Block Catalysts Synthesized by Burning Method for Exhaust Gases Neutralization

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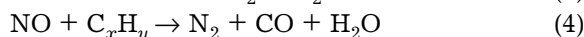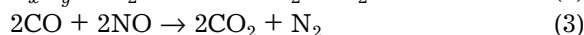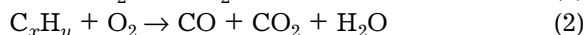
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Abstract

A novel synthetic approach had been worked out for block catalysts of compositions 0.1 % Pd–2.9 % CuO/γ-Al$_2$O$_3$ and 0.1 % Pd–2.9 % CuCo$_2$O$_4$/γ-Al$_2$O$_3$. Their catalytic properties had been investigated in neutralization reactions of toxic components of exhaust gases, *i.e.* CO oxidation, deep oxidation of hydrocarbons and NO$_x$ reduction by propane. It has been demonstrated that, due to higher specific surface area and dispersion of active components synthesized by burning method, the activity of these catalysts is significantly higher as compared to the samples yielded by a standard methods.

INTRODUCTION

The proportion of motor transport in a series of basic contaminants of the atmosphere steadily grows during the last decades. Catalytic technologies play the crucial part in neutralization of the majority of toxic compounds that are inherent to exhaust gases. Existing solutions to a problem of organic compounds catalytical removal from off-gas streams are usually coupled with CO and NO$_x$ neutralization. Catalytic transformation of the components of exhaust gases over a three-routing catalyst may involve the following reactions:

$$2CO + O_2 \rightarrow 2CO_2 \tag{1}$$
$$C_xH_y + O_2 \rightarrow CO + CO_2 + H_2O \tag{2}$$
$$2CO + 2NO \rightarrow 2CO_2 + N_2 \tag{3}$$
$$NO + C_xH_y \rightarrow N_2 + CO + H_2O \tag{4}$$

Effective passing of such a multichannel process in practice is difficult, since one needs an excess of oxygen to completely burn CO and CH, which in turn renders NO$_x$ reduction complicated. With the availability of effective catalysts, complete removal of ecologically dangerous components and poisons can be achieved by monitoring the air/fuel ratio in the region of stoichiometric quantities of oxygen and the components of the exhaust gas. Figure 1 presents the range of these values that corresponds to the fullest transformation of CO, CH and NO$_x$ and that is referred to as a λ-window.

Typical three-routing catalysts that are employed now include precious metals (Pt, Rh and Pd) deposited onto ceramic or metal blocks covered by an Al$_2$O$_3$ layer [1–3]. However, high
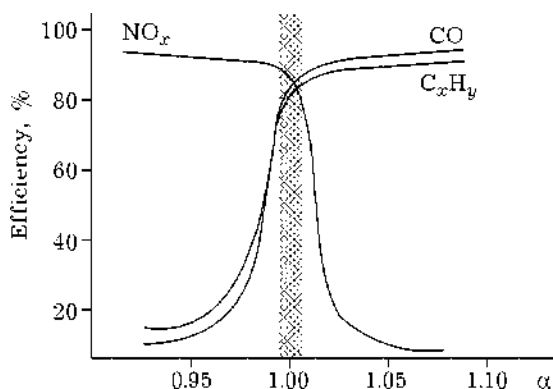

Fig. 1. Dependence of CO, CH and NO$_x$ conversion on air/fuel ratio using three-routing catalyst. α is the air/fuel ratio ($\alpha = 1$ at the air/fuel ratio equal to 14.6).

cost of these catalytic systems and their insufficient heat and poison stability stimulate scientific investigations to be conducted in order to create new catalytic neutralizers synthetic methods that will serve better from both economical and technological points of view.

One of the promising directions in this field is the development of catalysts with oxide components that partially substitute the precious metals [4−6]. Numerous literary data testify that deposited oxide catalysts doping increases catalytic activity and, to a certain extent, their thermal stability [7−14]. A function distribution between particular active superficial sites of catalysts is thought to be one of the reasons for an increase in the catalytic activity. It is a common knowledge that the energy of oxygen binding to the surface of an oxide is of critical influence on their activity in oxidation reactions. Acceleration of a certain process, for example, CO activation on Pd atoms, causes the concentration of electrons in the catalyst to increase, which in turn facilitates acceptor stage of the process − oxygen activation on metal oxides to form oxygen ions. Accordingly, several authors have found [12] that Pd and Pt doped oxides of cobalt and copper show an extraordinary activity in reactions of CO and light hydrocarbon oxidation and in NO_x reduction. In addition, recent investigations have demonstrated that palladium combination with oxides of transition elements shows a much higher stability in relation to sulphur-containing poisons than does Pd/Al_2O_3 [13].

Previously, we have shown [14−16] that superficial synthesis through burning is the promising way to prepare catalysts for neutralization of exhaust gases. The purpose of this work is to examine the physicochemical properties of block catalysts that were synthesized by this method with the following compositions: $0.1\ \% \ Pd−2.9\ \% \ CuO/\gamma\text{-}Al_2O_3$, $0.1\ \% \ Pd−2.9\ \% \ CuCo_2O_4/\gamma\text{-}Al_2O_3$ and examination of their catalytic properties in reactions of CO oxidation, hydrocarbons deep oxidation and NO_x reduction by propane.

EXPERIMENTAL

$Co(CH_3COO)_2$, $Cu(CH_3COO)_2$, $Cu(NO_3)_2$ and $Pd(NO_3)_2$ (Merck, 99.0 %) salts were used as precursors of active components; blocks from $\gamma\text{-}Al_2O_3$ with specific surface area $S = 150\ m^2/g$, as a substrate. The synthesis of catalysts was conducted following an earlier described procedure [15] that includes impregnation of substrate, followed by drying and initiation of exothermic oxidation-reduction reactions between the precursors of active components.

Radiographic investigations of reaction products have been executed with DRON-3 diffractometer with the use of monochromated CuK_α radiation in an interval of $2\theta = 20−60°$. A content of active components (C) was determined by the atomic absorption spectroscopy method. Measurements of surface area of catalysts was conducted using BET method, thermal desorption of argon in Sorpty apparatus (Carlo Erba, Italy).

The activity of the synthesized catalysts was studied in the reactions of carbon moxide oxidation, in reactions of deep oxidation of methane and propane in a flow-through setup with chromatographic analysis of the reaction products (Porapak Q). 1 cm^3 of a block catalyst was used for tests. A model reaction of carbon monoxide oxidation was conducted in a temperature range 20−300 °C with volume flow rate equal to $3 \cdot 10^4\ h^{-1}$ and with the following composition of the gas mixture, vol. %: 1 CO, 0.5 O_2 in nitrogen. Catalytic activity was characterized by the temperature of 100 % CO conversion ($T_{100\ \%}$). Reactions of deep oxidation of methane and propane were conducted in a similar way in an interval of temperatures 200−700 °C at the rate of volume flow of $1 \cdot 10^4\ h^{-1}$ and with the content of hydrocarbons in the initial gas mixture equal to 1 vol. %. Investigations of catalyst activities during selective NO_x reduction by propane were conducted in a setup of a flow-through type with an electrochemical Testo-33 gas analyzer (Germany) in a 70−550 °C temperature range. The composition of the reaction mixture, vol. %: NO 0.2, C_3H_8 0.1, O_2 5.0 in nitrogen; volume flow rate of the gas mixture $W = 11\ 250\ h^{-1}$.

RESULTS AND DISCUSSION

Over the course of 3−10 min, the synthesis through burning yields an active component on

the surface of a porous block substrate, the component being uniformly distributed and firmly bonded to the substrate. According to XRD, CuO (tenorite) with a fairly high dispersity $d_{c.s.a.} \approx 5$ nm represents a single product of the reaction in the first case during the burning of equimolar $Cu(CH_3COO)_2/Cu(NO_3)_2$ oxidation-reduction mixture. Specific surface area of the final catalyst in this case was as high as $S = 148$ m^2/g. A subsequent doping of the copper catalyst by palladium and calcination at 400 ^{o}C for 4 h did not result in a decrease of its specific surface area. When the catalyst of the same composition (0.1 % Pd$-$2.9 % CuO/γ-Al$_2$O$_3$) was prepared by the standard method (impregnation from nitrates of metals and calcination at 400 ^{o}C over the course of 6 h), a certain quantity of Cu_2O in addition to CuO was also found in the products, Cu_2O being less active in oxidation-reduction reactions. Specific surface area (S) of the catalyst in this case comprised 119 m^2/g, $d_{c.s.a.} \approx 20$ nm. It appears that dispersion of the active component occurs on the surface as a result of vigorous fuming in the course of a synthesis by burning, which allows obtaining catalysts with a more developed specific surface.

It is known that efficient catalytic burning is possible also at a low content of precious metals, since favourable synergetic effects of activity and stability [17] can be achieved for complex multicomponent catalysts. Previously, we have demonstrated that a non-additive increase in the catalytic activity as compared to simple oxides [16] is evidenced on the mixed cobalt-copper catalyst with Co : Cu = 2 : 1 ratio. As a consequence of the synthesis by burning, partial formation of $CuCo_2O_{4+\delta}$ spinel with an excess oxygen occurs from $Co(CH_3COO)_2/Cu(NO_3)_2$ oxidation-reduction mixture. Owing to

a change in the metal/oxygen ratio and to an electronic disordering in spinel structures, a great quantity of defects is likely to be formed, which are active sites in oxidation-reduction processes. Specific surface of the catalyst comprised 147 m^2/g in this case, $d_{c.s.a.} \approx 5$ nm.

Table 1 lists the temperatures of 50 and 100 % CO conversion on the catalysts that were synthesized by burning and standard methods.

As can be seen preparation method has a tangible influence on the activity of the copper-bearing catalyst doped by palladium. The temperature of the full CO conversion on the catalyst synthesized by burning method is 23 ^{o}C lower than on the sample that has been produced by the standard procedure, while on the mixed copper-cobalt catalyst, this temperature is achieved even at 98 ^{o}C, which is comparable to the activity of catalysts with palladium content 4$-$6 mass % [18].

Figure 2, a, b shows temperature dependences of deep oxidation of methane and propane on the catalysts that were prepared by various methods.

In reactions of deep oxidation of hydrocarbons, the highest activity is also reached on the catalyst of 0.1 % Pd$-$2.9 % $CuCo_2O_4$/γ-Al$_2$O$_3$ composition, synthesized by burning method. The temperature of 100 % conversion of CH_4 and C_3H_8 on the given catalyst was equal to 415 and 323 ^{o}C, respectively.

Figure 2, c displays the temperature dependences of NO conversion in N_2 on the catalysts that were prepared by various methods.

During selective catalytic reduction of NO_x by propane, the temperature of 50 % NO conversion on the catalyst 0.1 % Pd$-$2.9 % CuO/γ-Al$_2$O$_3$ synthesized by the burning method is 42 ^{o}C lower than on the sample that has been produced by the standard procedure. The palladium-doped cobalt-copper catalyst turned out to be the most

TABLE 1

Temperatures of 50 ($T_{50\,\%}$) and 100 % ($T_{100\,\%}$) CO conversion on the catalysts that were prepared by various methods, ^{o}C

Catalyst	Preparation method	$T_{50\,\%}$	$T_{100\,\%}$
0.1 % Pd$-$2.9 % CuO/γ-Al$_2$O$_3$	Synthesis by burning	85	112
0.1 % Pd$-$2.9 % CuO/γ-Al$_2$O$_3$	Standard*	96	135
0.1 % Pd$-$2.9 % CuCo$_2$O$_4$/γ-Al$_2$O$_3$	Synthesis by burning	72	98

*Calcination at 400 ^{o}C during 6 h.
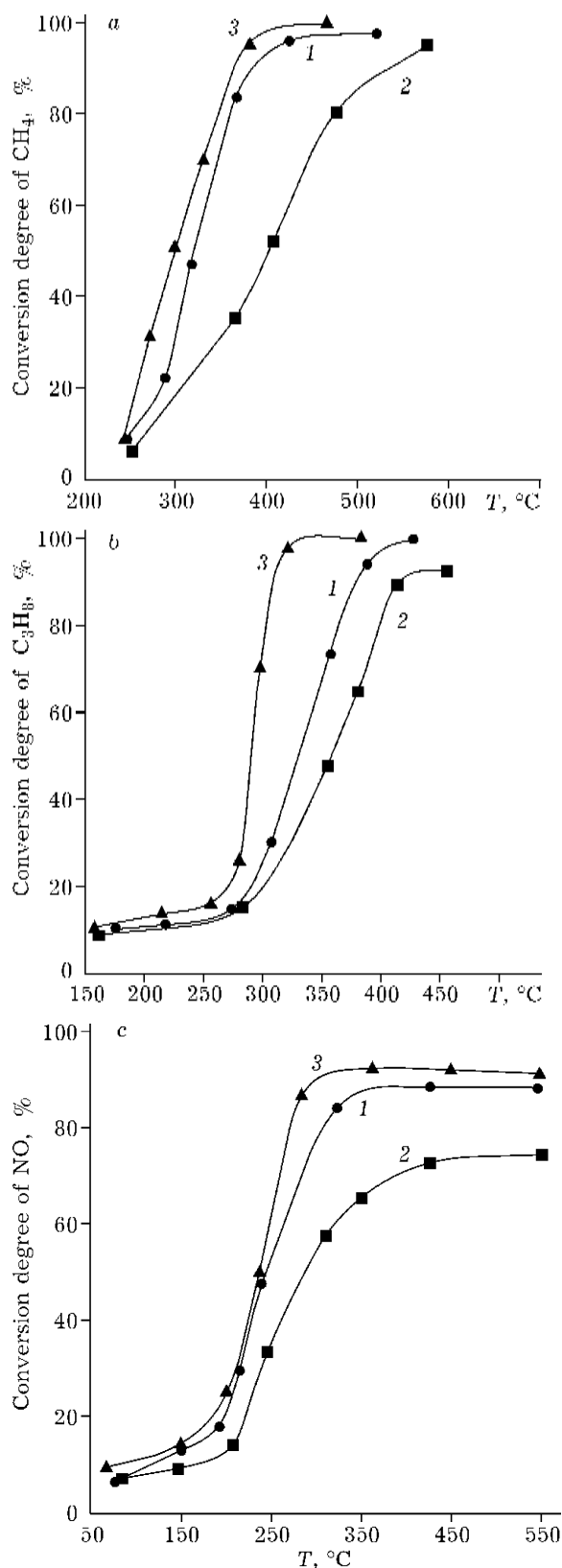
active in this reaction: 93 % conversion of NO was achieved on this catalyst at 306 °C.

CONCLUSION

Thus, owing to a higher specific surface area and dispersion of the synthesized active components, the activity of the catalysts, prepared by the method of superficial synthesis through burning, in the processes of toxic components removal from exhaust gases, is significantly higher as compared to the samples that were prepared by standard techniques. Harmlessness, low energy expenses and hardware simplicity of the process make it a promising candidate to implementation in block catalysts manufacturing for vehicles exhaust gases neutralization.

Acknowledgement

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Fig. 2. Temperature dependences of CH$_4$ (*a*), C$_3$H$_8$ (*b*) and NO in N$_2$ (*c*) conversion on the catalysts synthesized by burning and standard methods: *1* – Pd–CuO/Al$_2$O$_3$, *2* – Pd–CuO/Al$_2$O$_3$ standard, *3* – Pd–CuCo$_2$O$_4$/Al$_2$O$_3$.