Copper-Cerium Oxide Catalysts for the Selective Oxidation of Carbon Monoxide in Hydrogen-Containing Mixtures: I. Catalytic Activity

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Abstract—A series of copper–cerium oxide catalysts were prepared, and their properties toward the reaction of CO oxidation in hydrogen-containing gas mixtures were studied. It was found that the copper–cerium oxide catalysts are stable, active, and selective in this reaction. The conditions under which these catalysts decreased the concentration of CO from 1 to $<10^{-3}$ vol % in hydrogen containing water vapor and carbon dioxide were determined.

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INTRODUCTION

The development of highly active catalysts for the fine purification of hydrogen to remove CO with the use of selective CO oxidation is an important problem of the preparation of hydrogen for fuel cells with a polymer proton-conducting electrolyte. A hydrogen-containing gas mixture prepared by the steam or air reforming of hydrocarbon fuels followed by the CO water gas shift reaction usually contains 0.5-2 vol % CO. At the same time, it is well known that CO in this concentration is a poison for fuel cell electrodes, and the concentration of CO should be decreased to a level lower than 10-100 ppm. A serious attempt has been made to find inexpensive catalytic systems containing no noble metals for the fine purification of a hydrogen-containing gas to remove CO. Catalysts based on oxide coppercerium systems are of greatest current interest.

Avgouropoulos et al. [1] were the first to propose copper–cerium oxide catalysts for the reaction of CO oxidation in the presence of hydrogen. They studied CuO–CeO₂ catalysts prepared by a coprecipitation method. They found that the CuO–CeO₂ system is an active and selective catalyst for the oxidation of CO in the presence of H₂ and it can be used for the fine purification of a hydrogen-containing gas to remove CO. The subsequent publications [2–6] have fully confirmed this conclusion. Note that, along with the CuO–CeO₂ system, copper catalysts supported on CeO₂ doped with zirconium oxide or samarium oxide were studied [2–4, 6]. These catalysts were found to be less active and selective than CuO–CeO₂ in the reaction of CO oxidation in the presence of H₂. The catalytic properties of the CuO–CeO₂ system toward the reaction of CO oxidation in the presence of hydrogen were compared with the properties of other well-known Pt- and Au-containing catalysts [1, 7]. It was found that Au/ α -Fe₂O₃ was the most active (lowtemperature) catalyst for both a gas mixture free of H₂O and CO₂ and gas mixtures containing water and carbon dioxide, whereas CuO–CeO₂ was more active than Pt/ γ -Al₂O₃ and superior to all of these catalysts in selectivity.

In general, the above suggests that the $CuO-CeO_2$ system is a very promising catalyst for the fine purification of a hydrogen-containing gas to remove CO. Taking into account the fact that this system is free of noble metals, it is reasonable to study this system in more detail.

This work was devoted to a systematic study of the oxidation reaction of carbon monoxide in hydrogencontaining gas mixtures on Cu/CeO_{2-x} catalysts oriented to the determination of conditions for the fine purification of hydrogen to remove CO to a level of 10 ppm.

EXPERIMENTAL

Preparation of Cu/CeO_{2-x} Catalysts by the Coprecipitation Method

A concentrated aqueous solution of oxalic acid was rapidly added (for 1 min) to an aqueous solution of $Cu(NO_3)_2$ and $Ce(NO_3)_3$ with stirring at room temperature, and the mixture was stirred for 20 min with a mechanical stirrer. The resulting precipitate was allowed to stand for 30 min without stirring for aging. Thereafter, the supernatant solution was decanted and the precipitate was washed with distilled water, dried in air at 110°C for 4 h, and then calcined at a temperature from 400 to 900°C for 2 h.

Preparation of Cu/CeO_{2-x} Catalysts by the Impregnation Method

To prepare catalysts by this method, we initially prepared cerium oxide in accordance with the following procedure: A concentrated solution of oxalic acid was rapidly added (for 1 min) to an aqueous solution of $Cu(NO_3)_2$ with stirring at room temperature, and the mixture was stirred for 20 min with a mechanical stirrer. The resulting precipitate was allowed to stand for 30 min without stirring for aging. Thereafter, the supernatant solution was decanted and the precipitate was washed with distilled water and dried in air at 110°C for 4 h; then, the sample was calcined at 400°C in air for 2 h. The specific surface area of the resulting cerium oxide was 66 m²/g.

The cerium oxide powder thus prepared was incipient wetness impregnated with an aqueous solution of $Cu(NO_3)_2$. Then, the sample was dried in air at 110°C for 4 h and calcined at a temperature from 400 to 900°C for 2 h.

The powders prepared by coprecipitation and impregnation were pressed into pellets, which were then crushed. A fraction with a catalyst particle size of 0.25–0.50 mm was used in catalytic experiments.

The concentrations of the main components in the copper–cerium catalysts were determined by inductively coupled plasma atomic emission spectrometry on an Optima instrument from Perkin-Elmer. The analytical procedure involved the dissolution of a solid catalyst sample, the dilution of the resulting solution to a concentration required for spectrometric analysis, and photometric measurements using a calibration graph method. The copper content of a catalyst (at %) was determined from the equation $100N_{Cu}/(N_{Cu} + N_{Ce})$, where N_{Cu} and N_{Ce} are the numbers of copper and cerium atoms, respectively, in the test sample.

The specific surface areas (S_{BET}) and pore volumes (V_{pore}) of supports and catalysts were determined from the full isotherms of low-temperature nitrogen adsorption at 77 K, which were measured on an ASAP-2400 instrument (Micrometrics, United States).

The procedure used in the kinetic experiments was described in detail elsewhere [8]. The reaction was performed in a quartz flow reactor at atmospheric pressure. The reactor was a U-shaped tube 40 cm in length and 8 mm in i.d. with a wall thickness of ~ 1 mm. A thermocouple well 3 mm in o.d. was arranged at the center along the axis of the reactor. A weighed portion of the catalyst was mixed with powdered quartz (particle size of ~ 1 mm) and placed in the reactor. The length of the catalyst bed was 12 cm. Filters were placed at the reactor inlet and outlet to prevent small catalyst particles

from entering the capillary tube system of gas inlet and outlet lines with a gas flow. The temperature was measured with a Chromel–Alumel thermocouple, which was placed in the well at the center of the catalyst bed. No catalyst pretreatment processes were applied before the experiments.

The concentrations of reactants and reaction products at the reactor inlet and outlet were determined using a Kristall 2000 chromatograph (Russia) equipped with a thermal-conductivity detector and a flame-ionization detector with a methanator containing an NKM-4 nickel catalyst. The combination of a methanator and a flame-ionization detector allowed us to analyze any gaseous hydrocarbons present in the gas mixture in combination with CO and CO_2 with a high sensitivity. The test mixture was separated on a column with molecular sieves NaX (thermal-conductivity detector) and on a column with Porapak Q (flame-ionization detector). The sensitivity of the technique allowed us to measure the concentrations of CO, CH₄, and CO₂ to the level of ~10⁻⁴ vol % and O_2 to 10⁻³ vol %. The occurrence of the reaction of carbon monoxide oxidation in hydrogen-containing mixtures was characterized by the conversions of CO (X_{CO}) and O₂ (X_{O_2}) and selectivity (S), which were calculated from the equations

$$X_{\rm CO} = \frac{[\rm CO]_0 - [\rm CO]}{[\rm CO]_0} \times 100\%;$$
$$X_{\rm O_2} = \frac{[\rm O_2]_0 - [\rm O_2]}{[\rm O_2]_0} \times 100\%;$$
$$S = \frac{1}{2} \frac{[\rm CO]_0 - [\rm CO]}{[\rm O_2]_0 - [\rm O_2]} \times 100\%,$$

where $[CO]_0$ and $[O_2]_0$ are the concentrations of CO and O_2 , respectively, at the reactor inlet; [CO] and $[O_2]$ are the concentrations of CO and O_2 , respectively, at the reactor outlet.

RESULTS AND DISCUSSION

Activity and Selectivity of Cu/CeO_{2-x} Catalysts Prepared by Impregnation and Coprecipitation Methods

The reaction of CO oxidation in the presence of H_2 was studied on oxide copper–cerium catalysts containing from 2.5 to 30 at % Cu calcined in air at temperatures from 400 to 900°C.

It was found that catalysts containing ~15 at % Cu calcined at 400°C exhibited the highest activity and selectivity toward the oxidation reaction of CO in hydrogen-containing mixtures. Therefore, we report here the results obtained on the catalysts containing ~15 at % Cu calcined at 400°C. These catalysts, which were prepared using coprecipitation and impregnation, contained 14.4 and 14.6 at % Cu, respectively; they are

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subsequently referred to as $Cu/CeO_{2-x}(C)$ and $Cu/CeO_{2-x}(I)$, respectively.

Data given in Table 1 indicate that catalyst characteristics such as the copper content, specific surface area (S_{BET}), and pore volume (V_{pore}) were identical in catalyst samples before and after the reaction of CO oxidation in the presence of H₂; this suggests the stability of catalyst structures under reaction conditions.

Figure 1 shows the temperature dependence of the conversions of CO and O₂ and selectivity in the reaction of CO oxidation in the presence of hydrogen. It can be seen that, in all cases, the conversion of CO (X_{CO}) initially increased and than decreased with temperature. The maximum values of X_{CO} were as high as 99.9% at 170°C on the Cu/CeO_{2-x}(I) catalyst, 98% at 205°C on the Cu/CeO_{2-x}(C) catalyst, and only 60% at 330°C on pure CeO₂. The conversion of oxygen increased with temperature and reached 100% at $T \ge 170^{\circ}$ C on the Cu/CeO_{2-x}(I) catalyst, $T \ge 205^{\circ}$ C on the Cu/CeO_{2-x}(C) catalyst, and $T \ge 330^{\circ}$ C on pure CeO₂.

The 14.6 at % Cu/CeO_{2-x} catalyst prepared by impregnation was found to be the most selective catalyst toward CO oxidation in the presence of H₂. Almost 100% selectivity was observed on this catalyst at $T \le$ 140°C. A further increase in the temperature resulted in a dramatic decrease in selectivity to 33%.

The catalyst prepared by coprecipitation also exhibited high selectivity; however, its value was lower than that of the Cu/CeO_{2-x}(I) catalyst. It gradually decreased from 80 to 60% over the temperature range 130–190°C and then rapidly decreased to 33%. The selectivity of CeO₂ was much lower than that of oxide copper–cerium catalysts, and it gradually decreased from ~30 to 20% as the temperature was increased.

Thus, the experimental results suggest that cerium dioxide is not an inert material toward CO oxidation in the presence of H₂. However, it exhibited much lower activity and selectivity than those of oxide copper–cerium systems. Of these systems, the Cu/CeO_{2-x}(I) catalyst was found to be much more active and selective than Cu/CeO_{2-x}(C). Taking into account that the copper contents of both of the copper–cerium oxide catalysts were approximately equal, the above difference can be explained by the higher dispersion of copper in the catalyst prepared by impregnation, as compared with that in the coprecipitated catalyst. This conclusion is consistent with published data [1–3].

The subsequent studies of the reaction of CO oxidation in the presence of H₂ were performed with the 14.6 at % Cu/CeO_{2-x} catalyst prepared by impregnation, which is the most active and selective coppercerium catalyst.

Effect of the Composition of the Hydrogen-Containing Mixture on the Course of Reaction

To determine optimum conditions for the operation of the Cu/CeO_{2-x}(I) catalyst, we studied the effect of

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Table 1. Characteristics of oxide copper–cerium catalysts

Catalyst	$S_{\text{BET}},$ m ² /(g Cat)	$\frac{V_{\text{pore}}}{\text{cm}^3/(\text{g Cat})}$
CeO ₂	66	0.22
14.4 at % Cu/CeO _{2 - x} (C)	70	0.18
coprecipitation, before reaction		
14.4 at % Cu/CeO _{2-x} (C)	69	0.19
coprecipitation, after reaction		
14.6 at % Cu/CeO _{2-x} (I)	65	0.20
impregnation, before reaction		
14.6 at % Cu/CeO _{2 - x} (I)	65	0.20
impregnation, after reaction		

the composition of a hydrogen-containing mixture on the course of CO oxidation in the presence of H_2 . The experimental results are considered below.

Effect of CO_2 and H_2O vapor. We performed a number of experiments with the use of the following hydrogen-containing mixtures:

- (1) 1 vol % CO + 1 vol % O_2 + 65 vol % H_2 + balance He;
- (2) 1 vol % CO + 1 vol % O₂ + 65 vol % H₂ + 20 vol % CO₂ + balance He;
- (3) 1 vol % CO + 1 vol % O₂ + 65 vol % H₂ + 10 vol % H₂O + balance He;
- (4) 1 vol % CO + 1 vol % O₂ + 65 vol % H₂ + 20 vol % CO₂ + 10 vol % H₂O + balance He.

Figure 2 illustrates the experimental data. It can be seen that, with the use of a gas mixture free of CO_2 and H_2O , the conversion of CO increased and then decreased with temperature. A temperature window in which the conversion of CO was higher than 99.9% was observed over the temperature range 150–170°C. The conversion of O_2 increased much more slowly than the conversion of CO with temperature, and it reached ~50% at 130°C at almost 100% selectivity. By this is meant that the oxidation of hydrogen did not occur under these conditions. An increase in the temperature above 130°C resulted in a rapid growth of oxygen conversion to 100% and, correspondingly, a decrease in selectivity to 40% at 180°C.

The introduction of 20 vol % CO₂ or 10 vol % H₂O resulted in a decrease in the activity of the Cu/CeO_{2-x}(I) catalyst in the oxidation reaction of CO in the presence of H₂ and in a shift of the temperature dependence of CO and O₂ conversions and selectivity to the region of higher temperatures by ~30–70°C, as compared with the dependence obtained in a mixture containing no carbon dioxide and water vapor. In the presence of 20 vol % CO₂, a maximum conversion of CO (99.9%) was reached at 185–190°C. In the presence of 10 vol % H₂O, a maximum conversion of CO (99.6%) was observed at 185°C.

In the case that carbon dioxide and water vapor were simultaneously present in a mixture, a maximum conversion of CO was equal to 97.7% at $T = 195^{\circ}$ C. Thus,



Fig. 1. Dependence of the conversions of (a) CO and (b) O_2 and (c) selectivity on the reaction temperature of CO oxidation in the presence of H_2 on (1) CeO₂, (2) CuO/CeO_{2-x}(I), and (3) CuO/CeO_{2-x}(C). Gas mixture: 1 vol % CO, 1.5 vol % O_2 , 65 vol % H_2 , 3 vol % H_2 O, 20 vol % CO₂, and the balance He. Space velocity of the gas mixture: 12000 h⁻¹.

the presence of CO_2 and H_2O in a hydrogen-containing mixture resulted in a decrease in activity and in a narrowing of the temperature window of Cu/CeO_{2-x} cata-



Fig. 2. Dependence of the conversions of (a) CO and (b) O_2 and (c) selectivity on the reaction temperature of CO oxidation in the presence of H_2 on the CuO/CeO_{2-x}(I) catalyst for various gas mixtures: (*I*) 1 vol % CO, 1 vol % O_2 , 65 vol % H_2 , and the balance He; (2) mixture *I* + 20 vol % CO₂; (3) mixture *I* + 10 vol % H₂O; (4) mixture *I* + 20 vol % CO + 10 vol % H₂O. Space velocity of the gas mixture: 24000 h⁻¹.

lyst operation in the oxidation of CO in hydrogen-containing mixtures. Nevertheless, all of the hydrogencontaining mixtures used exhibited a temperature

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region in which almost 100% selectivity was reached: $T < 130^{\circ}$ C in the model mixture (without CO₂ and H₂O), $T < 140^{\circ}$ C in the presence of CO₂, $T < 140^{\circ}$ C in the presence of H₂O, or $T < 160^{\circ}$ C with the use of a real mixture (containing CO₂ and H₂O). A further increase in the temperature resulted in a rapid decrease of selectivity to 40%. Behavior of this kind, which is characteristic of copper–cerium oxide systems, was also found in previous studies [1–3].

To reveal the reason for the occurrence of a temperature region in which almost 100% selectivity was reached on the Cu/CeO_{2-x}(I) catalyst, we performed experiments on the separate oxidation of CO and the oxidation of H₂ both in the absence of CO₂ and H₂O and in the presence of 20 vol % CO₂ and 10 vol % H₂O. For this purpose, we used the following mixtures:

(1) 1 vol % CO + 0.5 vol % O_2 + balance He;

(2) 1 vol % CO + 0.5 vol % O₂ + 20 vol % CO₂ + 10 vol % H₂O + balance He in the reaction of CO oxidation and

(1) 65 H_2 + 0.5 O_2 + balance He;

(2) 65 H_2 + 0.5 O_2 + 20 vol % CO_2 + 10 vol % H_2O + balance He in the reaction of H_2 oxidation.

To compare the activity of a copper–cerium oxide catalyst in the reactions of CO and H_2 oxidation, the courses of both of the reactions were monitored by measuring the conversion of O_2 .

In Fig. 3, it can be seen that only the oxidation of CO occurred on the copper–cerium oxide catalyst in the absence of H_2O and CO_2 from the mixture to $T \sim 100^{\circ}C$, and the oxidation of H_2 was insignificant (it came into play only at a higher temperature).

In the presence of H_2O and CO_2 in the reaction mixture, the activity of the copper–cerium oxide catalyst in the oxidation of both CO and H_2 decreased. Nevertheless, the oxidation of CO primarily occurred to $T \sim 150^{\circ}C$, whereas the oxidation of H_2 was observed in the region of higher temperatures.

By this is meant that the activity of the $Cu/CeO_{2-x}(I)$ catalyst in CO oxidation was much higher than the activity in H₂ oxidation both in the absence and in the presence of CO₂ and H₂O in the reaction mixture. It is likely that, because of this, there is a temperature region in which almost 100% selectivity was observed in the reaction of CO oxidation in the presence of H₂. The selectivity considerably decreased at the instant the oxidation of H₂ came into play.

It is most likely that the catalyst activity in the presence of H_2O and CO_2 decreased because of the blocking of catalyst active sites by adsorbed CO_2 and H_2O molecules. This hypothesis is based on the following experimental data: No products were formed when a mixture of 20 vol % CO_2 and 80 vol % H_2 was supplied to the catalyst. By this is meant that the reverse CO water gas shift reaction does not occur under the reaction conditions of CO oxidation in the presence of H_2 .



Fig. 3. The temperature dependence of the conversion of O₂ in the course of the oxidation of (1, 3) CO and (2, 4) H₂ (1, 2) in the absence of H₂O and CO₂ or (3, 4) in the presence of 10 vol % H₂O and 20 vol % CO₂ on the CuO/CeO_{2-x} (I) catalyst. Gas mixtures in the reaction of CO oxidation: (1) 1 vol % CO, 0.5 vol % O₂, and the balance He; (3) mixture 1 + 20 vol % CO₂ + 10 vol % H₂O. Gas mixtures in the reaction of H₂ oxidation: (2) 65 vol % H₂, 0.5 vol % O₂, and the balance He; (4) mixture 2 + 20 vol % CO₂ + 10 vol % H₂O. The space velocity of the gas mixture was 24000 h⁻¹ in all of the experiments.

Effect of O_2 and CO. One of the main parameters affecting the efficiency of CO removal from hydrogencontaining mixtures is the initial concentration of oxygen. To choose optimum conditions, the minimum amount of oxygen required for decreasing the concentration of CO to 10 ppm should be known.

Figure 4 shows the dependence of the outlet concentration of CO, the conversion of O_2 , and the selectivity on the reaction temperature of CO oxidation in the presence of H₂ at various initial concentrations of oxygen (0.5–1.5 vol %) on the Cu/CeO_{2-x}(I) catalyst. It can be seen that an increase in the concentration of oxygen had no effect on the final concentration of CO at temperatures lower than 150°C. In this case, the values of selectivity for all of the three concentrations of oxygen were close to each other and insignificantly decreased from 100 to 90%.

From Fig. 4, it follows that, with the use of a stoichiometric mixture containing 1 vol % CO and 0.5 vol % O_2 , a minimum outlet concentration of CO (300 ppm) at 100% O_2 conversion was observed at 170°C. An increase in the concentration of oxygen to 1 vol % allowed us to decrease the final concentration of CO to 10 ppm at 180°C. However, in this case, the conversion of oxygen rapidly reached a value of 100% to result in a decrease in selectivity to 50%. At an initial oxygen concentration of 1.5 vol %, a minimum concentration



Fig. 4. Dependence of (a) the outlet concentration of CO, (b) the conversion of O₂, and (c) selectivity on the reaction temperature of CO oxidation in the presence of H₂ on the CuO/CeO_{2-x}(I) catalyst at O₂ concentrations of (1) 0.5, (2) 1.0, and (3) 1.5 vol % for a gas mixture of 1 vol % CO, 65 vol % H₂, 10 vol % H₂O, 20 vol % CO₂, and the balance He. Space velocity of the gas mixture: 6000 h⁻¹.

of CO (2 ppm) was reached at 185°C at 100% conversion of oxygen and 33% selectivity.

Note that a minimum outlet concentration of CO was observed over a very narrow temperature range

regardless of the initial concentration of oxygen, and even an insignificant increase in the temperature resulted in a rapid increase in the concentration of CO at the reactor outlet. For example, even at 210°C and an O_2/CO ratio of 0.5, 1.0, or 1.5, the outlet concentration of CO was equal to 2000, 1500, or 900 ppm, respectively. Thus, the temperature window in which the concentration of CO at the reactor outlet was lower than 10 ppm was narrow and equal to 10–15°C for the oxide copper–cerium catalyst.

Usually, after the low-temperature CO water gas shift reaction, the hydrogen-containing mixture contained from 0.5 to 2 vol % CO depending on reaction conditions. Because of this, the effect of the initial concentration of CO on the occurrence of CO oxidation in the presence of H₂ should be studied. Figure 5 shows the dependence of the conversion of CO and O₂ and the selectivity on the reaction temperature of CO oxidation in hydrogen-containing mixtures on the Cu/CeO_{2-x}(I) catalyst at CO concentrations varied from 0.5 to 2.0 vol % and a constant O₂/CO ratio of 0.5.

It can be seen that the temperature dependence of X_{CO} , X_{O_2} , and S was almost the same for all of the three gas mixtures. A maximum CO conversion of ~90% was reached at 180°C in gas mixtures containing 2.0, 1.0, and 0.5 vol % CO. A further increase in the temperature caused a rapid decrease in the conversion of CO.

An analogous dependence was also observed at other O_2/CO ratios. Table 2 summarizes the experimental results. It can be seen that a maximum conversion of CO was practically the same at various initial concentrations of CO and a constant O_2/CO ratio. The conversion of CO was increased only by an increase in the O_2/CO ratio.

Optimum conditions for the fine purification of hydrogen-containing mixtures to remove CO. Not only the data considered above but also data on the effect of the flow rate of a reaction mixture on the course of CO oxidation in the presence of O_2 are required for optimizing conditions for the fine purification of a hydrogen-containing gas to remove CO. The experiments were performed with the following mixture: 1 vol % CO, $O_2/CO = 0.5$, 65 vol % H₂, 10 vol % H_2O , 20 vol % CO_2 , and the balance He. As can be seen in Fig. 6, an increase in the flow rate shifted the temperature dependence of the final concentration of CO and the conversion of O_2 to the region of higher temperatures. In this case, the minimum concentration of CO increased. Thus, at a space velocity of 6000 h⁻¹, a minimum concentration of CO was equal to 300 ppm at 170°C, whereas it was equal to 1000, 2300, or 2700 ppm at a space velocity of 24000, 42000, or 60000 h^{-1} and a temperature of 180, 190, or 195°C, respectively. Note that the conversion of O_2 reached 100% at the specified temperatures. A further increase in the temperature resulted in a dramatic increase in the outlet concentration of CO at the complete conversion of oxygen. Note that, even at 220°C, the final concen-

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Fig. 5. Dependence of the conversions of (a) CO and (b) O_2 and (c) selectivity on the reaction temperature of CO oxidation in the presence of H_2 on the CuO/CeO_{2-x}(I) catalyst at CO concentrations of (1) 0.5, (2) 1.0, and (3) 2.0 vol % in a gas mixture also containing 65 vol % H_2 , 10 vol % H_2O , 20 vol % CO₂, and the balance He at $O_2/CO = 0.5$. Space velocity of the gas mixture: 24000 h⁻¹.

tration of CO was equal to ~4000 ppm at all of the flow rates.

An analogous dependence was also obtained at other initial O_2/CO concentration ratios. Table 3 sum-

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Fig. 6. Dependence of (a) the outlet concentration of CO, (b) the conversion of O₂, and (c) selectivity on the reaction temperature of CO oxidation in the presence of H₂ on the CuO/CeO_{2-x}(I) catalyst at space velocities of (*1*) 6000, (2) 24000, (3) 42000, and (4) 60000 h⁻¹. Gas mixture: 1 vol % CO, 0.5 vol % O₂, 65 vol % H₂, 10 vol % H₂O, 20 vol % CO₂, and the balance He.

marizes minimum outlet concentrations of CO and the reaction temperature depending on the rate of a gas flow and the initial O_2/CO concentration ratio. Based on these data, the following conclusions can be made:

Table 2. Maximum conversion of CO (%) at various O_2/CO ratios and initial CO concentrations in the oxidation of CO on the Cu/CeO_{2-x}(I) catalyst in the presence of H₂

O_2/CO ratio	T, ℃	Initial CO concentration, vol %		
		2.0	1.0	0.5
0.5	180	87.0	90.0	91.0
1.0	190	95.0	95.0	94.0
1.5	195	97.5	97.7	96.0

Note: The initial mixture contained 0.5–2 vol % CO, 0.25–3 vol % O₂, 65 vol % H₂, 10 vol % H₂O, 20 vol % CO₂, and the balance He. The space velocity of the gas mixture was 24000 h⁻¹.

• an increase in the flow rate resulted in an increase in the minimum concentration of CO at the outlet and in an increase in the temperature at which the minimum concentration of carbon monoxide was reached;

• an increase in the concentration of O_2 resulted in a decrease in the minimum concentration of CO at the outlet and in an increase in the reaction temperature at which this concentration was reached. This relation was true at all gas flow rates. For example, at a space velocity of 6000 h⁻¹, an increase in the initial O_2/CO concentration ratio by a factor of 3 decreased the outlet concentration from 300 to 2 ppm, whereas the addition of oxygen decreased the outlet concentration of CO from 2700 to 2000 ppm at a space velocity of 60000 h⁻¹.

Figure 7 shows the dependence of the outlet concentration of CO on the space velocity of the gas flow and the initial O_2/CO concentration ratio; this dependence was obtained at the optimum temperature (170–215°C), which was determined previously (see Figs. 4–6). The graph was subdivided into four regions with respect to the outlet concentrations of CO: 1000–10000, 100–1000, 10–100, and 1–10 ppm.

As can be seen in Fig. 7, the maximum gas-flow space velocity at which the removal of CO from the gas mixture below 10 ppm was reached was equal to ~14000 h⁻¹ at an O₂/CO ratio of no lower than 1.5. Either an increase in the velocity or a decrease in the initial concentration of O₂ resulted in an increase in the final concentration of CO. Thus, to remove CO at a level lower than 10 ppm and at a lower O₂/CO ratio, the

flow space velocity should be decreased. For example, the maximum space velocity was equal to 6000 h⁻¹ at $O_2/CO = 1$.

Comparison between the catalytic properties of Cu/CeO_{2-x} systems. The known published data on the oxidation of CO in the presence of H₂ on oxide coppercerium catalysts were obtained during the period when this study was performed. Therefore, it seemed reasonable to compare the above results with published data [1, 3, 5]. In the works cited, the reaction of CO oxidation in hydrogen-containing mixtures was studied on copper-cerium oxide catalysts prepared using various methods in both a model mixture with no CO_2 and H_2O and a mixture containing CO₂ and H₂O. It was found that catalysts containing 15-20 at % Cu exhibited the highest activity. We also found that the 14.6 at % Cu/CeO_{2-x} catalyst prepared by impregnation exhibited the highest activity and selectivity in CO oxidation in the presence of H_2 .

Avgouropoulos et al. [1] demonstrated that the 14.3 at % Cu/CeO₂ catalyst prepared by coprecipitation decreased the concentration of CO in a hydrogen-containing gas to 10 ppm in a gas mixture containing 1 vol % CO, 1.25 vol % O₂, 50 vol % H₂, and the balance He at $T = 130-150^{\circ}$ C and a space velocity of 10000 h⁻¹. In our experiments (see Fig. 2), the Cu/CeO_{2-x}(I) catalyst provided the above degree of CO removal from a hydrogen-containing gas under similar experimental conditions (inlet concentrations of 1 vol % CO, 1 vol % O₂, 65 vol % H₂, and the balance He; $T = 150-170^{\circ}$ C; and space velocity of 24000 h⁻¹).

Avgouropoulos et al. [1] also studied the effect of water and carbon dioxide on the course of CO oxidation in hydrogen-containing mixtures. These experiments were performed at a space velocity of 10000 h⁻¹. They found that the presence of 15 vol % CO₂ and 10 vol % H₂O in a model mixture resulted in a shift of the temperature dependence of CO and O₂ conversions by 15–70°C to the region of higher temperatures, as compared with the dependence observed in the model mixture. A maximum CO conversion of >99% at 40% selectivity was reached at 190°C. An analogous decrease in the activity of a copper–cerium oxide catalyst was also observed in our experiments on the Cu/CeO_{2-x}(I) cata-

Table 3. Minimum outlet concentrations of CO and reaction temperature depending on space velocity and initial O_2/CO concentration ratio in the course of CO oxidation on the Cu/CeO_{2-x}(I) catalyst in the presence of H₂

Space velocity, h ⁻¹	Inlet O ₂ /CO concentration ratio					
	0.5		1.0		1.5	
	<i>T</i> , °C	[CO] _{outlet} , ppm	T, ℃	[CO] _{outlet} , ppm	T, ℃	[CO] _{outlet} , ppm
6000	170	300	180	10	185	2
24000	180	1000	190	500	195	230
42000	190	2300	205	1200	210	580
60000	195	2700	210	2100	215	2000

Note: The initial mixture contained 1 vol % CO, 65 vol % H_2 , 10 vol % H_2 O, 20 vol % CO₂, and the balance He; $O_2/CO = 0.5-1.5$.



Fig. 7. Dependence of the outlet concentration of CO on the initial O₂/CO concentration ratio and the space velocity of a gas flow in the reaction of CO oxidation in the presence of H₂ on the CuO/CeO_{2-x}(I) catalyst. Gas mixture: 1 vol % CO, 0.5–1.5 vol % O₂, 65 vol % H₂, 10 vol % H₂O, 20 vol % CO₂, and the balance He.

lyst. A CO conversion of >99.9% and 38% selectivity were reached at 180°C in a mixture containing 1 vol % CO, 1.3 vol % O₂, 65 vol % H₂, 20 vol % CO₂, 10 vol % H₂O, and the balance He at a space velocity of 10000 h⁻¹.

Kim and Cha [5] found that the most active coppercerium oxide catalyst containing 20 at % Cu, which was prepared by the coprecipitation method, decreased the concentration of CO below 10 ppm in a mixture containing 1 vol % CO, 1 vol % O₂, 50 vol % H₂, 13.5 vol % CO₂, 20 vol % H₂O, and the balance He at a space velocity of 15000 h⁻¹ over the temperature range 167–176°C. In our experiments, the Cu/CeO_{2-x}(I) catalyst decreased the concentration of CO below 10 ppm in a mixture containing 1 vol % CO, 1.5 vol % O₂, 65 vol % H₂, 20 vol % CO₂, 10 vol % H₂O, and the balance He at a space velocity of 14000 h⁻¹ only over a narrow temperature window of 185–195°C.

The above comparison suggests that the coppercerium oxide catalysts studied in this work and described in the literature are similar in terms of both activity and selectivity in the reaction of CO oxidation in hydrogen-containing mixtures.

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