Chemistry for Sustainable Development **13** (2005) 819–825

Catalytic Systems for Hydrogen Purification from CO for Fuel Cells

V. F. TRETJAKOV, T. N. BURDEYNAYA, L. A. BEREZINA and R. A. LYUBUSHKIN

*Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,
Pr. Leninskiy 29, Moscow 119991 (Russia)*

E-mail: tretjakov@ips.ac.ru

Abstract

Comparative investigation of the activity of synthesized deposited Cu,Co/$Y_xCe_yZr_{1-x-y}O_2$ and Au-, Pt-containing catalytic systems in the reaction of a low-temperature selective CO oxidation in hydrogen-containing gas mixtures had been conducted. It had also been demonstrated that these systems provide a high CO conversion level and selectivity with respect to O_2 in an interval of temperatures up to 150 °C. It has been found that Au-containing catalyst is of the highest activity. The activity and selectivity of nanocrystalline Cu/$Y_xCe_yZr_{1-x-y}O_2$ catalysts in the mentioned reaction is higher as compared to Pt-containing catalysts, and they are comparable with an Au containing sample in their selectivity. It had been demonstrated that the use of these catalysts makes it possible to reach the degree of hydrogen cleansing from CO to the level of about 15 ppm, which meets the for fuel cells requirements.

INTRODUCTION

A car exhausts into the atmosphere as many as 200 various substances, half of which are hazardous to the human being and the environment. 40 million cars leave the car factory conveyors annually, and the tendency to increase the volumes of their production will be preserved [1]. This has a consequence that air pollution in big cities is about 80 to 95 % due to automobiles exhausts. Meanwhile, we may expect the production of the domestic automobile engines that meet the modern-day ecological requirements as late as 2010.

At present time, investigations are conducted all over the world to create new kinds of engine fuels that will meet both ecological and high performance requirements. The purpose of these works is the development of national concepts for production and employment of alternative engine fuels and creating the appropriate engines that are compatible with the most stringent world standards.

Polymer electrolyte membrane fuel cells (PEMFC) are considered as a promising energy source to replace the internal combustion engines in cars. Fuel cells belong to chemical current sources and perform the transformation between the fuel energy and electricity. The process that occurs in an oxygen-hydrogen fuel cell is a reverse in its nature to the electrolysis process. It is possible to distinguish the following of the advantages of fuel cells: continuous output of energy (unlike the accumulators that require a periodic replacement of the electrolyte); ecological compatibility of fuel cells and their waste products; high efficiency factor.

Meanwhile, the use of fuel cells involves a number of difficulties, the main of which is the hydrogen storage onboard the car. In this connection, it is suggested to produce hydrogen from methanol in various ways:

1. Catalytic decomposition of methanol:

$$CH_3OH \text{ (g.)} \rightarrow CO + 2H_2, \quad \Delta H = 91 \text{ kJ/mol}$$

2. Partial oxidation

$$CH_3OH \text{ (g.)} + 0.5O_2 \rightarrow CO_2 + 2H_2, \quad \Delta H = -192 \text{ kJ/mol}$$

3. Steam reforming

$$CH_3OH \text{ (g.)} + H_2O \rightarrow CO_2 + 3H_2, \quad \Delta H = 50 \text{ kJ/mol}$$

$$CH_3OH \text{ (g.)} \rightarrow CO + 2H_2, \quad \Delta H = 91 \text{ kJ/mol}$$

4. Autothermal reforming:
CH_3OH (g.) + $(1 - 2a)H_2O + aO_2$
$\rightarrow CO_2 + (3 - 2a)H_2$, where $0 \leq a \leq 0.5$, $H_2O/CH_3OH = 1.5 - 1.6$, $O_2/CH_3OH = 0.2 - 0.3$.

The composition of gas mixtures that are generated by these reactions is presented below, vol. %:

Catalytic decomposition	H_2 67, CO 33
Steam reforming	H_2 75, CO 1–2, CO_2, H_2O
Autothermal reforming	H_2 67, CO_2, CO

However, carbon monoxide generated as a by-product of methanol decomposition in the exhaust gases is not only an undesirable component, but it also poisons to the anode of a fuel cell. Therefore, prior to feeding the mixture in PEMFC, it is necessary to conduct an additional reaction of a selective catalytic oxidation of CO with the excess of hydrogen:

$$CO + 1/2O_2 \rightarrow CO_2, \quad \Delta H = -283.0 \text{ kJ/mol} \qquad (1)$$

Along with the target CO oxidation reaction, a side reaction is possible:

$$H_2 + 1/2O_2 \rightarrow H_2O, \quad \Delta H = -241.8 \text{ kJ/mol} \qquad (2)$$

Typically, the catalysts used in the process, based on platinum group metals or gold (Table 1), meet the basic requirements that are placed on the catalysts in this process: high activity in CO oxidation (reaction (1)) combined with low activity in H_2 oxidation (reaction (2)) in presence of CO_2 and water [2–4].

All of the above catalytic systems are expensive. In addition, full CO conversion on the catalysts that contain platinum metals is observed only at temperatures higher than 100 °C, and the selectivity of the process is low. Therefore, it is necessary to institute the investigations that are aimed to work out the catalysts that are suitable over a wide temperature range (25–200 °C) and that feature both high selectivity and low cost.

TABLE 1

Selective CO oxidation catalysts

Catalyst	T, °C	X_{CO}, %	S, %	Reference
5 % Au/Al_2O_3	100	65	74	[2]
5 % $Au/MgO/Al_2O_3$	50	95	90	[2]
1 % Pt/Al_2O_3	250	90	30	[3]
1.8 % Ru/Al_2O_3	200	30	15	[4]
1.8 % Rh/Al_2O_3	200	65	35	[4]

Note. X_{CO} is CO conversion degree, S is selectivity in respect to oxygen.

The promising systems in this regard are nanocrystalline catalytic systems containing transition elements deposited onto Ce containing support. The employment of nanocrystalline materials with the developed surface creates a wide field to prepare new generation multicomponent oxide catalysts and supports. Although cerium oxide, being a component of catalytic systems with high oxygen capacity, is able to maintain a substantial partial pressure of oxygen in a gas phase, it is characterized by a fast deactivation.

To raise the stability and oxygen capacity of Ce containing catalysts is possible through adding ZrO_2 and cations of various metals in their composition. It has been found that the quantity of latent lattice oxygen increases upon an introduction of ZrO_2 in the crystal lattice of cerium dioxide. It should be also noted that the ionic radii of cerium and zirconium are practically identical and both oxides show isomorphic structure; therefore, the formation of a mixture of solid binary solutions of oxides occurs in a wide interval of concentrations (10–90 mol. %) at the temperatures 100–400 °C:

$$CeO_2 + ZrO_2 \rightarrow Zr_{1-x}Ce_xO_{2-\delta} + Ce_{1-x}Zr_xO_{2-\delta} \qquad (3)$$

These binary mixtures are distinguished for high dispersion, since the particle size of the respective phases does not exceed 30–50 nm even in the temperature region of 700–1000 °C, whereas the particle size of the individual zirconium oxide is an order of magnitude higher [5]. Through a modification of $Ce_xZr_{1-x}O_2$ solid solutions by yttrium oxide, one can synthesize the system that features unique mechanical characteristics along with high thermal stability and enhanced oxidation-reduction characteristics that are inherent to $Ce_xZr_{1-x}O_2$ system [6, 7].

The purpose of this research was to create effective multicomponent nanocrystalline Co,Cu/Y–Ce–Zr oxide catalytic systems for the low-temperature selective CO oxidation in hydrogen containing gas mixtures. This was followed by an activity comparison between the synthesized systems and catalysts containing precious metals.

EXPERIMENTAL

In application to selective CO oxidation series of CeO_2, ZrO_2, $Ce_xZr_{1-x}O_2$, $Y_yCe_xZr_{1-x-y}O_2$ supported catalysts that incorporated Cu and Co as active components were studied along with Pt and Au containing catalytic systems. Samples of Co,Cu/Y–Ce–Zr had been obtained by impregnation of the supports synthesized by coprecipitation procedure. Pt- and Au-containing catalysts have been prepared by impregnation ($Au/Li_2O/CeO_x/Al_2O_3$, Pt/SiO_2) and ion-exchange methods (Pt/SiO_2). Table 2 presents the characteristics of the studied systems.

Testing of catalysts in the reaction of selective CO oxidation was conducted in a setup of a flow-through type in a temperature interval 20–240 °C at pressure 0.1–0.5 MPa, and volume flow rates $W = (3.6-25.0) \cdot 10^3\ h^{-1}$. Analysis of components of the gas mixtures that contained CO, O_2, H_2 and CO_2 was conducted by the gas-liquid chromatography method in a Chrom 5 chromatograph (thermal conductivity detector) with three columns within an accuracy limit of 70 ppm. For CH_4, CO_2, H_2O (He as gas-carrier) and H_2 (N_2 as gas-carrier) analyses Porapak Q was used; for O_2, N_2, CO (He as gas-carrier) analyses – 5A molecular sieves; for O_2, N_2, CO, CO_2 (H_2 as gas-carrier) – activated carbon. Low concentrations of CO were determined by means of electrochemical Testo-33 analyser (the accuracy limit 1–10 ppm).

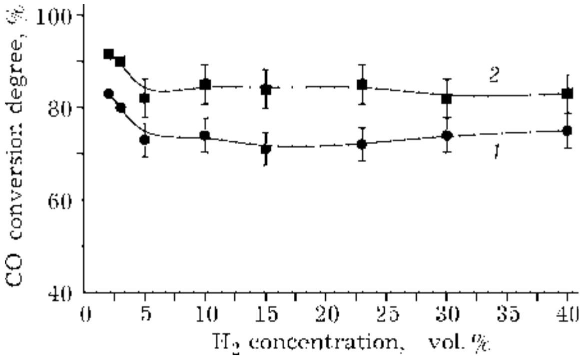

Fig. 1. Dependence of CO conversion degree on the hydrogen concentration in the mixture at 100 (*1*) and 120 °C (*2*). Composition of the mixture, vol. %: CO 1.0, O_2 1.4, H_2 2–40, N_2 up to 100. $P = 0.2$ MPa, $W = 25\,000\ h^{-1}$.

The effect of hydrogen concentration on the activity in selective CO oxidation has been studied with the catalyst of the following composition: 0.7 mass % $Au/MgAl_2O_4$ [8] (Fig. 1). It is evident that CO conversion level decreases at H_2 concentration from 0 to 5 vol. % and it is virtually stable as concentration increases to 40 vol. %. On the strength of the obtained results, the mixture of the following composition (vol. %) has been selected as a model one: CO 1.0, O_2 1.4, H_2 5, N_2 up to 100.

Reagents conversion degree X and process selectivity S in respect to oxygen were calculated by the formulae:

$$X = [(C_{in} - C_{out})/C_{in}] \cdot 100\ \% \qquad (4)$$

$$S = [1/2CO_2/(O_{2\,in} - O_{2\,out})] \cdot 100\ \% \qquad (5)$$

where C_{in}, C_{out} are concentrations of the mixture constituents at the inlet and the outlet of a reactor, respectively.

TABLE 2

Physicochemical characteristics of the studied catalysts

Catalyst	Specific surface of the carrier, m^2/g	Phase composition
1 mol. % Cu/CeO_2	24	Cubic
1 mol. % $Cu/Ce_{0.5}Zr_{0.5}O_{2-\delta}$	110	Tetragonal
1 mol. % $Cu/Y_{0.06}Ce_{0.44}Zr_{0,5}O_{2-\delta}$	78	Cubic
1 mol. % $Cu/Y_{0.1}Ce_{0.1}Zr_{0.8}O_{2-\delta}$	69	Tetragonal
1 mol. % Cu/ZrO_2	12	Monoclinic
1 mol. % Co/CeO_2	20	Cubic
1 mol. % $Co/Ce_{0.5}Zr_{0.5}O_{2-\delta}$	102	Tetragonal
1 mol. % Co/ZrO_2	10	Monoclinic
5 mass % $Au/Li_2O/CeO_x/Al_2O_3$	260	–
2 mass % Pt/SiO_2	200	–
2 mass % Pt/SiO_2	300	–

RESULTS AND DISCUSSION

Results of the completed investigation into the influence of temperature, pressure and volume flow rate on the activity and selectivity of Pt and Au containing catalysts in the reaction of selective CO oxidation in hydrogen-containing gas mixtures are presented in the work [8].

It has been found that the maximum conversion of CO on the catalysts with the composition of 2 mass % Pt/SiO_2 prepared by the impregnation and ion exchange methods does not exceed 90 % in 125–140 °C temperature interval, and its decrease is observed at the temperatures higher than 140 °C. By the use of the sample that has been obtained by the ion exchange method, a higher conversion level of CO over the region of temperatures lower than 120 °C has been attained as compared to the catalyst that was prepared by the impregnation method, and their activity is comparable at the temperatures higher than 120 °C. Selectivity with Pt-containing catalysts drops in the course of the temperature rise from 70 % at 100 °C to 40 % at 150 °C (0.5 MPa, 3600 h^{-1}). Study of the effect of water vapour (10 vol. %) has demonstrated that the activity and selectivity of catalysts throughout the whole interval of the examined pressures and temperatures is higher in the gas mixtures that contain water vapour. Accordingly, with the sample of 2 mass % Pt/SiO_2 that was prepared by the ion exchange method, $X_{CO} = 98$ % and $S = 60$ % at $P = 0.5$ MPa, $W = 3600$ h^{-1}, and $T = 135$ °C in the initial gas containing water vapour, and without water, 84 and 54 %, respectively.

For the catalyst of the composition of 5 mass % Au/Li_2O/CeO_x/Al_2O_3, a practically full CO conversion is achieved even at a temperature of 65 °C and that level is kept constant up to 150 °C. It is interesting to note that CO conversion level comprises 30 % even at 0 °C. For this sample the selectivity decreases with an increase of temperature ($S = 95$ % in the interval 0–35 °C), and it drops down to 32 % (0.2 MPa, 25 000 h^{-1}) during a further rise in the temperature to 150 °C. Addition of water vapour to the gas mixture leads to a decrease of CO conversion degree, which may be related to the fact that water blocks active sites of the catalyst that has the composition of 5 mass % Au/Li_2O/CeO_x/Al_2O_3 by means of poisoning the oxygen vacancies of CeO_x [9].

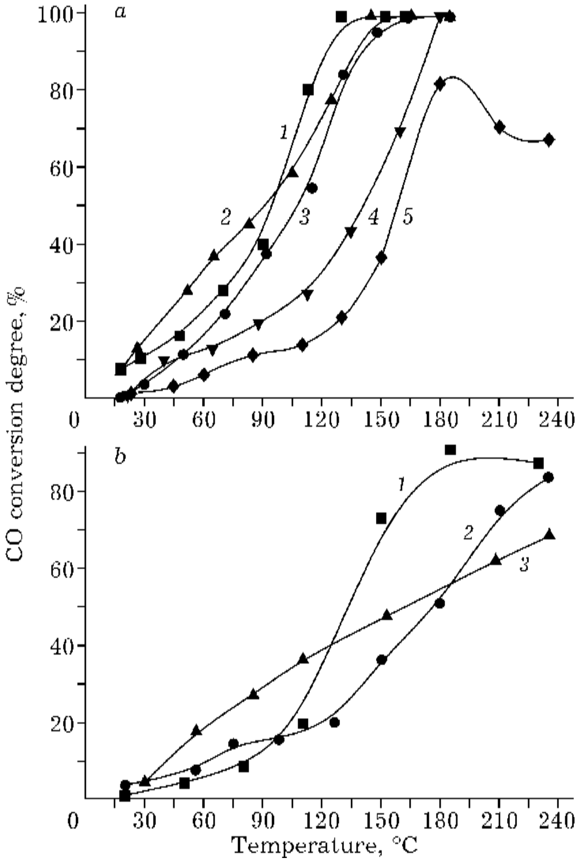

Fig. 2. Temperature dependences of CO conversion in CO oxidation on different catalytic systems ($P = 0.1$ MPa, $W = 10\,900$ h^{-1}): *a* – Cu (*1* – 1 % Cu/CeO_2, *2* – 1 % Cu/$Y_{0.06}Ce_{0.44}Zr_{0.5}O_2$, *3* – 1 % Cu/$Ce_{0.5}Zr_{0.5}O_2$, *4* – 1 % Cu/$Y_{0.1}Ce_{0.1}Zr_{0.8}O_2$, *5* – 1 % Cu/$ZrO_2$); *b* – Co (*1* – 1 % Co/CeO_2, *2* – 1 % Co/$Ce_{0.5}Zr_{0.5}O_2$, *3* – 1 % Co/ZrO_2).

Figure 2 presents the results of the study of Co,Cu/Y–Ce–Zr oxide catalysts in selective CO oxidation in hydrogen rich gas. It is evident that the conversion level is higher on Cu-containing samples as compared to Co-containing catalysts.

The activity of the studied Cu-containing catalysts decreases in a succession: Cu/$Y_{0.06}Ce_{0.44}Zr_{0.5}O_2$ > Cu/CeO_2 > Cu/$Ce_{0.5}Zr_{0.5}O_2$ > Cu/$Y_{0.1}Ce_{0.1}Zr_{0.8}O_2$ > Cu/ZrO_2, which is related to the features of $Y_xCe_yZr_{1-y-z}O_2$ solid solutions. On the one hand, superficial cations of cerium may be involved in the catalytic process. On the other hand, these solutions are typified by an increase in the mobility of oxygen in the crystal structure of the carrier upon the stabilization of ZrO_2 cubic phase by cerium oxide. It is known that in the reducing medium, cerium oxide releases the lattice oxygen at elevated temperatures thus forming non-stoichiometrical oxides CeO_{2-x} $(0 < x < 0.5)$ that are reoxidated in an oxidizing atmosphere to yield CeO_2.

Upon stabilization of ZrO_2 cubic phase by cerium oxide, the quantity of oxygen vacancies in the volumetric phase of the catalyst and the capability of the carrier to activate molecular oxygen of the gas phase increase, which causes CO oxidation rate to increase.

The incorporation of a modifying Y^{3+} cation in the lattice, the ionic radius of which is close to the critical radius of $Ce_xZr_{1-x}O_2$ (1.1015 and 1 Å, respectively), results in an increased defectiveness of the structure and in the stabilization of the low temperature cubic phase of ZrO_2.

Table 3 presents the data acquired with the studied catalytic systems regarding the temperatures of 50 % CO conversion (T_{50}) in relation to oxygen selectivity at this temperature.

Figure 3 presents temperature dependences of selectivity with respect to oxygen for Cu and Co containing systems in the reaction of CO oxidation in a hydrogen-rich gas. Except for the sample of 1 % Cu/ZrO_2, high selectivity (about 95–100 %) in 20–120 °C temperature interval is intrinsic for all Cu-based catalysts, while only the $Co/Ce_{0.5}Zr_{0.5}O_{2-\delta}$ sample among Co containing catalytic systems exhibits the selectivity as great as 95 %.

TABLE 3

Data regarding the temperatures of 50 % CO conversion (T_{50}) and selectivity (S) with respect to oxygen in the CO oxidizing reaction in hydrogen-containing gas

Sample	T_{50}, °C	S, %
1 % Cu/CeO_2	95	94.6
1 % $Cu/Ce_{0.5}Zr_{0.5}O_{2-\delta}$	108	96.4
1 % $Cu/Y_{0.06}Ce_{0.44}Zr_{0.5}O_{2-\delta}$	90	98.5
1 % $Cu/Y_{0.1}Ce_{0.1}Zr_{0.8}O_{2-\delta}$	141	71.1
1 % Cu/ZrO_2	165	37.8
1 % Co/CeO_2	132	24.6
1 % $Co/Ce_{0.5}Zr_{0.5}O_{2-\delta}$	162	41.8
1 % Co/ZrO_2	176	32.1

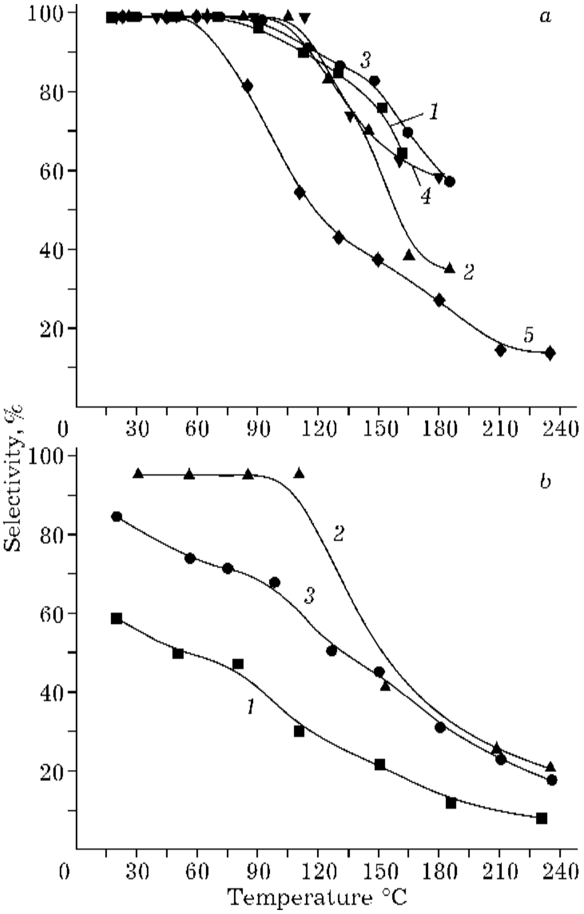

Fig. 3. Temperature dependences of selectivity in the reaction of CO oxidation in an excess of H_2 on different catalytic systems ($P = 0.1$ MPa, $W = 10\,900$ h^{-1}): *a* – Cu (*1* – 1 % Cu/CeO_2, *2* – 1 % $Cu/Y_{0.06}Ce_{0.44}Zr_{0.5}O_2$, *3* – 1 % $Cu/Ce_{0.5}Zr_{0.5}O_2$, *4* – 1 % $Cu/Y_{0.1}Ce_{0.1}Zr_{0.8}O_2$, *5* – 1 % Cu/ZrO_2); *b* – Co (*1* – 1 % Co/CeO_2, *2* – 1 % $Co/Ce_{0.5}Zr_{0.5}O_2$, *3* – 1 % Co/ZrO_2).

The work [10] presents one of the explanations for the high selectivity that has been achieved with Cu-based catalysts. The authors investigated a process of selective CO oxidation in an excess of hydrogen on Au, Pt and Cu (111) single crystals. It has been demonstrated that the energy barrier of activation of the CO oxidizing reaction on Au (111) and Cu (111) is equal to 0.18 and 0.82 eV, respectively is much less than the energy barrier of the hydrogen oxidizing reaction (0.9 and 1.28 eV, respectively. In the case when selective CO oxidation is carried out on Pt (111), a reverse situation was observed: the energy barrier of H_2 oxidation is lower than for the CO oxidation (0.83 and 0.96 eV, respectively); *i.e.* the reaction of H_2 oxidation will be of a higher likelihood for these single crystals.

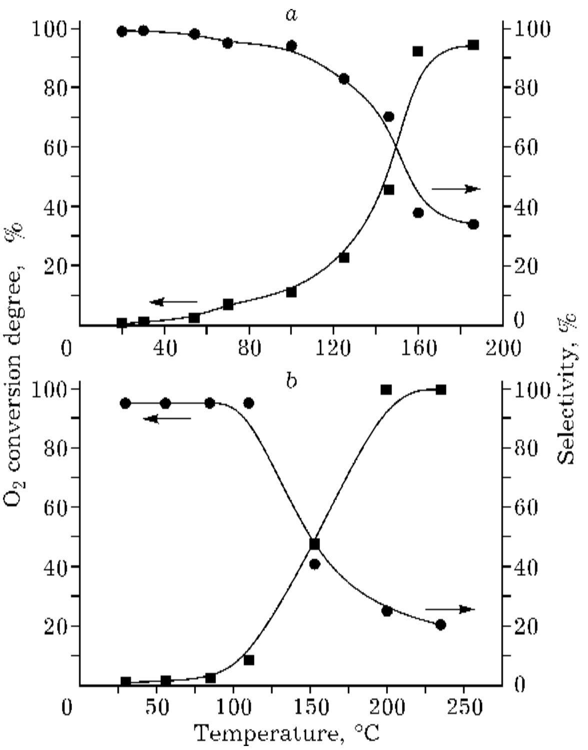

Fig. 4. Temperature dependences of the O_2 conversion and the selectivity in the CO oxidizing reaction on the 1 % $Cu/Y_{0.06}Ce_{0.44}Zr_{0.5}O_2$ (*a*) and 1 % $Co/Ce_{0.5}Zr_{0.5}O_2$ (*b*). $P = 0.1$ MPa, $W = 10\,900$ h^{-1}.

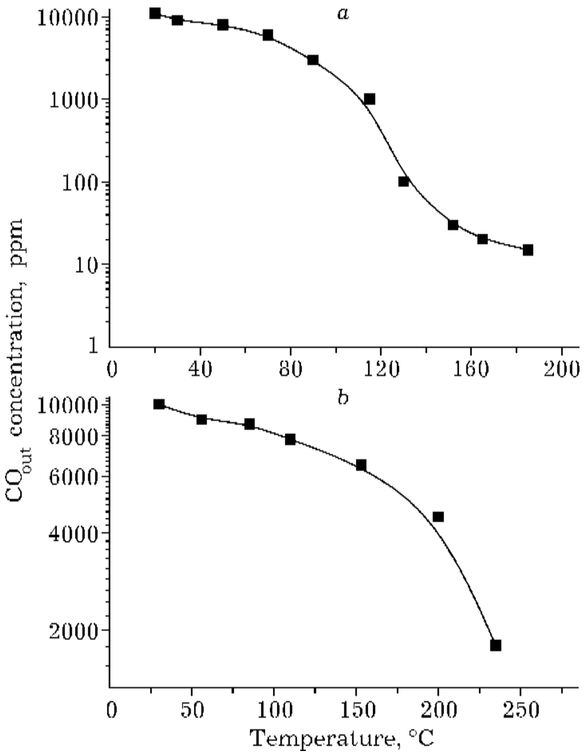

Fig. 5. Temperature dependences of CO concentration at the outlet from a reactor in the CO oxidizing reaction on 1 % $Cu/Y_{0.06}Ce_{0.44}Zr_{0.5}O_2$ (*a*) and 1 % $Co/Ce_{0.5}Zr_{0.5}O_2$ (*b*). $P = 0.1$ MPa, $W = 10\,900$ h^{-1}.

Based on the results of the performed research, we have found that the 1 % $Cu/Y_{0.06}Ce_{0.44}Zr_{0.5}O_2$ and 1 % $Co/Ce_{0.5}Zr_{0.5}O_2$ samples show the greatest activity among the studied Co,Cu/Y–Ce–Zr catalysts. Figure 4 displays temperature dependences of O_2 conversion degree and selectivity that have been achieved with 1 % $Cu/Y_{0.06}Ce_{0.44}Zr_{0.5}O_2$ and 1 % $Co/Ce_{0.5}Zr_{0.5}O_2$ catalytic systems. It is evident that at the temperatures below 100 °C, the O_2 conversion level does not exceed 10 % and the selectivity comprises more than 95 % (see Fig. 4). This implies that a little amount of oxygen is consumed under these conditions in the oxidizing reaction of hydrogen. As the temperature increases, the conversion level of oxygen increases and reaches 80–90 % at 160 °C, and the selectivity drops down to 50 % on the 1 % $Cu/Y_{0.06}Ce_{0.44}Zr_{0.5}O_2$ catalyst, and down to 30 % on 1 % $Co/Ce_{0.5}Zr_{0.5}O_2$. Thus, the basic way

TABLE 4

Data on the CO conversion degree (X_{CO}) and on selectivity (S) with respect to oxygen in the reaction of CO catalytic oxidation in a hydrogen-containing gas

Catalyst	Optimum operating conditions			X_{CO}, %	S, %
	P, MPa	W, h^{-1}	T, °C		
2 % Pt/SiO_2*	0.5	3600	125–140	85–90	56–50
2 % Pt/SiO_2**	0.5	3600	120–140	~90	60–55
5 % $Au/Li_2O/CeO_x/Al_2O_3$	0.2	25 000	40–60	90–100	85–80
1 % $Cu/Y_{0.06}Ce_{0.44}Zr_{0.5}O_{2-\delta}$	0.1	10 900	130–150	90–100	85–70

*Sample has been prepared by the impregnation method.

**Sample has been prepared by the ion exchange method.

of oxygen consumption at $T > 160\,^{\circ}\mathrm{C}$ is its interaction with hydrogen, hence the sharp decrease in the selectivity at these temperatures.

It follows from the data acquired (Fig. 5, *a*) that on the 1 % $\mathrm{Cu/Y_{0.06}Ce_{0.44}Zr_{0.5}O_2}$ catalyst, it is possible to achieve the degree of hydrogen cleansing from CO with a residual content of the latter of about 15 ppm. The residual content of CO on the 1 % $\mathrm{Co/Ce_{0.5}Zr_{0.5}O_2}$ sample comprises more than 1000 ppm in the wanted interval of temperatures (see Fig. 5, *b*).

Table 4 provides the comparison on conversion and selectivity in CO oxidation hydrogen-rich gas for the most active Cu-, Au-, and Pt-containing catalytic systems that have been obtained under their optimum operating conditions [8].

CONCLUSION

Results of the performed research on the reaction of selective CO oxidation in hydrogen-containing gas mixtures with deposited Cu, Cu,Co/Ce oxide catalysts have demonstrated that $\mathrm{Cu/Y_xCe_{1-x}Zr_yO_2}$ samples in 80–150 °C temperature interval are characterized by reliable, active and highly selective properties. The studied catalytic systems are comparable with precious metals based catalysts.

According to the experimental data, during hydrogen purification on synthesised catalysts, CO level can be decreased to 15 ppm, which complies with requirements stated by the PEMFC technology. The solution to the problem of pure hydrogen production can be thought of as one step towards the realization of the complex technological chain for creating ecology-friendly vehicles of new generation.

REFERENCES

1 Yu. N. Frolov, Zashchita okruzhayushchey sredy v avtotransportnom komplekse, Moscow, 1997.
2 R. J. H. Grisel and B. E. Nieuwenhuys, *J. Catal.*, 199 (2001) 48.
3 D. H. Kim, M. S. Slim, *Appl. Catal. A: Gen.*, 224 (2002) 27.
4 Y. Hasegawa, Y. Ueda. K. Kusakabe, S. Morooka, *Ibid.*, 225 (2002) 109.
5 A. S. Ivanova, E. M. Moroz, G. S. Litvak, *Kinetika i Kataliz*, 33 (1992) 1208.
6 C. E. Hori, H. Permana, K. Y. Simon *et al.*, *Appl. Catal. B*, 16 (1998) 105.
7 P. Fornasiero, R. Di Monte, G. Rango Rao *et al.*, *J. Catal.*, 151 (1995) 168.
8 V. F. Tretjakov, T. N. Burdeynaya, L. A. Berezina, *Neftekhimiya*, 44 (2004) 191.
9 E. D. Park, L. S. Sung, *J. Catal.*, 186 (1999) 1.
10 S. Kandoi, A. A. Gokhale, L. C. Grabow *et al.*, *Catal. Lett.*, 93 (2004) 93.