Application of the Catalysts Containing Ni, Cu, Zn, Mn Based on Alumocalcium Cement for Purification of the Exhaust of Internal Combustion Engines

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Abstract

The application of Ni, Cu, Zn, Mn-containing catalysts based on alumocalcium cement in catalyst converters of exhaust for motor transport is considered. The possibility of promoting the studied systems both by depositing a small amount of palladium and by charging palladium-free catalysts together with those containing a small amount of it.

INTRODUCTION

One of the most important directions of the global programme aimed at the improvement of the ecological status of the environment is purification of exhaust gas of automobile internal combustion engines (ICE) with the help of catalyst converters. The catalysts used for this purpose can be conventionally divided into three kinds, based on: 1) precious metals; 2) transition metals and their oxides; 3) transition metals and their oxides promoted by a small amount of a precious metal.

Due to the high degree of transformation of the toxic components of the gas to be purified, catalysts based on precious metals are widespread all over the world; more than 40 t of platinum alone is consumed for their production. The main disadvantage of these catalyst converters is high cost of the converter as a whole.

To investigate the possibility of using cheaper contacts in catalyst converters, we chose cement-containing catalysts with copper, nickel, zinc and manganese oxides added. The choice of these systems was based on a number of considerations, such as elimination or minimization of the use of precious metals; high activity in deep oxidation processes used in chemical industry; high strength and thermal stability due to the use of alumocalcium cement, which is especially important for the contacts operating in catalyst converters; wide use in different branches of chemical industry, and a good industrial basis for the commercial production of cement-containing catalysts [1–4].

EXPERIMENTAL

The catalysts were prepared by means of chemical mixing and by means of heterogeneous ion exchange. Deep interaction of the components (nickel and copper hydroxocarbonates with the high-alumina cement of Talyum grade) at the stage of preparation allows one to provide stabilization of the dispersed state of the active component

TABLE 1

Characteristics of NKO-2-3 catalysts

Characteristics	Grade 1, cylindrical dark-gray tablets	Grade 3		
		cylindrical dark-gray tablets	cylindrical dark-gray rings	cylindrical dark-gray granules
Size, mm:				
outer diameter	6.0	6.0	15.0	5.0 ± 1.0
inner diameter	–	–	7.0	–
height	4.5	4.5	10.0	–
length, not less than	–	–	–	5.0 ± 1.0
Packed density, kg/dm^3	1.2 ± 0.1	1.3 ± 0.1	1.0 ± 0.1	0.8 ± 0.2
Mechanical strength:				
collapsing force for crush at the butt-end, MPa	35.0 ± 5.0	35.0 ± 5.0	40.0 ± 5.0	–
cleavage strength, kg/mm of the granule diameter, not less than:	–	–	–	0.8
Concentration, mass %, calculated for:				
NiO	27.0 ± 4.0	27.0 ± 4.0	27.0 ± 4.0	27.0 ± 4.0
CuO	10.0 ± 2.0	10.0 ± 2.0	9.0 ± 3.5	10.0 ± 2.0
CaO	15.0 ± 3.0	15.0 ± 3.0	12.0 ± 3.0	15.0 ± 3.0
Al_2O_3	46.0 ± 4.0	46.0 ± 4.0	53.0 ± 5.0	46.0 ± 4.0
Thermal stability, °C		750		

during performance. Performance attributes of NKO-2-3 catalysts are listed in Table 1.

Manganese is introduced into the catalyst of NKO-2-4 grade.

RESULTS AND DISCUSSION

Increased reactivity of the components in the system based on $CaO-Al_2O_3$ cement in comparison with the catalysts based on Al_2O_3 is one of the reasons of spinel formation braking even at high temperature; this means that the active component is conserved. The active phase is both in the free and bound state during formation; so, a part of the active component is immediately reduced in cement-based catalysts while another part gets reduced gradually during performance, which ensures high thermal stability and long run of the catalysts. The introduction of manganese-containing components improves activity, stability and thermal stability of the catalysts. An increase in activity is due to the fact that manganese oxides simplify oxygen transport to the active centres. Stability and thermal stability increase due to the formation of compounds of manganese with the catalyst components, which hinders reduction of copper and nickel oxides and, as a consequence, their agglomeration. On the basis of the results of investigation of the effect of preparation conditions on texture, strength and catalytic properties of the samples, we proposed the optimal parameters of catalyst preparation by means of chemical mixing and hydrothermal synthesis. The catalysts were tested at the test benches of the Ministry of Motor Transport of Armenia and at the installations of the Research Institute of Chemistry of the Saratov State University.

Bench tests in the installations of Institute of Motors (Moscow) were carried out with a one-cylinder diesel engine Ch 15/16; the exhaust gases were analyzed before and after the converter for CO_2, hydrocarbon, NO and

NO_x content [2]. For comparison, the samples of APK-2 catalyst (palladium on aluminium oxide with palladium content 1.8–2.0 %) were tested. With these samples, high efficiency was achieved: the COP conversion degree was 60–80 %, NO_x 20–40 %. The nickel-alumocalcium catalyst of NKO-2-3 grade without palladium turned out to be not so efficient. At the same time, thermomechanical strength of the catalyst was satisfactory, in spite of the rather high temperature of exhaust gas (up to 800 °C). After promoting the surface of the NKO-2-3 catalyst with a small amount of palladium (0.026 %), the activity reached the level typical for the APK-2. It is interesting that the high efficiency of converter performance is conserved after a substantial part of APK-2 (up to 75 %) is replaced with NKO-2-3.

Moreover, after operation of the diesel engine for 3–5 h with the combined charge of NKO-2-3 and APK-2, the activity of the former catalyst increases to such a high level that further on, during the tests without APK-2, the efficiency of the converter reaches the same value as that characteristic of APK-2. A possible reason may be the formation of volatile surface compounds of palladium in the reaction medium and their transport onto the surface of NPK-2-3, which causes promotion of the latter. A similar effect was observed for the joint performance of NKO-2-3 not only with APK-2 but also with NMO-2-3 catalyst promoted with palladium (0.028 % Pd).

CONCLUSION

The results obtained in the investigation provide evidence that the high-strength and thermally stable catalytic system like NKO-2-3 is promising for use in catalyst converters, especially since a good industrial basis is available. To achieve high efficiency, it is necessary either to promote the surface with small (at a level of several hundredths of a per cent) amounts of palladium or charge a palladium-free catalyst together with a palladium-containing one.

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