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> PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

## Catalytic Activity of Electrodeposited Copper-containing Compounds in Conversion of Carbon Monoxide by Steam

M. V. Tesakova<sup>a</sup>, V. I. Parfenyuk<sup>a,b</sup>, and A. A. Il'in<sup>b</sup>

<sup>a</sup> Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, Russia <sup>b</sup> Ivanovo State University of Chemical Engineering, Ivanovo, Russia

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**Abstract**—Possibility of using an ultradisperse copper-containing powder produced by the electrolytic method as an efficient catalyst for conversion of carbon monoxide by steam was studied.

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The reaction of conversion of CO by steam, used in the technological cycle of hydrogen production in manufacture of ammonia is carried out at medium and low temperatures. The medium-temperature stage is commonly performed with a mixture of iron and chromium oxides as a catalyst, and the low-temperature stage, with copper-containing catalysts including CuO, ZnO, and Al<sub>2</sub>O<sub>3</sub>, prepared by the conventional methods of coprecipitation, mixing, decomposition of metal salts, and mechanochemical synthesis [1].

In this study, we suggest to obtain a catalytically active copper-containing powder by using an electrochemical method that is rather simple and practicable. The method can yield a product with a prescribed particle size and chemical composition by varying electrolysis parameters and the concentration of an aqueous-organic solvent [2].

Introduction of an organic solvent in an aqueous electrolyte solution makes it possible to obtain coppercontaining particles less than 100 nm in size and to vary the chemical composition of the powder (raise the content of copper oxides in the powder, compared with that produced from an aqueous solution). The presence of copper oxides in the powder provides its catalytic activity in conversion of CO in the low-temperature stage. The catalysis on small particles plays an extremely important part in industrial chemistry. Catalyzed reactions commonly occur at a lower temperature, compared with uncatalyzed reactions; use of a catalyst markedly raises the yield of the target product of the reaction.

The goal of our study was to examine the catalytic activity and operation selectivity of a nanosize coppercontaining powder produced by the electrochemical reduction method in the low-temperature conversion of carbon monoxide by steam in comparison with the activity of catalysts synthesized by other methods.

## EXPERIMENTAL

The nanosize copper-containing powder was produced by electrolysis of a copper sulfate solution in a water-isopropanol mixture [3, 4] in which the working concentrations of copper sulfate and isopropanol and the initial current density were found by analysis of polarization curves. The electrolysis was performed at the limiting current density at a constant voltage maintained across the electrodes, with soluble electrolytic-copper anodes a cylindrical steel anode. The soluble anodes enable electrolysis during a rather long time without adjustment of the electrolyte or any adverse changes in the composition and particle size of the powder obtained. The resulting precipitate was many times washed with twice-distilled water to a constant electrical conductivity of washing water and dried first in air at room temperature and then in a drying box at



**Fig. 1.** Electron micrographs of powders. (a) Without addition of an organic solvent, (b) with addition of isopropyl alcohol; the same for Fig. 2.

80°C for 20–30 min until a powder with a constant mass was formed.

The specific surface area of the catalysts obtained was determined by the BET technique from thermal desorption of argon for a helium–argon mixture. The shape and size of powder particles was determined by transmission electron microscopy (TEM); micrographs were obtained on an EMV-100L electron microscope with a resolution of 0.3 nm at an accelerating voltage of 100 keV (Fig. 1).

The chemical composition of the powders was analyzed by electron diffraction and thermogravimetric methods [5] and by X-ray phase analysis. The diffraction pattern formed by accelerated electrons was obtained on transmission electron microscope in the microdiffraction mode from areas up to 2  $\mu$ m in size. To determine the chemical composition of the samples under study, we measured ring diameters, calculated the corresponding interplanar spacings, and compared the results with reference data [6]. Among the probable phases, we found those in whose lattice the *d*<sub>hkl</sub> sequence we found is observed. The measurement accuracy of the electron diffraction patterns is about 0.1% relative to the measured value of interplanar spacings.

The X-ray diffraction analysis of the powders was made on a DRON-3M diffractometer with monochromatized CuK radiation ( $\lambda = 0.154$  nm) at angles in the range 20–70°. Diffraction spectra were obtained at a measurement step of 0.01° and scanning rate of 2 deg min<sup>-1</sup> on the scale. The phase composition was found by comparing the interplanar spacings obtained from diffraction patterns and the corresponding diffraction peak intensities with values from the PDF X-ray database [7].

The catalytic properties of the ultradisperse coppercontaining powders we obtained in the reaction of conversion of carbon monoxide by steam were determined on a flow-through installation in the temperature range  $180-240^{\circ}C$  [8]. The tests were made in a gaseous reaction mixture of composition (vol %): H<sub>2</sub> 55, CO 12, CO<sub>2</sub> 9, and He 24, at a steam : gas ratio of 0.7. A weighed portion of the catalyst was 0.5 g. The volumetric rate of gaseous mixture delivery to the catalyst was 5000 h<sup>-1</sup>. The catalyst was placed in a quartz glass reactor and heated in the reaction mixture, with temperature raised at a rate of 4 deg min<sup>-1</sup>. The compositions of the starting gaseous reaction mixture and the final gaseous reaction mixture after the reactor were determined chromatographically on a Tsvet-100 gas chromatograph.

The catalytic activity of the samples was evaluated by the conversion of CO in the reaction of conversion of carbon monoxide by steam and by the output capacity of the catalyst (for CO). The reaction of CO conversion is satisfactorily described by a kinetic equation of a first-order reaction [9]. To calculate the throughput P(ml g<sup>-1</sup> s<sup>-1</sup>) of the catalyst, we used the equation derived by transforming the equation for the rate constant of the first-order reaction, adapted to the process under study, in which CO is converted by steam [10]:

$$P = \frac{\ln \frac{1}{(1+X)} (1+n)R}{60g_{cat}},$$

where *R* is the flow rate of dry gas (ml min<sup>-1</sup>); X, CO conversion;  $g_{cat}$ , catalyst mass (g); and *n*, steam-to-gas ratio.

To find the amount of by-products formed in the conversion reaction and determine the operation selectivity of the catalyst, we subjected the condensate to a chromatographic analysis on a Kristall Lyuks chromatograph.

The results of our analysis of the granulometric composition of the powders obtained (Figs. 2a and 2b) suggest that key role is played in the formation of ultradisperse particles by the organic solvent and, in particular, isopropyl alcohol. Introduction of isopropyl alcohol into the electrolyte makes it possible to produce by the electrochemical method a copper-containing powder with a particle size smaller than 100 nm and a sufficiently narrow particle size distribution. As follows from Fig. 2b, only a small number of particles (about 10-15% of the total amount of particles) are more than 100 nm in size, with the main mass of powder particles (85-90%) having size smaller than 100 nm. The powder with <100-nm particles, produced from an aqueous-organic solution, was subjected to electron and X-ray diffraction analyses. The results of the electron diffraction analysis demonstrated that the powders contain metallic copper and oxides Cu<sub>2</sub>O and CuO (Table 1).

An analysis of the X-ray diffraction pattern in Fig. 3 confirmed that the powders contain Cu and Cu<sub>2</sub>O. A possible reason for the absence of peaks corresponding to copper(II) oxide found by electron diffraction analysis in the X-ray diffraction patterns is that copper(II) oxide covers copper-containing particles in the form of a thin layer and its amount is insufficient for being detected by X-ray phase analysis. The structure of an ultradis-

**Table 1.** Radii of rings in electron diffraction patterns, calculated interplanar spacings, and reference data for Cu,  $Cu_2O$ , and CuO

	$d_{hkl}$ , Å		Reference data			
<i>R</i> , mm		Compound	$d_{hkl}$ , Å	<i>I</i> , %		
17.54	2.06		2.08	100		
20.00	1.81		1.81	53		
33.15	1.09		1.09	33		
34.75	1.04	IJ	1.04	9		
12.00	3.01		3.00	3		
14.87	2.43		2.45	100		
24.00	1.51	$\left(\begin{array}{c} Cu_{2}O \end{array}\right)$	1.51	44		
28.00	1.29	J [	1.28	31		
14.50	2.49		2.51	100		
19.32	1.87		1.85	20		
21.00	1.72	$\left  \right\rangle$ CuO $\left  \right\rangle$	1.70	8		
23.00	1.57		1.57	8		
37.00	0.98	J (	0.98	3		

perse powder particle can be characterized as a druse of polycrystalline copper with oxidized surface. The X-ray diffraction method is less sensitive than the electron diffraction analysis. The sensitivity threshold of this method is 2–10 wt %. Presumably, the amount of copper(II)



**Fig. 2.** Histograms of the particle size distribution of the powders obtained. (*A*) Content.



Fig. 3. X-ray diffraction pattern of the ultradisperse coppercontaining powder.  $(2\theta)$  Bragg angle.

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oxide does not exceed this value and, therefore, cannot be determined in this way. The techniques we used mutually supplement each other and enable the most objective and fullest estimate of the qualitative composition of the powders obtained. The powders contain copper and copper oxides Cuo and Cu<sub>2</sub>O, with the amount of copper(II) oxide not exceeding 10 wt %.

Copper-containing catalysts are widely used in production of ammonia, methanol, and caprolactam. The catalytic conversion of copper monoxide with steam, catalyzed by copper-containing catalysts, is a constituent of the industrial process for hydrogen production from natural gas. The conversion of carbon monoxide by steam occurs in accordance with the reaction equation

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

The copper-containing powder exhibits a high catalytic activity in the reaction of CO conversion at a temperature of 200°C, which is due to its large specific surface area. With this catalyst, the conversion of CO in the reaction is 87% [11].

It can be seen in Table 2 that copper-containing powders produced by electrochemical precipitation surpass at low temperatures all catalysts obtained using other methods. At 180°C, the throughput of electrochemically precipitated copper-containing powders is more than two times that of the industrial KCO catalyst. At 220°C, the difference between catalysts of different types becomes less pronounced. At his temperature only the catalysts produced by the mechanochemical method is 6% better. In the range of optimal temperatures (200°C for the electrochemically precipitated powder and 240°C for the industrial catalyst), the catalyst we obtained has the best characteristics. The selectivity of the catalyst is also highly important for the process of CO conversion because the steam condensate can be repeatedly used in manufacture of ammonia [12]. The content of accumulated organic admixtures in the condensate should not exceed 15 mg l<sup>-1</sup>. Performing the technological cycle with recycling of the condensate saves raw materials and energy resources, diminishes the expenditure for preliminary water treatment and desalination, makes shorter the blowing stage, and lowers the loss of heat.

A chromatographic analysis of the reaction process demonstrated that, with the copper-containing powder produced by the electrochemical method used as a catalyst, the condensate contains no methanol, acetone, or butanol; the contents of acetaldehyde and 2-propanol are, respectively, seven and six times lower than those with the industrial sample (Table 3). The total content of impurities is 4.04 mg l<sup>-1</sup>. The presence of acetaldehyde, methyl acetate, ethyl acetate, ethanol, and 1- and 2-propanol in the condensate indicates that there occur side processes in which carbon monoxide is hydrogenated:

$$2CO + 4H_2 = C_2H_5OH + H_2O,$$
  

$$2CO + 3H_2 = CH_3COH + H_2O,$$
  

$$3CO + 6H_2 = C_3H_7OH + 2H_2O,$$
  

$$3CO + 4H_2 = CH_3COOCH_3 + H_2O,$$
  

$$4CO + 6H_2 = C_2H_5COOCH_3 + 2H_2O.$$

The electrolytically produced copper-containing powder has a high selectivity and surpasses in this regard the industrial sample, which is probably due to

	Catalyst throughput, ml g <sup>-1</sup> s <sup>-1</sup> , at indicated temperature, °C					
Catalyst preparation method	180	200	220	240		
Precipitation from ammonia carbonate solutions	4.9	_	8.7	12.4		
Industrial KCO sample	5.1	-	9.6	13.2		
Mechanochemical synthesis from salts	7.5	-	14.2	13.7		
Electrochemical precipitation	10.5	13.5	11.3	11.7		

**Table 2.** Activities of the copper-containing powder and catalysts produced by other methods in conversion of CO by steam at various temperatures

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Catalyst	Content in the condensate, mg l <sup>-1</sup>									
	acetaldehyde	methyl acetate	ethyl acetate	methanol	2-propanol	1-propanol	ethanol	acetone	butanol	$\begin{bmatrix} \Sigma, \\ mg l^{-1} \end{bmatrix}$
Copper-containing powder	0.76	2.09	0.17	-	0.77	0.07	0.18	-	_	4.04
Industrial KCO sample	5.52	_	_	0.48	4.85	_	_	0.48	0.28	11.77

Table 3. Yield of by-products in the test conversion of carbon monoxide by steam

the decrease in the reaction temperature to 200°C.

The high catalytic activity of the catalyst under study is due to the size-related characteristics of the powder and its chemical composition. The particle size smaller than 100 nm and the considerable amount of cuprous oxide in the powder predetermine its large specific surface area  $(51 \text{ m}^2 \text{ g}^{-1})$  and presence of a large number of active centers. Despite the wide application of copper-containing catalysts, the nature of their active centers remains a matter of discussion [13]. The published information about active forms of copper in the reaction of CO conversion is rather contradictory: in [14], it is assumed that metallic copper in finely dispersed state is assumed to be active; according to other data, the active centers include Cu<sup>+</sup> ions [15, 16] or Cu<sup>2+</sup> aggregates formed as a surface solid solution on ZnO on highly dispersed CuO and on the surface of metallic copper [13, 17].

Probably, copper in the oxidation state +1, which has high electron affinity, is responsible for the catalytic activity. Metal ions with  $d^{10}$  electron shell, to which belongs Cu<sup>+</sup>, easily pass from the upper *d* level to the upper *s* level under the action of thermal energy. Upon a transition of electrons to the *s* level, the *d* level becomes unoccupied. This free space (*d*-electron hole) has an electron affinity and can capture an electron from the adsorbed substance, which causes an activated adsorption on the metal [18]. Information about the structure of active centers is important for elucidating the reaction mechanism. In view of the assumption about the active centers of the catalyst, a probable mechanism is that constituted by a series of successive reactions [19]:

absorption of reactants

$$CO + K \rightleftharpoons KCO$$
,

$$H_2O + K \rightleftharpoons KH_2O;$$

surface reaction

$$KCO + KH_2O \rightleftharpoons KCO_2 + KH_2;$$

and desorption of reaction products

 $KCO_2 \rightleftharpoons K + CO_2,$  $KH_2 \rightleftharpoons K + H_2.$ 

## CONCLUSIONS

An electrolytically produced copper-containing powder used as a catalyst for conversion of carbon monoxide by steam makes lower the reaction temperature and diminishes the yield of by-products, compared with catalysts obtained using other methods.

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