

# THE NEW “ENHANCED NH<sub>3</sub>-SCR” REACTION FOR NO<sub>x</sub> EMISSION CONTROL

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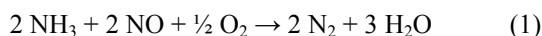
## Summary

NH<sub>3</sub>-Selective Catalytic Reduction (SCR) is applied worldwide to DeNO<sub>x</sub> of combustion exhausts from stationary and mobile sources, but a greater DeNO<sub>x</sub> activity at low temperatures is desired to meet forthcoming restrictive legislations. We have obtained high NO reduction efficiencies at 200 – 300 °C over commercial V-based and Fe-exchanged zeolite catalysts by reacting NO with both ammonia and nitrates (e.g. ammonium nitrate) according to a novel “Enhanced SCR” reaction,  $2 \text{NH}_3 + 2 \text{NO} + \text{NH}_4\text{NO}_3 \rightarrow 3 \text{N}_2 + 5 \text{H}_2\text{O}$ . This opens new pathways for low-T NO<sub>x</sub> reduction wherein the DeNO<sub>x</sub> activity is optimized by dosing an aqueous solution of nitrates to the SCR reactor feed stream.

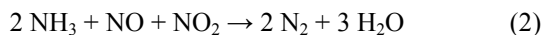
*Keywords:* Diesel exhaust aftertreatment, Diesel emission control, NH<sub>3</sub> SCR, NO<sub>x</sub> abatement.

## Introduction

The Selective Catalytic Reduction (SCR) technology is well established and used worldwide to control NO<sub>x</sub> emissions from power plants and other stationary sources, based on extruded honeycomb monolith catalysts consisting of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> [1-2]: it can be broadly described as passing a hot exhaust gas over a catalyst in the presence of a nitrogenous reductant, such as ammonia or urea (an ammonia carrier), which converts NO<sub>x</sub> to nitrogen according to the so called “Standard SCR” reaction (1),



Currently NH<sub>3</sub>- or urea-SCR is also being more and more employed to reduce NO<sub>x</sub> in the exhaust gases of internal combustion engines operated with excess air, such as Diesel engines installed on heavy-duty vehicles and passenger cars: zeolite-based catalysts promoted by transition metals, such as Fe and Cu, are considered for this application. One problem of SCR systems for vehicles however is the poor activity at low temperatures where most of the NO<sub>x</sub> are produced during e.g. cold start-up and on short travelling distances. The chosen method to boost the DeNO<sub>x</sub> activity of SCR catalysts for mobile applications at low temperature is to increase the NO<sub>2</sub>/NO molar feed ratio (NO<sub>2</sub> accounts only for few percents of total NO<sub>x</sub> in the exhaust gases), thus promoting the occurrence of the “Fast SCR” reaction (2) [3],

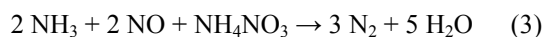


This is realized in practice by installing a Diesel oxidation catalyst (DOC) to convert a portion of NO to NO<sub>2</sub> upstream of the SCR converter, the oxidation catalyst typically consisting of precious metals carried on a flow-through honeycomb support: in this case considerable improvements in NO<sub>x</sub> conversion are achieved, the highest DeNO<sub>x</sub> efficiencies corresponding to the NO<sub>2</sub>/NO = 1/1 molar ratio associated with reaction (2) [4,5]. However, the oxidation activity of the DOC is strongly dependent on temperature and flow rate of the exhaust gases, so that the optimal NO<sub>2</sub>/NO unit feed ratio cannot be guaranteed for all possible engine operating conditions.

The purpose of the present contribution is to communicate the existence of a new, effective reaction for the Selective Catalytic Reduction of NO<sub>x</sub> with ammonia/urea (NH<sub>3</sub>-SCR), based on the use of nitrate species as oxidizing agents.

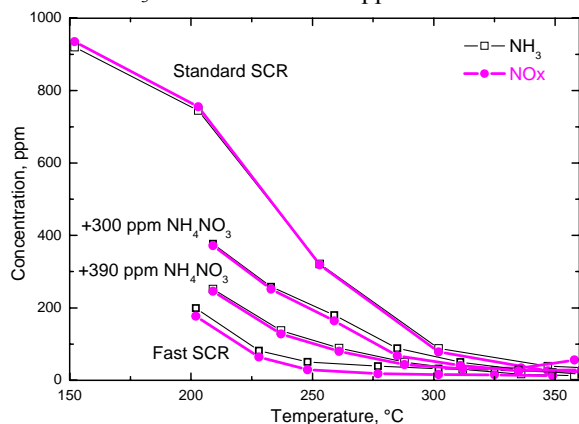
## Results

We present herein steady-state and transient data showing that addition of aqueous solutions of either NH<sub>4</sub>NO<sub>3</sub> or HNO<sub>3</sub> to a NO – NH<sub>3</sub> – O<sub>2</sub> feed results in the occurrence of the new “Enhanced SCR” reaction over both Fe-ZSM-5 and V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> commercial catalysts. Such a reaction involves the selective reduction of NO by NH<sub>3</sub> and nitrate species (e.g. ammonium nitrate) to N<sub>2</sub> as exemplified by



and is associated with superior NO reduction efficiencies in the 200 - 350°C temperature range, similar to those observed in the “Fast SCR” reaction: in this case however nitrate species rather than gaseous NO<sub>2</sub> are included in the feed stream. The new reaction is accompanied by total conversion both of the nitrates additives and of ammonia, when these are fed in sub-stoichiometric amounts: thus, the “Enhanced SCR” chemistry is also compatible with limits on the ammonia slip.

As an example, Figure 1 compares steady-state NOx and ammonia concentrations measured over V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> upon feeding 300 or 390 ppm of NH<sub>4</sub>NO<sub>3</sub> to those observed in runs with NOx feeds containing either only NO (Standard SCR, reaction (1)) or equimolar amounts of NO and NO<sub>2</sub> (Fast SCR, reaction (2)), respectively. The promoting effect of ammonium nitrate on the DeNOx activity as compared to the Standard SCR case is clearly apparent. Moreover, Figure 1 shows that the NOx removal efficiency was limited by the substoichiometric NH<sub>4</sub>NO<sub>3</sub> feed content (< 500 ppm) and increased with increasing NH<sub>4</sub>NO<sub>3</sub> feed concentration, approaching the optimal DeNOx activity of the Fast SCR reaction: the noted effect was in fact quite similar to the well-known effect of increasing the NO<sub>2</sub>/NOx feed ratio from 0 to 1/2 [3-5]. The enhancing effect of ammonium nitrate was most significant at low temperatures, and progressively decreased with growing temperature as total NOx and NH<sub>3</sub> conversions were approached.



**Figure 1** – Effect of NH<sub>4</sub>NO<sub>3</sub> feed concentration on the steady state NOx and ammonia concentrations over a V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst, in comparison to Standard and Fast SCR. GHSV = 33,000 h<sup>-1</sup>. Feed = 1000 ppm NOx, 1000 ppm NH<sub>3</sub>, 1% H<sub>2</sub>O, 2% O<sub>2</sub> in N<sub>2</sub>. Standard SCR runs: NO<sub>2</sub>/NOx=0; Fast SCR runs: NO<sub>2</sub>/NOx=1/2

## Discussion

Injecting nitrate species in order to reduce NOx is apparently paradoxical. Nevertheless, our data prove that this is indeed effective for NOx removal, likely due to the extreme oxidizing properties of such additives. In view of the well known red-ox nature of the NH<sub>3</sub>-SCR catalytic mechanism [6], it is believed that nitrogenous compounds with a high oxidation state can play a strong promoting role. The “Enhanced” DeNOx activity is in fact similar to that observed in the case of the well known “Fast SCR” reaction, but in this case nitrate species in aqueous

solution rather than gaseous NO<sub>2</sub> are included in the feed stream.

The present results open in principle new pathways for NOx abatement at low temperatures in SCR converters for Diesel vehicles. In fact, in existing technologies a Diesel oxidation catalyst (DOC) converts a portion of NO to NO<sub>2</sub> upstream of the SCR converter in order to promote the low-T SCR activity, the highest DeNOx efficiencies corresponding to a NO<sub>2</sub>/NO = 1/1 molar ratio. However, the DOC oxidation activity is strongly dependent on temperature and flow rate of the exhaust gases, so that the optimal NO<sub>2</sub>/NO unit feed ratio cannot be assured for all possible engine operating conditions. On the other hand, adoption of nitrate species rather than NO<sub>2</sub> as the promoting agent affords independent optimized dosage of the promoter for all conditions. Urea-ammonium nitrate (UAN) solutions of suitable compositions are commercially available. Likewise, the present concept appears to be promising also in relation to a number of modern stationary SCR applications, like incinerators with energy efficient configurations, which call for operation at the lowest possible temperature (≈ 200 °C) [7].

From a more fundamental viewpoint, the “Enhanced SCR” concept offers new perspectives for an improved understanding and modeling of the extended SCR catalytic chemistry: rationalization of the present results may likely motivate further significant research in this area [8].

## References

- (1) P. Forzatti, L. Lietti, E. Tronconi, "Nitrogen Oxides Removal - E (Industrial Processes and Relevant Engineering Issues)", in *Encyclopedia of Catalysis*, I.T Horvath, Ed. (Wiley, New York, 2003), vol. 5. pp. 298-343, and references therein contained.
- (2) I. Nova, A. Beretta, G. Groppi, L. Lietti, E. Tronconi, P. Forzatti, "Monolithic catalysts for NOx removal from stationary sources", in *Structured catalysts and reactors*, 2nd Edition, A. Cybulski and J.A. Moulijn, Eds. (Taylor & Francis, Boca Raton, 2006), 2nd Edition, Chap. 6, pp. 171-214.
- (3) A. Kato, S. Matsuda, T. Kamo, F. Nakajima, H. Kuroda, T. Narita, *J.Phys. Chem.* **85**, 4099 (1981).
- (4) M.Koebel, M.Elsener, G.Madia, *Ind. Eng. Chem. Res.*, **40**, 52 (2001).
- (5) S. Brandenberger, O. Kroecher, A. Tissler, R. Althoff, *Catal. Reviews* **50**, 492 (2008), and references therein contained.
- (6) M. Inomata, A. Miyamoto, Y. Murakami, *J. Catal.*, **62**, 140 (1980).
- (7) International Patent Application WO2008/126118, 23.10.2008.
- (8) P. Forzatti, I. Nova. E. Tronconi, *Angewandte Chemie*, in press (2009).