Glass-Fibre Catalysts to Clear Diesel Engine Exhausts

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Abstract

Results of laboratory and pilot studies of glass-fibre catalysts for the processes to clear off-gases of diesel engines from emissions of noxious substances have been presented. It has been demonstrated that these catalysts provide a high oxidation degree for CO and hydrocarbons as well as reduction of nitrogen oxides in the off-gases of real diesel engines.

INTRODUCTION

Clearing of automobile exhausts is one of the most important ecological problems both in Russia and all over the world, since they contain toxic impurities such as carbon monooxide (CO), hydrocarbons (CH) contain, soot particles, and nitrogen oxides (NO_x). It should be remarked that the problem to neutralize off-gases from nitrogen oxides and soot particles is seen to be the most urgent in connection with toughening the standards on automobile emissions [1].

Automobile exhausts are traditionally neutralized with the use of catalytic neutralizers that constitute ceramic blocks, onto which precious metals are applied. These catalysts are quite effective in oxidation of CO and CH; however, they do not provide a sufficiently high clearing degree from nitrogen oxides. The basic problems in this field are related to a low activity for removing NO_x with an excess of oxygen and water, as well as to a danger that the secondary contaminant, nitrogen oxide (I), is formed.

The present work deals with the development of a new generation of catalysts (so-called glass-fibre catalysts, or GFC) that represent precious metals that are applied in small quantities (of 0.01–0.1 mass %) onto glass-fibre carriers. As shown in [2, 3], the applied metals (platinum) under certain conditions can be implanted into the bulk of glass fibres to a depth of 100 Å and can be stabilised in an ultrafine (cluster) state, which is responsible for a higher catalytic activity as compared to traditional systems in a number of oxidizing processes [4]. In addition, their original geometrical form (Fig. 1), high mechanical strength, and flexibility in the organization of the structured layers of any form make it possible to perform radically new variants of catalytic processes.

A pilot production of GFC has been created and put into operation in the Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences (Novosibirsk).

LABORATORY INVESTIGATIONS

The efficiency of GFC operation in typical conditions for decontamination of diesel engine exhausts were studied on a laboratory setup with the use of a model gas mixture. According to the data of the tests (Fig. 2), GFC provide a high (more than 69 %) degree of NO_x conversion into molecular nitrogen in the reaction of the reduction of nitrogen oxides by propane with an excess of oxygen (see Fig. 2, curve *1*). As compared to traditional catalysts [5], effective reduction of nitrogen oxides on GFC occurs in a much wider temperature range

Fig. 1. Visual appearance of catalytic fibre glasses.

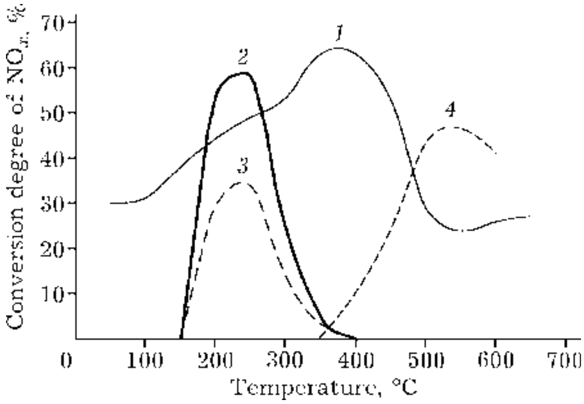

Fig. 2. Dependence of the reduction degree for nitrogen oxides by propane on GFC from the temperature (the volume rate of gas flow is 25 000 h^{-1}; the composition of the initial gas: O_2 10 %, NO 250 ppm, C_3H_8 250 ppm, SO_2 50 ppm, the rest is Ar): *1* – GFC (0.05 % Pt on fibre glass), *2* – the traditional platinum catalyst, *3* – the formation of N_2O on the traditional platinum catalyst, *4* – copper-zeolite Cu/ZSM-5 catalyst (curve *2–4*, the data of [5]).

and without the formation of N_2O (see Fig. 2, curve *3*), which is typical for traditional platinum neutralizers.

It has been also found that in view of specificity for the localization of the active component, GFC are extremely resistant to the influence of SO_2 that is a strong catalytic poison for the majority of the known automobile catalysts.

PILOT INVESTIGATIONS

The pilot tests of GFC in clearing the exhausts of the real diesel engine have been performed. With this end in view, a catalytic converter on the basis of GFC was mounted on a Toyota Crown car (produced in 1993) with a 2C-2500873 diesel engine instead of the resonator, the other muffler parts remained invariant. The converter consisted in two cylindrical "rolls" from that were arranged in succession and made from catalytically active glass fibre and from a corrugated metal belt. The outer diameter of each "roll" was 120 mm, the length of the fibre glass belt was 10 500 mm, the belt width was 90 mm, the total mass of the glass fibre was 215 g, the fabric thickness was 1 mm, the weaving density was 166 cells/cm^2, and platinum content in the fibre glass was 0.01 mass %. The height of a cell of the waved band comprised 1 mm in the first "roll", and 1.5 mm, in the second. The total volume of the converter was 2 l.

To analyse the composition of exhaust gases, two apertures for sampling have been made in the exhaust pipe. Samples were analysed by means of ECOM AC gas analyzer (manufactured in Beta Ltd.), the concentrations of O_2, CO, NO, NO_2, SO_2, and hydrocarbons were determined. The gas temperature at the inlet and outlet of the converter was measured by thermocouples.

The program of the tests included a periodic testing of the converter efficiency under idling and loaded (dinamometric) regimes after the car had run 0, 1500, and 5500 km with the mounted converter.

Tests at idling were conducted in PATC-3 (Novosibirsk, Russia). A car was placed on a platform; the measurements were conducted

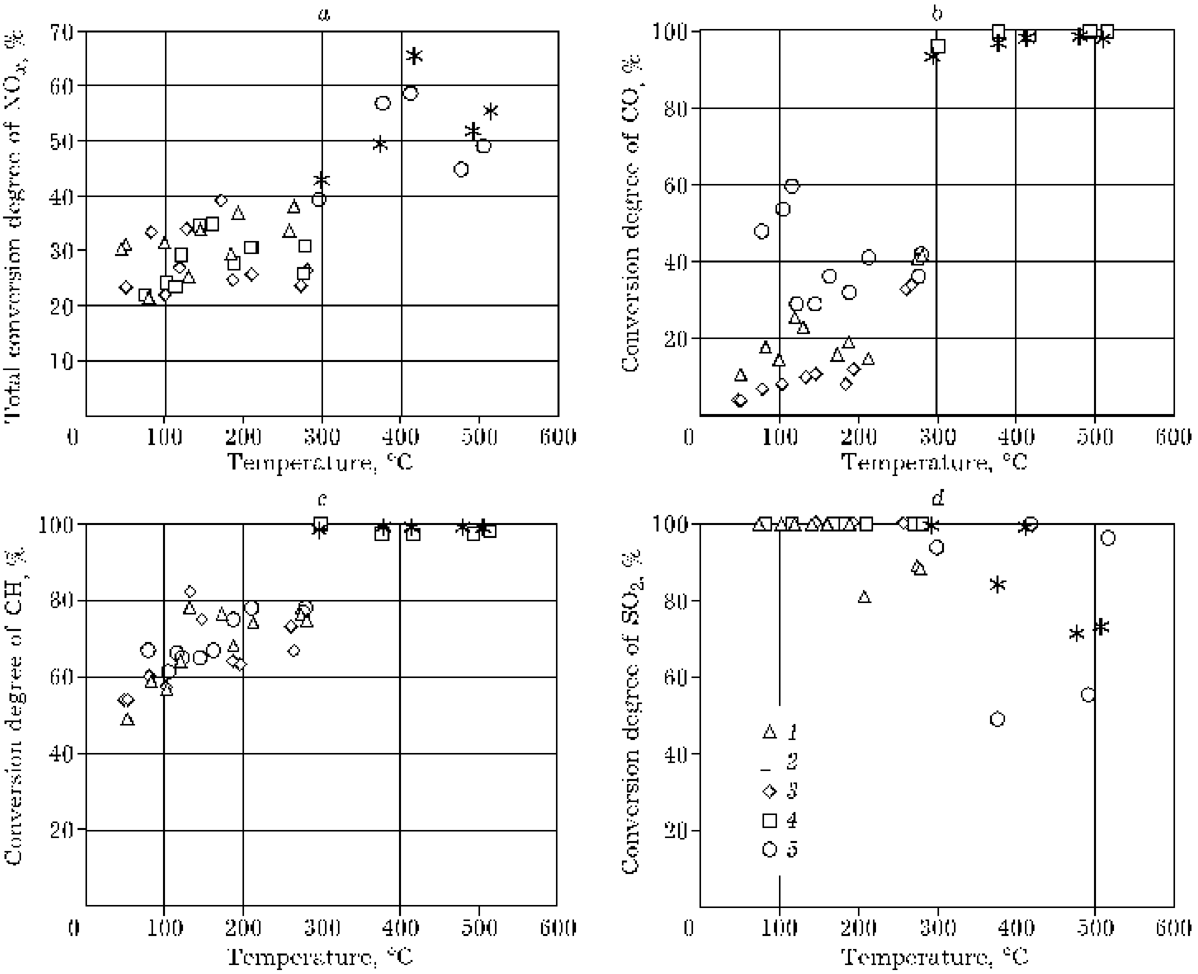

Fig. 3. Results of the pilot tests of GFC converter under various operating modes: *1* – idling, a fresh catalyst, *2* – loaded, a fresh catalyst, *3* – idling, after a path of 1500 km, *4* – idling, the path of 5500 km, *5* – loaded, the path of 5500 km.

at various engine speeds. Duration of each test comprised 30 min. For dinamometric tests (the motor depot of the NSC, Novosibirsk), a car was placed on rotating, the meterings were made at different rotation speeds of the rollers. The engine worked over the course of 1 h under each regime, the meterings were made every 30 min.

The engine speed frequency in the idling regime varied in a range of 800–4000 min^{-1}, and it was maintained constant (about 2000 min^{-1}) in the dinamometric tests. It has been found that the temperature at the inlet and the outlet of the converter increases practically linearly under idling (in the range of 50–280 °C) with the increasing speed. The gas temperature in the dinamometric regime varied from 200 to 500 °C depending on the engine load.

Reduction of NO_x

Efficiency of NO_x reduction was determined from the sum of NO and NO_2 concentrations. A typical NO_x content at the converter inlet for an idling and dinamometric regimes comprises 80–150 and 170–420 ppm, respectively. It can be seen (Fig. 3, *a*) that the NO_x conversion level at idling is as great as 20–40 % and it raises up to 40–65 % in a dinamometric regime due to a rise in the temperature of off-gases. The maximum conversion was observed in the temperature region of 350–500 °C. The acquired data are in a good agreement with the results of the laboratory studies.

It should be remarked that the efficiency of removal of nitrogen oxides on a fresh catalyst and on the catalyst after a path of 5500 km is virtually identical.

Oxidation of CO and CH

Carbon monoxide content of exhaust gases comprises 100–900 ppm depending on the test conditions.

From Fig. 3, *b* one can see that CO conversion level rises with an increase of temperature and it practically reaches 100 % at a temperature of 300 °C and over. No deactivation of the catalyst is observed, and the CO conversion level in the field of low temperatures even increases with an increase of the path.

Analogous regularities are also evidenced as regards the oxidation of hydrocarbons (see Fig. 3, *c*), the content of which in the exhaust gases is 700–2300 ppm. Practically full oxidation occurs at the temperatures of more than 300 °C.

It is remarkable that a sufficiently high conversion level of CH (no less than 50 %) is evidenced throughout the temperature range, including the field of low temperatures.

Removal of SO_2

A content of sulphur dioxide in exhausts comprised 0–70 ppm depending on the fuel quality.

From Fig. 3, *d* it is evident that practically complete removal of SO_2 was achieved at low temperatures (below 300 °C). At higher temperatures, the conversion level dropped down to 50–80 %.

Efficiency of the oxidation of soot particles

We did not determine the content of soot particles in the exhausts; however, indirect data make it possible to judge that rather effective oxidation of carbon black (at least, of its soluble organic phase) proceeds on GFC. This is evidenced, particularly, by the visible absence of carbon black from the surface of a waste GFC (the glass fibre has retained the initial color that is close to white).

Thus the test data have demonstrated that practically full conversion of CO and hydrocarbons is attained at the temperatures higher than 300 °C, while the efficiency of NO_x removal in a temperature range of 300–500 °C is as great as 60–65 %. It should be remarked that no any deactivation of the catalyst has been revealed that would be at all noticeable during the tests.

BENCH TESTS

Tests of neutralizers with GFC have been conducted at certificated stands of FGUP NIKTID (Vladimir, Russia) on various types of diesel engines: RM-120, D-245.12C, and D-120-44. The converter was made in the form of a punched cylinder with radial gas distribution through catalyst beds [6] (Fig. 4).

The results acquired during the tests have shown a high performance of GFC in the process of clearing the off-gases of diesel engines and they are suited to requirements of normative documents (State Standard GOST R 41.96–99, GOST R 17.2.2.05–97, the UNECE regulations No. 96). No deactivation of the catalyst was observed during the tests (more than 400 h), while the level of the hydraulic resistance of the neutralizer remained stable,

Fig. 4. Visual appearance of the neutralizer with a radial flow of gases (on the right) and of a catalytic glass fibre.

which tells for the efficient oxidation of soot particles.

Next, the GFC were tested at a certificated stand of KamAZ JSC with diesel engines of the KamAz 740.50-360 lorries, No. 2274395, with a power of 300 h. p. According to these tests, the application of GFC ensures that the norms of the EURO-3 standard are complied with (on the engine of EURO-2 standard) regarding all of the basic indices (CO, hydrocarbons, soot), except for nitrogen oxides. The last-mentioned is related to a strong shortage of a reducer, *i.e.* the NO_x/CH stoichiometric ratio is 5–6 times lower. To solve this problem, a special device for additional injection of hydrocarbon reducers (steams of diesel fuel) in the flow of the off-gases is scheduled to be made.

CONCLUSION

Based on the results of the laboratory experiments and the pilot tests with real exhaust gases of diesel engines, one can argue that, as compared to traditional types of catalytic neutralizers, the developed catalysts ensure:

– a substantial decrease in the cost of the catalyst, since the noble content in GFC is considerably (by hundreds of times) lower;

– high efficiency due to a high conversion degree in NO_x reduction, in oxidation of CO and hydrocarbons, in removal of SO_2;

– effective, long-term, and stable operation in a considerably wider temperature range;

– a stable, long-term service in the presence of SO_2 with no any noticeable decrease of the activity.

Acknowledgements

The authors express their thanks to L. G. Simonova, A. V. Toktarev, V. B. Goncharov, A. P. Suknev, E. A. Paukshtis (the Boreskov Institute of Catalysis, SB RAS), A. V. Kachkin, L. A. Kalinina, T. V. Borisova (Katalizator JSC, Novosibirsk), to S. V. Paponov, A. G. Korotnev (NIKTID Enterprise, Vladimir), and to A. R. Kulchitskiy (the Vladimir Tractor Plant) for their active involvement in this work.

The performed work was financed by internal grants of the Boreskov Institute of Catalysis, SB RAS, and within the framework of the programme "National technological base of the Russian Federation".

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