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 (Al2O3, ZrO2), 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, Al2O3, ZrO2, 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 C3H8). The decrease of inhibiting effect of SO2, O2 and H2O 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) In2O3 / Co3O4 / Al2O3 (ZrO2) / kaolino-aerosil (KA) on their activity in the process of simultaneous reduction of N2O and NO with carbon monoxide. The influence of oxygen, water vapor and SO2 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 Al2O3 and ZrO2. 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 / Al2O3 takes place may be the positive effect of In2O3 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 H2O (fig. 1, tabl. 1).

In reaction mixtures containing excessive amounts of oxidizing agents /N2O + NO + CO2 + H2O + O2/, along with 99% conversion of NO and CO, low conversion of N2O (17-45% at 570 °C) can be explained with the competition of oxidant molecules N2O, NO, and O2 (H2O) for the active sites of the catalyst. Clusters of cobalt(II) oxide in the Co-In / Al2O3 and isolated Co2+ ions in In-, Co- HZSM-5 (FER) zeolite catalysts [2] are the active sites for NO oxidation by molecular oxygen to NO2 – the most reactive oxidant with respect to CO in the series: NO2 > O2 > NO. This may explain the high activity of 5% In2O3 / 5% Co3O4 / Al2O3 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 N2O and NO by carbon monoxide.
Fig. 1. Temperature dependences of N₂O (solid lines) and NO (dashed lines) conversion on the catalysts In₂O₃,Co₃O₄/Al₂O₃ for reaction mixtures: 0.5% N₂O + 0.2% NO + 1.5% CO in He.

Table 1

| Catalysts (Specific surface area, m²/g) | Conversion of N₂O[NO],%/T, °C for reaction mixtures: |
|----------------------------------------|--------------------------------------------------|
|                                        | N₂O+NO+CO | N₂O+NO+CO+H₂O | N₂O+NO+CO+H₂O+O₂ |
| 5% In₂O₃/Al₂O₃ (80)                    | 90/480 [83/570] | 93/560 [61/580] | 17/570 [99/450] |
| 5% In₂O₃/ZrO₂ (67)                    | 55/550 [52/550] | 55/550 [52/550] | - |
| 5% In₂O₃/5% Co₃O₄/Al₂O₃ (74)           | 90/450 [98/500] | 90/500 [91/500] | 23/570 [99/310] |
| 2.5% In₂O₃/10% Co₃O₄/80% ZrO₂/20% Al₂O₃ (140) | 90/580 [90/570] | 90/570 [90/570] | 45/580 [99/380] |
| 0.1% Pd/5% In₂O₃/7% Co₃O₄/9% ZrO₂/KA   | 90/450 [99/450] | 90/450 [99/450] | 86/500 [90/500] |

¹ for reaction mixtures: 0.5% N₂O + 0.2% NO + 1.5% CO + 2% H₂O + 0.01% SO₂.

Conclusion

Developed granular and structured catalysts of 0.1% Pd / 2.5-5% In₂O₃ / 5% Co₃O₄ / ZrO₂ / (KA) showed high activity in the reaction of N₂O + NO + CO (90-99% conversion of N₂O and NO is achieved by temperature 450 °C), tolerance to the influence of moisture and sulfur compounds.

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