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CATALYSIS
AND ENVIRONMENT PROTECTION

Catalysis in the Automotive Industry: Mutual Development and State-of-the-Art

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Abstract—In this paper, the development of catalytic technologies used aboard a vehicle for purifying exhaust gases is estimated and forecasted. According to forecasts, in the next decade, the total production of vehicles will exceed 1 billion units and 75% of them will be equipped with internal combustion engines, which should necessarily be accompanied by an exhaust gas purification system. The development of catalytic technologies for purifying vehicle exhaust gases is mutually stimulated by the tightening of environmental standards and improving the internal combustion engines. For example, to date, the European standards have gone from Euro 1 to Euro 6d. The introduction of Euro 7 standards in Europe and the introduction of their counterparts in a number of countries by 2025 is planned. In addition, this paper discusses the concepts of systems that purify the exhaust gases of gasoline and diesel engines to meet the Euro 7 standards.

Keywords: exhaust gas purification system, internal combustion engine, three-way catalyst, ammonia selective catalytic reduction system, environmental standards

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INTRODUCTION

In discussing relationships between catalysis and vehicles, the first thing that comes up is catalytic petroleum refinery technologies for the production of automotive fuels and synthetic structural materials. In this paper, catalytic technologies used directly aboard a vehicle will be discussed. Let us begin with exhaust gas aftertreatment catalysts. They have been used for more than 50 years, of which for more than 25 years they have been produced in Russia by the Automotive Catalyst Plant, which earlier was part of AO Ural Electrochemical Plant (Novouralsk, Sverdlovsk oblast). In December 2010, the Automotive Catalyst Plant was withdrawn from AO Ural Electrochemical Plant and reorganized into OOO Ecoalliance, which is still operating and developing.

The use of exhaust gas purification systems is obviously a compulsory measure. Unacceptable air pollution caused, in particular, by the accelerated increase in the number of vehicles, has given rise to a number of legislative initiatives: the adoption of amendments to the Clean Air Act by the US Congress in 1990 [1], the tightening of environmental standards in California [2, 3] and Europe [4], and the Kyoto agreement on climate change concluded in 1997 [5]. After that, the large-scale introduction of exhaust gas purification devices for vehicles with various types of internal combustion engines (ICEs) began all over the world. Engine management systems have been significantly improved, and the relationship between the vehicle chemistry and electronics has been strengthened. Fuel purification technologies have been developed to provide a significant improvement in the fuel quality.

Currently, ICE vehicles are being replaced by electric vehicles or competing hydrogen-powered vehicles, the only emission of which is water. Over the past 30 years, this is the third attempt to switch to electric vehicles, which is initiated by the largest automobile concerns. Just like today, optimistic forecasts of an imminent technological revolution were voiced. However, the technologies did not reach a critical level, and the industry continued to develop naturally. To date, European political forces, while spurring their own industrial enterprises, have cut off their path of retreat to existing technologies. Huge subdivisions of automakers have refocused on the development of electric vehicles. In June 2021 Executive Vice President of the Renault Group Giles De Born wrote, “If we do not bring an affordable electric vehicle to the market, then we are finished” [6]. However, there is still a lot of research and development to be done before the large-scale implementation of all these technologies. To date, vehicles equipped with ICEs still occupy a major share of the global vehicle fleet.

Currently, the annual sales volume of road vehicles equipped with ICEs is about 78 million units [7].

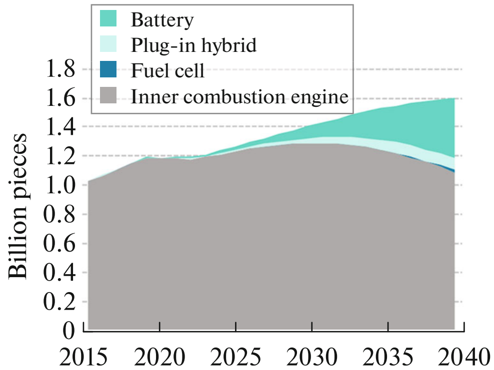

Fig. 1. Forecast of global production of light vehicles with different types of power units (BNEF data) [9].

Today many people are predicting an imminent "death" of ICEs. For example, the European Commission proposed to completely switch to electric vehicles from 2035 and ban the production of conventional fuel vehicles in the European Union [8]. However, according to the Bloomberg NEF estimates shown in Fig. 1, between 2020 and 2030, the total production of vehicles will exceed 1 billion, and 75% of them will be equipped with ICEs [9]. Thus, ICE should not lose a significant market share even by 2040.

Due to the economic and political situation in the world in 2022, it becomes difficult to assess and forecast the development of any industry. Therefore, this paper discusses the state-of-the-art of catalytic technologies for purifying exhaust gases of ICE vehicles until 2022; the development forecast is made without taking into account recent events.

CATALYTIC PURIFICATION OF EXHAUST GASES

The pioneering catalytic converters were designed exclusively to oxidize CO and HC and were commonly used in conjunction with an air pump, which provided the addition of a sufficient amount of air to maintain the excess oxygen required for efficient oxidation, regardless of how the engine was running. However, these catalysts overheated and rapidly failed in transient operating modes. In addition, by the early 1980s, NO_x emission standards in the United States have been tightened to such an extent that measures to decrease NO_x emissions by reducing the compression ratio or exhaust gas recirculation became insufficient for most vehicles. Therefore, in addition to these measures, a catalyst for the simultaneous oxidation of CO and HC and the reduction of NO_x was required.

Thus, the era of three-way catalysts (TWCs) began. This type of catalyst required maintaining an exact stoichiometric ratio between fuel and oxygen, which was not provided by the use of a carburetor. Therefore, the global automotive industry began to significantly complicate the gasoline engine and, accordingly, increase the cost of it via replacing the carburetor with an injector with electronic control of numerous engine operation parameters, in particular, the oxygen content in the exhaust gases. In addition, this technological leap made it possible to abruptly increase the fuel efficiency of the engine; however, the main driving motive was to provide an efficient on-stream behavior of exhaust purification catalysts. The use of TWCs provided a relationship between electronics and chemistry, which, unlike many relationships, enhanced over time.

It is noteworthy that the control of oxygen content is also implemented by catalytic technologies. An oxygen sensor (λ-probe) is a fuel cell with a solid oxide electrolyte, the catalyst of which mediates oxygen ionization [10–13].

The situation with aftertreating emissions from diesel engines is more complicated. In this case, the exhaust gases contain excess oxygen, a significant amount of NO_x, and carbon black. The task of oxidizing CO and CH with excess oxygen is easily solved by installing an oxidation catalyst (diesel oxidation catalyst (DOC)), whereas the efficiency required to remove NO_x is provided only by a system of selective catalytic reduction (SCR) with ammonia produced on board a vehicle by the thermal decomposition of urea. In this case, it is necessary to remove excess ammonia, which is implemented by its decomposition–oxidation in the presence of an appropriate catalyst (ammonia slip catalyst (ASC)). For the removal of carbon black, the most common and highly effective solution is a ceramic particulate filter (diesel particulate filter (DPF)), in which carbon black accumulates and undergoes oxidation (exclusively thermal or thermocatalytic) to CO_2 at regular intervals. The use of these technologies, as in the case of a gasoline engine, required significant modifications of the diesel engine, which also increased its efficiency.

Methane, which is the main component of natural gas, is one of the most important energy resources of the future [14]. In terms of environmental safety, methane-powered ICEs are considered to be more promising than conventional gasoline or diesel engines, because they provide lower levels of carbon dioxide and carbon black emissions. At the same time, according to the US Environmental Protection Agency estimates, the contribution of methane to the total greenhouse effect is at least 25 times higher than that of carbon dioxide [15]. For the further oxidation of unburned methane at the outlet of ICEs operating under excess air conditions, expensive catalysts with a high content of platinum metals are required. The tightening of environmental regulations with respect to nitrogen oxides gives an impetus to switching to a stoichiometric engine, which provides the occurrence of the process over a TWC. In turn, the degree of com-

Country/ Region	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026 and further
	Euro 6b		Euro 6d-TEMP/WLTC+RD					Euro 6d			Euro 7	
	Trier 2		Trier 3/LEV III									Trier 4/LEV IV
	LEV III											
	JC08			WLTP								
	Euro-5									Euro-6		
	China 4/China 5				CN6a			CN6b				CN7
	KLEV II	KLEV III / Euro 6b										
	Bharat IV					Bharat VI						Bharat VII
	Proconve L6							Proconve L7				Proconve L8

Fig. 2. Dynamics introducing the requirements to vehicle emissions in the different countries of the world.

plexity of this stoichiometric engine is significantly higher than that of a gasoline engine, because it is necessary to solve the problem of high heat generation and maintaining a narrower stoichiometry window [16].

CURRENT REQUIREMENTS TO VEHICLE EXHAUST EMISSIONS

The development of catalytic technologies for purifying exhaust gases is mutually stimulated by the tightening of environmental standards and the improvement of ICEs. For example, to date, European standards have gone from Euro 2 to Euro 6d, and Euro 7 is under development. However, the dynamics of the implementation of standards regulating vehicle exhaust emissions is not uniform in the countries of the world (Fig. 2). In the Russian Federation and the states of the Eurasian Economic Union, the implementation of European standards is somewhat lagging. From 2015 to the present, the Euro 5+ standards have been in force [17]. To date, India, China, South Korea, Japan, and Brazil have implemented their own counterparts of the Euro 6 standards.

In determining the specific emissions of a light- or medium-duty commercial vehicle, tests for a specific platform (vehicle type, weight, engine calibration version) are conducted on a chassis dynamometer system in accordance with a certain formalized cycle in compliance with strictly regulated environmental climatic conditions. Emissions of exhaust gases from a vehicle running on a chassis dynamometer in a cycle are collected into special packages and analyzed. Emissions during real driving are also analyzed. The results are expressed in terms of substance grams per kilometer of run (g/km).

Figure 3 shows two types of cycle. The New European Driving Cycle (NEDC) is valid for Euro 2 to Euro 6b standards [18]. This cycle consists of an urban and an extra-urban test phase. A relatively small set of engine operating modes is involved in these tests. These conditions have a low adequacy to real operating conditions; in addition, they allow a modern engine management system recognizing this type of test and switching to an “environmentally friendly” mode, for example, during certification. However, the results of this test can be used to determine whether the catalyst coped with the problem of “cold start” and whether it is sufficiently effective to aftertreat emissions at maximum space velocities of the vehicle. The Worldwide harmonized Light vehicles Test Cycle (WLTC) is more “realistic.” It includes a significantly larger number of transient processes, which require an expansion of the working area of exhaust gas aftertreatment systems [19]. The expansion of the operating mode boundaries, which are subject to increased requirements, contributes to the development of an engine with an aftertreatment system as a single unit.

Spheres of different sizes in Fig. 4 indicate the maximum allowable emissions of toxic components of exhaust gases for gasoline ICEs, which change with the development of environmental standards. The modern standards provide not only the presence of a catalyst, but also the control of the catalyst efficiency by an on-board diagnostic system. Starting with Euro 6, these parameters are comparable to the standards

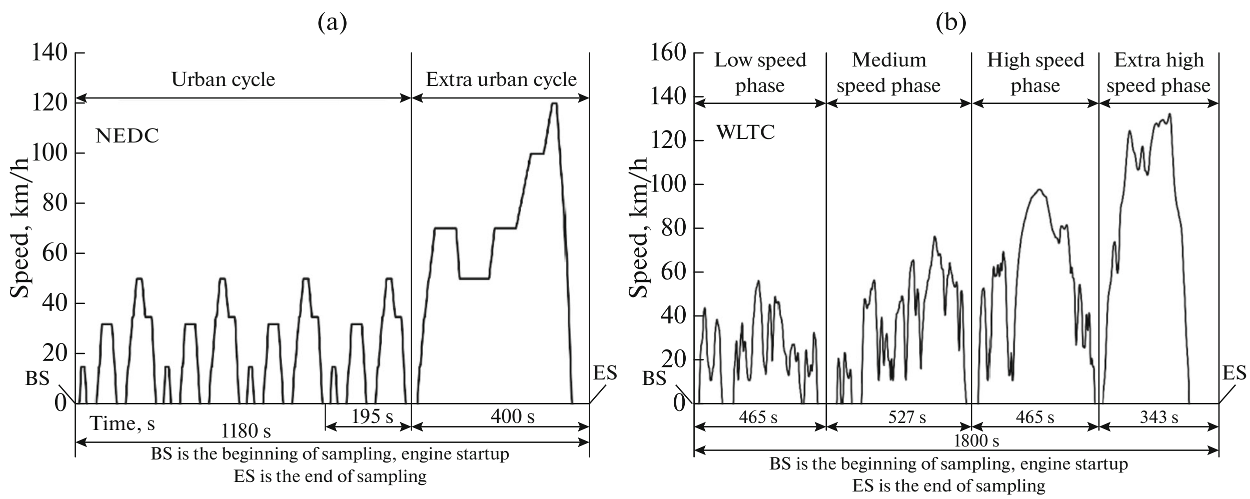

Fig. 3. Driving cycles in testing a vehicle on a chassis dynamometer system: (a) NEDC and (b) WLTC.

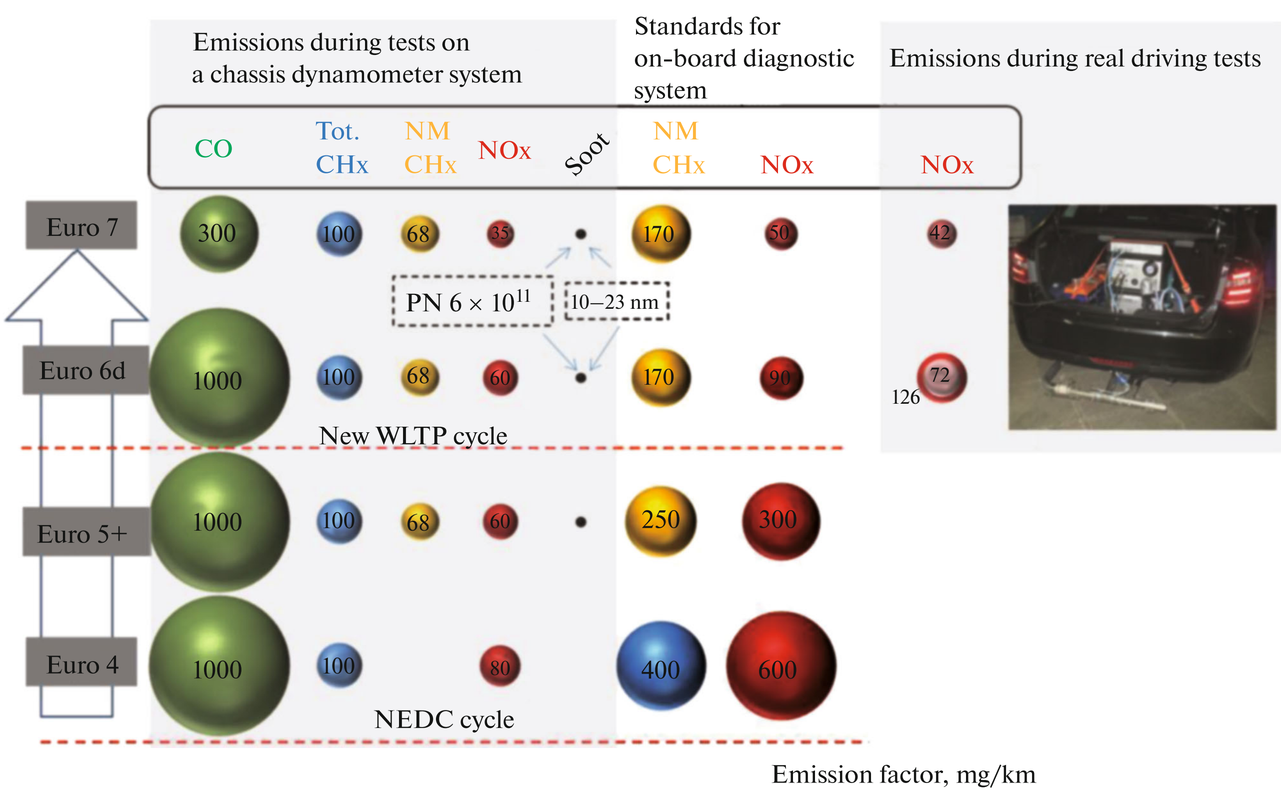

Fig. 4. Development of vehicle emission requirements (Euro standards).

for a serviceable vehicle; that is, a modern on-board diagnostic system should inform about catalyst failure in advance. Today, this aim is achieved by installing an extra TWC. It is mounted behind the diagnostic oxygen sensor, which detects a malfunction of the main TWC from oxygen transmission, while the supplementary TWC provides the compliance with the standards until the main TWC is replaced.

An increase in the energy efficiency of gasoline ICEs has led to the use of the direct fuel injection technology [20]. However, it necessitated the removal of carbon black using particulate filters (gasoline particulate filter (GPF)) [21]. In addition, the standards regulate not only the mass of carbon black, but also the number of carbon black particles; this requirement is attributed to the particularly harmful effect of small dust particles [22].

In 2015, it was found that the software installed in some vehicles did not display nitrogen oxide emissions correctly. This case is referred to as "Dieselgate" [23–26]. Subsequently, this event led to the tightening of test cycles and the introduction of special tests under real driving conditions (Real Drive Emission (RDE)) [27]. In addition to the fact that the Euro 7 standards abruptly tighten the requirements for maximum allowable emissions of toxic substances regulated by previous standards, they imply an increased control of some more pollutants, namely, NH_3, N_2O, and formaldehyde [28, 29]. This, in turn, involves an improvement in the selectivity of the aftertreatment system. Figure 5 shows extra pollutants to be controlled in the modern version of the Euro 7 standards.

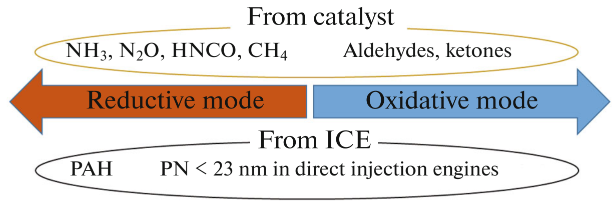

Fig. 5. New controlled pollutants in Euro 7 and mode of their occurrence.

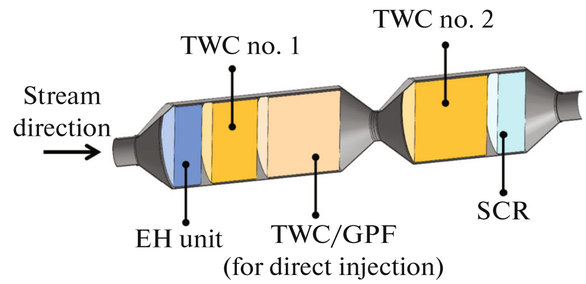

Fig. 6. Diagram of an exhaust gas purification system for gasoline ICEs to comply with the Euro 7 standards.

CONCEPTS FOR EXHAUST GAS PURIFICATION SYSTEMS FOR THE EURO 7 STANDARDS

Figure 6 shows the assumed composition of a gasoline ICE emission purification system to comply with the Euro 7 standards. Increasing attention to cold start efficiency inevitably leads to the use of an electric heating (EH) unit at the inlet. The TWC and GPF units are sequentially mounted behind it. A GPF is used only for direct fuel injection engines. Next, an extra TWC unit is mounted to provide predictive diagnostics of catalyst efficiency. Ammonia can be formed on the TWC due to the interaction of nitrogen monoxide and hydrogen in a hydrocarbon-enriched air–fuel mixture. In view of the introduction of ammonia emission limits within the framework of Euro 7, an ammonia decomposition unit should be mounted in the least hot zone.

In the case of a diesel engine operating under excess oxygen conditions, the exhaust gas aftertreatment system is significantly more complicated. Its general form is shown in Fig. 7; it is a fusion of all prior catalytic technologies commercially used to aftertreat emissions from diesel engines. It also implies the installation of an EH unit to solve the cold start problem. In addition, it involves a Lean NO_x Trap (LNT) catalyst combined with a DOC for the adsorption of nitrogen oxides in cold-mode operation (engine start or idling). The DOC, in addition to oxidizing CO and total hydrocarbons, mediates the conversion of NO to NO_2 to accelerate the SCR reaction. The EH unit, together with the DOC, in addition to solving the cold start problem, mediates the periodic regeneration of the particulate filter. Due to the variety of transient modes, it is supposed that the SCR technology should be a two-stage process, and urea should be injected at each of the stages. The quite recently commercialized SCR technology involving a particulate filter is also used here. The problem of controlling emissions of ammonia that is not consumed in the SCR process is solved by installing an extra catalyst for the decomposition of excess ammonia (ASC).

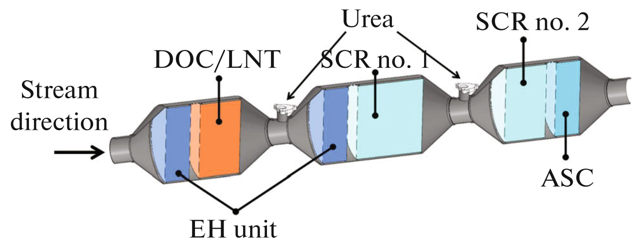

Fig. 7. Diagram of an exhaust gas purification system for diesel ICEs to comply with the Euro 7 standards.

WHAT WILL FOLLOW EURO 7?

According to Emission Analytics, the Euro 7 standards are not the end point of environmental regulation in the field of aftertreatment of vehicle exhaust gases, because the class of volatile organic compounds is still not subject to regulation [30]. Most of these substances are emitted during engine start-up and warm-up; therefore, it is necessary to develop adsorbing catalyst systems, which should be resource-sustainable [31]. The European regulatory framework in the field of cabin air control is being developed. Therefore, the cabin ventilation system will undergo significant changes, which will inevitably include the introduction of catalytic technologies.

CONCLUSIONS

On the verge of the implementation of Euro 7 requirements, the vehicle exhaust gas aftertreatment system is the most science-intensive and costly part of it. The large-scale application of catalytic technologies has made motor transport the largest consumer of platinum metals today, which inevitably leads to their shortage and a raise in their prices. At the same time, the automotive industry “exists” under conditions of fierce competition and, being focused on the end consumer, is forced to constantly update the model range and reduce the cost of the current model range. This fact stimulates efforts to develop cheaper and more efficient catalysts. In Russia, these activities are constantly being conducted at OOO Ecoalliance; they are vigorously supported by leading scientific institutions.

The forced switching to electric vehicles will certainly lead to the development of alternative power generation and new technologies. However, the necessity of an abrupt increase in power generation capacities will not allow abandoning hydrocarbon fuels, which will require further development of catalytic technologies for the effective greening of these fuels. Another way to achieve zero emissions—switching to hydrogen fuel—is hampered by the complexity of storing hydrogen on board a vehicle. In this context, it appears promising to use hydrocarbon fuel reformed to synthesis gas, which is further converted to electricity in fuel cells.

Increasing environmental requirements stimulate the development of catalytic processes and new technologies. Their particularly dynamic development is observed in the automotive industry, and it will continue in the future.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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