Influence of composition (Pd) In-, Co-containing aluminia- and zirconia-based catalysts on simultaneous reduction of nitrogen(I, II) oxides by CO

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It is shown that binary In-, Co-oxide supported catalysts show high activity in the reactions of simultaneous reduction of nitrogen(I, II) oxides by CO, which depends on the nature support (Al_2O_3, ZrO_2), a sequence of the active components introduction. Structured Pd-containing In-, Co-oxide catalysts are characterized by high activity, moisture and sulfur resistance, low content of Pd (0.1) and can be used for complex purification of waste gases from nitrogen oxides and CO.

Keywords – DeNOx, In-Co-oxide catalysts, Al_2O_3, ZrO_2, CO, Pd, moisture resistance

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). 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.

Results

This paper presents the results of study of the effect of composition of In-, Co-oxide catalysts of zirconium and aluminia base as well as doped Pd (0.1%), also formed on carriers with honeycomb monoliths (Pd) In_2O_3 / Co_3O_4 / Al_2O_3 (ZrO_2) / kaolino-aerosil (KA) on their activity in the process of simultaneous reduction of N_2O and NO with carbon monoxide. The influence of oxygen, water vapor and SO_2 in the reaction mixture on the activity of catalysts were also studied.

It was shown that catalytic properties of composites with binary active phase differ significantly from the individual In-, Co-oxides deposited on Al_2O_3 and ZrO_2. Binary catalysts exhibit higher activity in the investigated process, which depends on the sequence of active components introduction (cobalt and indium oxides), the nature of the catalyst carrier, acidic properties of the surface. The high catalytic activity of In-Co / Al_2O_3 takes place may be the positive effect of In_2O_3 on the stabilization of cobalt in the state of Co(II) in the composition of highly dispersed cobalt oxide clusters [1]. This catalyst also characterized by greater moisture resistance: 90-98% conversion of reagents is achieved at temperatures of 450–500 °C in reaction mixtures with H_2O (fig. 1, tabl. 1).

In reaction mixtures containing excessive amounts of oxidizing agents /N_2O + NO + CO_2 + H_2O + O_2/, along with 99% conversion of NO and CO, low conversion of N_2O (17-45% at 570 ° C) can be explained with the competition of oxidant molecules N_2O, NO, and O_2 (H_2O) for the active sites of the catalyst. Clusters of cobalt(II) oxide in the Co-In / Al_2O_3 and isolated Co^{2+} ions in In-, Co- HZSM-5 (FER) zeolite catalysts [2] are the active sites for NO oxidation by molecular oxygen to NO_2 – the most reactive oxidant with respect to CO in the series: NO_2> O_2> NO. This may explain the high activity of 5% In_2O_3 / 5% Co_3O_4 / Al_2O_3 catalyst with respect to NO: at 310 ° C, 100% conversion of nitrogen monoxide and CO is achieved (tabl. 1).

The introduction of 0.1 mass % palladium into In-, Co-, Zr oxide composites significantly enhances their activity in the reduction of N_2O and NO by carbon monoxide.

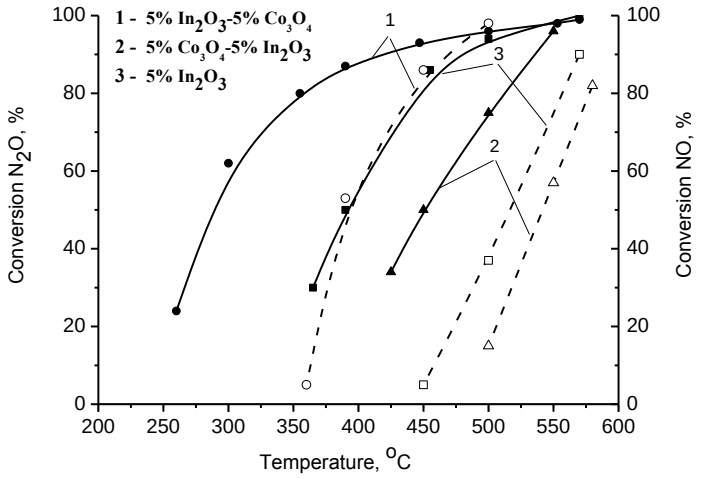

Fig.1. Temperature dependences of N_2O (solid lines) and NO (dashed lines) conversion on the catalysts In_2O_3,Co_3O_4/Al_2O_3 for reaction mixtures: 0.5% N_2O + 0.2% NO + 1.5% CO in He.

Table 1

Simultaneous reduction of nitrogen(I, II) oxides by CO in the presence of oxidizing agents (H_2O, O_2) / 0.5% N_2O + 0.2% NO +1.5% CO + 2% H_2O (5% O_2) in He; W = 6000 h^{-1}/

Catalysts (Specific surface area, m^2/g)	Conversion of N_2O[NO],%/T, °C for reaction mixtures:		
	N_2O+NO+CO	N_2O+NO+CO +H_2O	N_2O+NO+CO +H_2O+O_2
5% In_2O_3/Al_2O_3 (80)	90/480 [83/570]	93/560 [61/580]	17/570 [99/450]
5% In_2O_3/ZrO_2 (67)	55/550 [52/550]	55/550 [52/550]	-
5% In_2O_3/5% Co_3O_4/Al_2O_3 (74)	90/450 [98/500]	90/500 [91/500]	23/570 [99/310]
2.5% In_2O_3/10% Co_3O_4/ 80% ZrO_2+20% Al_2O_3 (140)	90/580 [90/570]	90/570 [90/570]	45/580 [99/380]
0.1%Pd/5%In_2O_3/7%Co_xO_y/9%ZrO_2/KA	90/450 [99/450]	90/450 [99/450]	86/500[90/500][1]

[1]/ for reaction mixtures: 0.5% N_2O + 0.2% NO+1.5% CO + 2% H_2O + 0.01% SO_2.

Conclusion

Developed granular and structured catalysts of 0.1% Pd / 2.5-5% In_2O_3 / 5% Co_3O_4 / ZrO_2 / (KA) showed high activity in the reaction of N_2O + NO + CO (90-99% conversion of N_2O and NO is achieved by temperature 450 °C), tolerance to the influence of moisture and sulfur compounds.

References

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