ISSN 0023-1584, Kinetics and Catalysis, 2009, Vol. 50, No. 1, pp. 18–25. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © V.A. Kirillov, E.I. Smirnov, Yu.I. Amosov, A.S. Bobrin, V.D. Belyaev, V.A. Sobyanin, 2009, published in Kinetika i Kataliz, 2009, Vol. 50, No. 1, pp. 22–30.

FIFTY YEARS OF THE BORESKOV INSTITUTE OF CATALYSIS

Reduction of Nitrogen Oxides in Diesel Exhaust: Prospects for Use of Synthesis Gas

V. A. Kirillov, E. I. Smirnov, Yu. I. Amosov, A. S. Bobrin, V. D. Belyaev, and V. A. Sobyanin
Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia
e-mail: vak@catalysis.ru

Received February 27, 2008; in final form, April 8, 2008

Abstract—Already commercialized and some of the most promising technologies of nitrogen oxide reduction in automotive diesel exhaust are compared. The Boreskov Institute of Catalysis (Siberian Branch, Russian Academy of Sciences) is developing an advanced method for the selective catalytic reduction of NO_x with synthesis gas produced on board by the catalytic conversion of diesel fuel. The activity of the Ag/Al_2O_3 catalytic system in NO_x reduction by H_2 + CO admixtures is studied for both a model composition of the exhaust gas and under real diesel operation conditions.

DOI: 10.1134/S0023158409010030

INTRODUCTION

At the present stage of technological development, the diesel engine is the most fuel-efficient internal combustion engine. In the last forty years, its efficiency has increased considerably due to various design efforts. Now the diesel engine has the greatest potential for reduction of automotive CO_2 emissions into the atmosphere. However, as for NO_x and soot particles, diesel engines suffer from a higher level of emissions than their gasoline counterparts equipped with a three-way catalyst.

Today the soot emission standards are satisfied primarily owing to the perfection of the fuel injection and combustion systems in the diesel engines and owing to the application of catalysts and recirculation systems for the oxidation of unburned hydrocarbons in the exhaust. The ultimate and the most efficient solution of the problem of reducing soot emissions is use of catalytic soot traps in all diesel-engined vehicles, including passenger cars. Note that such traps have already been commercialized and they reduce soot in the exhaust below its concentration in urban air.

While a way to reduce soot emissions has been found, the problem of NO_x reduction in diesel exhaust is still among the topical environmental challenges. Today's European NO_x emission standard (EURO-4) cannot be met only by improving the design or changing the operation regime of the diesel engine without a substantial (5–7%) loss of its fuel efficiency. In the future, the exhaust emission standards will inevitably be more stringent, so the optimal solution of the NO_x problem is use of catalytic exhaust neutralization systems.

Under oxygen excess conditions typical of diesel exhaust, nitrogen oxides can be converted into nitrogen using reducing agents (selective catalytic reduction, SCR). Present-day commercial technologies for removal of nitrogen oxides from diesel exhaust use urea or diesel fuel in the SCR process [1–3]. Another approach to the problem is to use the adsorption–catalytic reduction (ACR) technology. The principle of this technology is the storage of nitrogen oxides in the catalytic system under oxygen excess conditions and the reduction of concentrated NO_x upon desorption under periodically created fuel excess conditions [2–4].

In this work, we compare already commercialized technologies and some of the most promising newer technologies for nitrogen oxide reduction in diesel exhaust. The Boreskov Institute of Catalysis (Siberian Branch, Russian Academy of Sciences) is developing an NO_x SCR technology using synthesis gas obtained on board by the catalytic conversion of diesel fuel. Here, we demonstrate the potential of this method.

NO_x REDUCTION IN DIESEL EXHAUST

NO_x SCR Using Urea

The idea of using ammonia or urea in the removal of NO_x from automotive exhaust has been under development for several decades. The use of a eutectic aqueous solution of urea in the SCR reaction in diesel exhaust is attractive for reasons of storage and transportation safety and convenience and the high reducing power of ammonia obtained from urea on board.

Ammonia is prepared in two steps [5, 6]. The first step is noncatalytic, and it takes place in a hot engine exhaust stream:

(1) injection of fine droplets of an aqueous solution of urea into the gas stream;

(2) water evaporation during droplet motion in the stream, resulting in the formation of solid or melted urea droplets,

$$NH_2–CO–NH_2\ (l) + H_2O\ (l) \longrightarrow NH_2–CO–NH_2\ (s/l) + H_2O\ (g); \qquad (I)$$

(3) heating and thermal decomposition of urea in the gas stream

$$NH_2–CO–NH_2\ (s/l) \longrightarrow NH_3\ (g) + HNCO\ (g). \qquad (II)$$

As a result, an equimolar mixture of ammonia and isocyanic acid, which is very stable in the gas phase, is obtained at the first stage.

The hydrolysis of isocyanic acid, which can be carried out in the presence of various solid oxides, is the second, catalytic step of ammonia preparation:

$$HNCO + H_2O \longrightarrow NH_3 + CO_2. \qquad (III)$$

Theoretically, 2 mol of ammonia must be produced by the complete decomposition of 1 mol of urea and the hydrolysis of the resulting isocyanic acid. Thus, ~0.5 mol of urea per mole of NO_x in the exhaust should be supplied to the catalytic reduction unit (i.e., ~0.9 g of urea per gram of nitrogen oxides).

The commercial catalysts for NO_x SCR with ammonia are systems containing vanadium as the active component: V_2O_5/TiO_2, $V_2O_5/WO_3/TiO_2$, and $V_2O_5/MoO_3/TiO_2$. Under oxygen excess conditions, the catalytic reduction of individual nitrogen oxides can proceed as follows:

$$2NH_3 + 2NO + 0.5O_2 \longrightarrow 2N_2 + 3H_2O, \qquad (IV)$$

$$4NH_3 + 3NO_2 \longrightarrow 3.5N_2 + 6H_2O. \qquad (V)$$

The simultaneous reduction of NO and NO_2 occurs at a considerably higher rate than reactions (IV) and (V) [5]:

$$2NH_3 + NO + NO_2 \longrightarrow 2N_2 + 3H_2O. \qquad (VI)$$

Usually the NO_2 concentration in diesel exhaust is 5–10% of the entire volume of NO_x and the NO concentration is about 90% or higher. At these concentrations of individual nitrogen oxides, the vanadium-based catalytic systems afford a very high NO_x conversion and nitrogen selectivity only above 250–300°C. Below 200°C, its activity is rather low. By directing the NO_x reduction process via the high-rate route (VI), one can substantially increase the conversion of nitrogen oxides in the low-temperature region. This can be attained by an increase in the NO_2 fraction in the exhaust gas, for example, by partial oxidation of NO on a platinum catalyst:

$$NO + 0.5O_2 \longrightarrow NO_2. \qquad (VII)$$

The replacement of pure NO with an NO + NO_2 mixture (1 : 1) was shown [5] to increase the conversion of nitrogen oxides at 200°C from 21 to 93% (at a flow rate of 52000 h^{-1} and an ammonia breakthrough concentration of 10 ppm).

Obviously, any mobile NO_x removal system has a very small space for the droplet evaporation and urea decomposition processes. Because of the limited duration of these processes, the decomposition of urea in the gas stream may be incomplete. Serious problems can arise in NO_x mixing with the reducing agent (ammonia) because of the short residence time. Thus, the slow decomposition of urea at a low exhaust temperature can lead to incomplete NO_x reduction and to considerable concentrations of ammonia and isocyanic acid in the "reduced" gas stream.

On the other hand, various macromolecular byproducts capable of suppressing the catalytic activity and decreasing the NO_x conversion form on the walls of the catalytic reduction unit and on the catalyst surface at exhaust temperatures above 300°C. Isocyanic acid can react with urea and ammonia or polymerize to yield biuret, cyanuric acid, melamine complexes, and other products [7]. There is evidence that hydrocyanic acid (~10 ppm above 250°C) forms on the NO_x reduction catalyst [8]. This is explained by the fact that, under oxygen excess conditions, ammonia can react with methane, whose concentration in the exhaust can be about 10–100 ppm:

$$NH_3 + CH_4 + 1.5O_2 \longrightarrow HCN + 3H_2O. \qquad (VIII)$$

To enhance droplet evaporation, the thermal decomposition of urea, and flow stirring, the space between the injection system and the NO_x reduction catalyst can be filled with an inert packing. In this case, almost complete urea decomposition can be achieved at a residence time of 0.1 s of the mixture in the inert layer and at $T =$ 350°C [9]. However, this does not eliminate the problem of undesirable by-products, which can form and decompose (depending on the temperature regime) on the inert layer surface [7]. Thus, there are deviations from the stoichiometric ratio necessary for efficient NO_x reduction yielding 2 mol of ammonia per mole of urea. Under different engine operation conditions, this results in a decrease in the NO_x conversion or in the breakthrough of ammonia and other nitrogen-containing pollutants through the NO_x reduction catalyst. This breakthrough can be prevented by introducing another platinum catalyst into the NO_x reduction unit for oxidation of the nitrogen-containing pollutants.

When applied to trucks, this exhaust treatment scheme is often simplified. A typical consequence of this simplification is a decrease in the average NO_x conversion to ~80% at medium temperatures and flow rates of up to 50000 h^{-1}. Nevertheless, although the breakthrough of ammonia and other nitrogen-containing pollutants is higher in this case, it still meets the certification requirements for cargo transport.

For instance, it was demonstrated that 20 l of a vanadium honeycomb catalyst alone is sufficient to reduce NO_x emissions to the EURO-5 level for a 12-l diesel engine with a power of 400 hp [10]. The engine was optimized to decrease soot emissions and fuel consumption, which was 198 g kW^{-1} h^{-1} when using the European Transient Cycle (ETC) test. In this case, the average NO_x emission was 8.5 g kW^{-1} h^{-1} at the combustor outlet and 1.5 g kW^{-1} h^{-1} after the exhaust gases were passed through the catalytic reduction unit.

The literature pays special attention to the sulfur poisoning resistance and operating stability of vanadium catalysts. For example, more than 20 diesel engines equipped with a vanadium-based catcon were subjected to ETC certification tests [11]. The NO_x conversion was shown to be almost unchanged after a >200000-km-long run.

Although there are problems below 200°C and above 400°C, an unquestionable advantage of this method of NO_x removal from the exhaust gas is the high reducing power of ammonia. This makes it possible to considerably extend the urea refilling interval over that used for less reactive reducing agents. With the comparatively low level of NO_x emissions from the modern diesel engines, an automobile can be refilled with a urea solution at the same intervals as are adopted for conventional servicing, such oil change [3]. European producers stated that they would use this method of NO_x reduction in exhaust from cargo automobiles [12, 13]. For this purpose, the European Union is developing the necessary refilling infrastructure. At present, researchers are seeking more active catalytic systems for NO_x reduction with ammonia, including zeolite-based systems [14].

When considering the possibility of applying this technology in Russia, one should take into account the fact that the freezing point of the eutectic aqueous solution of urea is too high (–11°C). This causes additional technical problems in the use of catalytic converters in winter. The freezing temperature can be decreased by adding modifiers to the solution [15]. However, their influence on urea decomposition and NO_x reduction needs further investigation.

Thus, the use of urea in NO_x SCR in diesel exhaust has a high potential for cargo transport, for which the space necessary for an extra tank, a catalytic unit, a dosage system, and other equipment is not a crucial limiting factor. Today the key problems are that of decreasing the freezing temperature of the reductant solution and that of precisely controlling the dosage of the solution in the transient modes of engine operation. The urea-based SCR systems ensure a high NO_x conversion and selectivity and are operable in a wider temperature range (~200–500°C) than any other system for removal of nitrogen oxides from diesel exhaust. The factor limiting the activity of the system at low temperatures is urea decomposition into ammonia and isocyanic acid in the exhaust gas stream [6]. Recently, Hitachi proposed using a heated bypass channel through which part of the exhaust is passed for urea decomposition [16]. No heating is required to decompose urea when the temperature of the exhaust gases is rather high. This device will possibly shift the lower temperature limit of the operation of the urea-based SCR systems to 150°C. This would have a favorable effect on the efficiency of the system at low and medium engine loads, such as in the urban driving cycle.

NO_x SCR Using Diesel Fuel

The expected advantages of the SCR process using diesel fuel are that it needs no extra tank for a reducing agent and no refilling infrastructure and is technologically simple. With diesel fuel as the reducing agent, NO_x SCR can be carried out on various catalytic systems, which can be grouped as follows:

(1) zeolite-based systems, (2) systems based on oxide composites, and (3) systems based on Ag/Al_2O_3.

Each of these three groups is characterized by its specific mechanism of nitrogen oxide reduction. Their common problem is the competition between the nitrogen oxides and oxygen at the hydrocarbon oxidation stage:

$$C_yH_z + NO_x + O_2 \longrightarrow CO_2 + H_2O + N_2, \quad \text{(IX)}$$

$$C_yH_z + O_2 \longrightarrow CO_2 + H_2O. \quad \text{(X)}$$

Because of this, hydrocarbons should be added to the exhaust gases so that the CH/NO_x ratio is many times higher than the stoichiometric ratio necessary for the oxidation of hydrocarbons by nitrogen oxides via route (IX). Furthermore, a larger amount of the catalyst than would be required for NO_x reduction should be used to prevent the presence of considerable amounts of unreacted hydrocarbons at the outlet of the exhaust treatment system. As a result, the competition between routes (IX) and (X) can lead to a significant decrease in the efficiency of the system.

The three types of catalytic systems for SCR using diesel fuel are briefly considered below.

The systems based on zeolites with supported transition metal cations and/or platinum group metals show a rather high efficiency and operation stability in the SCR of nitrogen oxides with hydrocarbons in dry model mixtures. In real water-containing diesel exhaust, the zeolite catalysts are prone to deactivation because of their hydrothermal instability resulting in dealumination. The instability of zeolite systems hampers their application. Nitrogen oxides are reduced on zeolite-based systems in two steps: initially, NO is oxidized to NO_2 on active metal sites, and then it reacts more rapidly with hydrocarbons on acid sites of the zeolites and is reduced to nitrogen. Among the zeolite systems suitable for NO_x SCR using hydrocarbons, Cu/ZSM-5 has attracted the greatest attention from researchers [17, 18]. It was shown [18] that an improved system containing Cu/ZSM-5 ensures ~50% NO_x conversion in the exhaust gas in reduction by heavy hydrocarbons (CH/NO_x = 6 mol/mol) in the medium-temperature region at a flow rate of 30000 h^{-1}.

In addition to hydrothermal instability, degradation because of sulfurization is another flaw of the zeolite-based systems.

The catalytic systems based on alumina, zirconium dioxide, and complex oxide compositions with supported platinum group metals and/or transition metal cations show a high stability in the SCR of nitrogen oxides in real exhaust gases. However, in the presence of water vapor and sulfur dioxide, the region of efficient operation of most nonplatinum catalysts in the SCR process using diesel fuel shifts to higher temperatures (400–600°C) [19, 20]. The efficiency of the system can be increased by adding platinum to the active components. As a result, high activity is achieved in the medium-temperature region and the N_2O selectivity increases sharply [21, 22]. These systems require further investigation and still cannot be regarded as competing for use in NO_x removal from exhaust gases.

The Ag/Al_2O_3 catalytic system is considered to be the best for NO_x SCR by heavy hydrocarbons [23, 24]. This system is particularly attractive because the longest hydrocarbon chains ensure the highest catalytic activity in the SCR of nitrogen oxides. Equal activities are observed in the reduction of NO_2 and NO. The Ag/Al_2O_3 system makes it possible to attain >70% NO_x conversion in SCR by heavy hydrocarbons in the temperature range from 350 to 450°C at a flow rate of 60000 h^{-1} and $CH/NO_x = 6$ [25], implying a 4.7% increase in fuel consumption. Optimization of the performance of the system in NO_x conversion–fuel efficiency terms demonstrated that the $CH/NO_x = 4.5$ ratio is the best. In this case, a NO_x conversion of 60–70% is achieved at an extra fuel consumption of 3.5%. This is one of the highest fuel efficiencies attained for the catalytic systems used in SCR by heavy hydrocarbons. However, the Ag/Al_2O_3 system also involves unsolved problems, namely, insufficient activity of the catalyst below 300°C and the inhibition of the catalyst by aromatic hydrocarbons present in real diesel fuel.

Thus, the problems common to all of the existing SCR systems using diesel fuel are the low efficiency of fuel consumption for NO_x reduction and an insufficient activity in oxygen-rich mixtures even in the medium-temperature region.

Important points in the development and application of this technology are the way of converting part of the diesel fuel into synthesis gas and the use of the resulting synthesis gas as a more reactive reductant of nitrogen oxides. The application of this NO_x SCR scheme will be considered below.

NO_x ACR Technology

The efficiency of the adsorption–catalytic reduction technology can vary widely, depending on the nature and molecular weight of the reducing agent [2]: H_2 and CO have the highest reducing power, followed by heavy hydrocarbons. The reductive medium necessary for NO_x conversion is periodically created directly in the catalytic converter by removing free oxygen from the system. As a rule, an additional catalyst, such as Pt/Al_2O_3, is used for this purpose. Part of the diesel fuel is oxidized on this catalyst after evaporation in the exhaust gas stream. Note that the amount of fuel injected into the catalytic unit should be sufficient for the complete removal of both free oxygen from the exhaust and oxygen stored by the catalytic system during operation under the oxygen excess conditions. The unoxidized fuel is spent on NO_x desorption and reduction. The considerable increase in the temperature of the system that occurs during fuel conversion accelerates NO_x desorption and reduction. Since the engine continually works under oxygen excess conditions, when the conversion of the injected portion of fuel is complete, the system cools and returns to the NO_x adsorption mode. Thus, the operation of the catalytic system under periodically created favorable conditions (reductive medium and high temperature) makes it possible to attain an almost complete NO_x conversion at the reduction stage of the cycle. By repeating this stage more frequently, it is possible to reach a nearly 100% cycle-average conversion. On the other hand, the fuel consumption for reduction depends directly on the durations of the lean- and rich-mixture operation intervals, so, when choosing an operation regime, one has to find a compromise between the NO_x conversion and the fuel efficiency.

The most popular commercial catalyst for the adsorption and catalytic reduction of NO_x from internal combustion engines is $Pt/Ba/Al_2O_3$, which was developed by Toyota. Rhodium and palladium are often used together with Pt [26, 27]. The modern ACR systems using diesel fuel are characterized by high activity in the medium-temperature region of 250 to 450°C, in which an NO_x conversion higher than 80% is achieved at an extra fuel consumption of 3–4% of the diesel fuel consumption [2, 3]. The required amount of catalyst is comparable to the amount necessary for an SCR system using urea.

A drawback of this technology is the sensitivity of the catalysts to the sulfur content of the fuel [2, 3, 27], which is demonstrated in the fact that the sorption capacity of the system decreases as sulfates form on the catalytic sites active in sorption. Desulfurization should be carried out at intervals under reductive medium conditions above 600°C to restore the sorption capacity.

Marked progress in the ACR technology has been made by applying a method involving the conversion of diesel fuel and use of the conversion products with high CO and H_2 contents (synthesis gas) as reducing agents for nitrogen oxides [28, 29]. The expected advantages of the ACR technology using synthesis gas are the following: fast catalyst ignition, the possibility of temperature control, fast and/or low-temperature desulfurization, and a low level of extra fuel consumption.

Below, we consider two examples of the application of the NO_x ACR process using the autothermal conversion of diesel fuel. The first example is the approach suggested by Catalytica Energy Systems Inc. [30–32]. A fuel processor placed immediately upstream of the ACR catalyst is used to carry out the fast low-temperature regeneration and periodic desulfurization of the catalyst. During catalyst regeneration, a mixture of the exhaust gas with injected diesel fuel is converted in the fuel processor, producing a ~6% H_2 + CO mixture. This approach offers the following advantages: high NO_x conversion at $(H_2 + CO)/NO_x \geq 3$, ACR catalyst regeneration at low temperatures (starting at 150°C), and a small amount of the catalyst sufficient for the process owing to the complete regeneration and restoration of its sorption capacity by very reactive reducing agents (H_2 and CO).

Obviously, the minimum extra consumption of fuel for NO_x reduction can be achieved by minimizing the amount of fuel required for oxygen removal from the exhaust. This can be done by controlling the operation of the engine. Tests showed that engine operation can be optimized so as to decrease the oxygen content of the exhaust to 5% at the point of switching to the ACR catalyst regeneration stage [30]. In this case, the typical engine operation cycle was as follows: 60 s in the lean fuel mixture mode and then several seconds in the enriched fuel mixture mode. The use of the fuel processor in combination with engine operation control made it possible to reduce the extra fuel consumption to <3% at 90% NO_x conversion. However, if this method is used without engine operation control, i.e., if the exhaust contains 8–15% oxygen, the extra fuel consumption will increase to 5–8% [32].

The fuel consumption for the creation of a reductive medium for ACR catalyst regeneration can be considerably decreased by using a system with two catalyst-containing hoses. A system with a single hose can also be used if there is a possibility of bypassing the catalytic converter for some period of time. In this case, during regeneration the exhaust gas stream can be directed via an alternative pathway and synthesis gas can be used in catalyst regeneration and NO_x reduction. The fuel processor should be a separate device capable of distributing the products of diesel fuel conversion between the other components of the system according to a given operation cycle. Part of the diesel exhaust should be used as a source of oxygen, water, and heat for fuel conversion to enhance the energy efficiency of the system.

Precisely this approach is considered below as the second example of the ACR process using the autothermal conversion of diesel fuel. The HydrogenSource Company suggested a similar approach [33]. In their method, the ACR catalyst is regenerated at a low temperature and 90% NO_x conversion is achieved at 150 to 450°C. Unfortunately, the efficiency of the system was estimated only by model tests at 300°C. In this case, the extra fuel consumption for NO_x reduction was ~1.5%.

However, it should be mentioned that present-day ACR technologies using both diesel fuel and synthesis gas require catalysts containing platinum group metals in amounts of ≥ 2 g/l, which markedly raises the cost of the NO_x removal system.

NO_x SCR on Ag/Al_2O_3 Using Synthesis Gas

As was noted above, Ag/Al_2O_3 is among the best catalysts in terms of activity and fuel efficiency for NO_x SCR systems using hydrocarbons. However, the insufficient activity of the catalyst at temperatures below 300°C, at which various hydrocarbons (from C_1 to C_{12} and diesel fuel) are used as reducing agents, is an insuperable obstacle on the way to its automotive application. In recent years, researchers involved in solving the NO_x emission problem have given special attention to catalytic systems based on Ag/Al_2O_3. This is explained by the pronounced promoting effect of hydrogen on the activity of the silver catalyst in the NO_x SCR processes using ammonia or urea [34] and hydrocarbons [35, 36]. Not only the simple summation of the effects from the two separate SCR routes, but also a synergic effect was observed, because pure hydrogen shows a low activity in NO_x reduction on the silver catalyst under oxidative conditions.

The studies performed at the Boreskov Institute of Catalysis show that hydrogen-containing synthesis gas is an efficient reducing agent for NO_x in the medium-temperature region. Synthesis gas can be obtained on board from diesel fuel, mixed with engine exhaust, and then fed into the SCR unit.

Initially, the activity of the 3.6% Ag/Al_2O_3 catalytic system was studied at the following model composition of the exhaust gas (hereafter, the concentrations are given in volume units): O_2, 9.8%; NO, 350 ppm; CO_2, 5.9%, H_2O, 2%; N_2, the balance. In order to simulate synthesis gas admixtures, CO and H_2 were added to the mixture at concentrations of 600 and 2100 ppm, respectively. The studies were carried out in a quartz flow reactor of a kinetic setup under atmospheric pressure at temperatures of 100 to 600°C and volumetric flow rates of 9000 to 26000 h^{-1}.

At a flow rate of 9000 h^{-1}, the reduction of nitrogen oxides by the synthesis gas is initiated at 150°C. As the temperature increases, the conversion of NO_x increases, passes through a maximum (~60%) at 200°C, and then falls off. At 300°C its value is ~30%. This behavior is due to the fact that, above 120°C, hydrogen and carbon monoxide are oxidize by oxygen from the gas mixture. Above 300°C, almost no reducing agents remain in the mixture and, as a consequence, the active oxidation of NO to NO_2 begins.

Taking into account that the Ag/Al_2O_3 catalyst is good for the SCR of NO_x by heavy hydrocarbons above 300°C and that the catalytic activity is enhanced by hydrogen, it was reasonable to continue the tests performed at the Boreskov Institute of Catalysis by using a combined reducing agent containing synthesis gas and the heavy hydrocarbon decane (as a model of the diesel fuel). In order to simulate the combined reducing gent, CO and H_2 at concentrations of 600 and 2100 ppm, respectively, and decane at concentrations of 75 to 200 ppm were added to the initial mixture of the exhaust gas, whose composition was specified above.

As was expected, the use of the complex reducing agent considerably increases the catalytic activity and extends the temperature interval of efficient catalyst operation. For instance, at 180–350°C the conversion of NO into nitrogen is higher than 95% at a decane content of 150 ppm and a volumetric flow rate of 9000 h^{-1}. As the temperature is further increased, the NO conversion decreases to 80% at 400°C, and to ~70% at 450°C. When the model exhaust gas contains 110 ppm decane, the NO conversion is above 80% at 180–350°C and remains above 70% as the temperature is raised to 400°C.

Note that, at 200°C, the NO conversion is about 60% with synthesis gas alone. With decane alone (150 ppm), the NO conversion is lower than 30%. In the case of the combined reducing agent consisting of synthesis gas and decane, the conversion at 200°C is nearly 100%.

Bench tests of the NO_x reduction system using the Ag/Al_2O_3 catalyst under real diesel operation conditions are being performed now. The real exhaust of any diesel contains unburned hydrocarbons (about 100 ppm with respect to the diesel fuel), CO, and H_2. For this reason, adding only synthesis gas to the exhaust, we expect to obtain approximately the same effect as in the case of the combined reducing agent with a decane content of >110 ppm, specifically, an NO_x conversion of at least 80% between 180 and 400°C.

At the moment of writing this article, preliminary bench tests had been carried out. In these tests, synthesis gas produced by the autothermal conversion of diesel fuel (~2.8 l STP of (H_2 + CO) from 1 g of diesel fuel), with H_2/CO ~ 3.5, was added to the exhaust of a 100-kW diesel working at its nominal power. The synthesis gas generator was designed and made at the Boreskov Institute of Catalysis. Detailed information about the catalysts and the technical characteristics of the generator will be published after patenting. The main component and nitrogen oxide concentrations in the exhaust were as follows: O_2, 10.1%; CO_2, 6.9%; H_2O, 6.6%; N_2, 76%; NO_x, 460 ppm. The temperature of the mixture at the inlet of the catalytic converter was 350°C, and the mixture consumption rate was about 470 kg/h. A vertical cylindrical 25-l reactor with a fixed catalyst bed (spherical granules of 2% Ag/Al_2O_3 2.5 mm in diameter) was used as the NO_x removal unit.

The preliminary bench tests showed that the consumption of diesel fuel for the production of synthesis gas for NO_x SCR is ~4.6 g per gram of reduced nitrogen oxides at conversions higher than 80%. The fuel consumption is above the expected value. This is due to the fact that diesel operation was not optimized in the preliminary tests and the CH/NO_x ratio in the exhaust was too small. Because of this, to achieve an NO_x conversion higher than 80%, it was necessary to produce ~1.5 times more synthesis gas than was planned.

The effects of the CH/NO_x ratio were considered [37] for the case of a diesel fuel–hydrogen mixture as the reducing agent. For instance, it was demonstrated that, at a hydrogen concentration of 3200 ppm, the optimum CH/NO_x ratio is ~2, the deactivation and reduction of the Ag/Al_2O_3 catalyst are at equilibrium, and a high activity of the catalyst is retained (the NO_x conversion is higher than 80% at 300°C).

Based on these studies, we can claim that an NO_x conversion of at least 80% in the 180–400°C temperature range and an extra fuel consumption of about 3 g per gram of reduced nitrogen oxides (3–4% of the fuel consumed by the diesel) can be attained provided that a CH/NO_x ratio favorable for the operation of the silver catalyst is established in the exhaust. The published data show that this does not require changes in the design or other technical improvements of the engine, but can be achieved by optimizing the operation of the diesel.

CONCLUSIONS

A comparison between the three most competitive technologies for the reduction of nitrogen oxides in diesel exhaust and technology of NO_x reduction with synthesis gas that is being developed at the Boreskov Institute of Catalysis is presented in the table.

The SCR technology using urea is the most efficient from the standpoint of the reducing agent consumption and cost. Nevertheless, the application of this technology in Russia involves some serious problems. Firstly, the freezing point of aqueous urea is too high for the winter conditions even in the European part of Russia. Heating of the tank filled with the urea solution during the operation of the engine and a warm garage become necessary conditions for automobile exploitation. Secondly, no infrastructure for mass filling of automobiles with a urea solution exists in Russia today and nothing is planned in future. Thirdly, since it is necessary to mount an extra heated tank, a catalytic unit, a dosing system, and other equipment on the automobile, this technology is less competitive for passenger cars.

The obvious advantage of the technologies using synthesis gas as a reducing agent is that they reduce the catalyst "ignition" temperature to 150–180°C, which is especially important under urban driving cycle conditions typical of the exploitation of passenger cars. It is also significant that these technologies do not require storing any extra reducing agent on board.

Comparison of technologies for nitrogen oxide reduction in diesel exhaust

NO_x reduction technology of	Necessity of an extra reducing agent on board	Temperature range in which the NO_x conversion is >80%, °C	Reducing agent consumption, wt % of the fuel consumed by the engine	Platinide content of the catalyst
SCR using urea	Yes (urea)	200–500	~1% urea	No
ACR using diesel fuel	No	250–450	3–4% diesel fuel	≥2 g/l
ACR using synthesis gas	No	150–450	1.5–3% diesel fuel	≥2 g/l
SCR using synthesis gas (being developed at the Boreskov Institute of Catalysis)	No	180–400	Estimated at 3–4% diesel fuel	No

Concerning the NO_x ACR technology (using both diesel fuel and synthesis gas as reducing agents), we can conclude that the high platinide content of the existing ACR catalysts limits its large-scale application, especially in cargo automobile transport, because the cost of the catalyst alone for a small truck with a 10-l class diesel would be above $1000 (on the basis of the average cost of platinum in January 2008, namely, $50 for 1 g [38]). Since the catalyst is progressively deactivated and should be replaced after a ~200 000-km run, even the exploitation of a passenger car with an NO_x ACR system is expensive.

The SCR technology using synthesis gas is less expensive. The use of the Ag/Al_2O_3 catalyst has a number of advantages in addition to the low cost [37, 39], namely, a low SO_2 oxidation activity providing a high sulfur-poisoning resistance, a rather high thermal and hydrothermal stability, and a high nitrogen selectivity in NO_x reduction. In addition, this exhaust treatment method is continuous and is, therefore, technically simpler. Recent studies, including those carried out at the Boreskov Institute of Catalysis, suggest an optimistic prognosis concerning the creation of an efficient diesel exhaust treatment system based on NO_x SCR using synthesis gas obtained by the conversion of diesel fuel on board.

REFERENCES

1. Twigg, M.V., *Appl. Catal., B*, 2007, vol. 70, p. 2.
2. Liu, Z. and Woo, S.I., *Catal. Rev.*, 2006, vol. 48, p. 43.
3. Jobson, E., *Top. Catal.*, 2004, vol. 28, p. 191.
4. Forzatti, P., Castoldi, L., Nova, I., Lietti, L., and Tronconi, E., *Catal. Today*, 2006, vol. 117, p. 316.
5. Koebel, M., Elsener, M., and Kleeman, M., *Catal. Today*, 2000, vol. 59, p. 335.
6. Birkhold, F., Meingast, U., Wassermann, P., and Deutschmann, O., *Appl. Catal., B*, 2007, vol. 70, p. 119.
7. Fang, H.L. and DaCosta, H.F.M., *Appl. Catal., B*, 2003, vol. 46, p. 17.
8. Sluder, S., Storey, J., Lewis, S., and Lewis, L., *Report of Oak Ridge National Laboratory at the 10th Annual DEER Workshop*, Coronado, Calif., 2004.
9. Yim, S.D., Kim, S.J., Baik, J.H., Nam, I.S., Mok, Y.S., Lee, J.H., Cho, B.K., and Oh, S.H., *Ind. Eng. Chem. Res.*, 2004, vol. 43, p. 4856.
10. Gekas, I., Gabrielsson, P., Johanssen, K., Bjorn, K.J.I., Husted-Kjeer, J., Reczek, W., and Cartellieri, W., *SAE Tech. Pap. Ser.*, 2002, no. 2002-01-2885.
11. Ammon, B. and Keefe, G., *SAE Tech. Pap. Ser.*, 2001, no. 2001-01-1931.
12. *ACEA Statement on the Adoption of SCR Technology to Reduce Emissions Levels of Heavy-Duty Vehicles*, 2003.
13. Gabrielsson, P.L.T., *Top. Catal.*, 2004, vol. 28, p. 177.
14. Bartholomew, C.H. and Farrauto, R.J., *Fundamentals of Industrial Catalytic Processes*, Hoboken, N.J.: Wiley-Interscience, 2006, p. 739.
15. Solla, A., Westerholm, M., Soderstrom, C., Tormonen, K., Harma, T., Nissinen, T., and Kukkonen, J., *SAE Tech. Pap. Ser.*, 2004, no. 2004-05FL-150.
16. Kowatari, T., Hamada, Y., Amou, K., Hamada, I., Funabashi, H., Nakagome, K., and Takakura, T., *SAE Tech. Pap. Ser.*, 2006, no. 2006-01-0642.
17. Patent EP 0445408B1, 1990.
18. Marshall, C.L., *Report of Argonne National Laboratory at the 9th DEER Conf.*, Newport, R.I., 2003.
19. Li, N., Wang, A., Wang, X., Zheng, M., Cheng, R., and Zhang, T., *Appl. Catal., B*, 2004, vol. 48, p. 259.
20. Sato, K., Yoshinari, T., Kintaichi, Y., Haneda, M., and Hamada, H., *Appl. Catal., B*, 2003, vol. 44, p. 67.
21. Burch, R. and Ottery, D., *Appl. Catal., B*, 1996, vol. 9, p. 19.
22. Corro, G., Fierro, J.L.G., Montiel, R., Castillo, S., and Moran, M., *Appl. Catal., B*, 2003, vol. 46, p. 307.
23. US Patent 06045765, 1996.
24. Eranen, K., Lindfors, L-E., Klingstedt, F., and Murzin, D., *J. Catal.*, 2003, vol. 219, p. 25.
25. Klingstedt, F., Eranen, K., Lindfors, L-E., Andersson, S., Cider, L., Landberg, C., Jobson, E., Eriksson, L., Ilkenhans, T., and Webster, D., *Top. Catal.*, 2004, vols. 30/31, p. 27.
26. Dou, D. and Ballard, J., *SAE Tech. Pap. Ser.*, 2002, no. 2002-01-0734.
27. Gill, L.J., Blakeman, P.G., Twigg, M.V., and Walker, A.P., *Top. Catal.*, 2004, vol. 28, p. 157.
28. Kong, Y., Crane, S., Patel, P., and Taylor, B., *SAE Tech. Pap. Ser.*, 2004, no. 2004-01-0582.
29. Wu, M.C., Han, T., and Fisher, G.B., *SAE Tech. Pap. Ser.*, 2005, no. 2005-01-3878.

30. Dalla Betta, R., Sheridan, D., and Cizeron, J., *Report of Catalytica Energy Systems Inc. at the 10th DEER Conf.*, Coronado, Calif., 2004.
31. Dalla Betta, R., Boleda, T., Cizeron, J., and Sheridan, D., *Report of Catalytica Energy Systems Inc. at the 11th DEER Conf.*, Chicago, 2005.
32. Yee, D., Adair, B., Boleda, A., Berry, B., Caron, T., Cizeron, J., Kinney, T., Lundberg, K., and Dalla Betta, R., *Report of Catalytica Energy Systems Inc. at the 11th DEER Conf.*, Chicago, 2005.
33. *Report of Hydrogen Source Inc. at the 9th DEER Conf.*, Newport, R.I., 2003.
34. Shimizu, K. and Satsuma, A., *Appl. Catal., B*, 2007, vol. 77, p. 202.
35. Breen, J.P., Burch, R., Hardacre, C., Hill, C.J., and Rioche, C., *J. Catal.*, 2007, vol. 246, p. 1.
36. Arve, K., Backman, H., Klingstedt, F., Eranen, K., and Murzin, D.Yu., *Appl. Catal., B*, 2007, vol. 70, p. 65.
37. Houel, V., Millington, P., Rajaram, R., and Tsolakis, A., *Appl. Catal., B*, 2007, vol. 77, p. 29.
38. http://www.platinum.matthey.com.
39. Breen, J.P., Burch, R., Hardacre, C., Hill, C.J., Krutzsch, B., Bandl-Konrad, B., Jobson, E., Cider, L., Blakeman, P.G., Peace, L.J., Twigg, M.V., Preis, M., and Gottschling, M., *Appl. Catal., B*, 2007, vol. 70, p. 36.