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Catalysis Today 59 (2000) 335–345

CATALYSIS TODAY

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Urea-SCR: a promising technique to reduce NO_x emissions from automotive diesel engines

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Abstract

Urea-SCR, the selective catalytic reduction using urea as reducing agent, has been investigated for about 10 years in detail and today is a well established technique for $DeNO_x$ of stationary diesel engines. It is presently also considered as the most promising way to diminish NO_x emissions originating from heavy duty vehicles, especially trucks.

The paper discusses the fundamental problems and challenges if urea-SCR is extended to mobile applications. The major goal is the reduction of the required catalyst volume while still maintaining a high selectivity for the SCR reaction over a wide temperature range. The much shorter residence time of the exhaust gas in the catalyst will lead to higher secondary emissions of ammonia and isocyanic acid originating from the reducing agent. Additional problems include the control strategy for urea dosing, the high freezing point of urea, and the long term stability of the catalyst.

Keywords: Urea-SCR; NO_x emissions; Diesel engines

1. Introduction

Forthcoming European legislation pertaining to heavy duty diesel engines aims at the simultaneous reduction of the emissions of particles and NO_x. It is generally assumed that the EURO 4 emission standards proposed for the year 2005 will be no longer feasible by primary measures but will require additional exhaust gas after treatment techniques.

Urea-SCR, the selective catalytic reduction using urea as reducing agent, has been investigated in detail for about 10 years and today is a well established technique for $DeNO_x$ of stationary diesel engines [1,2]. It is presently considered as the most promising way to diminish NO_x emissions originating from heavy duty vehicles, especially trucks [3]. In the following we will discuss some challenges and selected problems that arise if the SCR process will be adopted to mobile diesel engines.

2. Main SCR reactions with ammonia

NO_x in diesel exhaust is usually composed of >90% NO. Therefore, the main reaction of SCR with ammonia will be

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \quad (1)$$

This reaction implies a 1:1 stoichiometry for NH_3 and NO and the consumption of some oxygen. The reaction consuming no oxygen is much slower and is therefore not relevant in lean combustion gases:

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O \quad (2)$$

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0920-5861/00/$ – see front matter
PII: S0920-5861(00)00299-6

On the other hand, the reaction rate with equimolar amounts of NO and NO_2 is much faster than that of the main reaction (1):

$$4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O \qquad (3)$$

It should be mentioned that the reaction with pure NO_2 is again slower than reactions (1) and (3):

$$4NH_3 + 3NO_2 \rightarrow \tfrac{7}{2}N_2 + 6H_2O \qquad (4)$$

At high temperatures (>400°C) the commonly used catalysts based on TiO_2–WO_3–V_2O_5 tend to form nitrous oxide. One of the possible reactions leading to nitrous oxide is

$$4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O \qquad (5)$$

At still higher temperatures, ammonia may be oxidized to NO, thus limiting the maximum NO_x conversion:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (6)$$

3. Basic requirements for a mobile DeNO$_x$ system

A stationary diesel engine is operated at constant (usually full) load and there is no restriction concerning the size of the SCR catalyst. Therefore, the SCR catalyst is usually generously sized. This allows to attain very high values of NO_x reduction (DeNO$_x$) at very low ammonia slip. It should be emphasized here that a high DeNO$_x$ alone is of no practical value if the ammonia slip is high. High values of ammonia slip will result if the catalyst is not generously sized and if the stoichiometric ratio $\alpha = NH_3/NO_x$ is too high.

The requirements for a mobile diesel engine in a car or truck are different. Firstly, load and engine speed will vary often and abruptly, and this will cause permanent changes of flow and temperature of the exhaust gas. A sophisticated control for the dosage of the reducing agent will be therefore necessary. Moreover, the space occupied by a mobile DeNO$_x$ system is very limited. This space is mainly given by the catalyst volume which becomes decisive at low loads/temperatures as the kinetic rate constants diminish.

4. Problems and challenges

4.1. Reduced catalyst volumes of selective catalysts

Typical space velocities GHSV in three-way catalysts (spark-ignited engines) amount to ≈100 000 h^{-1}. Correspondingly, the necessary catalyst volume will be of the order of the engine cylinder volume. On the other hand, typical space velocities in stationary SCR catalysts are only of the order of 10 000 h^{-1}. The problem of necessary catalyst size is further aggravated by two unfavorable features of the diesel engine: (a) the widely varying exhaust gas temperatures and (b) the diesel process is operated always under excess stoichiometric air, thus leading to larger exhaust volume flows than the Otto process (gasoline engine).

Fig. 1 shows the temperatures and the exhaust gas flows for a turbocharged diesel engine with an intercooler of 6.6 l cylinder volume at 1500 rpm. It is seen that the temperatures vary from 200 to 535°C for a load range of 10–100 kW corresponding roughly to 10–100%. This range will further widen to about 100–650°C if lower loads and higher rpm are taken into consideration. The corresponding exhaust flows are 420 m_N^3/h at 100% load and 240 m_N^3/h at 10%.

If a mobile diesel engine is to be equipped with an SCR system, space velocities much higher than 10 000 h^{-1} must be achieved. Therefore, the volumetric activity of the catalysts must be improved and this may be realized by the following means:

(a) *Increase the intrinsic activity of the SCR catalyst*. If a high selectivity for N_2-formation is to be kept, i.e. little formation of N_2O and NO_x at higher temperatures, the standard SCR catalyst systems based on TiO_2–WO_3–V_2O_5 or TiO_2–MoO_3–V_2O_5 are still the systems of choice. Their drawback is a limited activity, which is especially evident at the lowest loads/exhaust temperatures of the engine. The concentration of vanadia may be increased to boost the intrinsic activity, but concentrations above ≈3% will lead to a loss of selectivity of these catalysts.

(b) *Increase of the cell density of the monolith*. This will cause an increase of the geometric surface-to-volume ratio of the catalysts. For example, going from a cell density of 36 to 300 cpsi is accompanied by an increase of the volumetric surface from ≈770 to ≈2200 m^2/m^3. SCR extruded catalysts based on TiO_2–WO_3–V_2O_5 with cell densities up to 300 cpsi

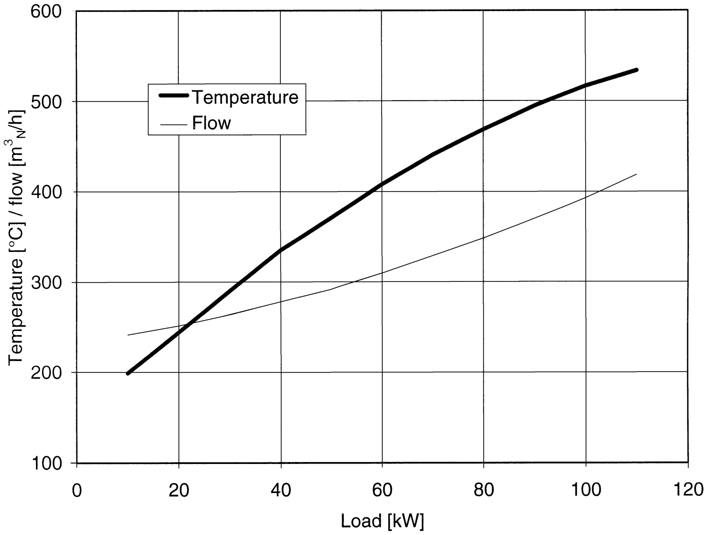

Fig. 1. Typical exhaust temperatures and flows (humid) for a 6.6 l turbocharged diesel engine with intercooler at 1500 rpm.

have been developed recently by some manufacturers. Still higher cell densities can be realized by coating techniques using cordierite or metallic substrates [4]. This is due to the fact that cordierite or metal foils have much better mechanical properties and therefore allow thinner walls of the monolith. In extruded catalysts, the entire wall consists of TiO_2–WO_3–V_2O_5 plus admixtures of binders and glass fibers to increase the mechanical properties.

This measure will be especially effective at high temperatures, where the SCR reaction proceeds mainly in the top layer of the catalyst. This has been shown in previous work, where the performance of SCR catalysts has been calculated for various conditions [5]. Fig. 2 shows the relative concentration profile of NO and NH_3 in the wall of a 200 cpsi extruded catalyst at 250 and 450°C. It is evident that the reaction takes place mainly in the top layer of the catalyst at 450°C. This is no longer true at 250°C: At this temperature, even in the center of the wall (x=200 μm), the relative concentration of NO or NH_3 still amounts to ≈0.5. We can further see that due to the much higher reaction rates at 450°C the mass transfer resistance is important at 450°C but negligible at 250°C (relative concentrations at x=0 are ≈0.8 and ≈0.97, respectively). Therefore, an increased geometric surface per volume will be especially effective at higher temperatures. Because at 450°C the deeper layers of the catalyst have almost no contribution to the SCR reaction, an extruded and a thinly coated catalyst will be practically equally effective. This is no longer true at low temperatures, where the deeper layers of the catalyst contribute to the SCR reaction and therefore increase the SCR performance.

(c) *Make use of the increased reaction rate of reaction* (3). This may be achieved by increasing the fraction of NO_2 in the exhaust. Figs. 3 and 4 compare the performance of catalyst K51 under identical conditions with NO and with a 1:1 mixture of NO+NO_2. Because practically no oxidation of ammonia is observed the NH_3/NO_x inlet ratio α is given by $DeNO_x/100$ at low values of ammonia slip. Catalyst K51 is a coated type with 370 cpsi developed in our laboratory [4]. The tests were performed at a GHSV=52 000 h^{-1} and the test gas further contained 5% H_2O, 10% O_2 and varying amounts of NH_3, balance N_2. Comparing the results for 10 ppm NH_3 slip at 200°C, only ≈21% $DeNO_x$ are obtained with pure NO but ≈93% with the NO–NO_2 mixture. The mixture even allows to work at 150°C where still a $DeNO_x$ of ≈43% is obtained.

The fraction of NO_2 in a typical diesel exhaust amounts to 5–10% only. This fraction may be increased by passing the gas over a strong oxidation catalyst containing platinum as the active component. However, it is difficult to obtain useful fractions of

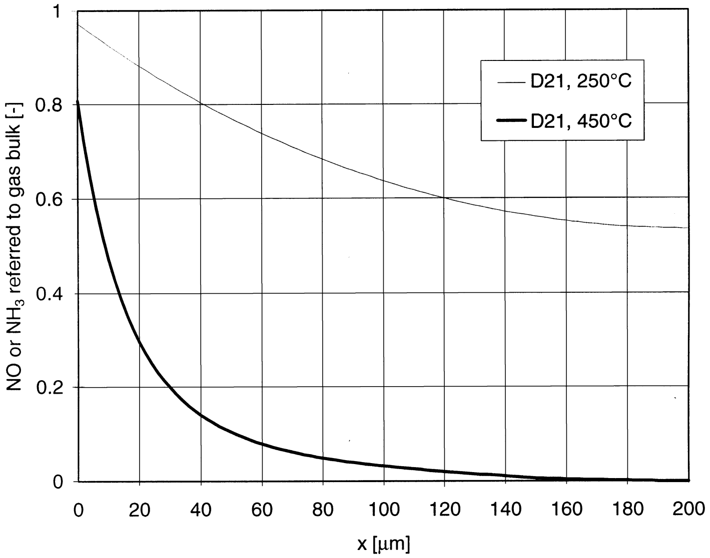

Fig. 2. Calculated concentration profiles at 250 and 450°C in the catalyst wall of a 200 cpsi extruded catalyst at GHSV=25 000 h^{-1} and 1000 ppm each of NO and NH_3.

NO_2 at temperatures below 200°C at high space velocities. Therefore, there is considerable interest in improving the oxidation activity of such pre-catalysts. Due to the thermodynamic equilibrium the possible NO_2 fraction is limited at higher temperatures (Fig. 5). This thermodynamic limitation is useful because the oxidation rate of NO increases with rising temperature and because NO_2 fractions above 50% will lead to a decrease of the reaction rate of the SCR reaction due to the low rate of reaction (4).

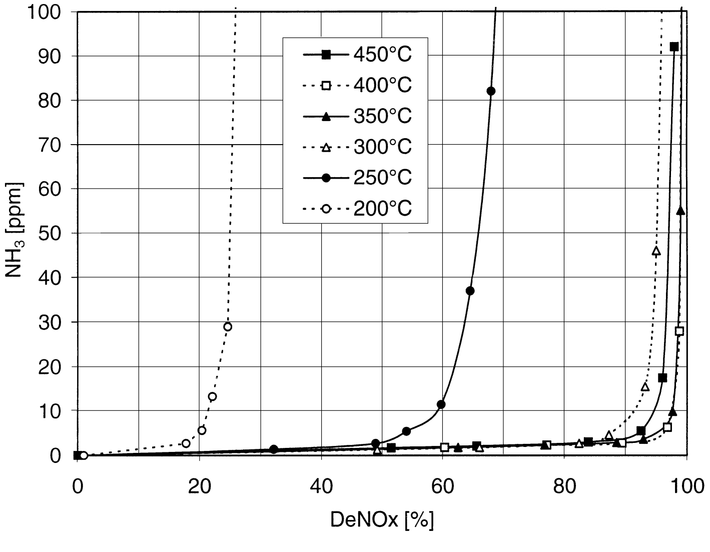

Fig. 3. Performance of the coated SCR catalyst K51 in pure NO. GHSV=52 000 h^{-1}.

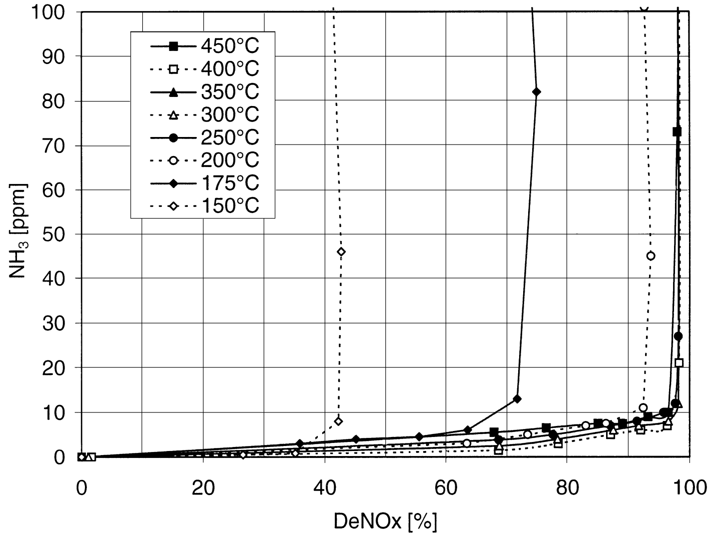

Fig. 4. Performance of the coated SCR catalyst K51 in a 1:1 mixture $NO+NO_2$. GHSV=52 000 h^{-1}.

4.2. *Reactions of urea: generation of the SCR reactive reducing agent NH_3*

For reasons of safety and toxicity, urea is the preferred selective reducing agent for mobile SCR applications. If urea is used instead of ammonia the $DeNO_x$ chemistry involves isocyanic acid as an important intermediate which will lead to a complication of the SCR chemistry.

Urea is usually applied in urea-SCR as an aqueous solution. If this solution is atomized into the hot exhaust gas stream the first step is the evaporation of water from the droplets, thus leading to solid or molten urea:

$$NH_2\text{–CO–}NH_2(\text{aqueous}) \rightarrow NH_2\text{–CO–}NH_2(\text{solid}) + x\,H_2O(\text{gas}) \quad (7)$$

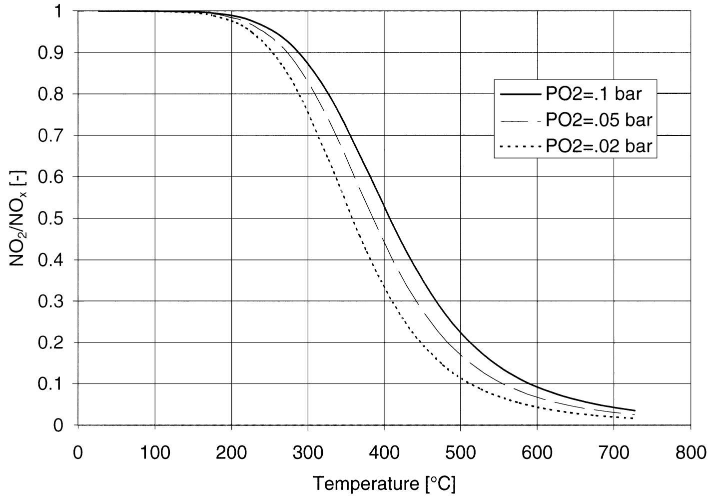

Fig. 5. Thermodynamic equilibrium of the reaction $NO+\frac{1}{2}O_2 \rightarrow NO_2$ for oxygen partial pressures of 0.1, 0.05 and 0.02 bar.

Pure urea will then heat up and decompose thermally according to

$$\mathrm{NH_2{-}CO{-}NH_2(solid)} \rightarrow \mathrm{NH_3(gas)} + \mathrm{HNCO(gas)}, \quad \Delta H^{298} = 186\,\mathrm{kJ} \tag{8}$$

Equimolar amounts of ammonia and isocyanic acid are thus formed. Isocyanic acid is very stable in the gas phase, but hydrolyzes easily on many solid oxides with water vapor originating from the combustion process:

$$\mathrm{HNCO(gas)} + \mathrm{H_2O(gas)} \rightarrow \mathrm{NH_3(gas)} + \mathrm{CO_2(gas)}, \quad \Delta H^{298} = -96\,\mathrm{kJ} \tag{9}$$

SCR catalysts are also effective for this reaction. Reactions (7) and (8) are endothermic and can occur already in the gas phase ahead of the catalyst. The hydrolytic reaction (9) is exothermic and will proceed on the SCR catalyst itself.

We have shown that the rate of HNCO hydrolysis is much higher than the rate of the SCR reaction at low to medium temperatures on the usual SCR catalysts [6,7]. Therefore, we believe that NH_3 is the active reducing agent also in the case where urea is the reducing agent.

In order to speed up the thermohydrolytic decomposition of urea the use of a hydrolyzing catalyst in front of the SCR catalyst has been proposed [8]. However, the hydrolysis of HNCO is not the only reaction contributing to the delayed liberation of ammonia, but all three reactions require additional time. A mobile SCR system will have only a short distance between the engine exhaust (where urea may be injected) and the catalyst entrance. This leads to short residence times of urea in this section and therefore steps (7) and (8) will not be completed at the catalyst entrance. As a result, a mixture of NH_3, HNCO and urea will be fed to the catalyst. Fig. 6 shows the relative amounts of these

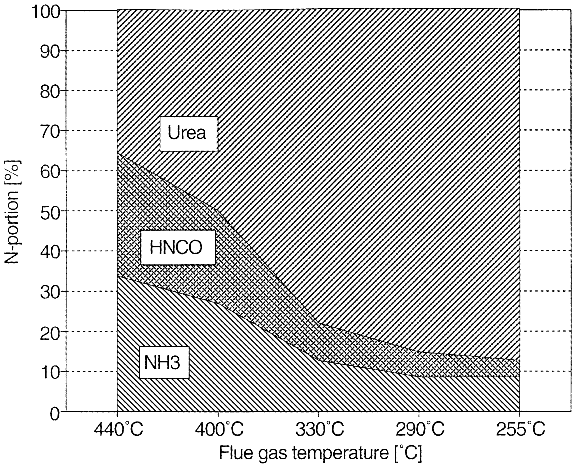

Fig. 6. Ammonia, isocyanic acid and urea at various temperatures at the catalyst entrance. Residence time urea injection — catalyst entrance=0.09 s at 440°C.

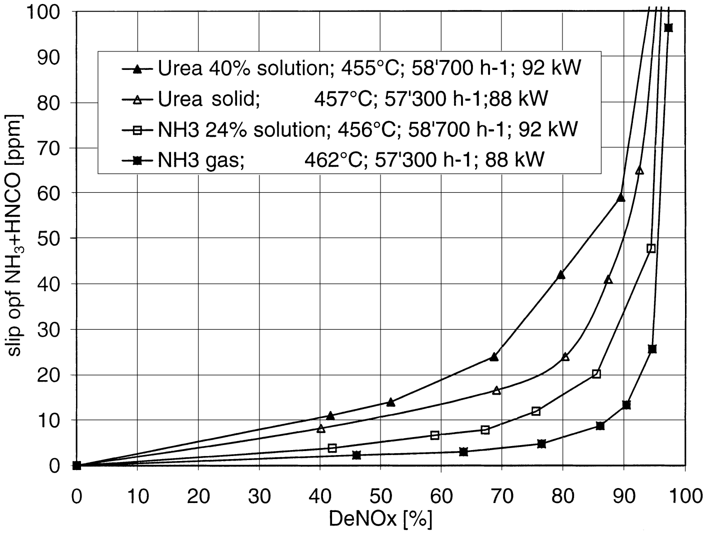

Fig. 7. Performance of coated catalyst K53 with various reducing agents at 460°C.

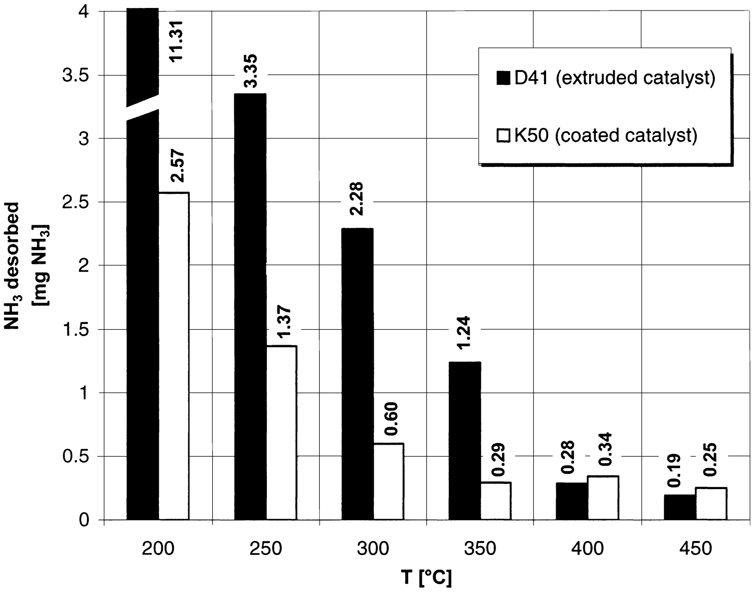

Fig. 8. Comparison of the total ammonia adsorption of coated catalyst K50 and extruded catalyst D41 under SCR conditions: $c(NH_{3,in})=c(NO_{in})=1000$ ppm. Catalyst volume=7 cm^3.

three components at the catalyst entrance measured in a typical experiment on the diesel test stand at PSI.

The delayed liberation of ammonia will cause a loss of SCR performance compared to the use of ammonia. This effect is particularly pronounced at high space velocities and at high temperatures as shown in Fig. 7 for various reducing agents at 460°C: the best performance is obtained with gaseous ammonia, followed by ammonia solution, solid urea, and urea solution. It is evident that ammonia outperforms urea.

It should be further mentioned that aiming at compact DeNO$_x$ systems will lead to short residence times ahead of the SCR catalyst. This causes considerable mixing problems for NO$_x$ with the reducing agent. The mixing problem is further aggravated if an additional pre-catalyst for oxidizing NO is used. In this case urea can only be injected after the oxidation catalyst leading to even shorter mixing and residence times.

4.3. Minimizing ammonia slip

When urea is used as reducing agent the main emission is still ammonia. Because exhaust gas temperatures may vary from ≈100°C at idle up to ≈650°C at full load the catalyst temperature will vary correspondingly and this leads to varying amounts of ammonia adsorbed on the catalyst.

Typical NH_3 adsorption capacities for an extruded and a coated catalyst are shown in Fig. 8. These values were determined under laboratory conditions for an identical catalyst volume of 7 cm^3. It can be seen that the quantity of adsorbed ammonia decreases strongly with temperature. The extruded catalyst adsorbs much higher quantities than the coated catalyst due to the fact of having about five times more active mass. Due to the method of determination, i.e. under SCR conditions with NO present, this expected difference is only visible at low temperature. For further details the reader is referred to a separate publication on the subject of ammonia adsorption [9].

Fig. 9 shows the effect of a fast load increase in a diesel test stand experiment. A considerable ammonia peak is obtained if the dosage of urea is increased abruptly with load. Much better results are obtained if the actual catalyst activity is taken into account, i.e. the actual catalyst temperature. Still better results are possible by a closed feedback control. In the present example the slip of NH_3 was measured and taken as the controlling parameter.

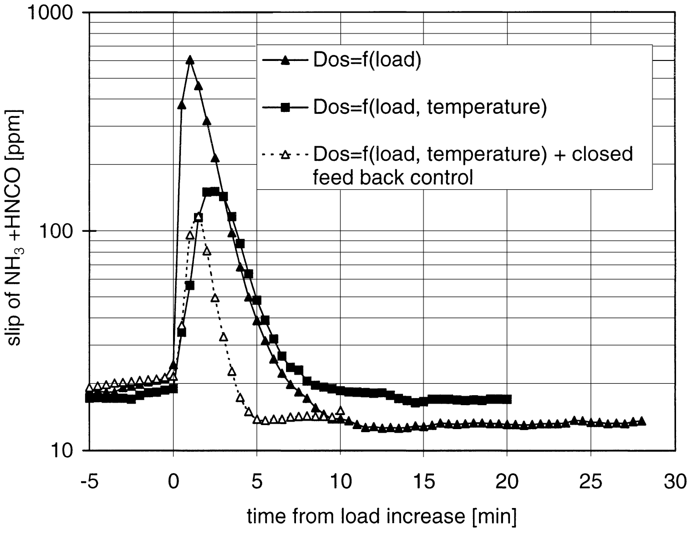

Fig. 9. Load increase 25→75 kW corresponding to a temperature increase 230→400°C. Effect of varying dosing strategies.

Summarizing, we may say that the following measures can reduce these ammonia peaks and consequently the total ammonia emission in a test cycle:

(a) *The use of coated instead of extruded catalysts* (*less active mass/catalyst volume*). The disadvantage of such catalysts will be a reduced performance at lower temperatures. Extruded catalysts possess more active mass/volume, which contributes to performance at lower temperatures.

(b) *Use of an optimized dosing strategy*. The dosing rate of urea should not only be governed by the actual mass flow of NO_x, but should at least take into account the actual catalyst activity which is determined mainly by its actual temperature.

(c) *The addition of an oxidation catalyst downstream of the SCR catalyst will oxidize any surplus* NH_3. Hug et al. [1] have described such a two-catalyst system for off-highway exhaust gas after treatment. An oxidation catalyst is also used in the so-called “VHRO-system” discussed by Jacob [10]. In addition to increasing the costs of the system, selective and highly active selective catalytic oxidation (SCO) catalysts (SCO to N_2) are not known at the present time. The most active types are again based on Pt metals. Their oxidation activity is strongly dependent on temperature requiring relatively large volumes for ammonia oxidation below 250°C. At rising temperatures their oxidation power increases and this leads to the formation of N_2O and NO. Especially undesired is their strong tendency to form N_2O at intermediate temperatures (250–300°C) if the gas coming from the SCR catalyst also contains unreacted NO which allows for reaction (5).

4.4. Other difficulties related to the use of urea

Urea is generally considered to be the safest and least toxic selective reducing agent. The main problems caused by its decomposition chemistry have been outlined above. In a recent study the properties of four selective reducing agents have been compared: pure ammonia, ammonia solution, urea solution and ammonium carbamate [11]. According to this study urea also has some disadvantages:

(a) *Emission of isocyanic acid*. As mentioned in Section 4.2 the emission of isocyanic acid may be considerable at very low and at very high temperatures (typically up to 50 ppm at high α values). No detailed information on the toxicity of HNCO could be found. However, the fact that organic isocyanates have become well known for inducing hyperreactive respiratory diseases in recent years (see e.g. [12]) calls for investigation of possible physiological effects of HNCO.

(b) *The high freezing point of aqueous urea solutions*. The proposed eutectic solution has a concentration of 32.5% urea and a freezing point of only −11°C. This poses technical problems in winter use. It has therefore been suggested to use solid urea. However, the use of solid urea will require a dosing unit for solid urea which is an expensive and critical component. Further, the introduction of solid urea into the exhaust gas stream and the mixing operation are far more difficult to achieve than with urea solution.

(c) *Possible formation of high molecular weight products*. The isocyanic acid formed as an intermediate may react with urea or with itself and lead to higher products like biuret, melamine, cyanuric acid, etc. This problem has been carefully studied earlier due to possible clogging of atomizing nozzles and deposit formation in the flue gas duct. It can be handled technically and the secondary emission of higher products is very small [2].

4.5. Long term stability of SCR catalysts

SCR catalysts based on the ternary system TiO_2–WO_3–V_2O_5 are presently the preferred type for mobile SCR. This system is resistant to sulfur oxides originating from fuel sulfur. At temperatures below 250°C some deactivation due to condensation of ammonium sulfate may be observed. This deactivation is reversible if the catalyst is operated again at higher temperatures.

A more serious problem is the sensitivity of these catalysts to basic compounds and to phosphorous. Both are present in the usual motor oil formulations: ZDDP, the very common antiwear booster, contains both Zn and P. An alkalinity reserve is usually provided by the addition of soaps of alkaline earth metals. Tests over 1000 h on the PSI diesel test stand have therefore shown a considerable drop in SCR performance. Fig. 10 shows the performance of the extruded catalyst D41 on the diesel test stand after 100 and 1000 h, i.e. the slip of NH_3 or (NH_3+HNCO) as a function of NO_x conversion. Because the increase of (NH_3+HNCO) with aging is much more pronounced than the increase of NH_3 slip alone, we may conclude that the hydrolyzing activity has degraded more than the SCR activity. The loss in hydrolyzing activity is especially pronounced at the highest temperature.

Finally, high temperature stability is also important. The catalysts usually stand up temperatures up to 600°C, but above this temperature deactivation becomes possible. This is mainly due to the phase transformation of TiO_2 (anatase) into TiO_2 (rutile) and consequent loss of BET surface. On the other hand, exhaust temperatures may go up to 700°C at very high power output. Such operating conditions are certainly rare and only of short duration. Nevertheless, optimizing high temperature stability of the catalysts still remains a goal in catalyst development.

5. Outlook

Urea-SCR has high potential for the application in diesel driven vehicles. The main emphasis is presently put on the development of systems for heavy duty vehicles, especially trucks. In the case of diesel passenger cars the requirement of an additional reagent (urea) will hardly be accepted by the consumers and the average exhaust temperatures in a typical test cycle are so low that only modest reductions of NO_x are feasible. In the case of the diesel passenger car the NO_x storage-reduction catalyst could be a more convenient choice.

Siemens has developed the $SINO_x$-system [3]. A number of these systems have been tested by trucking companies since 1996. The present development aims at reducing the size of the system and the series introduction for heavy duty vehicles is planned for the year 2000 [13]. This system uses a single SCR catalyst of the extruded type.

A much more sophisticated system has been proposed by MAN [10]. The “VHRO-system” (Fig. 11) uses a structured catalyst consisting of four catalytic sections optimized for the various reactions:

Vorkat (pre-catalyst, NO oxidation)

$$NO+\tfrac{1}{2}O_2 \rightarrow NO_2 \qquad (10)$$

H-Kat (hydrolyzing or urea catalyst)

$$NH_2\text{–}CO\text{–}NH_2 + H_2O \rightarrow 2NH_3 + CO_2 \qquad (11)$$

$$NH_2\text{–}CO\text{–}NH_2 + NO + NO_2 \rightarrow 2N_2 + CO_2 + 2H_2O \qquad (12)$$

R-Kat (reducing, i.e. SCR catalyst)

$$2NH_3+2NO+\tfrac{1}{2}O_2 \rightarrow 2N_2 + 3H_2O \qquad (13)$$

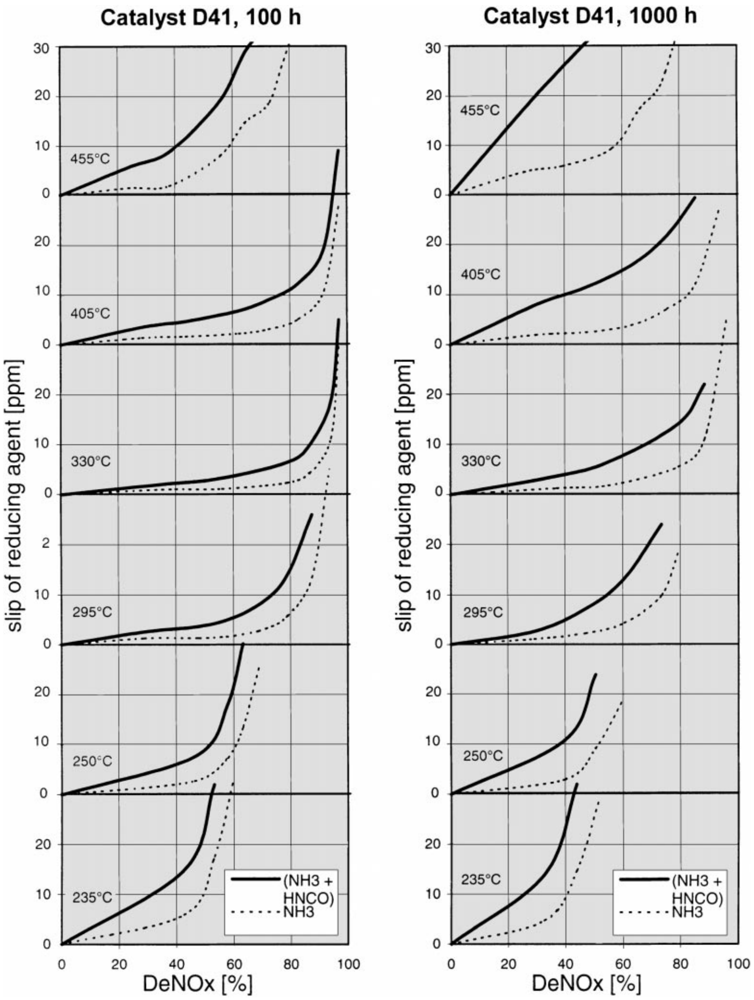

Fig. 10. Performance of catalyst D41 after 100 and 1000 h at various temperatures.

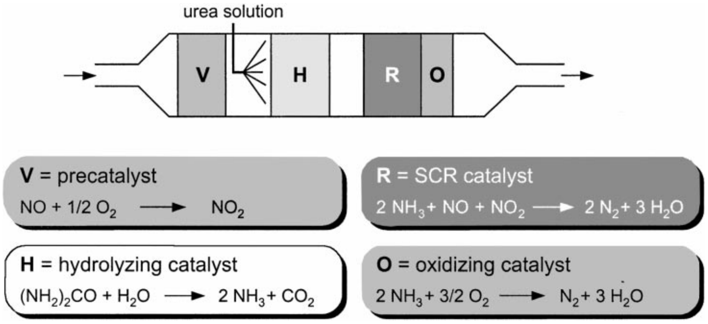

Fig. 11. Scheme of the “VHRO-system” according to MAN [10].

$$2NH_3+NO+NO_2 \rightarrow 2N_2+3H_2O \qquad (14)$$

O-Kat (oxidizing catalyst for limiting NH_3-slip)

$$4NH_3+3O_2 \rightarrow 2N_2+6H_2O \qquad (15)$$

Coated catalysts of high cell density are used in all sections. The total catalyst volume therefore amounts to only 24 l (diesel engine with 12 l cylinder volume/400 PS).

A similar system is also the subject of investigation of the project "GD-Kat". This is a joint project of the German car manufacturers and the leading component suppliers. The goal is to show the feasibility of urea-SCR also for the diesel passenger car.

Acknowledgements

The financial support of the Swiss Federal Office of Energy (BEW) is gratefully acknowledged.

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