehyde, glyoxal surpasses it in chemical properties. Partial oxidation of ethylene glycol on polycrystalline silver catalysts, performed in the continuous flow mode, is the most ecnomically feasible and facile procedure for preparing glyoxal. In this case, the alcohol conversion is as high as 90%, and the selectivity with respect to glyoxal reaches 55–60% [2, 3]. Promotion of the surface or introduction of certain additives into the reaction mixture with the subsequent treatment of the catalyst are the best ways to enhance the activity of the catalytic systems. Various promoters are used in catalysts for partial oxidation of organic compounds, e.g., alkali metals [4] and phosphorus-containing compounds [5]. The promoting effect of halogen-containing hydrocarbons on the partial oxidation of methanol to formaldehyde in the presence of silver catalysts was studied in [6, 7]. It was found that, with addition of microamounts of iodine-containing promoters into the reaction mixture, the alcohol conversion and yield of formaldehyde increase, whereas the yield of the products of deep oxidation decreases. Taking into account that the processes of partial oxidation of methanol and ethylene glycol are largely similar, in this study we examined the catalytic synthesis of glyoxal in the presence of ethyl iodide promoter.

EXPERIMENTAL

Silver crystals were prepared at the Institute of High-Temperature Electrochemistry (Ural Division, Russian Academy of Sciences, Yekaterinburg, Russia) by electrolysis of a $KNO_3 + NaNO_3 + AgNO_3$ melt in an open electrolysis bath using rotating cathode [8]. The crystal surface was finely cleaned by the procedure described elsewhere [9]. The catalyst was prepared by pressing of silver crystals with paraformaldehyde and subsequent annealing in an air flow at 650°C for 3 h.

The catalytic activity of silver was studied in a flow catalytic installation with a fixed catalyst bed by the procedure described in [10]. The height of the catalyst bed was 20 mm, and the reactor diameter was 16 mm. The gaseous and liquid products obtained in the course of oxidation were analyzed chromatographically [11, 12].

The surface morphology of the silver samples was studied using a JEOL 6460LV field-emission high-vacuum scanning electron microscope (energy of the primary electron beam 20 keV). To improve the image contrast, the sample surface was coated with gold (film thickness up to 0.05 μm).

Data on the partial oxidation of ethylene glycol into glyoxal in the absence of ethyl iodide and with its addition to the reaction mixture in relation to the oxygen content in the reaction mixture are plotted in Fig. 1a. The molar content of the promoter added was 6 ppm with respect to ethylene glycol. The oxygen/ethylene glycol (O_2 : EG) molar ratio was varied from 0.8 to 1.8. As seen, with increasing oxygen content in the promoter-free reaction mixture the alcohol conversion increases (Fig. 1a, curve *1*), whereas the selectivity of the glyoxal formation passes through a maximum (Fig. 1a, curve *3*). Addition of the promoter into the reaction mixture improves the selectivity with respect to the desired product in a broader range of

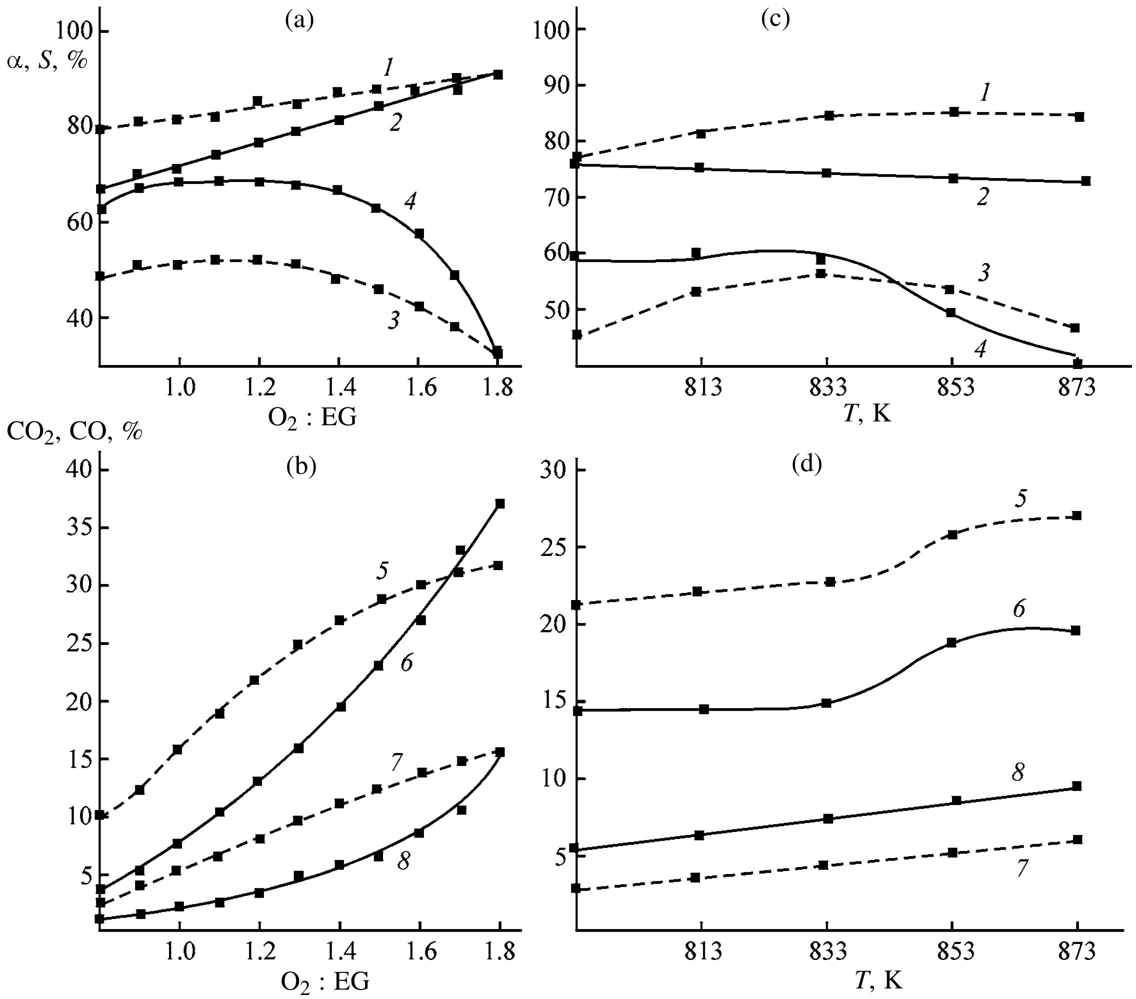

Fig. 1. (*1, 3, 5, 7*) Catalytic activity of silver catalyst without iodine-containing promoter and (*2, 4, 6, 8*) with addition of promoter into the reaction mixture as a function of the (a, b) O_2 : EG molar ratio and (c, d) temperature *T*. (α) (*1, 2*) Conversion of ethylene glycol; (*S*) (*3, 4*) selectivity with respect to glyoxal; yields of (*5, 6*) CO_2 and (*7, 8*) CO.

the compositions of the reaction mixture as compared to the initial sample (Fig. 1a, curve *4*).

It should be noted that, with addition of the iodine-containing promoter into the reaction mixture, the yields of the products of deep oxidation decrease (Fig. 1b), which is probably due to changes in the chemical composition of the silver crystal surface. Atomic iodine formed by the ethyl iodide decomposition is adsorbed on the silver surface and, occupying the adsorption centers, decreases adsorption of the oxygen atoms responsible for the deep oxidation [13]. This assumption is confirmed by certain decrease in the ethylene glycol conversion in the presence of the promoter (Fig. 1a, curve *2*).

The effect of temperature on the activity of the silver catalyst in the course of ethylene glycol oxidation is illustrated in Figs. 1c and 1d. As seen, with increasing temperature of treatment of the silver catalyst with the promoted reaction mixture, the selectivity with respect to glyoxal decreases (Fig. 1c, curve *4*), whereas the conversion of ethylene glycol remains essentially constant (Fig. 1c, curve *2*). This decrease in the selectivity with respect to glyoxal is probably due to the increasing rate of the iodine desorption from the catalyst surface and rearrangement of the centers of deep oxidation.

In the case of promoted reaction mixtures, the yields of the products of deep oxidation are lower than those in the promoter-free systems at the same temperatures (Fig. 1d). These data suggest that, in the presence of the promoter, the process is stable in the broader range of experimental conditions. On the whole, the silver catalyst in the presence of the iodine-containing promoter is characterized by higher yield

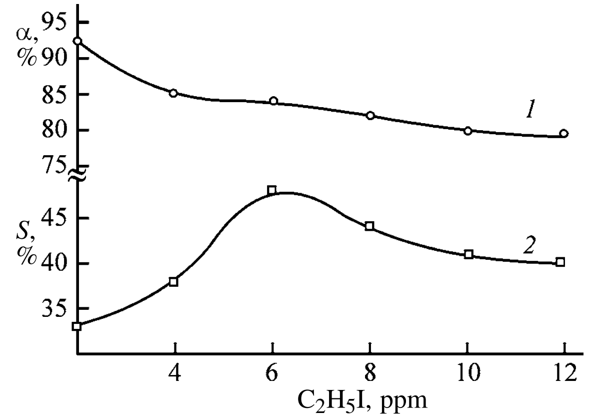

Fig. 2. Catalytic activity of silver as a function of the promoter (C_2H_5I) concentration in the reaction mixture (molar ratio to ethylene glycol). Composition of the reaction mixture: EG : O_2 : N_2 : H_2O 1.0 : 1.0 : 10.0 : 3.4, *T* 560°C. (α) (*1*) Conversion and (*S*) (*2*) selectivity.

of the desired product and high stability in a wide range of experimental conditions.

The dependence of the catalytic activity of silver on the content of the iodine-containing promoter in the reaction mixture is shown in Fig. 2. As seen (Fig. 2, curve *1*), the ethylene glycol conversion decreases with increasing promoter content in the reaction mixture. This is probably due to the fact that iodine competing with oxygen in the adsorption on the silver surface decreases the content of adsorbed atomic oxygen which provides selective oxidation of ethylene glycol. Also, poisoning of the catalyst surface with iodine due to excess removal of oxygen cannot be excluded.

The dependence of the selectivity with respect to glyoxal on the promoter concentration passes through a maximum, which is observed at a molar ratio of ethyl iodide to ethylene glycol of about 6 ppm (Fig. 2, curve *2*). This is probably due to the following reasons. At a molar ratio smaller than 6 ppm, the promoter content is insufficient for the selective conversion, i.e., at low concentrations of the promoter in the reaction mixture significant amounts of oxygen are retained on the catalyst surface in the form of surface oxide Ag_2^SO, which can participate in further oxidation of the final product by the following reaction:

Catalytic activity of the silver samples before and after regeneration; composition of the reaction mixture: EG : O_2 : N_2 : H_2O 1.0 : 1.0 : 10.0 : 3.4, *T* 560°C

Sample	Ethylene glycol conversion, %	Selectivity to glyoxal, %
Ag	90	55
Ag/I	80	66
Ag/I:		
prolonged treatment	70	45
after regeneration	80	64

$$C_2H_2O_2 + 3Ag_2O \rightarrow 2CO_2 + H_2O + 6Ag.$$

On the other hand, at molar ratios of ethyl iodide to ethylene glycol higher than 6 ppm, the catalyst activity decreases due to poisoning of both the oxidation centers on the silver surface participating in the deep oxidation and oxygen-containing centers of the O_α type participating in the selective oxidation of ethylene glycol into glyoxal. Participation of the O_α centers of adsorbed oxygen in the glyoxal formation was confirmed in [14].

Upon prolonged treatment of the catalyst with the reaction mixture containing ethyl iodide in amounts greater that 6 ppm, the process characteristics deteriorate owing to poisoning of the active centers on the silver surface. We studied the possibility of the regeneration of catalyst after prolonged treatment with the iodine-containing promoter. For this purpose, the spent catalyst was annealed in an air flow at 600°C. After this treatment, the experiments on the catalytic oxidation were repeated; the results are listed in the table.

As seen from the table, annealing in an air flow at 600°C ensures almost complete regeneration of the activity of the silver catalyst. This is probably due to the iodine desorption from the sample surface and regeneration of the centers of alcohol selective oxidation. Thus, we found that the catalyst activity can be enhanced by adding an iodine-containing promoter (ethyl iodide) and the spent silver catalyst can be readily regenerated.

An electron-microscopic examination was performed to study the mechanism of promotion of the iodine-containing additive and the effect of the reaction mixture containing ethyl iodide on the morphology of the silver catalyst. The surface of the initial sample is shown in Fig. 3a. The samples prepared by electrolysis of the silver nitrate melt are elongated particles (5–7 μm wide and 40–60 μm long). The particle surface is smooth and well-rounded along the edges. The structure of the sample surface is determined by the side topochemical processes occurring during electrolysis of the molten mixture of KNO_3, $NaNO_3$, and $AgNO_3$ [15].

The surface morphology of the silver catalysts strongly changes after treatment with both initial and promoted reaction mixtures (Figs. 3b and 3c). As seen, after treatment with the initial reaction mixture EG : O_2 : N_2 : H_2O = 1.0 : 1.0 : 10.0 : 3.4 at 873 K, channels 0.2–1.0 μm in diameter are formed on the silver catalyst surface (Fig. 3b), and their amount upon treatment in the presence of the iodine-containing promoter is significantly smaller (Fig. 3c). It was found [14, 16] that these channels are formed in the near-surface silver layers in the course of treatment due to the adsorption of C-containing reagents providing accumulation of the oxocarbon structures able to diffuse into the sample bulk with increasing temperature. Under the action of the oxygen-containing reaction mixture, the oxocarbon fibers formed in the near-surface layer are burnt out, causing formation of channels.

In accordance with the electron-microscopic data, prolonged contact of the catalyst with the reaction mixture leads to the formation of carbon deposits (particles about 2 μm long and 0.5 μm thick, Fig. 3d). This effect is due to the adsorption of carbon-containing reagents participating in the catalytic process [17]. Addition of ethyl iodide does not cause changes in the silver crystal morphology (Fig. 3e). No pronounced carbonization was observed after treatment under the conditions similar to that of the initial sample.

Moreover, we observed almost no adsorption of carbon structures, no formation of the carbonization products, and no development of channels upon treatment of silver with the iodine-containing reaction mixture. This is most probably due to a decrease in the content of oxygen adsorbed on the catalyst surface, which directly participates in carbonization, because no accumulation of the carbonization products on the silver surface is observed in the oxygen-free systems [14].

In the reaction of ethyl iodide with the oxidized silver surface, along with competitive adsorption, removal of the surface oxygen is also possible by the following reactions:

$$2Ag_2O + 4C_2H_5I \rightarrow 4AgI + 2C_4H_{10} + O_2,$$

$$\Delta G_{298} = -564 \text{ kJ};$$

$$Ag_2O + 2C_2H_5I \rightarrow 2AgI + 2C_4H_{10}O, \Delta G_{298} = -450 \text{ kJ}.$$

In a study of the interaction of ethyl iodide with the surface of a preoxidized silver single crystal, the reaction products (butane, diethyl ether) used in the ther-

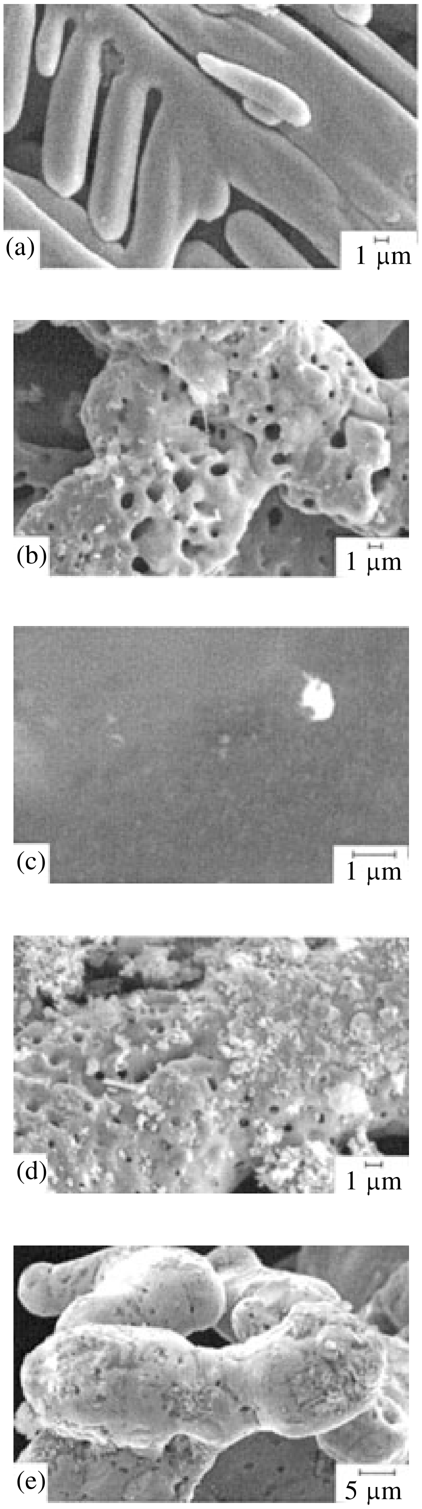

Fig. 3. Morphology of the silver catalyst surface: (a) initial sample, (b) sample treated with the initial reaction mixture, (c) catalyst treated with the promoted reaction mixture, (d) sample treated with the initial reaction mixture for a long period, and (e) sample treated with the promoted reaction mixture a long period.

mochemical calculations were detected by gas chromatography–mass spectrometry [18].

CONCLUSIONS

(1) The catalytic and physicochemical experimental data showed that addition of an iodine-containing promoter into the reaction mixture increases the selectivity with respect to glyoxal by 5–10%.

(2) The catalytic activity increases owing to a decrease in the contribution of the carbonization and profound oxidation in the presence of the iodine-containing additives.

(3) Promoter decreases the concentration of the centers of adsorbed oxygen responsible for the formation of carbonization products and occurrence of deep oxidation of ethylene glycol. In this case, the amount of oxygen participating in the selective conversion of alcohol decreases only slightly, leading to only insignificant decrease in the ethylene glycol conversion.

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