Using the Naturally Occurring Oxides for Developing the Catalysts of Carbon (II) Oxide Oxidation

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Abstract

Catalysts for carbon (II) monoxide low-temperature oxidation were studied. It is demonstrated that wastes from water treatment plants those are formed in the course of water purification from iron can be used as catalysts in the mentioned process.

Key words: carbon (II) monoxide oxidation, catalysts, hopcalite

INTRODUCTION

The reaction of carbon (II) monoxide oxidation is one of the simplest oxidation reactions which is considered as a model for studying the general laws of oxidation processes. In addition, the investigation of this reaction is also of practical interest, since the carbon monoxide (CO) is one of toxicants entering into the atmospheric air as the result of natural disasters and human activities. The development of low temperature and stable catalytic CO oxidation systems is a direct way to create efficient respiratory devices for the protection of respiratory organs [1]. At the present time, for CO oxidation by means of atmospheric oxygen at a room temperature, heterogeneous catalysts are generally offered; noble metal nanoclusters, including those applied onto different carriers are under active investigation [2]. One could consider a group of supported metal complex catalysts based on platinum, palladium and copper [3]. Gold-containing catalysts capable of removing CO at a low temperature are widely used [4], but one does not succeed in achieving the parameters required for the activity, stability and durability thereof. At the same time, replacing the catalysts based on noble metals by cheaper oxide catalysts is urgent. Of the greatest interest in this in this connection are catalytic systems based on transition metals (Fe, Co, Ni) [5, 6].

One of the most famous CO oxidation catalysts operating at a room temperature is presented by hopcalite [7, 8]. The hopcalite is a mixture of oxides (MnO, CuO, and Ag_2O) applied onto different carries that is used in breathing masks to protection respiratory organs against carbon monoxide. The main disadvantage of hopcalite catalysts consists in the fact that they are inactivated in the presence of water vapour, which confines to a considerable extent the practical use thereof.

As far as CO oxidation catalysts are concerned, to all appearance, there could be of interest also some naturally occurring oxohydroxides and oxides of transition metals. For example, in regions with high iron content in groundwater, the wastes of water treatment plants (in the course of purifying the water from iron) are mainly presented by iron and manganese oxides applied onto natural carriers (sand, clay, and burnt rock).

In the Tomsk Region, there is one of the largest deposits of iron located, that influences to a great extent upon the composition of water therein. The interaction of minerals and rocks with groundwater is accompanied by a significant mineralization of water, so all the groundwaters of the Tomsk Region contain large amounts of iron, often 20−30 mg/L. In the course of water purification from iron, a significant amount of a precipitate is formed, that is mainly composed of different of iron and manganese oxide and oxyhydroxide species. The traditional methods for the disposal of wastes from water deironing stations are based primarily on a small size of precipitate particles. The disparity level of naturally occurring oxides is high enough: the particle size inherent in a precipitate dried at 25 °C mainly ranges within 0.02−0.03 μm, which corresponds to a nanosized state of substances [9]. There is information available in the literature concerning the use of wastes taken from water treatment plants, activated at different temperature values, as an active sorbent for water purification from petroleum products and phenols [10] and as catalysts for the oxidation of hydrocarbons [11].

EXPERIMENTAL

The catalysts were prepared from the wastes taken from water treatment plants those purify water from the iron as it follows. A precipitate of the mixture of metal oxides and oxohydroxides formed as the result of the underground water aeration was deposited on the filter (quartz sand). The wet precipitate was stirred-up to separate coarse particles from fine ones *via* sedimentation with further obtaining two fractions (I and II) those were dried at 25 °C.

The fraction I was dried to grind using an agate mortar with further separating phase I with the particle size of 0.1−0.15 μm (HR TEM) by means of sedimentation. The composition of phase I: 85 % MnO, the rest SiO_2, Al_2O_3, $CaCO_3$, $MgCO_3$. In the course of making the catalysts the phase I was used completely, with no isolation of SiO_2, Al_2O_3, $CaCO_3$, $MgCO_3$, because these oxides and salts are not active in the oxidation reaction.

From the fraction II, we isolated phase II with a particle size of 0.02−0.03 μm that contains 98.0−99.0 % of amorphous iron oxohydroxide with small amounts (0.1 %) of other metal oxides (Si, Sr, Ca, Mn, Zn, Ba) [12].

In order to investigate the phase composition of the phases I and II, the samples were dried at the temperature of 25, 100, 200, 250, 300, 500 °C in atmospheric air in a WS 31 drying box and a PM-10 muffle oven.

The phase composition was determined by means of X-ray diffraction analysis (Shimadzu XRD-6000 diffractometer, CuK_α radiation, database PCPDFWIN).

The specific surface area of mixed oxides and oxohydroxides was determined using a method of nitrogen thermal desorption employing a "Sorbtometr M" unit with calculation according to a multipoint BET method in automatic mode.

The size and shape of the particles inherent in the compositions under investigation was determined using transmission electron microscopy technique with the use of a JEM-100 CX II JEOL electron microscope.

The activity of the catalyst systems in the oxidation of CO was measured at 20, 30, 35, 40 °C and atmospheric pressure in a glass flow-through reactor (the volume of the catalyst loaded was constant amounting to 12 cm^3). A reaction mixture containing about 5.0 % of CO, and about 95.0 % of air was preliminarily thermostated at a temperature required to supply it to the reactor with the flow rate of 1200 h^{-1}. From the results of analysis, we calculated CO and CO_2 mole fractions of in the initial (IM) and the final (FM) reaction mixtures. The CO conversion was calculated as a ratio of the difference between the molar fraction of CO in the IM to the molar fraction of CO in the IM. The CO concentration at the inlet and at the outlet was measured using a K-100 electrochemical carbon monoxide gas analyzer.

The reference catalyst K-1 similar to hopcalite was prepared from active manganese dioxide (MnO_2), copper oxide (CuO) and silver oxide (Ag_2O). The oxides composing the catalyst were synthesized according to the techniques described by the authors of [13].

RESULTS AND DISCUSSION

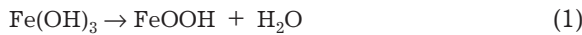The mineral precipitate formed in the course of iron removal (oxidation) of mineral salts
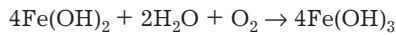
TABLE 1

Chemical composition of precipitate

Main	Concentration, %	
components	Fraction I	Fraction II
SiO_2	3.56	12.90
Al_2O_3	7.99	19.03
Fe_2O_3	12.59	31.80
MnO	39.10	5.98
$CaCO_3$	8.93	6.17
$MgCO_3$	9.99	1.10

Note. Fraction I − coarse phase of precipitate; fraction II − dispersed phase of precipitate.
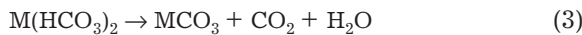
inherent in the groundwater of the Tomsk Region in the wet state represents a creamy yellow-brown substance. The formation of the precipitate can be described by the following processes:

$$Fe(HCO_3)_2 \rightarrow Fe(OH)_2 + 2CO_2$$
$$4Fe(OH)_2 + 2H_2O + O_2 \rightarrow 4Fe(OH)_3$$
$$Fe(OH)_3 \rightarrow FeOOH + H_2O \qquad (1)$$

The overall reaction could be expressed as it follows:

$$4Fe(HCO_3)_2 + O_2 \rightarrow 4FeOOH + 8CO_2 + 2H_2O \qquad (2)$$

In parallel, there occurs a process

$$M(HCO_3)_2 \rightarrow MCO_3 + CO_2 + H_2O \qquad (3)$$

where $M^{2+} = Mn^{2+}$, Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, Pb.

The chemical composition of the precipitate isolated in the course of water purification after drying at 25 °C is presented in Table 1 [9].

After heating from 25 to 500 °C the composition of the iron oxide phase (phase II) and the specific surface area thereof changes to a considerable extent (Table 2). It can be seen that the specific surface area decreases with increasing the heating temperature. The prevailing
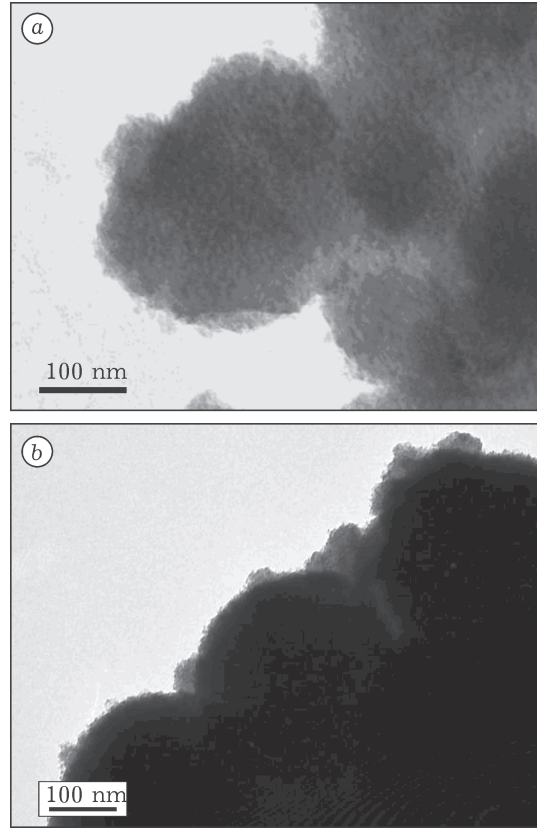
Fig. 1. Electron microscopy images (HR TEM) for iron oxohydroxide activated at 25 (*a*) and 500 °C (*b*).

phase in the samples calcined up to the temperature of 300 °C is amorphous, with appearing the trace amounts of crystalline structures upon heating. The precipitate activated at 500 °C exhibits 50 % of crystalline structures, whose 21 % are presented by mineral magnetite (Fe_3O_4). The structural composition of the phase I remains almost unchanged.

TABLE 2

Phase composition and specific surface area (S_{sp}) of iron oxohydroxide (IOH) at different processing temperature values

Samples*	Content, %							S_{sp}, m^2/g
	Amorphous phase	γ-Fe_2O_3	α-Fe_2O_3	α-FeOOH	β-FeOOH	γ-FeOOH	Fe_3O_4	
OGZ-25	95−98	traces	−	−	−	−	−	230
OGZ-100	95−98	traces	−	−	−	−	−	206
OGZ-200	95	traces	traces	−	−	−	−	197
OGZ-250	90	4.3	5.5	−	−	−	−	172
OGZ-300	90	traces	traces	−	5.1	5.2	−	142
OGZ-500	50	traces	1.0	4.0	6.0	12.0	21.0	128

Note. Dash − absent.

* The name indicates the sample drying temperature.

TABLE 3

Composition of the catalysts for carbon monoxide oxidation

Samples	Concentration, %				
	MnO	Phase I	FeOOH	CuO	Ag$_2$O
K-1	65.0	–	–	30.0	5.0
K-2	–	70.0	25.0	–	5.0
K-3	–	75.0	20.0	–	5.0
K-4	–	70.0	–	25.0	5.0
K-5	–	60.0	–	35.0	5.0

Note. Dash – absent.

The electron microscopy images (HR TEM) of the precipitate dried at 25 and 500 °C (Fig. 1) demonstrate that the sample dried at 25 °C has a granular structure with very fine grain size (5–10 nm) (see Fig. 1, *a*). Initial formations are strongly agglomerated, but the agglomerates are loose enough with oval or round shape. There are also more dense inclusions observed those become more compacted with increasing the temperature, to all appearance, due to inter-molecular forces.

In the case of making catalysts K-2–K-5 with the use naturally occurring oxide as a main component, we took phase I that was mixed with the iron oxides (phase II), copper and silver oxides in different proportions. Furthermore, as the reference sample, a catalyst was prepared identical in composition with the catalyst that is used in a hopcalite cartridge (sample K-1). The composition of the catalysts is presented in Table 3.

The activity of the samples was investigated in the reaction of carbon monoxide oxidation. Figure 2 presents the conversion level of carbon (II) oxide in the case catalysts K-1–K-5
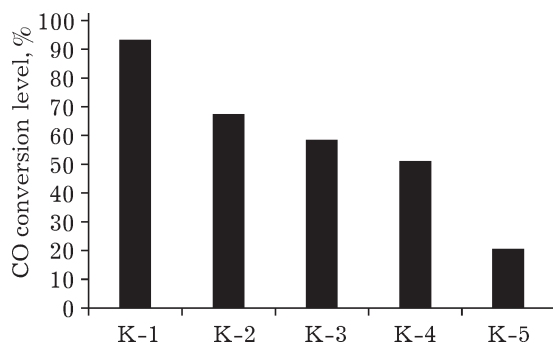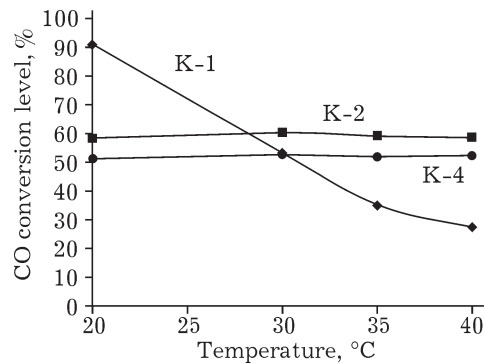
Fig. 3. Level of carbon monoxide conversion into carbon dioxide depending on the temperature in the presence of catalysts K-1, K-2, K-4.

at 20 °C. It can be seen that the conversion level of CO on the catalyst similar to hopcalite (K-1) is equal to about approximately 90 %. The samples prepared from the wastes of water treatment plants exhibit a lower activity level (%): K-2 66, K-3 58, K-4 51, K-5 20.3. Thus, at a room temperature, the activity of the samples prepared from the wastes of water treatment plants, is somewhat lower in comparison with the activity of a catalyst such as hopcalite. However, a slight increase in the temperature of a catalyst such as hopcalite results in an abrupt decrease in the level of CO conversion, whereas in the case of the catalyst prepared basing on the wastes taken from water treatment plants, the conversion level remains constant (Fig. 3). The decrease of the conversion level in this case could be explained by the deactivation of catalyst K-1 because increasing the vapor pressure of water in the course of preliminary heating the gas mixture.

The catalysts based on the wastes of water treatment plants retain their activity.

To all appearance, changing the structure of natural oxohydroxides occurs at the stage of precipitate formation under the influence of external factors (water, oxygen, air, organic compounds). These assumptions were made by the authors of [12] basing on studying the IR spectra of a mineral sediment obtained in the course of purifying the artesian water from iron.

CONCLUSION

Thus, the results obtained demonstrate that it is promising to use iron and manganese

Fig. 2. Conversion level of carbon (II) oxide on different catalysts at the temperature of 20 °C.

oxohydroxides obtained from waste water treatment plants in the course of water purification from iron, as catalysts for the oxidation of carbon (II) monoxide.

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