Adsorption Catalytic Neutralization of Exhaust Gases from Diesel Engines

I. V. MISHAKOV, A. A. VEDYAGIN, A. M. VOLODIN and M. S. MYAKISHEVA
Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 5, Novosibirsk 630090 (Russia)
E-mail: mishakov@catalysis.ru

Abstract

The basic aspects of environmental protection from hazardous gaseous impurities present in the exhaust gases of diesel engines are considered. Approaches used for the development of fundamental investigation of adsorbents and catalysts for afterburning CO and hydrocarbons are outlined. Results of the investigation of adsorption capacity of zeolites BEA and Y types with respect to heavy hydrocarbons (decane and toluene) obtained with the help of the gravimetric microanalyzer TEOM are presented. It is shown that both zeolites possess comparable capacities with respect to toluene, while the presence of mesopores in BEA zeolite determines its substantially larger adsorption capacity with respect to decane. For Pd/Al₂O₃ catalysts as example, the effect of the nature of precursor of active component and treatment conditions on the activity of the catalysts in the oxidation of CO is considered. It is demonstrated that in the case of the mass fraction of deposited chloride components up to 0.25–0.5 % atomically dispersed forms of palladium are formed; they are responsible for the high activity of palladium catalysts.

Key words: diesel engines, neutralizers, exhaust gases, afterburning catalysts, adsorbents, zeolites, TEOM

INTRODUCTION

The modern level of motor transport threatens to turn from the achievement of progress into ecological disaster for the inhabitants of megalopolises. Tens millions personal automobiles fill the streets of cities and highways, traffic jams many kilometres long every now and then, enormous amount of fuel is burnt improperly, air is poisoned by automobile exhaust gases; in many cities their amount exceeds total emissions from industrial enterprises. Unlike for foreign countries, the growth of the Russian motor stock proceeds under the conditions of substantial lag of home and second-hand foreign cars in ecological parameters and lag of motor fuel used in Russia from the world level [1].

Each automobile emits about 200 different components with exhaust gases into the atmosphere. Exhaust gases contain carbon monoxide CO, hydrocarbons CₓHₙ, nitrogen oxides NOₓ, benzo(a)pyrene, aldehydes. Due to incomplete combustion of fuel in car engines, a part of hydrocarbons is transformed into soot containing tarry matter. The amount of soot and tar formed is especially high when a driver forces the engine and decreases the ratio of air to fuel in order to obtain so-called rich mixture [2].

In diesel engines, hydrocarbons CₓHₙ partially remain in combustion chamber due to the heterogeneity of the mixture, that is, the flame shuts down in a very rich mixture where air is deficient due to incorrect turbulence, low temperature of poor spraying. Hydrocarbons get oxidized in the air and interact with nitrogen oxides; toxic compounds can be formed. Some of them are carcinogenic and cause cancer in humans after long-term contact [3].

During a long time within which the problem of air pollution with automobile exhaust gases exists, many methods were developed that allow one to decrease the amount of exhaust gases or to decrease heir toxicity. Neutralization of worked out gases in the outlet system became a widespread method. In this case, toxic vapour going out from engine cylinders gets mitigated before it is emitted into the atmosphere. Mitigation of exhaust gases with the help of catalysts occurs in devices called catalytic neutralizers [4]. Neutralizers are mount-
ed into the exhaust system of engine without any
changes and provide efficient purification from
the major toxic components within a broad tem-
perature range for worked out gases (150–900 °C).

The basic element of automobile converter
(neutralizer) is a catalytic reactor, usually made
as a monolith of block-honeycomb structure,
which provides optimal hydrodynamic condi-
tions of gas flow and high efficiency of the
interaction of impurities with the catalyst. The
first sample of a catalytic block-honeycomb con-
verter was developed in the USA as early as in
the middle of the 60es of past century, and in
middle 1970es the neutralizers of this kind had
become widely used in motorcar construction
practice in the world [5].

Screens, compensators and other elements
that are used in different designs of neutraliz-
ers usually play auxiliary functions and serve
to solve partial problems.

As a rule, a modern neutralizer is a ceramic
or metal block of honeycomb structure with
catalytically active layer deposited on the inner
surface of its channels [6]. This allows one to
increase the catalyst surface, decrease the con-
sumption of expensive metals (Pt, Pd, Rh) and
prevent recrystallization and sintering of the
active component at high temperature. Particle
size of the metal supported catalysts to a high
extent depends on the type of the support used.
Supports are usually synthetic (active coal, sil-
ica gel, Al2O3, aluminosilicate, MgO, ZrO2) and
more rarely natural (natural clay, pumice, di-
atomite, asbestos) solids with highly developed
specific surface and porosity [7].

COLD START PROBLEM:
ADSORPTION OF HYDROCARBONS ON ZEOLITES

As we have already mentioned, the problem
of exhaust neutralization is generally reduced
to the removal of CO, hydrocarbons and nitro-
gen oxides from the exhaust gases. While cata-
lysts are active towards the transformation of
NOx and CO within a broad temperature range,
hydrocarbon oxidation starts at a temperature
above 120–150 °C. For this reason, so-called cold
start problem arises. To solve it, zeolites are used
in world practice; their amount in afterburning
catalysts can reach 40 mass % [10].

During the first minutes of engine opera-
tion, non-burnt hydrocarbons are captured in
the porous matrix of zeolite. During further
heating of the catalytic converter, non-burnt
hydrocarbons get liberated from zeolites and
are oxidized on the catalyst. In this connection,
the developers of neutralizers face the prob-
lem to choose a zeolite so that a number of
requirements due to the specificity of after-
burning catalyst operation could be met.

To study adsorption properties of zeolites,
different gravimetric devices are used in prac-
tice. One of the most suitable devices is a Rup-
precht and Patashnik TEOM 1500 PMA (USA).
The basic principle of TEOM (Tapered Element
Oscillating Microbalance) operation is the prin-
ciple of pendulum, the form of which is im-
plemented in a cone reactor with the sample
under test at the end. Changes of the mass of
pendulum (sample) cause a square change of
oscillation frequency, which is recorded with
the help of optics in the real time mode (Fig. 1).
The use of TEOM procedure, unlike other
gravimetric techniques, allows one to achieve
100 % contact of reaction flow with the
weighed portion of the sample. In addition, this
method provides a high sensitivity to mass
(5 · 10^-6 g) and high frequency of recording in
the automatic mode (up to 10 measurements
per second).
Initially developed for measuring the concentration of solid particles in the air [11], the gravimetric microanalyzer TEOM has been used successfully for more than 10 years to study adsorption, diffusion, as well as deactivation and regeneration of catalysts [12–14].

In addition, TEOM microanalyzer has occupied important position in monitoring solid particles of automobile exhaust along with the investigation and development of new adsorbents and materials for automobile neutralizers [15]. This device is included in the complex of analytic equipment used for stand tests of experimental samples of afterburning devices mounted on real automobiles. In addition, TEOM has won active application in laboratory tests at the stage of choosing adsorbents and investigating their characteristics. For this purpose, one can use either model mixtures imitating real automobile exhaust or individual components which are of the highest interest for investigation (see Fig. 1).

In the work, we present the results of the investigation of zeolite samples of structural types BEA and Y; their texture characteristics are listed in Table 1. All zeolite samples were preliminarily calcined at 600 °C directly before the start of experiment.

Non-branched decane and toluene were used as model hydrocarbons that are usually present in the exhaust gases of diesel automobiles. The concentration of decane vapour in the flow of carrier gas (air) was 1200 ppm, and toluene 500 ppm. Adsorption of hydrocarbon vapour was carried out at a temperature of 30 °C. Desorption was performed using two methods: at 30 °C and through rapid heating of the sample to 250 °C in air flow.

Two experimental curves on decane adsorption (at 30 °C) and desorption in air flow at an-

<table>
<thead>
<tr>
<th>Parameters</th>
<th>BEA</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface, m²/g</td>
<td>585</td>
<td>790</td>
</tr>
<tr>
<td>Total pore volume, cm³/g</td>
<td>0.31</td>
<td>1.40</td>
</tr>
<tr>
<td>Volume of micropores, cm³/g</td>
<td>0.24</td>
<td>0.21</td>
</tr>
<tr>
<td>Concentration of micropores, %</td>
<td>78</td>
<td>15</td>
</tr>
</tbody>
</table>

Fig. 1. Gravimetric microanalyzer TEOM and the areas of its application in the development and investigation of catalytic converters of exhaust gases.

Fig. 2. Adsorption (30 °C) AND DESORPTION (250 °C) of decane on zeolites of BEA (1) and Y (2) types.
TABLE 2
Generalization of the results on adsorption/desorption of decane and toluene on BEA and Y type zeolites

<table>
<thead>
<tr>
<th>Parameters</th>
<th>BEA</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Decane</td>
<td>Toluene</td>
</tr>
<tr>
<td>Adsorption capacity at 30 °C, mass %</td>
<td>13.1</td>
<td>15.0</td>
</tr>
<tr>
<td>Residue after desorption at 30 °C, mass %</td>
<td>10.0</td>
<td>9.8</td>
</tr>
<tr>
<td>Residue after desorption at 250 °C, mass %</td>
<td>1.5</td>
<td>2.3</td>
</tr>
<tr>
<td>Specific surface, m²/g, after desorption</td>
<td>350</td>
<td>535</td>
</tr>
<tr>
<td>Total pore volume, cm³/g, after desorption</td>
<td>0.21</td>
<td>0.30</td>
</tr>
</tbody>
</table>
responding value for BEA type zeolite is 78\% (see Table 1). This fact explains the substantial difference between these zeolite types in their adsorption capacity with respect to decane.

**PALLADIUM CATALYSTS IN THE OXIDATION OF CARBON OXIDE**

In the investigation of the catalytic properties of afterburners, the most interesting aspect is their activity in the oxidation of the most toxic component of exhaust gases – carbon monoxide. In our studies we prepared the Pd/Al\(_2\)O\(_3\) catalyst using as support γ-Al\(_2\)O\(_3\) (Condex, \(S_{\text{BET}} = 200 \text{ m}^2/\text{g}\), granule size 0.25–0.5 mm) calcined in the air at 700 °C. Palladium was deposited in the amount of 0.03–1 mass \% by means of impregnation for moisture capacity from aqueous solutions of \(\text{H}_2\text{PdCl}_4\) (below designated as Pd(Cl)/Al\(_2\)O\(_3\)) and palladium nitrate (Pd(NO\(_3\))/Al\(_2\)O\(_3\)). The samples were dried at first at room temperature, then in a muffle at 100 °C for 12 h, and after that the sample were calcined in the air at a temperature of 600 °C for 10 h.

Determination of the activity of catalyst samples was carried out using a flow-type set-up. A sample of catalyst with a mass of 300 mg (fraction 0.25–0.5 mm) was placed in a quartz U-shaped reactor. Temperature in the reactor was risen from 60 to 300 °C at a rate of 10 °C/min. Reaction flow rate was 300 mL/min. Each catalyst was subjected to three cycles of heating–cooling, which allowed us to evaluate the stability of catalyst functioning. A criterion for comparing the activity was \(T(50)\), which is temperature of 50 % conversion of CO.

Reaction flow was a model mixture of the following composition, vol. %: H\(_2\)O 5, CO 0.15, O\(_2\) 14, NO 0.01, C\(_x\)H\(_y\) (a mixture of hydrocarbons) 0.0081; N\(_2\) – balance. The stability of catalysts to the action of high temperature was tested by means of hydrothermal treatment of samples at 800 °C in humid air (volume concentration of H\(_2\)O: 10 \%) for 14 h.

Important feature of palladium catalysts is their activity in the oxidation of CO, starting from very low concentrations of deposited metal. It is noteworthy that an increase in the oxidative activity stops sharply when palladium concentration of 0.25 mass \% is achieved (Fig. 4).

Taking into account \(S_{\text{BET}}\) of aluminium oxide used (200 m\(^2/g\)), the concentration of 0.25 mass \% corresponds to the degree of support surface filling with palladium ions not higher than 0.5 \% of monolayer. This allows us to conclude that stabilization of the active forms of Pd is due to the presence of special centres on the surface of γ-Al\(_2\)O\(_3\), and the concentration of these centres is insignificant.

We studied the effect of palladium deposition procedure and the nature of precursors (nitrate and chloride complexes) on the activity of Pd/Al\(_2\)O\(_3\) catalyst in the oxidation of CO. The values of parameter \(T(50)\) for these catalysts containing 0.25 mass \% Pd are listed in Table 3. Attention should be paid to substantially higher activity of the catalyst prepared from palladium nitrate in comparison with the sample prepared from the chloride precursor after calcination in the air at 600 °C. One can see that hydrothermal treatment of the latter allows one to improve the activity substantially.

The activity of palladium catalysts with low platinum content was also compared with the reference sample containing 2 \% platinum (see Table 3). One can see that the sample with treatment temperature 800 °C (0.25 \% Pd(Cl)/Al\(_2\)O\(_3\)-800) in the first cycles exhibits higher activity than the reference sample, in spite of substantially lower concentration of the active metal. Nevertheless, platinum catalyst demonstrates good stability from one cycle to another, while
The obtained results provide evidence of higher dispersity of supported palladium in the samples prepared from the chloride precursor. Calcination of these samples in the air at 800 °C causes baking of the active component and to the appearance of PdO phase (see Fig. 5, sample $T_{act} = 800$ °C (Cl)). TPR results are in good agreement with EXAFS [21] and spin probe data [22] for Pd/Al$_2$O$_3$ catalysts, which confirms the presence of atomically dispersed ion clusters Pd$^{2+}$ in chloride samples when the concentration of supported Pd is up to 0.5 mass %.

In spite of the high dispersity of palladium in chloride catalysts, its activity in CO oxidation turned out to be low in comparison with the nitrate samples. This is due to the presence of residual chloride ions in these samples. Experiments showed that its removal is possible as a result of hydrothermal treatment of catalysts at 500–550 °C. Data shown in Table 3 provide evidence that chloride samples subjected to the standard hydrothermal treatment procedure give extremely high activity exceeding the $T(50)$ parameter for nitrate samples.

### TABLE 3

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Palladium precursor</th>
<th>Treatment conditions</th>
<th>$T(50)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cycle 1</td>
<td>Cycle 2</td>
</tr>
<tr>
<td>0.25 % Pd(NO$_3$)/Al$_2$O$_3$</td>
<td>Nitrate</td>
<td>10 h, 600 °C</td>
<td>129</td>
</tr>
<tr>
<td>0.25 % Pd(Cl)/Al$_2$O$_3$</td>
<td>Chloride</td>
<td>10 h, 600 °C</td>
<td>235</td>
</tr>
<tr>
<td>0.25 % Pd(Cl)/Al$_2$O$_3$-800</td>
<td>Chloride</td>
<td>14 h, 800 °C, 10 % H$_2$O</td>
<td>115</td>
</tr>
<tr>
<td>2 % Pt/Al$_2$O$_3$ (reference sample)</td>
<td>–</td>
<td>14 h, 800 °C, 10 % H$_2$O</td>
<td>165</td>
</tr>
</tbody>
</table>

Fig. 5. TPR spectra of catalysts 0.5 % Pd/Al$_2$O$_3$ prepared from chloride and nitrate precursors after calcination in the air at different temperatures.
CONCLUSION

At present, integrated solution of the ecological problem of air pollution with exhaust gases is impossible without the application of adsorption and catalytic approaches. The use of adsorbents is due to the necessity to capture hydrocarbons in the cold cycle of engine operation, while catalysts provide complete neutralization of hazardous impurities at increased temperature.

The most evident candidates for adsorption trap are zeolite materials; however, not all of them satisfy requirements dictated by rigid conditions of neutralizer functioning. These criteria are first of all, the adsorption capacity with respect to a broad range of hydrocarbons, as well as the ability to regenerate pores and high thermal stability. We demonstrated that zeolites of BEA and Y types having comparable toluene capturing ability exhibit substantial differences in the sorption capacity for non-branched decane. In this case, determining factor is the porous structure of zeolite. Higher adsorption capacity of BEA type zeolite towards decane is due to the presence of substantial volume of mesopores, which are almost absent in zeolite Y.

Investigation of palladium catalysts Pd/Al2O3 showed that it is atomically dispersed ion forms of palladium stabilized on specific centres of the support that are responsible for the high activity of samples in the oxidation of CO. The use of chloride precursor in combination with subsequent hydrothermal treatment of the catalyst allows one to conserve highly dispersed state of supported palladium thus providing the high catalytic activity.

Unfortunately, it must be stated that in spite of extremely high activity in the first cycles of tests, palladium catalysts do not exhibit stability which characterizes platinum catalysts. Gradual transformation of active Pd forms into PdO leads to permanent decrease in activity from one cycle to another in longevity tests. For this reason, the efforts of many researchers are directed at present to the development of alloyed catalysts combining high activity with acceptable stability. Replacement of even a small amount of platinum by palladium will allow one to reduce the total cost of the converter in view of more than 3-fold difference between these metals in price.

REFERENCES

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