

# Toward Improved Catalytic Low-Temperature NO<sub>x</sub> Removal in Diesel-Powered Vehicles

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Received October 28, 2005

## ABSTRACT

The potential of different catalytic after treatment techniques to meet future diesel emission standards, which are strongly shifted toward urban driving conditions including cold start, are critically discussed in this Account and evaluated for their suitability for commercial applications. The dominating techniques in this field are NO<sub>x</sub> storage, urea-selective catalytic reduction (SCR), and HC-SCR. Each of these techniques have significant disadvantages such as sulfur sensitiveness and regeneration requirements of NO<sub>x</sub>-storage materials, infrastructure issues and formation of ammonium nitrate (at low temperatures) for urea-SCR, and low-temperature activity of HC-SCR catalysts. Ways to overcome these disadvantages in commercial applications may involve optimized regeneration strategies, reactor modifications, flow reversal, closed-loop NO<sub>x</sub> feedback systems, nonthermal plasma, and/or hydrogen-assisted catalyses, etc.

## 1. Introduction

Lean-burn gasoline and direct injected common rail turbo-charged diesel engines have significant fuel economy benefits compared to gasoline engines, operating under

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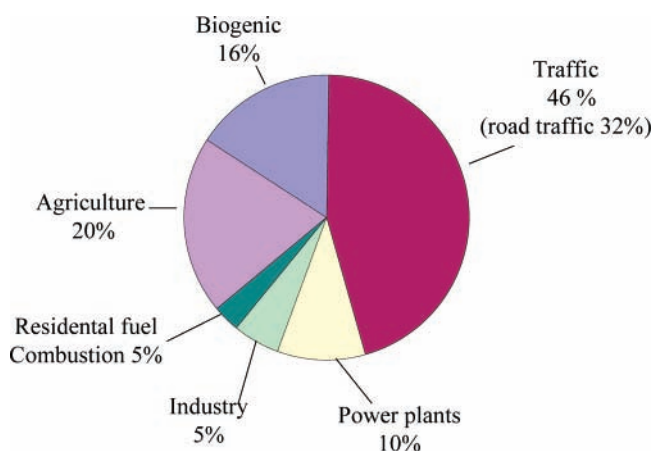


FIGURE 1. Nitrogen oxide emission in the 15 EU countries in 2000.

a stoichiometric air/fuel ratio ( $\lambda = 1$ ). Dependent upon the load, air/fuel ratios are typically above 1.5 and, for instance, during idling, the air/fuel ratio of a modern diesel engine can be an order of magnitude higher than that of stoichiometric engines, i.e.,  $\lambda > 10$ .<sup>1</sup> However, the full worldwide expansion of such engines is hindered by the difficulties in effective NO<sub>x</sub> and particulate removal. In Europe, traffic is the major source of the total NO<sub>x</sub> emissions<sup>2</sup> (Figure 1) and first emission regulations for diesel engines were introduced in 1988.<sup>3</sup> This first regulation mainly concerned the particle emissions, but later regulations beginning with the Euro I regulation in 1992 also included standards for HC, CO, and NO<sub>x</sub> emissions. Tables 1 and 2 contain a summary of the emission standards for heavy-duty diesel truck and bus engines as well as diesel-powered passenger cars and their implementation year.<sup>4,5</sup> Similar or even stricter regulations are in use in the United States.

Standardized test procedures are necessary to obtain repeatable and comparable emission results. The emissions are measured using engine or vehicle test cycles. In these test cycles, speed and load are varied in well-defined steps to simulate the real driving condition for a given application. Emissions measured on vehicle dynamometers are expressed in grams of pollutant per unit of traveled distance, for example, g/km, and emissions measured on engine dynamometers are expressed in grams per mechanical energy delivered by the engine, for instance, g/kWh.<sup>6</sup>

The ECE test cycle, also known as UDC, represents urban driving with low speed and load. The EUDC (Extra Urban Driving Cycle) is characterized by higher speeds, with the maximum being 120 km/h. Most of the modern test cycles incorporate today a cold-start phase into the transient driving cycle. In Euro 3, the test cycle was modified, eliminating an engine warm-up period. This modified ECE + EUDC cycle is also called "The New European Driving Cycle" (NEDC). In Figure 2, the temperature profile over a Ag/alumina catalytic converter

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**Table 1. Emission Standards for Heavy-Duty Diesel Truck and Bus Engines in Europe<sup>a</sup>**

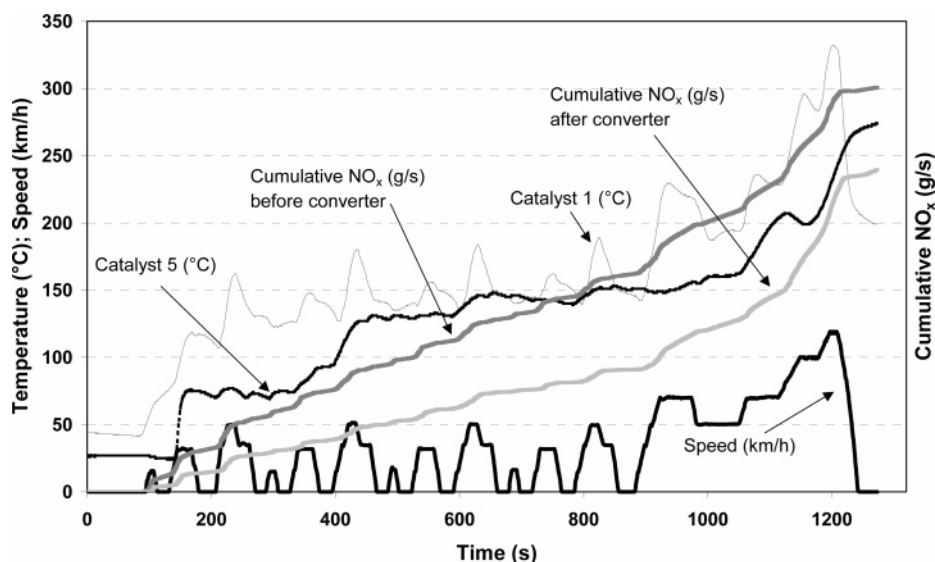
	year	test cycle	CO (g/kWh)	HC (g/kWh)	NO <sub>x</sub> (g/kWh)	PM <sup>b</sup> (g/kWh)	smoke (m <sup>-1</sup> )
Euro I	1992, <85kW	ECE R-49	4.5	1.1	8.0	0.612	
	1992, >85 kW	ECE R-49	4.5	1.1	8.0	0.36	
Euro II	1996	ECE R-49	4.0	1.1	7.0	0.25	
	1998	ECE R-49	4.0	1.1	7.0	0.15	
Euro III	2000	ESC + ELR	2.1	0.66	5.0	0.10	0.8
		ETC	5.45	0.78	5.0	0.16	
Euro IV	2005	ESC + ELR	1.5	0.46	3.5	0.02	0.5
		ETC	4.0	0.55	3.5	0.03	
Euro V	2008	ESC + ELR	1.5	0.46	2.0	0.02	0.5
		ETC	4.0	0.55	2.0	0.03	

<sup>a</sup> Reproduced from ref 3 with kind permission from DieselNet.com. <sup>b</sup> PM, particulate matter; ECE R-49, steady-state engine test cycle; ESC, European stationary cycle; ELR, European load response test; ETC, European transient cycle. For type approval according to the Euro IV limit values, the emissions have to be determined on both the ETC and ESC/ELR tests.

**Table 2. Emission Standards for Diesel-Powered Passenger Cars in Europe<sup>3 a</sup>**

	year	test cycle	CO (g/km)	HC (g/km)	HC + NO <sub>x</sub> (g/km)	NO <sub>x</sub> (g/km)	PM (g/km)
Euro 1	1992	ECE15 + EUDC	2.72		0.97		0.14
Euro 2	1996	ECE15 + EUDC	1.0		0.70		0.08
Euro 3	2000	ECE15 + EUDC	0.64		0.56	0.50	0.05
Euro 4	2005	ECE15 + EUDC	0.50		0.30	0.25	0.025

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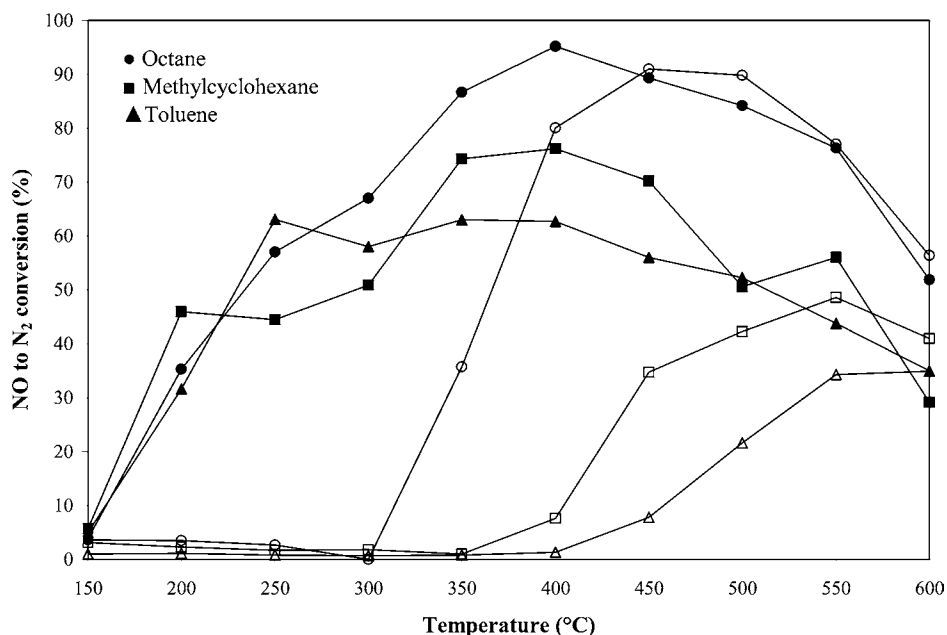
**FIGURE 2.** Cold-started EUDC test using a Ag/alumina converter. Reproduced from ref 6 with kind permission from Springer Science and Business Media.

during the NEDC test cycle is illustrated.<sup>7</sup> As can be seen in the test, the temperature of the catalyst remains below 150 °C in approximately 70% of the driving cycle. This means that most of the NO<sub>x</sub> generated in the first part of the test will not likely be removed to a great extent by the existing catalytic solutions of today. However, NO<sub>x</sub> emissions are a function of the engine load and speed. During the first stages of the test cycle, the load is quite low, which obviously will affect the amount of NO<sub>x</sub> emitted. This means that it is not very straightforward to correlate the operation activity of the catalyst only based on the temperature of the cycle because the emissions are expressed in g/km or g/kWh.

Three major catalytic techniques are widely proposed and used for removal of NO<sub>x</sub> emissions from lean-burn and diesel-operated vehicles: NO<sub>x</sub> storage, urea-selective catalytic reduction (SCR), and HC-SCR. Each of these techniques have significant disadvantages such as sulfur

sensitiveness and regeneration requirements of NO<sub>x</sub>-storage materials, infrastructure issues and formation of ammonium nitrate (at low temperatures) for urea-SCR, and low-temperature activity of HC-SCR catalysts. In this Account, we will critically discuss and present the potential of the different catalytic after treatment techniques to meet future emission standards, which are nowadays strongly shifted toward urban driving conditions, including cold start.

As will be shown below, a big progress was made in the recent years to prepare active and selective catalysts for NO<sub>x</sub> removal in diesel-powered vehicles with a potential to be applied commercially. However, the rational design of efficient catalysts active at a low-temperature domain requires the understanding of processes on the molecular level. This field of environmental catalysts still awaits detailed mechanistic studies, including identification of surface and gas-phase intermediates, application



**FIGURE 3.** Activity test over 2 wt % Ag/alumina in the presence (●, ■, and ▲) and absence (○, □, and △) of 1 vol % H<sub>2</sub>. GHSV = 60 000 h<sup>-1</sup>, HC<sub>1</sub>/NO = 6, and total volumetric flow = 550 mL/min.

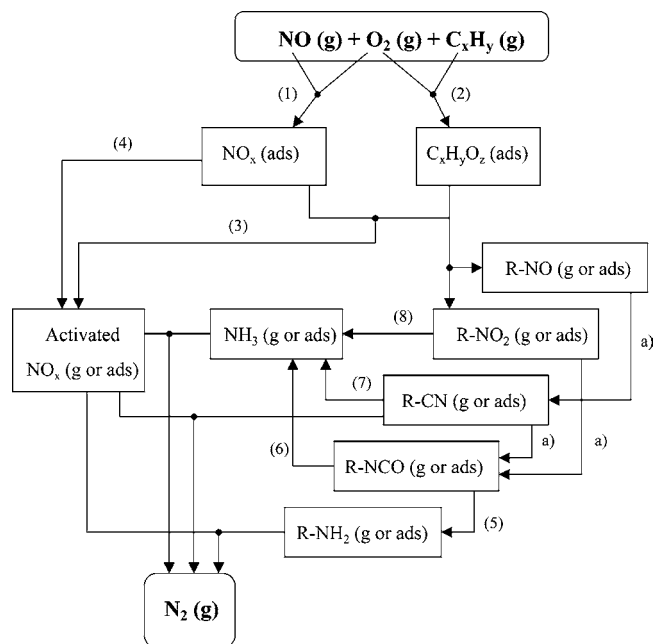
of computational chemistry, as well as molecular and kinetic modeling.

## 2. HC-SCR

For a car manufacturer, the most attractive method to abate NO<sub>x</sub> emissions is through self-decomposition of NO over a suitable catalyst. However, the major problem connected with this technique is the well-known severe inhibition effect on the reaction rate caused by oxygen, which is produced by the reaction or is present in the feed. Another elegant solution is HC-SCR, which makes use of existing hydrocarbons in the exhaust (passive control) or added fuel (active control) in front of the converter to reduce NO<sub>x</sub>. In 1990, Held et al.<sup>8</sup> and Iwamoto et al.<sup>9</sup> independently discovered that copper ion-exchanged ZSM-5 was active in the selective reduction of NO with alkanes and alkenes in the presence of oxygen. Since this discovery, the research on the topic has been extensive and several catalytic formulations have been suggested. Smedler et al.<sup>10</sup> have listed some formulations and their peak NO<sub>x</sub> conversions and corresponding temperatures in laboratory tests. The NO<sub>x</sub> conversion at 400 °C was reported to decrease as follows: Ag/alumina (80%) > SnO<sub>2</sub> (67%) > H-mordenite (62%) > Cu-ZSM5 (60%) using C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, or C<sub>2</sub>H<sub>4</sub> as reducing agents. It is worth mentioning that the performance of the different formulations is likely to depend upon the reducing agent used. However, most of the proposed materials developed for this technique suffer from almost nonexistent low-temperature activity (below 300 °C), with Pt/alumina being an exception. On the other hand, Pt/alumina has a very shallow activity window and a tendency to selectively produce large amounts of N<sub>2</sub>O.<sup>11</sup> In a recent study, Yentekakis et al.<sup>12</sup> showed that Na-modified Pt/alumina catalysts were significantly more selective toward the formation of N<sub>2</sub> than

the corresponding unmodified catalyst. In the same study, Na was shown to widen the operation window of the C<sub>3</sub>H<sub>6</sub> + NO + O<sub>2</sub> reaction by improved low-temperature activity. Patrick et al.<sup>13</sup> have on the other hand suggested that gold on alumina catalysts are highly selective toward the formation of N<sub>2</sub> and have peak NO<sub>x</sub> reduction activities at 200 °C. Such materials combined with a suitable high-temperature catalyst (i.e., Cu-ZSM-5 and/or Ag/alumina) may broaden the operating window for effective NO<sub>x</sub> removal. With the low temperatures (below 150 °C) recorded during the driving cycle illustrated in Figure 2 kept in mind, it seems that the traditional materials developed for HC-SCR will not likely remove NO<sub>x</sub> to a great extent during the cold-started driving cycle if used in a single-bed (reactor) approach. As a summary, it can be mentioned that before the commercialization of the HC-SCR technique a suitable catalyst or a combination of catalysts able to reduce NO<sub>x</sub> at temperatures below 200 °C need to be developed.

**2.1. H<sub>2</sub>-Assisted HC-SCR over Ag/Alumina.** Hydrogen in combination with hydrocarbons has been reported to boost significantly the low-temperature activity of silver catalysts.<sup>14–18</sup> High activities in laboratory conditions are achieved at temperatures as low as 150 °C.<sup>10</sup> We have investigated the effect of hydrogen in combination with different reductants such as octane, toluene, and methylcyclohexane<sup>19</sup> (Figure 3). In the absence of hydrogen, the ring-containing hydrocarbons were poor reductants for NO below 450 °C and the maximum conversion of NO to N<sub>2</sub> at 550 °C remained as low as 40–45%. Octane on the other hand gave rise to high NO to N<sub>2</sub> conversion in the temperature range of 400–600 °C (with a maximum around 90%). In the presence of hydrogen, high activity in the removal of NO<sub>x</sub> was achieved already below 200 °C in the case of all three reductants. This result is especially



**FIGURE 4.** Schematic illustration of the proposed reaction mechanism during HC-SCR over Ag/alumina. Reactions 1–4 are accelerated by the addition of hydrogen. Higher concentrations of ammonia and amines are formed in the presence of water in steps 5–8. Steps 5 and 6 proceed at 250 °C, but at 400 °C, step 5 is not taking place. The transformation of nitrile to NH<sub>3</sub> in step 7 is restricted to high temperatures. Step 8 is pronounced at high temperatures. Reproduced from ref 18 with kind permission from Elsevier.

interesting because several of the diesel fuels on the market contain considerable amounts of aromatic and cyclic hydrocarbons, which in the absence of hydrogen reversibly deactivate the Ag/alumina catalyst.

Shibata et al.<sup>16</sup> discussed that hydrogen increased the concentration of acetate but decreased the concentration of nitrates on the catalyst surface during reaction conditions. Moreover, they found that the formation rates of nitrates and acetates were increased. In a recent paper, Richter et al.<sup>20</sup> have proposed that hydrogen generates short-term scale zero-valent silver. Reactive O (and/or OH) species are formed via dissociative interactions of O<sub>2</sub> (and H<sub>2</sub>) with these metallic silver species. These reactive oxygen atomic species should then accelerate the necessary oxidative transformation of gaseous NO to adsorbed nitrite/nitrate species. In our recent paper,<sup>18</sup> dealing with HC-SCR over Ag/alumina, we proposed a schematic mechanism (Figure 4) including the possible effect of hydrogen. The role of hydrogen on the HC-SCR process is dual. First of all, improved oxidation of all components involved is obtained. Second, hydrogen was shown to activate NO over the Ag/alumina catalyst to react with amines and ammonia or with other N-containing species in the gas phase. Further, in the same study, it was discussed that hydrogen may boost the formation rate of isocyanate and hereby enhance the low-temperature activity during the HC-SCR process.

Burch<sup>11</sup> has proposed that hydrogen has a specific chemical function, which is to destroy nitrate species that are strongly adsorbed on silver sites, thus poisoning them.

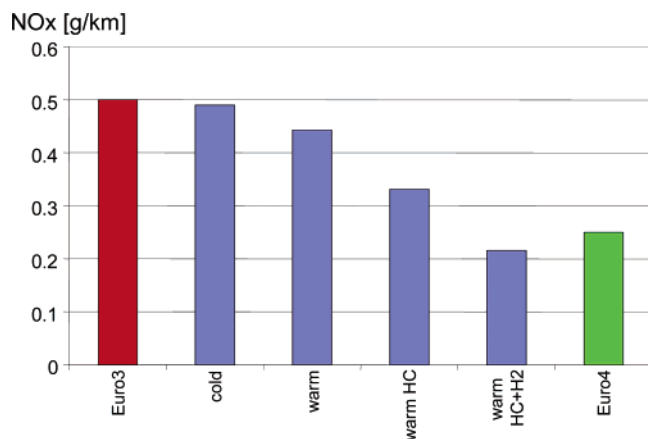
A further conclusion in ref 11 was that from the standard Gibbs free-energy relationship for the formation of silver nitrite and silver nitrate it is clear that the nitrite is thermodynamically much less stable. Therefore, if hydrogen reduces silver nitrate to the nitrite, this could spontaneously decompose, thus freeing up silver sites for the HC-SCR reaction. In line with this, Bentrup et al.<sup>21</sup> have shown that hydrogen co-fed favors the formation of reactive nitrite, nitrite, and nitro species.

Satsuma et al.<sup>22</sup> proposed that the formation of cationic Ag clusters, by the addition of a small amount of H<sub>2</sub>, drastically enhances NO reduction activity at lower temperatures for HC-SCR with light hydrocarbons over Ag/Al<sub>2</sub>O<sub>3</sub>. Shibata et al.<sup>23</sup> concluded on the basis of UV–vis and Ag *K*-edge XANES/EXAFS results that, during the NO + C<sub>3</sub>H<sub>8</sub> + O<sub>2</sub> + H<sub>2</sub> reaction over Ag zeolites at 573 K, part of the Ag<sup>+</sup> ions are converted to Ag<sup>δ+</sup> clusters, whose average structure can be close to Ag<sub>4</sub><sup>2+</sup>.

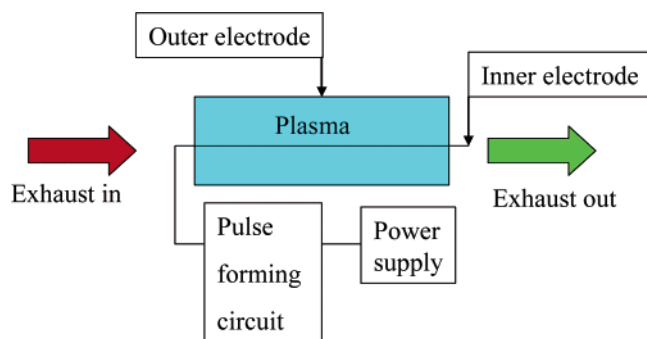
Although Wicterlová et al.,<sup>24</sup> Sazama et al.,<sup>25</sup> and Breen et al.<sup>26</sup> have shown in their recent papers that the enhanced activity from the addition of hydrogen to the NO<sub>x</sub>-SCR mixture cannot be attributed exclusively to the formation of Ag clusters, they proposed that hydrogen is rather directly involved in the reaction mechanism. Our latest kinetic studies on the hydrogen-assisted HC-SCR over Ag/alumina support the conclusions made in refs 24–26 and indicate that the role of hydrogen is to enable the hydrocarbon adsorption on the silver surface at a lower temperature than in hydrogen-free HC-SCR. The effect is thought to be due to the partial reduction of silver nitrates to metallic silver and aluminum nitrates.

The comprehensive reason for the significant boosting effect of small additions of hydrogen into the HC-SCR process is still unclear. However, because the improvement by hydrogen is so significant, the technique should be investigated on a larger scale to find out if future emission standards can be reached by it. As a matter of fact, preliminary results from H<sub>2</sub>-assisted HC-SCR in full scale were obtained during a recent research project financed by the EU (KNOWNOX).<sup>27</sup> In the steady-state mode at 260 °C, around 25% NO<sub>x</sub> conversion was recorded over the Ag/alumina converter system, when only diesel fuel (Swedish MK1) was used as the reducing agent (HC<sub>1</sub>/NO = 4.5). When 0.25% hydrogen was added to the feed, the NO<sub>x</sub> conversion rose immediately above 90%. The hydrogen effect was also investigated in European transient cycle (ETC) tests using a full-scale vehicle equipped with a Ag/alumina system. The preliminary results indicated that it is possible to convert more than 50% of the engine out of NO<sub>x</sub> emissions and meet the Euro 4 limits, in the warm-started ETC cycle, if hydrogen is added in combination with diesel fuel having a low content of sulfur (Figure 5).

Diesel fuel itself is an obvious source for hydrogen, which could be produced through reforming or partial oxidation. In this case, the need for extra storage tanks is avoided. However, the on-board production and use of hydrogen should not increase the overall fuel penalty more than 3–5%, otherwise this technique would not be



**FIGURE 5.** Vehicle tests with a Ag/alumina system from warm- and cold-started ETC tests. HC = diesel fuel (Swedish MK1 quality). From "Results from Knownox—A European cooperation project" presented at FISITA2004, Barcelona, Spain, and reproduced from ref 27 with kind permission from FISITA.



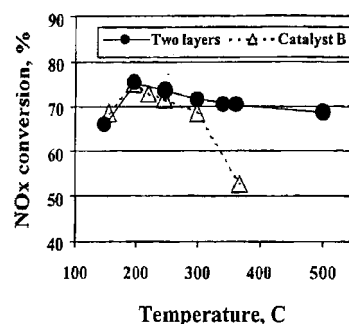
**FIGURE 6.** Simplified scheme of the NTP reactor.

competitive against urea-SCR. Therefore, the injection of hydrogen together with the fuel should be limited to the cold-start period to minimize the fuel penalty. As a summary, the H<sub>2</sub>-assisted HC-SCR technique offers a promising way to meet stricter emission limits, while the fundamental understanding of the role of hydrogen in boosting the rate of HC-SCR at low temperatures remains a challenge.

## 2.2. Nonthermal Plasma (NTP)-Assisted Catalysis.

NTP has been a proven mainstay for the "smoke stack" industry, and the challenge has been to scale down and adapt the technique to mobile units such as passenger cars and trucks.<sup>28</sup> Studies show that all electrical discharge plasma reactors produce a plasma with an electron kinetic energy of around 3–6 eV.<sup>29</sup> During plasma treatment of simulated diesel exhaust, NO is oxidized to NO<sub>2</sub> and the reactions involve N, O, OH, and HO<sub>2</sub> radicals (Figure 6). Hydrocarbons are transformed into oxygenates (mainly aldehydes), and the radicals inducing the transformation are mainly O and OH.<sup>28–31</sup> Plasma can also oxidize NO without oxidizing SO<sub>2</sub>, thus making the process tolerant against the sulfur content in the fuel.<sup>29</sup>

NTP in combination with an appropriate catalyst can provide NO<sub>x</sub> emission reduction efficiency of 60–80% from mobile or stationary sources.<sup>32</sup> Potential advantages of a plasma-catalyst after treatment system include low-temperature activity (~150 °C), a relatively wide temper-

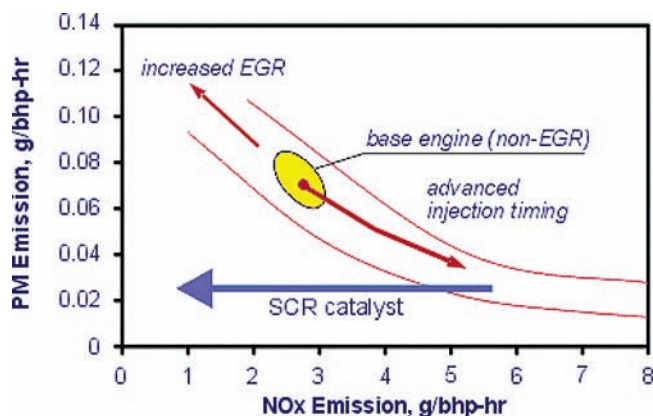


**FIGURE 7.** Temperature dependence of NO<sub>x</sub> conversion over NTP-assisted two-layer (zeolite–alumina) catalyst bed (—) and zeolite catalyst (---). NO = 200 ppm, CO = 400 ppm, C<sub>3</sub>H<sub>8</sub> = 715 ppm, O<sub>2</sub> = 8%, CO<sub>2</sub> = 7%, H<sub>2</sub>O = 2%, and N<sub>2</sub> balance. Reproduced from ref 30 with permission from SAE Paper 2000-01-2964, copyright 2000, SAE International.

ature window (150–500 °C), and the use of non-noble metal catalysts (base metal zeolite and alumina based) for the reduction of NO<sub>x</sub>.<sup>32</sup> To realize the fuel economy benefits offered by diesel and lean-burn engines, the fuel and electrical power required by a NTP system must be kept to a minimum. If too much energy is spent reducing NO<sub>x</sub> in the exhaust stream, the benefit of using such a system and a more efficient engine is diminished.<sup>31</sup>

Panov et al.<sup>30</sup> have investigated NO<sub>x</sub> reduction under simulated lean-burn conditions using a NTP in combination with a dual-bed catalyst system consisting of a zeolite and an alumina catalyst. The zeolite in combination with plasma showed high activity in the 150–300 °C region, whereas the alumina catalyst was most active at temperatures above 250 °C. The combination of the two catalysts in separate beds widened the temperature range for significant NO<sub>x</sub> removal to 150–500 °C (Figure 7).<sup>30</sup> The result is especially interesting because more than 60% of NO<sub>x</sub> is removed in the whole temperature range. However, the experiments were carried out at relatively low gas hourly space velocity (GHSV) = 12 000 h<sup>-1</sup> (catalyst), which necessarily does not give the right picture of the suitability of this system in real application. In addition, the concentration of the hydrocarbon (C<sub>3</sub>H<sub>8</sub>) was fairly high (715 ppm), resulting in a HC<sub>1</sub>/NO ratio of approximately 10. This means that the fuel penalty originating from the hydrocarbon addition in combination with the plasma addition will be quite high or that the engine has to be operated in a very nonefficient manner to release such high amounts of unburned HCs. The authors<sup>30</sup> explained that the mechanism of plasma-assisted catalysis was different for the two materials. In both cases, NO was converted to NO<sub>2</sub> in the plasma reactor. However, over the zeolite catalyst, NO<sub>2</sub> was reduced by propylene, and over the alumina catalyst, the reduction agents were products formed in the plasma, possibly formaldehyde.<sup>30</sup>

In another study,<sup>28</sup> a two-stage system with a unique NTP reactor combined with a zeolite-based catalyst was shown to work over a broad range of temperatures. Exhaust from a 2.0 L Opel direct injection (DI) diesel engine was treated, and at least 60% NO<sub>x</sub> conversion



**FIGURE 8.** Emission strategy for SCR systems. Reproduced from ref 35 with kind permission from DieselNet.com.

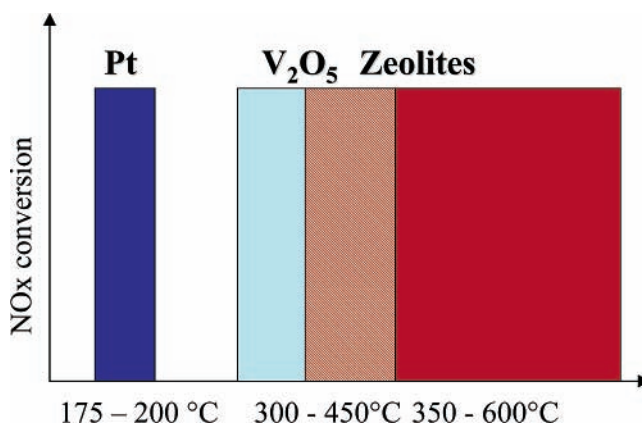
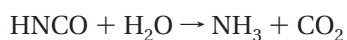
efficiency was reached at idle using a slipstream device. In addition a larger device, treating the entire exhaust, was shown to occur in similar results. It is worth mentioning that these results were obtained without the addition of reductants into the exhaust gas, when operated at the proper power level.

It can be concluded that NTP alone will unlikely be a commercialized technique for NO<sub>x</sub> controlling in real applications, but in combination with a suitable catalyst, it is a promising technique to achieve high activity in NO<sub>x</sub> removal already at temperatures around 150 °C. To implement such systems into full-scale vehicles, one needs to evaluate the impact of the power generated in the plasma in combination with HC addition on the total fuel consumption.

### 3. Ammonia/Urea-SCR

Selective catalytic reduction by ammonia, commonly referred to as SCR, is a well-developed and proven technique in industrial stationary applications since the 1970s. SCR is widely considered as the only technique to meet future emission standards in mobile applications. For obvious reasons, it would not be possible to use NH<sub>3</sub> as a selective reductant on a lean-burn gasoline- or diesel-powered car, i.e., it is corrosive, toxic, a primary and secondary pollutant, and a gas difficult to handle (except aqueous ammonia).<sup>33</sup> Therefore, urea-SCR has been selected as the choice for meeting both the Euro IV (2005) and Euro V (2008) limits of 3.5 and 2 g/kWh, respectively, for heavy-duty trucks and bus engines.<sup>34</sup> The most attractive emission strategy when using SCR involves a calibration of the engine for low particulate matters (PMs) and using the SCR catalyst to reduce the increased NO<sub>x</sub> (Figure 8). Such an approach brings benefits in the fuel economy in comparison to the competing exhaust gas recirculation (EGR) technique.<sup>35</sup>

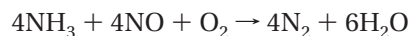
Aqueous urea solution hydrolyses easily at relatively low temperatures to NH<sub>3</sub> (via formation of HCNO) as follows:<sup>34</sup>



**FIGURE 9.** Main working temperatures for a different urea-SCR catalyst for vehicle applications.

However, the U.S. clean air authorities have voiced concerns about the SCR technology. From the regulatory perspective, SCR poses enforcement problems, both in terms of ensuring that the reductant (urea) is available together with diesel fuel throughout the nationwide distribution network and that it is always timely replenished by vehicle operators.<sup>35</sup>

NO<sub>x</sub> in diesel exhaust is mainly composed of NO (>90%), which means that the main reaction of SCR with ammonia will be<sup>34</sup>



However, the reaction rate and low temperature SCR can be significantly improved by having equimolar amounts of NO and NO<sub>2</sub> as follows:<sup>34</sup>



Therefore, the amount of NO<sub>2</sub> is in some diesel SCR systems purposely increased, e.g., with a suitable oxidation catalyst, to achieve better low-temperature activity.<sup>34</sup>

Dependent upon the conditions, SCR includes several competitive, nonselective reactions with oxygen, producing secondary emissions such as N<sub>2</sub>O, NO, NH<sub>4</sub>NO<sub>3</sub>, NH<sub>4</sub>-NO<sub>2</sub>, NH<sub>4</sub>HSO<sub>4</sub>, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.<sup>36</sup> Explosive ammonium nitrate has a tendency to form at low temperatures (100–200 °C) through a reaction between NO<sub>2</sub> and NH<sub>3</sub>. It may deposit in liquid or solid form in the pores of the catalyst, leading to its temporary deactivation.<sup>36</sup> The formation of ammonium nitrate can be avoided by making sure that the temperature stays above 200 °C or by dosing less ammonia than is stoichiometrically required. Sulfur in the diesel fuel is a source for the formation of SO<sub>2</sub> and consequently SO<sub>3</sub> during the highly oxidative conditions. A combination of SO<sub>3</sub> with NH<sub>3</sub> forms ammonium sulfates, which may foul the catalyst and cause deactivation of it.<sup>35</sup> The problem with ammonium sulfate formation is severe because it accumulates and causes irreversible damages in the catalytic units.

SCR catalysts can commonly be divided on the basis of their peak activity in (Figure 9): low-temperature (Pt; 175–250 °C), medium-temperature (V<sub>2</sub>O<sub>5</sub>; 300–450 °C), and high-temperature (zeolite; 350–600 °C) catalysts.<sup>35</sup>

Attribution of materials to different temperature regions is not rigid because additives and modifiers can significantly affect the activity region. Zeolites, for example, show high activity at low temperature when ion-exchanged with a suitable metal.<sup>35</sup> On the other hand, zeolites are known to undergo de-alumination induced by high temperatures (above 600 °C) and steam. This could hinder the implementation of them into practical SCR systems, because the regeneration of the particulate trap as well as extra urban driving conditions might give rise to elevated temperatures.

It has been demonstrated in several studies that the SCR catalyst is capable of reducing diesel NO<sub>x</sub> emissions ranging from about 55 to 90% depending upon the application and test method.<sup>35</sup> Steady-state cycles such as the ESC result in high conversion. The transient cycles on the other hand are more challenging because of the lower exhaust temperatures and problems in the urea injection strategy. In a full-scale test with a 2.5 L light-duty diesel engine, NO<sub>x</sub> conversions of up to 60% were reported on the ECE + EUDC cycle and up to 83% on the FTP-75 cycle.<sup>37</sup> However, the open-loop systems have not been able to reduce the NO<sub>x</sub> emissions to meet the USA EPA Tier 2 Bin 5 limit. It seems that for heavy-duty vehicles a closed-loop system with NO<sub>x</sub> sensors is necessary to meet the transient test cycles.<sup>35</sup>

As a summary, SCR by urea seems to be one of the best techniques to meet the future emission standards, but to be able to implement the technique into mobile vehicles, the following issues need to be solved:<sup>35</sup>

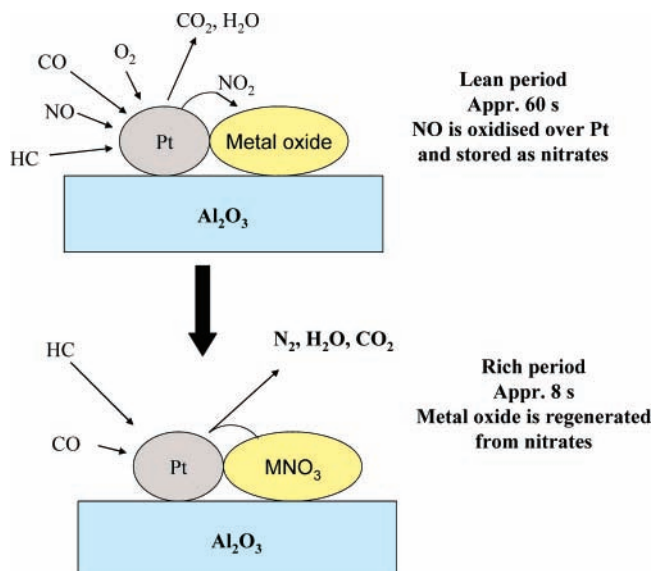
Mobile diesel engines work under highly transient conditions, which require that the catalytic-converter system should operate in a wide temperature window. Catalysts presently available cannot span such a broad temperature range. Low-temperature activity may present a problem, both in terms of NO<sub>x</sub> activity and catalyst durability (deactivation by ammonium nitrate and sulfate).

The transient operation in the engine influences the urea injection strategy as well and makes it challenging to control ammonia slip and secondary emissions. Therefore, a closed-loop NO<sub>x</sub> feedback system including NO<sub>x</sub> sensors is needed to meet the strict NO<sub>x</sub> limits.

There is apparently a lack of a urea distribution net. Another problem associated with urea is that it has a freezing point around -11 °C, which is not acceptable for winter conditions in many countries.

#### 4. NO<sub>x</sub> Adsorption

NO<sub>x</sub> adsorber catalysts operate under alternating lean and rich periods during which NO<sub>x</sub> is stored and reduced. During a long lean period (around 60 s), NO is oxidized to NO<sub>2</sub> over a suitable noble metal (Pt and/or Pd) and adsorbed as nitrates in the storage component (e.g., Ba- or Sr-containing material such as aluminate, perovskite, and zeolite).<sup>38</sup> When the catalyst is saturated, the fuel rich period (8 s) assists in decomposing the stored nitrates into nitrogen<sup>39</sup> (Figure 10). The drawback of the NO<sub>x</sub>-storage catalyst is its high affinity to sulfur compounds in the



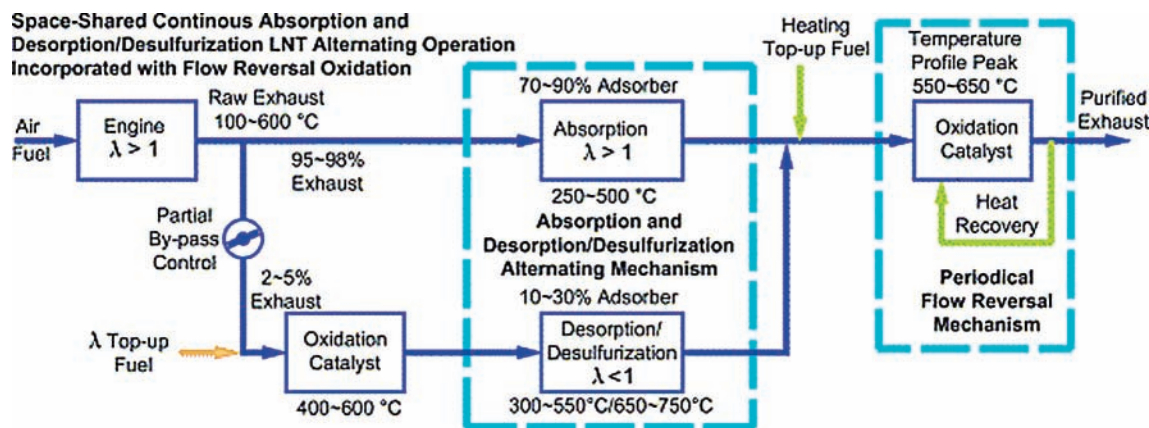
**FIGURE 10.** Simplified scheme of the NO<sub>x</sub>-storage catalyst. During the lean mode, NO is oxidized to NO<sub>2</sub> and stored as nitrates on the metal oxide parallel to CO and HC oxidation. During the rich mode, nitrates are reduced by hydrocarbons over the noble metal.

exhaust. SO<sub>2</sub> in the flue gas is converted to sulfates on the adsorber material via an analogous mechanism to NO<sub>x</sub> storage. The SO<sub>3</sub> is preferentially adsorbed rather than NO<sub>2</sub>, because of the higher thermodynamic stability of sulfate species compared to corresponding nitrates. A higher temperature is required for decomposing the sulfates than the nitrates, which means that sulfur effectively blocks the sites on the catalyst.<sup>39</sup> Rohr et al.<sup>40</sup> have shown that desulfation at 700 °C on a synthetic gas bench leads to a removal of 50% of the sulfur. The residual sulfur is evenly distributed along the length of the catalyst compared to the sulfur profile in the sulfated catalyst.

Recent work on NO<sub>x</sub>-storage catalysts suggest that the storage function and the oxidation of NO to NO<sub>2</sub> should be separated.<sup>41</sup> The oxidation of NO to NO<sub>2</sub> is slow at low temperatures on the adsorber catalyst and can be significantly accelerated on a separated specially designed oxidation catalyst.

An important parameter in the NO<sub>x</sub>-storage system is the length of the rich cycle. In ref 39, it was demonstrated that over 90% NO<sub>x</sub> conversion can be reached at 300 °C over an oxidation catalyst combined with the NO<sub>x</sub>-adsorber catalyst, if a rich period of 8 s (60 s lean) was applied. In the same study, it was discussed that, at lower temperatures, the lower NO<sub>x</sub> mass flow would enable shorter regeneration periods, resulting in greater fuel efficiency. Improving the adsorption capacity is the fundamental issue to be solved for making the NO<sub>x</sub>-storage technique economically more competitive.

Sulfur poisoning and thermal aging are unavoidable factors contributing to deactivation of NO<sub>x</sub>-storage systems. The sensitivity for sulfur poisoning varies greatly depending upon the formulation of the catalyst and is in most cases reversible. However, the thermal deactivation is permanent regardless of its cause, i.e., desulfation or diesel particulate filter regeneration.<sup>42</sup> In ref 39, it was



**FIGURE 11.** Novel arrangement for a lean NO<sub>x</sub> storage system. Reproduced from ref 1 with kind permission from Elsevier.

demonstrated that a state-of-the-art NO<sub>x</sub>-adsorber catalyst, which was subjected to a simulated sulfation/desulfation procedure corresponding to a 160 000 km road travel, still removed close to 70% of the NO<sub>x</sub> emissions at 280 °C. The NO<sub>x</sub> conversion of the fresh catalyst was slightly above 70%. Such results demonstrate the possibility of NO<sub>x</sub>-storage catalysts to operate efficiently in a modern diesel vehicle without the risk for severe deactivation/poisoning. In the same study, it was proposed that a NO<sub>x</sub>-adsorber catalyst can be combined with a diesel particulate filter according to a patent by Brisley et al.<sup>43</sup> The system, also called four-way emissions control technology, was shown to reduce NO<sub>x</sub> and PM by 80%.

To sum up, a NO<sub>x</sub>-storage catalyst combined with particulate filters shows a potential to reduce NO<sub>x</sub> emissions to a great extent in future test cycles. The drawback still is their sensitiveness for sulfur poisoning requiring desulfation at elevated temperatures and hereby causing possible thermal deactivation. Because the levels of sulfur are to be reduced in future diesel fuels, the interest to implement NO<sub>x</sub> adsorption catalysts in diesel-powered vehicles will rise. A question mark is also the activity of NO<sub>x</sub> adsorption catalysts at low temperatures, which are present in modern test cycles during the urban driving conditions. Most of the reports on NO<sub>x</sub>-storage catalysts show NO<sub>x</sub> removal activity starting at around 200 °C. However, as was discussed also above, the mass flow of NO<sub>x</sub> is quite small at low load and speed (low temperature), resulting in longer adsorption periods and shorter regeneration.

## 5. Reactor Modifications

The efficiency of diesel after treatment systems can be significantly improved by means of periodic switching, reactor modifications, and active thermal management.<sup>1,7,44</sup> In ref 1, a novel arrangement for a lean NO<sub>x</sub>-storage system was considered according to Figure 11. The system utilizes the flow through the structure of a monolith to divide the exhaust flow into two streams, and the smaller stream is enriched with a secondary fuel. A rotating catalytic cartridge or a rotating exhaust gas divider can be configured as an embedment. In addition, the system involves a periodic flow reversal control, which cyclically

alternates the direction of the exhaust flow and hereby produces a thermal wave along the catalyst.<sup>1</sup> A similar flow reversal approach has been suggested by Jirat et al.,<sup>44</sup> in which they showed that periodic switching helped to create a temperature window for the NO reduction. The proposed active after treatment system (Figure 11) has the potential to be more energy-efficient because of two aspects: the partially restricted flow saves supplemental energy during regeneration/desulfurization and the periodic flow reversal for exhaust energy recovery during oxidation.

In our recent work,<sup>45</sup> we showed that by dividing a Ag/alumina single bed into four layers (cascade reactor), with intermediate spacing in between, the NO<sub>x</sub> to N<sub>2</sub> activity was significantly improved at lower temperatures. The reason for the improved conversion was attributed to the longer residence time in the cascade reactor, enabling important heterogeneously mediated gas-phase reactions to take place. In the same study,<sup>45</sup> the experimental results recorded over single and cascade Ag/alumina catalysts were investigated by means of neural network modeling.

As a continuation of the work presented in ref 45, we showed that, when a Ag/alumina and Cu-ZSM-5 catalyst were combined, the low temperature activity was significantly improved over the cascade system.<sup>46</sup> Moreover, it was demonstrated that the improved activity was not just because of combining these two catalysts together but because of the synergetic reaction mechanism.

Reactor optimization and modification does not alone help to solve problems associated with less than required catalytic activity at low temperatures. However, they are essential in combination with the development of new diesel catalysts to have a complete converter system, which takes into account several aspects such as energy efficiency, mass transfer limitations, regeneration, deactivation, gas-phase reactions, etc. Using, for example, the flow reversal approach, one may gain the needed 50 °C temperature to meet emission limits at low temperatures.

## 6. Conclusions

The potential of different catalytic after treatment techniques to meet future diesel emission standards, which are strongly shifted toward urban driving conditions



including cold start, was discussed. The dominating techniques in this field are NO<sub>x</sub> storage, urea-SCR, and HC-SCR. Besides several advantages, each of these techniques have significant drawbacks, such as sulfur sensitivity and regeneration requirements of NO<sub>x</sub>-storage materials, infrastructure issues and formation of explosive ammonium nitrate (at low temperatures) for urea-SCR, and low-temperature activity of HC-SCR catalysts. Ways to overcome these disadvantages and meeting the future emission limits seem to involve optimized regeneration strategies, reactor modifications, flow reversal, closed-loop NO<sub>x</sub> feedback systems, NTP, and/or hydrogen-assisted catalysis, among others. The challenge is to find new materials (catalysts) and systems, which are able to effectively remove NO<sub>x</sub> emissions at low temperatures (<150 °C) without sacrificing too much of the efficiency of the modern diesel engine.

*The financial support from the European Union through the Ammonore project (GRD-CT 2001-00595) and from the National Graduate School of Materials Research is gratefully acknowledged. This work is part of the activities at the Åbo Akademi Process Chemistry Centre within the Finnish Centre of Excellence Programmes (2000–2011) by the Academy of Finland.*

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AR050185K