# Effect of the Nanoparticle Size of Supported Copper-Containing Catalysts on Their Activity in the Selective Oxidation of CO in an Excess of H<sub>2</sub>

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Abstract—The catalytic properties of systems prepared by the supporting of CuO onto CeO<sub>2</sub>, ZrO<sub>2</sub>, and Zr<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>2</sub> with particle sizes of 15–25 nm (nitrate pyrolysis (p)) and 5–6 nm (microemulsion method (me)) in the reaction of CO oxidation in an excess of H<sub>2</sub> were studied. In the latter case, the supports had an almost homogeneous surface and a small number of defects. The catalytic activity of (me) and (p) supports was low and almost the same, whereas the catalytic activity of CuO/(CeO<sub>2</sub>, ZrO<sub>2</sub>, and Zr<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>2</sub>)(me) samples was lower than that of CuO/(CeO<sub>2</sub> and ZrO<sub>2</sub>)(p). The maximum CO conversion (~100% at 125°C) was observed on 5% CuO/CeO<sub>2</sub>(p). The CO and CO<sub>2</sub> adsorption species on (p) and (me) catalysts were studied by TPD. Differences in the compositions of copper-containing centers on the surfaces of (p) and (me) systems were found using TPR. The nature of the active centers of CO oxidation and the effect of support crystallite size on the catalytic activity were considered.

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## **INTRODUCTION**

The purification of commercially produced hydrogen to remove an impurity of CO, whose concentration is 0.5-2 vol % CO, is mandatory for the use of this hydrogen in new fuel cells, which can replace internal combustion engines [1, 2]. The concentration of CO in mixtures with hydrogen should be lower than 10 or 100 ppm in operations with cells containing platinum electrodes or bimetallic catalysts like PtRu, respectively [3–5]. The low-temperature catalytic oxidation of CO in an atmosphere of hydrogen with oxygen or air is most promising for the removal of CO impurities from the mixtures. Various supported catalytic systems involving Pt, Ru, Pd, and Au [3, 6-9] or Co [10-13]and Cu oxides [14-22] were proposed. In the latter case, with the use of CeO<sub>2</sub> and ZrO<sub>2</sub> dioxides and  $Zr_xCe_{1-x}O_2$  solid solutions as supports, the CuO/CeO<sub>2</sub> catalysts were found the most effective in this process. On the surface of these catalysts, highly active oxygen, which is capable of oxidizing CO at 100–160°C, was formed as a result of the strong interaction of CuO-CeO<sub>2</sub> oxides. It was found [19] that Cu–O–Ce clusters were formed on the surface of  $CuO/CeO_2$ , and CO was adsorbed at these clusters with the formation of CO-Cu<sup>+</sup> carbonyl complexes and the subsequent CO oxidation by the oxygen of these clusters. In the study of the oxidation of CO in an excess of hydrogen [19], it was found that the conversion of CO increased with increasing CuO concentration (from 0.5 to 6 wt %) and reaction temperature to reach a maximum of 99.5% at a 5-6 wt % CuO concentration and 140150°C. At the temperature T > 150°C, the conversion of CO dramatically decreased because of the dissociative adsorption of hydrogen and the blocking of active centers by adsorbed water. The temperature range in which a high CO conversion (90–99.5%) was retained was very narrow, only 20 K. It was found that, upon the addition of Fe and Ni oxides, which are inactive in this reaction, to the CuO/CeO<sub>2</sub> system, the conversion of CO increased at a lower concentration of CuO (2.5%) [20] and the temperature range of a maximum conversion simultaneously broadened to 40–50 K toward both low and high temperatures.

The studies of nanosized catalytic systems synthesized based on materials with high surface areas and uniform crystallite sizes in the range of 3–10 nm [23] and containing supported small metal or oxide particles are currently underway. There are published data on the effect of the size of such supported particles on the catalytic activity of the systems [24–26] in dehydrogenation and oxidation reactions. It was noted that a decrease in the particle size of a catalyst can lead to either an increase or a decrease in the catalytic activity. New methods have been developed for the preparation of nanodispersed oxides; these are the thermal decomposition of an organometallic precursor in a flow reactor [27], the sol-gel synthesis [28], and the microemulsion method [29], which was used to synthesize CeO<sub>2</sub>, ZrO<sub>2</sub>, and Zr<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>2</sub> [30]. Il'ichev et al. [30] used X-ray diffraction (XRD) analysis, temperatureprogrammed desorption (TPD), and EPR spectroscopy to find that these oxides have a high specific surface area of ~100 m<sup>2</sup>/g and consist of uniform particles with a crystallite size of ~5 nm. The use of such oxides for preparing supported catalysts for CO oxidation in the presence of hydrogen makes it possible to study the influence of the particle size of a catalyst on its activity because the number of supported atoms accessible to the reaction increases with the dispersity. On the other hand, the probability of formation of active centers that include several metal and oxygen atoms arranged in a certain manner on the surface decreases with decreasing support particle size, and this can lead to a decrease in the catalytic activity.

The aim of this work was to comparatively study copper-containing catalytic systems in which the CeO<sub>2</sub>, ZrO<sub>2</sub>, and Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> supports differed in crystallite sizes (15–25 and ~5 nm in the case of (p) samples and samples prepared by (me) synthesis, respectively) in the reaction of CO oxidation in an excess of H<sub>2</sub>. The effects of the particle sizes of the catalysts on their structure, bond strength of oxygen with the surface, catalytic activity, and CO and CO<sub>2</sub> adsorption species were studied using XRD analysis, temperature-programmed reduction (TPR), and TPD.

#### **EXPERIMENTAL**

The cerium and zirconium dioxides ( $CeO_2$  and  $ZrO_2$ ) were prepared by two different methods: (1) the pyrolysis of nitric acid salts (p) and (2) a microemulsion method (me). In the former case,  $CeO_2$  was obtained from  $Ce(NO_3)_3 \cdot 6H_2O$  on heating in air to 500°C at a rate of 7 K/min and the subsequent calcination at this temperature for 2 h, and ZrO<sub>2</sub> was obtained from zirconium(IV) oxide nitrate  $(ZrO(NO_3)_2 \cdot 6H_2O)$ by consecutive thermal decomposition in air at  $30\overline{0}^{\circ}C$ for 2 h and at 500°C for 3 h. In the latter case, CeO<sub>2</sub>,  $ZrO_2$ , and  $Ce_{0.5}$   $Zr_{0.5}O_2$  were synthesized using a microemulsion procedure, which was described elsewhere [30]. The emulsions were prepared by mixing the aqueous solutions of the salts  $Ce(NO_3)_3 \cdot 6H_2O$  and  $ZrOCl_2 \cdot 8H_2O$  or their mixture (with the ratio Zr: Ce = 1 between the cations) and N(CH<sub>3</sub>)<sub>4</sub>OH  $\cdot$  5H<sub>2</sub>O with an organic solution containing hexane, hexanol, and the surfactant Triton X-100. Commercial reagents from Aldrich were used. The reaction was carried out with stirring the corresponding emulsions for 24 h; after this, the products were separated by centrifugation, washed in methanol, dried at room temperature, then heated in air at a constant heating rate of 2 K/min to 500°C, and kept at this temperature for 2 h.

CuO was supported onto the resulting systems by impregnating them with a copper nitrate solution; thereafter, they were dried at  $150^{\circ}$ C and calcined at  $500^{\circ}$ C for 2 h. The samples contained 2.5 and 5 wt % CuO.

The specific surface areas  $(S_{sp})$  of the samples were measured by the BET method using the low-temperature adsorption of argon. The values of  $S_{sp}$  for CeO<sub>2</sub> (p) and (2.5, 5)%CuO/CeO<sub>2</sub> (p) were 67 and 65–63 m<sup>2</sup>/g, respectively, and for  $ZrO_2(p)$  and  $(2.5, 5)\%CuO/ZrO_2(p)$ , 55–50 m<sup>2</sup>/g, respectively. For the samples prepared by the (me) method,  $S_{sp}$  was much higher: 100 m<sup>2</sup>/g in  $ZrO_2$  (me) or 80 m<sup>2</sup>/g in CeO<sub>2</sub> (me) and  $Zr_{0.5}Ce_{0.5}O_2$  (me). Upon supporting 2.5 and 5 wt % CuO onto the (me) systems, the values of  $S_{sp}$  decreased by 5–7 m<sup>2</sup>/g.

The phase composition was studied by XRD analysis on a Dron-3M diffractometer over the angle range of  $2\theta = 8-70^{\circ}$  (Cu $K_{\alpha}$  radiation; graphite monochromator), which was calibrated with the use of the (112) line of SiO<sub>2</sub> powder ( $\alpha$ -quartz; interplanar spacing, 1.818 Å). All of the calculations and the processing of spectra were performed using computer programs.

The catalytic properties of the synthesized samples in the reaction of CO oxidation in an excess of hydrogen were studied in a flow-type system over the temperature range of 20-400°C. The reaction mixture containing 98 vol % H<sub>2</sub>, 1 vol % CO, and 1 vol % O<sub>2</sub> was passed through a quartz tube reactor (3 mm in diameter) with a catalyst (20 mg) at a flow rate of 40 ml/min; the temperature was increased stepwise. A thermocouple was arranged outside the reactor at a level of the center of a catalyst bed (whose height was 4-5 mm). In the course of the analysis of reaction products at each particular temperature, which was kept for 20-30 min, no increase in the catalyst temperature as a result of heat release during exothermic reactions of CO and H<sub>2</sub> oxidation was detected. The reaction products were analyzed by chromatography; they were separated on two columns packed with molecular sieves NaX (13 Å) and Porapak QS. Katharometers were used as detectors. The reaction was characterized by the degree of conversion, the temperature at which a maximum conversion of CO into  $CO_2$ was reached  $(T_{\text{max}})$ , and the selectivity for oxygen. This selectivity was determined as the fraction of oxygen (on a consumed basis) used for the formation of  $CO_2$ .

The TPR of the catalysts was performed in a flow of a 6%H<sub>2</sub>/Ar mixture at a rate of 100 ml/min. Heating over the temperature range of 20–650°C was performed at a rate of 12 K/min. Before the experiments, the samples (100 mg) were calcined at 500°C in a flow of air for 1 h. Water vapor released upon reduction was absorbed in a trap packed with Anhydrone and arranged immediately after the reactor. A katharometer was used as a detector. The amount of absorbed hydrogen was determined from TPR peak areas to within ~10%.

The adsorbed CO and CO<sub>2</sub> species on copper oxide supported on (me) and (p) samples were studied using TPD. A sample (50 mg) was placed in a quartz ampoule, evacuated to  $10^{-4}$  Pa, heated to  $500^{\circ}$ C for 1 h, oxidized in O<sub>2</sub> for 30 min (P = 600 Pa), cooled to  $20^{\circ}$ C, and evacuated once again. After this, the adsorption of CO (P = 30 Pa) was performed for 10 min; then, the gas phase was pumped out for 15 min, and the sample was heated at the constant rate  $\beta = 10$  K/min in the course of evacuation. The TPD spectrum as the dependence of the pressure of des-



Fig. 1. (a) Conversion of CO into  $CO_2$  and (b) process selectivity for oxygen on the catalysts (*1*) 2.5% CuO/CeO<sub>2</sub> (p), (2) 2.5% CuO/CeO<sub>2</sub> (me), (3) 5% CuO/CeO<sub>2</sub> (p), (4) 5% CuO/CeO<sub>2</sub> (me), (5) CeO<sub>2</sub> (p), and (6) CeO<sub>2</sub> (me).

orbed gas (W) on temperature (T) was measured using a Pirani gage [31] in a temperature range from 20 to 500°C.

#### RESULTS

## XRD Analysis of the Samples

According to XRD data, cerium dioxide  $(CeO_2)$ crystallized in a cubic modification (C) regardless of preparation procedure; this crystal structure was retained upon supporting 2.5 and 5 wt % CuO onto it. In the synthesis of  $ZrO_2(p)$ , a monoclinic modification (M) was mainly formed; in addition, low-intensity reflections due to a tetragonal modification (T), whose concentration was no higher than 10%, were detected in a diffraction pattern. The phase composition of the catalyst remained unchanged upon supporting 2.5 and 5 wt % CuO. On the contrary, only a metastable T phase was detected in the sample of  $ZrO_2(me)$ ; this is characteristic of crystallites with a size of  $\sim 5$  nm [30]. The formation of 20–25% M phase was noted after supporting 5% CuO; that is, the imperfection of the sample increased. In the case of  $Zr_{0.5}Ce_{0.5}O_{2}(me)$ , a solid solution is formed, which was, probably, a pseudoisometric phase with a lattice parameter intermediate between the lattice parameters of  $CeO_2$  (me) and  $ZrO_2$  (me). The phase composition of the sample after supporting CuO remained unchanged. The crystallite sizes of the synthesized samples were determined from XRD data using the

## Catalytic Activity of (p) and (me) Samples in the Reaction of CO Oxidation with Oxygen in an Excess of Hydrogen

**Supports.** The conversion of CO on CeO<sub>2</sub>(p) came into play at 200°C and reached 30% at 350°C; it was almost the same as the conversion of CO on CeO<sub>2</sub>(me).

Both of the samples of  $ZrO_2$  (me) and  $ZrO_2$  (p) were inactive in the range of  $20-300^{\circ}C$ ; the oxidation of CO on them was observed at temperatures higher than  $300^{\circ}C$ ; in this case, the conversion was higher than 3-4%. The mixed oxide  $Zr_{0.5}Ce_{0.5}O_2$  (me) occupied an intermediate place between the individual oxides in terms of catalytic activity: the oxidation of CO came into play at temperatures higher than  $200^{\circ}C$ , as on  $CeO_2$  (me); however, the conversion of CO was lower by a factor of about 2, namely, ~17% at 350°C.

The conversion of CO on the samples containing the supported copper oxide CuO depended on both CuO concentration on the surface and the nature of the support.

 $CuO/CeO_2$ . As can be seen in Fig. 1a, the conversion and the temperature range of a maximum conversion  $(T_{max})$  depend on both the amount of CuO supported on the surfaces of (p) and (me)  $CeO_2$  samples and the CeO<sub>2</sub> preparation method. For all of the CuOcontaining samples, the temperature dependence of CO conversion is an extremal function. In the oxidation of CO on a sample of 2.5% CuO/CeO<sub>2</sub>(p) (Fig. 1a, curve I), the conversion increased from 5 ( $80^{\circ}$ C) to 95% to reach a maximum at  $T_{\text{max}} = 145^{\circ}\text{C}$  decreased as the temperature was further increased. On 2.5%  $CuO/CeO_2$  (me) (curve 2), the conversion of CO increased in the range of 100-180°C to reach a maximum value of 87% at  $T_{\text{max}} = 180-200^{\circ}\text{C}$  and also decreased at higher temperatures. As the amount of supported copper oxide (CuO) was increased from 2.5 to 5%, the conversion of CO increased and  $T_{\rm max}$ decreased on both (p) and (me) samples. On the 5%  $CuO/CeO_2(p)$  catalyst, the maximum conversion was ~100% at  $T_{\text{max}} = 125^{\circ}$ C (curve 3); in this case, the temperature range of a maximum conversion broadened and shifted to the region of low temperatures. The accuracy of the measurement of a minimum residual concentration of CO in a gas mixture was about 0.005%, that is, ~50 ppm. Thus, the residual concentration of CO was no higher than 50 ppm on the 5% CuO/CeO<sub>2</sub> (p) sample under optimum conditions at a CO conversion of ~100%. The same behavior was also observed in the 5% CuO/CeO<sub>2</sub> (me) sample: the conversion increased to 99% with a simultaneous decrease in  $T_{\text{max}}$  to 160°C (curve 4). In this case, the residual concentration of CO was no higher than 100 ppm. Figure 1a (curves 5, 6) shows the conversion of CO on (p) and (me) CeO<sub>2</sub>.

Data on the catalytic activity of samples based on  $\text{CeO}_2$  show that the catalysts obtained by supporting copper oxide on  $\text{CeO}_2$  (p) were more active than the samples with  $\text{CeO}_2$  (me). Note that the extremal temperature dependence of CO conversion was also characteristic of other supported copper oxide catalysts [20–22], and a decrease in the conversion of CO at  $T > T_{\text{max}}$  was not related to an irreversible change in the catalyst because the conversion increased to a maximum value once again as the reaction temperature was decreased to  $T_{\text{max}}$ . Furthermore, the stable operation of (p) and (me) samples at  $T_{\text{max}}$  was retained for 2 h.

Figure 1b shows the selectivity for oxygen of the process on the samples based on CeO<sub>2</sub>. For the (me) samples (curves 2, 4), the selectivity in the low-temperature region of  $80-150^{\circ}$ C was much higher (100-65%), as compared with 64-45% for the (p) samples (curves 1, 3). A change in the amount of copper oxide supported onto the surface from 2.5 to 5% had almost no effect on the value of selectivity both in the case of CuO/CeO<sub>2</sub> (p) (curves 1, 3) and in the case of CuO/CeO<sub>2</sub>(me) (curves 2, 4).

 $CuO/ZrO_2$ . The catalytic systems in which  $ZrO_2$  (p) and (me) are used as the supports are less active than the systems with CeO<sub>2</sub>; however, the temperature dependences of conversion also exhibited an extremal character. The activity of  $CuO/ZrO_2$  (p) catalysts (Fig. 2a, curves 1, 2) is determined by the copper oxide content of the sample. Thus, the oxidation of CO on 2.5%CuO/ZrO<sub>2</sub> (p) came into play at a temperature higher than 100°C, and the conversion passed through a maximum at 190°C. As the concentration of CuO on the surface of  $ZrO_2(p)$  increased by a factor of 2 (from 2.5 to 5%), the maximum conversion also increased by a factor of 2 from 32% (190°C) to 65% (170°C), and  $T_{\rm max}$  decreased by 20 K. A further increase in the amount of supported CuO to 10% had almost no effect on the degree of CO conversion and  $T_{\text{max}}$ . This effect of the concentration of CuO on the catalyst activity was not observed in  $CuO/ZrO_2$  (me) samples. The conversion of CO came into play at 130°C to reach a maximum value of 29 or 32% at  $T_{\text{max}} = 190^{\circ}$ C on 2.5% CuO/ZrO<sub>2</sub> (me) (Fig. 2a, curve 3) or 5% CuO/ZrO<sub>2</sub> (me) (Fig. 2a, curve 4); then, it rapidly decreased and was no higher than 5% at 250°C. Figure 2a (curves 5 and 6) shows data on the conversion of CO on  $ZrO_2(p)$  and (me).

The process selectivity for oxygen (Fig. 2b) on  $CuO/ZrO_2(p)$  and (me) samples increased considerably as the concentration of CuO on the surfaces of  $ZrO_2(p)$  and (me) was increased from 2.5 to 5%. As can be seen in Fig. 2b, a maximum selectivity of 100% was observed at low temperatures of 100–120°C upon supporting 5% CuO onto both (p) and (me)  $ZrO_2$ (curves 2, 4). The process selectivity on these catalysts



**Fig. 2.** (a) Conversion of CO into  $CO_2$  and (b) process selectivity for oxygen on the catalysts (*1*) 2.5% CuO/ZrO<sub>2</sub> (p), (*2*) 5% CuO/ZrO<sub>2</sub> (p), (*3*) 2.5% CuO/ZrO<sub>2</sub> (me), (*4*) 5% CuO/ZrO<sub>2</sub> (me), (*5*) ZrO<sub>2</sub> (p), and (*6*) ZrO<sub>2</sub> (me).

rapidly decreased with temperature to be 45-50% in the temperature range of  $160-190^{\circ}$ C, where a maximum conversion of CO was observed. On the 2.5% CuO/ZrO<sub>2</sub> (p) and (me) samples, the selectivity was much lower (Fig. 2b, curves *I*, *3*), and its value depended on the ZrO<sub>2</sub> preparation procedure: (p) or (me). In the case of the 2.5% CuO/ZrO<sub>2</sub>(p) sample, the selectivity increased from 8% at 130°C to 38% at 190°C and then decreased (curve *I*), whereas an almost constant selectivity of 42-45% was observed on the 2.5% CuO/ZrO<sub>2</sub> (me) sample at  $120-190^{\circ}$ C (curve *3*). As the temperature was further increased, the selectivity decreased, as in the case of other catalysts.

**CuO/Zr<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>2</sub>.** Figure 3 shows data on the oxidation of CO on the samples of  $Zr_{0.5}Ce_{0.5}O_2$  (me) (curve 1) and 2.5 and 5% CuO/Zr<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>2</sub> (me) (curves 2 and 3, respectively). The regularities of CO oxidation on CuO/Zr<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>2</sub> (me) are similar to oxidation on CuO/CeO<sub>2</sub> (me), although the activity of the latter is much higher. The surface concentration of copper oxide influences the conversion of CO: for 2.5% CuO, a maximum conversion was 36% at  $T_{max} = 220^{\circ}$ C (Fig. 3a, curve 2), whereas it was 51% for 5% CuO at  $T_{max} = 180^{\circ}$ C (Fig. 3a, curve 3); that is, the conversion of CO increased by a factor of 1.5 and  $T_{max}$  decreased by 40 K with increasing the amount of supported copper oxide.

For these samples, the selectivity of  $O_2$  consumption for the oxidation of CO (Fig. 3b) depended on the concentration of CuO on the surface of  $Zr_{0.5}Ce_{0.5}O_2$ 



**Fig. 3.** (a) Conversion of CO into  $CO_2$  and (b) process selectivity for oxygen on the catalysts (1)  $Zr_{0.5}Ce_{0.5}O_2$  (me), (2) 2.5%  $CuO/Zr_{0.5}Ce_{0.5}O_2$  (me), and (3) 5%  $CuO/Zr_{0.5}Ce_{0.5}O_2$  (me).





(me) only in the low-temperature region of 80– 150°C; moreover, the process selectivity on the sample containing 2.5% CuO was higher (curve *1*) than that on the catalyst with 5% CuO (curve *2*). The selectivity of both of the samples was almost the same at temperatures higher than 150°C.

#### Temperature-Programmed Reduction (TPR) of (p) and (me) Samples with Hydrogen

The study of the (p) and (me) nanodispersed systems by TPR with hydrogen allowed us to reveal differences in the reduction of both CeO<sub>2</sub>, ZrO<sub>2</sub>, and Zr<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>2</sub> supports synthesized by different methods and the copper oxide catalysts obtained on their basis. Figure 4 indicates that the reduction temperature of the  $CeO_2$  (me) sample (spectrum 1) was considerably lower than that of  $CeO_2$  (p) (spectrum 2). In both cases, the TPR spectra exhibited two peaks: spectrum 1, at 270 and 345°C and spectrum 2, at 400 and 526°C. Two peaks of the oxidation of hydrogen by oxygen of the catalyst suggest two stages of the reduction process. Note that the total amounts of hydrogen absorbed by (p) and (me) samples were almost the same (see Table 1):  $5.3 \times 10^{-4}$  and  $4.9 \times 10^{-4}$  mol/g, respectively. Assuming that H<sub>2</sub> is completely oxidized by oxygen from the surface of oxides, the amount of reacted oxygen per unit surface area is  $(4-4.3) \times 10^{18}$  molecule/m<sup>2</sup>, which corresponds to the interaction of hydrogen with approximately 60%of surface oxygen ions. According to published data [21, 30], at the first stage the reduction of CeO<sub>2</sub>, hydrogen is oxidized by surface oxygen, and oxidation at the second stage was accompanied by the formation of nonstoichiometric surface oxides  $CeO_x$ . As can be seen in Table 1, both of the processes effectively occurred on the  $CeO_2(p)$  sample, whereas the consumption of hydrogen on  $CeO_2$  (me) at the first stage was higher than that at the second stage by a factor of 10. This fact suggests that the surface of  $CeO_2(me)$  was more uniform than that of the  $CeO_2(p)$  sample.

The TPR spectra of the  $CuO/CeO_2$  (me) and  $CuO/CeO_2$  (p) samples were also strongly different (Fig. 4, curves 3-6). Spectrum 3 of the 2.5% CuO/CeO<sub>2</sub> (me) sample contained three peaks. The first of them at 137°C belongs to the reduction of surface finely dispersed copper oxide particles [32, 33]. The second peak at 173°C is likely due to the reduction of Cu-O-Ce clusters formed at the CuO- $CeO_2$  boundary, whereas the third peak at 226°C belongs to the reduction of  $CeO_2$  (me). As the concentration of CuO was changed from 2.5 to 5% (curves 3 and 6, respectively), the number of reduced finely dispersed copper oxide particles increased, and the amount of the reacted surface oxygen of  $CeO_2(me)$  did not increase. At the same time, the amount of oxygen in Cu–O–Ce clusters cannot be accurately estimated as a result of the overlapping of peaks at 137 and 173°C; it likely remains constant. The spectrum of the 2.5% CuO/CeO<sub>2</sub>(p) sample (Fig. 4, curve 4) also contained three peaks at 127, 153, and 340°C. Characteristic peaks due to the surface reduction of the  $CeO_2(p)$ support at 400 and 526°C were absent from this spec-

\* TPR up to 650°C.

\*\* Fraction of ceria reduced in the absence of CuO.

\*\*\* The peak number in the TPR spectrum is given in parentheses; sh = shoulder, and w = weak.

 $T_{\rm max}$ , °C  $H_2$  consumption ×10<sup>4</sup>, mol/g Degree of reduction, % Sample 400 2.6  $CeO_2(p)$ 526 <u>2.7</u> Σ5.3\*  $CeO_2(me)$ 270 4.5 345 <u>0.4</u> Σ4.9 127 2.5% CuO/CeO<sub>2</sub>(p) 1.7  $100(CuO \rightarrow Cu^0)$ 153  $100(\text{CeO}_2 \longrightarrow \text{Ce}_2\text{O}_3)^{**}_{\text{surf}}$ 5.5 1.2 340  $\Sigma 8.4$ 2.5% CuO/CeO<sub>2</sub> (me) 137(sh) Σ7.5  $100(CuO \rightarrow Cu^0)$ 173  $90(\text{CeO}_2 \rightarrow \text{Ce}_2\text{O}_3)^{**}_{\text{surf}}$ 226 316(w)  $5\% CuO/CeO_2(p)$ 114 2.8  $100(CuO \rightarrow Cu^0)$ <u>6.9</u> 150  $84(\text{CeO}_2 \longrightarrow \text{Ce}_2\text{O}_3)^{**}_{\text{surf}}$ Σ9.7  $5\% CuO/CeO_2$  (me) 138 Σ11.0  $100(CuO \rightarrow Cu^0)$ 228  $100(\text{CeO}_2 \longrightarrow \text{Ce}_2\text{O}_3)^{**}_{\text{surf}}$  $ZrO_2(p)$ \_ \_ \_ 0.3  $ZrO_2(me)$ 326 2.5% CuO/ZrO<sub>2</sub>(p) 149(1)\*\*\* 1.7(1) \*\*\*  $81(CuO \rightarrow Cu^0)$ 207(2) <u>0.8</u> (2+3) 311(3)  $\Sigma 2.5$ 2.5% CuO/ZrO<sub>2</sub> (me) 162(1) 2.4(1+2) $78(CuO \rightarrow Cu^0)$ 202(sh, 2) <u>0.3</u>(3) Σ2.7 319(3)  $5\% CuO/ZrO_2(p)$ 4.5(1)142(1) $98(CuO \rightarrow Cu^0)$ 192(2) 1.6(2+3)Σ6.1 212(3) Σ 6.0  $5\% \text{ CuO/ZrO}_2(\text{me})$ 150 97 (CuO  $\rightarrow$  Cu<sup>0</sup>) 325  $Zr_{0.5}Ce_{0.5}O_{2}$  (me) (me) 376 4.4 2.5% CuO/Zr<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>2</sub> (me) 173 Σ8.6  $100 (CuO \rightarrow Cu^0)$ 278 100 (Ce-Zr-O)<sup>\*\*</sup><sub>surf</sub>  $5\% \text{ CuO/Zr}_{0.5}\text{Ce}_{0.5}\text{O}_2$  (me) 147 Σ10.4  $100 (CuO \rightarrow Cu^0)$ 286 98 (Ce-Zr-O)\*\*

**Table 1.** TPR data for the CuO/(CeO<sub>2</sub>,  $ZrO_2$ , and  $Zr_{0.5}Ce_{0.5}O_2$ ) samples



Fig. 5. TPR spectra of (1)  $ZrO_2$  (me), (2) 2.5%  $CuO/ZrO_2$  (me), (3) 2.5%  $CuO/ZrO_2$  (p), (4) 5%  $CuO/ZrO_2$  (me), and (5) 5%  $CuO/ZrO_2$  (p).

trum. At the same time, the temperatures of peak maximums in the spectrum depends on the amount of CuO on the surface: a change in the concentration of CuO from 2.5 to 5% (Fig. 4, curve 5) led to a shift in the temperature of the first maximum from 127 to 114°C or from 153 to 150°C for the second maximum. Furthermore, a peak at 340°C disappeared. As in the case of the  $CuO/CeO_2$  (me) samples, the first and the second peaks were due to the reduction of finely dispersed copper oxide particles and Cu–O–Ce clusters, respectively. A comparison of spectra 3-6 (Fig. 4) shows that the number of Cu-O-Ce clusters in the (2.5-5%) CuO/CeO<sub>2</sub> (p) samples was greater than that in the corresponding (me) samples. It should be noted that the amount of hydrogen absorbed by both  $CuO/CeO_2$  (p) and (me) samples during the reduction was considerably greater than that required for the complete reduction of supported copper from the state  $Cu^{2+}$  to  $Cu^{0}$  (see Table 1), and it was also sufficient for 100% reduction of the surface ions Ce<sup>4+</sup> that are reduced in the absence of CuO to  $Ce^{3+}$  (see Table 1).

Figure 5 shows the TPR spectra of the (p) and (me) samples of  $ZrO_2$  and  $CuO/ZrO_2$ . Unlike  $ZrO_2$  (p), which was not reduced in hydrogen to 650°C, the TPR spectrum of  $ZrO_2$  (me) exhibited a small narrow peak of the absorption of hydrogen at 326°C (Fig. 5, curve *I*). The amount of oxygen removed from the sample corresponding to this peak was no higher than 3% on a surface oxygen ion basis; it was most likely due to defects formed upon the synthesis of the sample [30].

In the (2.5-5)% CuO/ZrO<sub>2</sub> (p) samples (Fig. 5, spectra 3 and 5), the absorption of hydrogen occurred

in the two regions of 140–150 and 190–210°C. According to Firsova et al. [22], the low-temperature peak belongs to the reduction of copper cations that strongly interact with the surface defects of  $ZrO_2$  to form Cu–O–Zr clusters, and the second group of peaks at ~200°C belongs to the reduction of the surface particles of a CuO phase. The concentration of clusters on the surface increased with the copper content of the sample.

Analogous behaviors were observed in the (2.5-5)% CuO/ZrO<sub>2</sub> (me) samples (Fig. 5, spectra 2 and 4). In this case, the reduction of clusters occurred at a higher temperature of 150–160°C and the reduction of the particles of a CuO phase occurred at ~200°C.

Note that the total amount of hydrogen absorbed by the (p) and (me) samples was approximately the same (see Table 1).

Figure 6 shows the TPR spectra of the  $Zr_{0.5}Ce_{0.5}O_2$ (me) (curve *I*) and 2.5 and 5% CuO/Zr<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>2</sub> (me) samples (curves 2 and 3, respectively). As is evident, spectrum *I* exhibits one peak at  $T_{max} = 376^{\circ}C$  analogously to the spectrum of CeO<sub>2</sub> (me) (Fig. 4, curve 2) with a peak at  $T_{max} = 270^{\circ}C$ ; the amount of absorbed hydrogen was almost the same as that observed during the reduction of CeO<sub>2</sub> (me). On this basis, we can assume that the surface of the solid solution  $Zr_{0.5}Ce_{0.5}O_2$  (me) was enriched in CeO<sub>2</sub>, and an increase in the temperature of its reduction by ~100 K, as compared with that of CeO<sub>2</sub>, was due to the strong interaction of Ce and Zr cations, which strengthened the bond of surface oxygen [30]. In the TPR spectra of the 2.5 and 5% CuO/Zr<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>2</sub> (me) samples, two



**Fig. 6.** TPR spectra of (1)  $Zr_{0.5}Ce_{0.5}O_2$  (me), (2) 2.5% CuO/ $Zr_{0.5}Ce_{0.5}O_2$  (me), and (3) 5% CuO/ $Zr_{0.5}Ce_{0.5}O_2$  (me).

peaks were observed. One of these peaks at 173°C for 2.5% CuO (curve 2) or 147°C for 5% CuO (curve 3) was due to the reduction of surface copper oxide, and the other at 286 or 278°C for 2.5 and 5% CuO, respectively, was due to the reduction of  $Zr_{0.5}Ce_{0.5}O_2$  (me). In this case, a decrease in the support reduction temperature under the action of supported copper oxide was also observed.

## Study of the CO and CO<sub>2</sub> Adsorption Species on CuO/(CeO<sub>2</sub>, ZrO<sub>2</sub>, and $Zr_{0.5}Ce_{0.5}O_2$ )(p) and (me) Samples

TPD spectra were obtained for the oxidized supports and copper-containing samples after the adsorption of CO on them (P = 30 Pa;  $T = 20^{\circ}$ C; adsorption time, 10 min). Desorption from the (p) and (me) CeO<sub>2</sub> oxides was observed only at  $T > 400^{\circ}$ C. The number of desorbed molecules per unit surface area was almost the same for both of the sample (approximately  $2.0 \times$  $10^{16} \text{ m}^{-2}$ ). The only product of desorption was CO<sub>2</sub>, which, probably, resulted from the decomposition of surface carbonates formed upon the adsorption of CO. This conclusion was supported by the absence of any peaks from the TPD spectra of the oxidized samples without the adsorption of CO. At the same time, the temperature range of the observed desorption of  $CO_2$ coincides with the region of the decomposition of carbonates on  $CeO_2$  [34].

Figure 7 shows the TPD spectra of the oxidized CuO/(CeO<sub>2</sub>, ZrO<sub>2</sub>, and Zr<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>2</sub>) samples after CO adsorption on them. The intensity of the spectrum depends on the nature of the support and the method of its preparation. Thus, the intensity of the spectrum of desorption from the 5% CuO/CeO<sub>2</sub> (p) sample (Fig. 7, curve *I*) is 1.5 times higher than that of the 5% CuO/CeO<sub>2</sub> (me) sample (curve 2). The amount of desorption products from the 5% CuO/ZrO<sub>2</sub> (me)

(curve 3) and 5% CuO/ $Zr_{0.5}Ce_{0.5}O_2$  (me) (curve 4) samples are substantially lower; moreover, for the latter sample, it is even lower than that of 5% CuO/CeO<sub>2</sub> (me) by a factor of 2 (see curves 2, 4).

Using mass-spectrometric analysis, we found that the products of desorption are CO (28 amu) and CO<sub>2</sub> (44 amu) and their TPD spectra overlap. To separate spectra, we performed analogous TPD experiments and recorded the spectra of CO desorption without CO<sub>2</sub>. For this purpose, in the process of desorption,  $CO_2$  was frozen in a trap cooled with liquid nitrogen, which was arranged between the reactor and a manometer. The desorption spectrum of  $CO_2$  was obtained by the subtraction of the spectrum of CO from the overall spectrum. The results of this analysis are given in Fig. 8 for the 5%  $CuO/CeO_2(p)$  sample. Curve 1 in Fig. 8 shows the total TPD spectrum  $(CO + CO_2)$ . Spectrum 2 corresponds to CO desorption, which occurred in the range of 20-200°C with a maximum rate of desorption at  $T_{\text{max}} = 110^{\circ}$ C. Spectrum 3, which is the difference of spectra 1 and 2, relates to the desorption of CO<sub>2</sub>, which occurs in the range of 50–400°C with  $T_{\text{max}} = 150$ °C. In the range of 200–400°C, it is likely that the wing of the  $CO_2$  desorption spectrum consists of two additional peaks with  $T_{\rm max}$  at 240 and 300°C. Similar peaks of CO and CO<sub>2</sub> desorption at  $T_{\text{max}} = 100-110$  and ~150°C, respectively, were also observed for the other copper oxide catalysts containing the (me) supports: CeO<sub>2</sub>, ZrO<sub>2</sub>, and  $Zr_{0.5}Ce_{0.5}O_2$ . However, as can be seen in Figs. 7 and 8, the desorption of  $CO_2$  on them occurs only to 300°C. Table 2 summarizes the total amounts of desorbed molecules N(CO) and  $N(CO_2)$  per unit surface area of the samples. It turned out that CO and  $CO_2$ were desorbed in approximately the same amounts from the surfaces of each of the (me) samples, although the total desorption (see Fig. 7) was different and depended on the nature of the support.



**Fig. 7.** TPD spectra of the oxidized samples after the adsorption of CO on them: (1) 5% CuO/CeO<sub>2</sub> (p), (2) 5% CuO/CeO<sub>2</sub> (me), (3) 5% CuO/ZrO<sub>2</sub> (me), and (4) 5% CuO/Zr<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>2</sub> (me).  $T = 20^{\circ}$ C;  $\tau = 10$  min.

Table 2 also summarizes data on CO<sub>2</sub> desorption (N<sub>20</sub>(CO<sub>2</sub>)), which occurred at 20°C in the course of CO adsorption (P = 30 Pa; T = 20°C; and  $\tau = 10$  min) before the onset of TPD. In this case, the amount of adsorbed CO was determined from a pressure change upon its adsorption, and the amount of CO<sub>2</sub> was determined by measuring the amount of frozen gas in the trap. The largest amount of CO<sub>2</sub> ( $4.3 \times 10^{17}$  m<sup>-2</sup>) was obtained from the 5% CuO/CeO<sub>2</sub> (me) sample. It was comparable with the amount of CO<sub>2</sub> desorbed from the catalyst upon TPD. In other samples, the amounts N<sub>20</sub>(CO<sub>2</sub>) were smaller than N(CO<sub>2</sub>).

Note that the adsorption of CO is activated. As the temperature of CO adsorption on the 5% CuO/CeO<sub>2</sub> (me) sample was increased to 100°C, the amount of CO and CO<sub>2</sub> upon desorption increased by a factor of about 1.4. The same effect was observed with a change in the pressure of CO in the course of adsorption from 30 to  $1.7 \times 10^3$  Pa. A change in the temperature of CO adsorption from 20 to 100°C on the 5% CuO/Zr<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>2</sub> (me) sample also led to an increase in the amounts of CO upon TPD from  $1.2 \times 10^{17}$  to  $5.6 \times 10^{17}$  m<sup>-2</sup> and of CO<sub>2</sub> from  $1.5 \times 10^{17}$  to  $2.8 \times 10^{17}$  m<sup>-2</sup>. It is likely that the activated nature of CO adsorption and its low value at 20°C on 5% CuO/Zr<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>2</sub> (me), as compared with other samples, was due to the strong interaction of Zr and Ce cations in the mixed oxide Zr<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>2</sub> (me) [30].

For explaining the mechanism of  $CO_2$  formation on TPD, we studied  $CO_2$  desorption from the preoxi-



**Fig. 8.** TPD spectra of the 5% CuO/CeO<sub>2</sub> (p) sample after the adsorption of CO on it: (1) CO + CO<sub>2</sub>, (2) CO, and (3) CO<sub>2</sub>.  $T = 20^{\circ}$ C.

dized 5% CuO/CeO<sub>2</sub> (me) sample after the TPD of CO. In both cases, after the adsorption of CO<sub>2</sub> (P = 30-60 Pa;  $T = 20^{\circ}$ C; and CO<sub>2</sub> = 10 min), the desorption of CO<sub>2</sub> from the samples was observed only in the region of 20–200°C. It did not exceed 15% of the amount of CO<sub>2</sub> obtained upon the TPD of CO as a result of its oxidation by oxygen of the catalyst surface N(CO<sub>2</sub>) =  $4.4 \times 10^{17}$  m<sup>-2</sup>. This fact suggests that the observed temperature dependence of the desorption of CO<sub>2</sub> in the region of 50–400°C, which is given in Fig. 8, is caused by the activation energy of the oxidation reaction of adsorbed CO by oxygen surface ( $E_r$ ) rather than by the activation energy of the desorption of CO<sub>2</sub>.

The activation energy of the desorption and oxidation of CO can be estimated using the expression  $E_d = 25RT_{max}$ , where R = 8.3143 J K<sup>-1</sup> mol<sup>-1</sup> is the gas constant, and  $T_{max}$  is the temperature (*T*, K) that corresponds to the maximum rate of desorption [35]. Thus, for the desorption of CO at  $T_{max} = 383$  K, the activation energy of desorption is  $E_d = 79$  kJ/mol, the activation energy of the oxidation of CO for the desorption peak of CO<sub>2</sub> at  $T_{max}(CO_2) = 423$  K is  $E_r = 88$  kJ/mol, and  $E_r =$ 130 kJ/mol for  $T_{max}(CO_2) = 623$  K.

In the process of TPD, approximately a half of adsorbed CO is moved away upon desorption in the region of 20–200°C, and the remaining part is oxidized by surface oxygen to CO<sub>2</sub>, whose desorption is observed at 50–400°C. It should be noted that, on the 5% CuO/CeO<sub>2</sub> (me) sample, CO is oxidized to CO<sub>2</sub>

Sample	$N(CO) \times 10^{-17}, m^{-2}$	$N(CO_2) \times 10^{-17}, m^{-2}$	$N_{20}(CO_2) \times 10^{-17}, m^{-2}$
5% CuO/CeO <sub>2</sub> (p)	7.2	10.1	0.34
$5\% \text{ CuO/CeO}_2 \text{ (me)}$	5.4	4.4	4.3
5% CuO/ZrO <sub>2</sub> (me)	3.7	4.1	0.4
5% CuO/Zr <sub>0.5</sub> Ce <sub>0.5</sub> O <sub>2</sub> (me)	1.2	1.5	0.6

Table 2. Amounts of CO and CO<sub>2</sub> molecules desorbed in TPD after the adsorption of CO on the test samples

Sample	$N(CO) \times 10^{-17}, m^{-2}$	$N(CuO) \times 10^{-18}, m^{-2}$	N(CO)/ N(CuO) × 100%
5% CuO/CeO <sub>2</sub> (p)	17.5	4.5	39
$5\% \text{ CuO/CeO}_2 \text{ (me)}$	14.0	4.6	30
$5\% \text{ CuO/Zr}_{0.5}\text{Ce}_{0.5}\text{O}_2 \text{ (me)}$	5.4	6.0	9
$5\% \text{ CuO/ZrO}_2(\text{me})$	7.9	4.1	19

 Table 3. Ratios between the amounts of adsorbed CO and CuO particles on the samples

during adsorption even at room temperature ( $20^{\circ}$ C), and the amount of CO<sub>2</sub> is comparable with that formed in the TPD process (see Table 2).

The total number of adsorbed CO molecules on the surface of 5% CuO/CeO<sub>2</sub> (p) is greater than that on (me) samples (see Table 3). If we consider the uniform surface coverage of the support with copper oxide, the number of CuO molecules per unit surface area is almost the same on (p) and (me) samples; however, the relationships between the amounts of adsorbed CO and CuO particles on the investigated samples (Table 3) are essentially different: it is maximal for 5% CuO/CeO<sub>2</sub> (p) or 5% CuO/CeO<sub>2</sub> (me) among (me) samples.

### DISCUSSION

The catalytic activity of  $CuO/(CeO_2, ZrO_2)$  in the reaction of CO oxidation in the presence of hydrogen depends on both the amount of supported copper oxide and the particle size (preparation procedure) of  $CeO_2$  and  $ZrO_2$ . A considerable decrease in the reaction temperature on these samples, as compared with temperatures observed in the oxidation of CO on the supports and the copper oxide CuO, and also an increase in the conversion of CO are consistent with previously obtained data [19, 20, 26, 36, 37]. In these publications, it is assumed that an increase in the activity of the supported copper oxide catalysts is due to the formation of the new active centers, which are formed and stabilized on the surface as a result of the strong interaction of CuO clusters with the support (a synergetic effect).

According to TPR data, the following two types of centers were detected on the surface of the supported copper oxide catalysts: the clusters of finely dispersed copper oxide and the centers formed at the interface of the CuO clusters and the support. These latter contain the cations of copper and the support Cu<sup>2+</sup>-O<sup>2-</sup>-Ce<sup>4+</sup> or  $Cu^{2+}-O^{2-}-Zr^{4+}$ ; in accordance with the above, they can be the centers of the low-temperature oxidation of CO. It is well known [8-12, 38-40] that strong carbonyl complexes with only Cu<sup>+</sup> cations are formed upon the adsorption of CO. Therefore, copper cations in the active center on the oxidized catalyst surface will occur in this state. According to Krylov [35], this takes place in the structure of the cluster  $Cu^{2+}-O^{2-}-Cu^{2+}$ , where the effective charge of copper is  $Cu^+$ . Upon the formation of boundary clusters, one of the copper cations is replaced by  $O^{2-}-Ce^{4+}$  or  $O^{2-}-Zr^{4+}$ , and the second copper cation remains in the effective state  $Cu^+$ , which is necessary for the adsorption of CO. At the same time, the  $Cu^+$  cations can be formed from  $Cu^{2+}$  by the interaction with negatively charged anionic vacancies, which appear in the course of CO oxidation by surface oxygen [39].

The systems containing 5% CuO can be arranged in the following order of decreasing catalytic activity (the maximum conversions and the corresponding values of  $T_{\text{max}}$  are given in parentheses):

$$\begin{aligned} \text{CuO/CeO}_{2}(\text{p}) \ (\sim 100\%, \ 125^{\circ}\text{C}) > \text{CuO/CeO}_{2}(\text{me}) \\ (99\%, \ 160^{\circ}\text{C}) > \text{CuO/ZrO}_{2}(\text{p}) \ (65\%, \ 170^{\circ}\text{C}) \\ > \text{CuO/ZrO}_{2}(\text{me}) \ (32\%, \ 190^{\circ}\text{C}). \end{aligned}$$

Note that copper oxide catalysts in which  $CeO_2$  was used as a support are more active regardless of support preparation procedure (and hence support particle size). This is likely due to both the lower strength of the bond of oxygen in the centers  $Cu^{2+}-O^{2-}-Ce^{4+}$ , as compared with  $Cu^{2+}-O^{2-}-Zr^{4+}$ , and the greater number of active centers on the surface of  $CeO_2$ . The above data indicate that the catalytic activity of the supported copper oxide systems also changes depending on the particle size of the support,  $CeO_2$  or  $ZrO_2$ .

In the case of  $CeO_2$ , the catalytic activity of (me) samples is lower than that of (p) samples at the same concentration of CuO on the surface. It was found by XRD analysis that CeO<sub>2</sub> crystallized in the K modification with constant unit cell parameters regardless of preparation procedure and particle size. This means that the catalytic properties changed not due to a change in the support structure. According to TPR data (Fig. 4, Table 1), a change in the concentration of CuO on the surface of  $CeO_2(p)$  from 2.5 to 5% leads to an increase in the number of Cu-O-Ce clusters and a decrease in the temperature of their reduction with hydrogen, which confirms the occurrence of a synergetic effect for these samples. According to TPR data, the 5% CuO/CeO<sub>2</sub> (me) sample contained a much greater amount of the finely dispersed particles of surface copper oxide in comparison with the 2.5% CuO/CeO<sub>2</sub> (me) sample, and the number of Cu–O–Ce (me) clusters remained almost unchanged. Moreover, a considerable fraction of the free  $CeO_2$ (me) surface was retained in both of the samples. Probably, a smaller number of Cu–O–Ce clusters was formed on the uniform surface of  $CeO_2$  (me), which

consists of small nanoparticles (~5 nm), upon the interaction with supported copper oxide. These clusters are active centers for the reaction of CO oxidation [20], and these clusters are smaller than those on a more defective surface of  $CeO_2(p)$  with a crystallite size of ~15 nm. This may be consistent with TPD data, which show that the number of CO molecules adsorbed on  $CuO/CeO_2$  (p) per unit surface area (at almost the same numbers of supported CuO particles) is much greater than that on  $CuO/CeO_2$  (me). Furthermore, according to TPR data, the reduction of copper oxide (me) samples occurs at a higher temperature than that of (p) samples (see Fig. 4 and Table 1). This can be due to an increase in the binding energy of cluster oxygen with the surface and a weakening of the synergetic effect in the case of (me) catalysts. All of these results explain the smaller activity of the  $CuO/CeO_2$  (me) sample with particle sizes of 5-6 nm, as compared with  $CuO/CeO_2(p)$ , which has a particle size of 15 nm. The selectivity of CO oxidation (see Fig. 1b) on (me) samples is higher than that on (p) samples and almost independent of the amount of supported copper oxide. This may serve as an additional support to the greater uniformity of the surface of  $CuO/CeO_2$  (me) catalysts, as compared with (p) samples.

The dependence of the conversion of CO upon the concentration of CuO on the surface of ZrO<sub>2</sub> was detected only on (p) samples: as the amount of supported CuO was changed from 2.5 to 5%, the conversion of CO increased from 32 to 66%, whereas it remained unchanged on the (me) catalyst (see Fig. 2). According to Il'ichev et al. [30], the concentration of coordinatively unsaturated Zr4+ cations and acidbase pairs  $(Zr^{4+}-O^{2-})$  was two times higher than that on  $ZrO_2$  (me). Assuming the formation of Cu–O–Zr active centers on such defects, we can explain the higher activity of the 5%  $CuO/ZrO_2$  (p) sample in comparison with 5% CuO/ZrO<sub>2</sub> (me). According to TPR data, raising the CuO content of the (me) samples from 2.5 to 5% results primarily in an increase in the surface concentration of fine-particle CuO, as in the case of the  $CuO/CeO_2$  (me) surface.

As noted previously [22], the number of active centers on the surface of CuO/ZrO<sub>2</sub>(p) (clusters like Cu–O–Zr) is substantially smaller than that of Cu–O–Ce in the case of CuO/CeO<sub>2</sub>(p); this fact explains its low activity. As the particle size of ZrO<sub>2</sub> was decreased from 20– 25 nm in CuO/ZrO<sub>2</sub> (p) to 5–6 nm in the case of CuO/ZrO<sub>2</sub> (me) with a simultaneous increase in the surface uniformity of the support, the number of Cu– O–Zr clusters also decreased. Upon supporting higher concentrations of CuO, only the fraction of finely dispersed surface copper oxide increased.

In the study of CuO/Zr<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>2</sub> (me), we found that  $Zr_{0.5}Ce_{0.5}O_2$  (me) is a solid solution, whose surface is enriched in CeO<sub>2</sub> (according to TPR data), and the binding energy of surface oxygen in  $Zr_{0.5}Ce_{0.5}O_2$  (me) is greater than that in CeO<sub>2</sub> (me) at the same size of crystallites. These data suggest the strong interaction of Zr and Ce ions, which is consistent with published data [30]. Taking into account this fact, we can assume that the copper oxide on the surface of  $Zr_{0.5}Ce_{0.5}O_2$  (me) forms centers for the oxidation of CO {(Zr)Ce<sup>4+</sup>-O<sup>2-</sup>-Cu<sup>2+</sup>}, in which the surface ions of Ce interact with the ions of Zr from a near-surface layer. It is likely that this interaction leads to a strengthening of the bond of cluster oxygen and hence to an increase in  $T_{max}$  and a decrease in the conversion of CO.

Thus, the copper oxide catalysts prepared based on the synthesized (me) supports were found less active than  $CuO/(CeO_2,ZrO_2)(p)$  in the oxidation of minor CO impurities in an excess of H<sub>2</sub>.

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