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DESIGN OF (Pd), Co, Ce, Zr - METAL-OXIDE CATALYSTS FOR NITROGEN (I), (II) OXIDES REDUCTION BY CARBON MONOXIDE

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Introduction

One of the most important challenges for scientific and applied researches is reduction of nitrogen oxides in gas emissions mobile and stationary sources, as evidenced by the introduction of morestrict norms for emissions into the environment (EURO-VI) [1]. One of the most efficient methods for neutralization of nitrogen(I, II) oxides in exhaust gases is catalytic reduction with various reducing agents (CO and C_nH_m). The decrease of inhibiting effect of SO_2, O_2 and H_2O to be the critical factor in the design of catalysts of elimination of nitrogen oxides from "tail" gases. Now the main attention is focused on structured catalysts in the form of monolithic blocks, in particular, because of the wide selection of options for constructive solutions, low gas-dynamic resistance, easy placement in reactor [2].

Platinum group metals (PGM) (Pt, Pd, Rh) in the composition of TWC catalysts (CO/NO/C_nH_m) are active for the reactions of CO + NO (N_2O). One the way for reducing of the PGM content is their partial replacement by other substances such as transition metal oxides with high mobility of surface oxygen [3, 4]. Rare earth oxide (REO) doping may increase the activity of transition metal oxide catalysts. It is known that the catalytic systems containing cobalt oxide (Co_3O_4) with REO (CeO_2, La_2O_3), which demonstrate high activity in oxidation of CO, hydrocarbons and in reduction of NO, may be used for purification of automobile exhaust gases [5-7]. The high catalytic activity of Co_3O_4 and CeO_2 mixtures is attributed to the formation of Co-O-Ce surface clusters during preparation [5, 8].

This paper presents the results of study of the effect of composition of palladium-cobalt-cerium-oxide catalysts supported on zirconia as well as over structured honeycomb monoliths Pd/(Co_3O_4+CeO_2+(ZrO_2))/cordierite on their activity in the reduction of nitrogen(I),(II) oxides with carbon monoxide. Structure-sized characteristics (phase composition, dispersion) and redox properties of the composites Pd/CeO_2-Co_3O_4/cordierite (with different preparation methods) and their effect on the catalytic properties of metal-oxide catalysts were also studied.

1 Experimental

Monolithic ceramic blocks of synthetic cordierite ($2Al_2O_3 \cdot 2MgO \cdot 5SiO_2$) with a honeycomb structure and zirconia were used as a catalyst support. The formation of catalytic coating catalysts was carried by impregnation (in the case of cordierite – on

moisture capacity) from aqueous solution of $(NH_4)_2Ce(NO_3)_6$, $Co(NO_3)_2 \cdot 6H_2O$, $Pd(NO_3)_2$ followed by drying in air at 110^0C and calcining at 600 °C. The multicomponent catalysts were prepared by the deposition of the active components in the following order: (1) cerium oxide, cobalt oxide (successive deposition, SD), palladium; (2) cerium oxide with cobalt oxide (co-deposition, CD), palladium. The following catalyst samples formed on cordierite and zirconia were prepared: $0.1\%Pd/5\%Co_3O_4$, $0.1\%Pd/2\%Co_3O_4+3.5\%CeO_2(CD)$, $0.1\%Pd/2\%Co_3O_4/3.5\%CeO_2(SD)$, $0.1\%Pd/2\%Co_3O_4 + 2.7\%CeO_2 + 0.8\%ZrO_2(CD)$. Bulk samples with the same ratios and the same order of component deposition as for the supported catalysts were prepared to evaluate structural, dimensional characteristics and morphology of the catalyst surface by X-ray diffraction and transmission electron microscopy.

The catalytic activity of the samples was characterized by the conversion of N_2O and NO to nitrogen which was determined in a continuous-flow system with a gradientless quartz reactor under atmospheric pressure in the temperature range 150 – 400 °C. The following reaction mixtures were used (vol. %): N_2O – 0.2; NO – 0.2; CO – 0.2 and 0.8; the rest – helium. Gas hour space velocity was 6.000 h^{-1}. The sample (fraction 1–3 mm) was roasted prior to testing at 550 °C for 1h. The components and reaction products were analyzed by gas chromatography with conductometer detector and CaA column (for N_2, NO, CO, O_2), Polisorb-1 column (for N_2O, CO_2).

The morphology of the sample surface was studied using transmission electron microscope (TEM). The specific surface (S_{sp}, m^2/g) was determined chromatographically by thermal argon desorption on a GKh-1 instrument.

2 Results and discussion

The activity of the (Pd), Co-, Ce-, Zr-oxides catalysts, also over the monoliths with honeycomb structure, in reactions of nitrogen(I), (II) oxides reduction with carbon monoxide is presented in the Table. Introduction of palladium (0.1 %) into 5 % Co_3O_4/ZrO_2 catalyst leads to an increase in its activity. High conversions of NO and CO (90 %) are achieved at lower temperatures (at ~160 °C) in the presence of cerium-containing sample $Pd/Co_3O_4 + CeO_2/ZrO_2$; 85 % conversion of nitrogen(I) oxide is achieved at 300 °C. The difference in temperatures of high conversion of nitrogen oxides under conditions of their combined reduction with carbon monoxide may be due to the competition of N_2O and NO molecules for an active site of the catalyst as was observed in the combined reduction of N_2O + NO with C_3–C_4 alkanes [9]. The activity of palladium-doped catalysts formed on the surface of cordierite in reduction of N_2O + NO with CO is changed in following order: $Co_3O_4 - CeO_2 > Co_3O_4 - CeO_2 - ZrO_2 > Co_3O_4$.

Decrease in NO and N_2O conversion on the structured catalysts in comparison with granulated, probablly, is related to some decrease in specific and consequently also an active surface of the samples.

Modification of the palladium-cobalt-oxide structured catalyst by cerium oxide enhances its activity in CO + NO reaction. A more significant increase in

catalytic activity is achieved by co-deposition of cobalt oxide and cerium oxide, in comparison with successive deposition of the components (Table).

Table. Catalytic activity of (Pd), Co-, Ce-, Zr-oxides catalysts in reactions of nitrogen(I) (II) oxides reduction by carbon monoxide (GHSV = 6,000 h^{-1})

Catalyst (method of preparation)	S_{sp}, m^2/g	N_2O[NO] conversion,%/T^oC ($T_{50\%}$) for reaction mixtures:	
		0.2%N_2O+0.2%NO+ +0.8%CO	0.2%CO+ +0.2%NO
5%Co_3O_4/ZrO_2	6.7	83/400 (270) [82/250]	-
0.1%Pd/5%Co_3O_4/ZrO_2	5.7	85/350 (200) [99/200]	-
0.1%Pd/2%Co_3O_4+3.5%CeO_2 /ZrO_2 (CD)	5.8	85/300 (190) [99/160]	-
0.1%Pd/5%Co_3O_4/cordierite	1.5	78/350 (275) [99/300]	99/250 (230)
0.1%Pd/2%Co_3O_4+ 3.5%CeO_2/cordierite (CD)	2.7	78/300 (180) [99/200]	99/155 (123)
0.1%Pd/2%Co_3O_4/ 3.5%CeO_2/cordierite (SD)	2.2	-	99/200 (169)
0.1%Pd/2%Co_3O_4+2.7%CeO_2 +0.8%ZrO_2/cordierite(CD)	3.5	75/325 (240) [99/260]	99/190 (130)

It is known that doping of cobalt oxide spinel structure with a small amount of cerium oxide (Ce/Co = 0.05) increases the surface Co_3O_4 and assists the reduction Co^{3+} to Co^{2+}, thus facilitating the desorption of surface oxygen – the limiting stage of nitrous oxide decomposition on the catalysts of this type [10]. Cobalt is stabilized on the separation boundary between Co_3O_4 and CeO_2 in an oxidation state higher than stoichiometric, there is an increase in the Co–O bond length at the sites of contact of the cobalt and cerium nanoparticles and the surface oxygen on the interface between of the oxide phases becomes more mobile than the bulk oxygen of the individual oxides [5].

The results of a SEM study indicated a rather homogeneous distribution of the Pd/Co_3O_4 and $Pd/(Co_3O_4$+$CeO_2)$ compositions on the cordierite surface. Formation of ring-like structures of the active components is observed for 0.1%$Pd/(Co_3O_4$+$CeO_2)$/cordierite. This may be taken as an argument to support the hypothesis that the components form a homogeneous structure containing a mixture of pure phases. These results are in accord with the XPA results and literature data [6, 7].

The values of the specific surface of the catalyst samples deposited on a structurized cordierite support and bulk samples indicate high dispersion of the active phase in the case of co-deposition of Co_3O_4 and CeO_2 (ZrO_2) components (Table).

The mechanism for the reduction of NO with carbon monoxide over platinum group metals, in particular over palladium, involves a step featuring the dissociative adsorption of nitric oxide (II) [11]. Bol'shakov et al. [3] have shown that palladium in the Pd-Co/γ-Al_2O_3 catalyst provides for spillover of the oxygen formed onto cobalt oxide where it reacts with carbon monoxide. As a consequence, oxygen passivation of the Pd-Co/γ-Al_2O_3 catalyst is overcome and high activity in

the reduction of nitrogen oxides is achieved. Whereas modification of the palladium–cobalt oxide catalyst with cerium oxide increases activity in the reaction $NO + CO$, we may also assume that the addition of CeO_2 to the $Pd–Co_3O_4$ catalyst facilitates spillover of oxygen onto the cobalt oxide surface due to an increase in the number of oxygen vacancies on the separation boundary of the Co_3O_4 and CeO_2 phases and a reduction in the bonding energy of the bond of oxygen to the surface.

The activity relative to NO for the mechanical mixtures depends on the amount of cobalt component in the catalyst. A doubling of the cobalt component in the catalysts with zeolite support leads to an increase in the NO conversion by a factor of 2.5 (37% at 455 °C). A tripling of the cobalt component in the catalyst with $(CoO/ZrO_2 + Fe_2O_3/H-ZSM-5)$ leads to an increase in the NO conversion from 24% to 31% at 350 °C. High yields (50-90%) conversions of N_2O at 370-500 °C are achieved on all catalysts tested (mechanical mixtures of different composition). Platinum group metals are characterized by low metal-oxygen binding energy [4], so, oxygen is rapidly desorbed from the surface of such metals as a result of the reaction that occurs at lower temperatures.

3. Conclusions

Modification of the palladium–cobalt oxide catalysts with cerium oxide enhances its activity in reaction of nitrogen(I), (II) oxides reduction with carbon monoxide and caused by increasing the mobility of surface oxygen of catalyst. The most significant increase in activity for the catalyst prepared by co-deposition of ceria and cobalt oxide takes place due to the more disperse components in the catalytic composition according to the results of XRD, TEM and SEM.

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