

Removal of NO_x from Diesel Exhausts: The New “Enhanced NH₃-SCR” Reaction

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Pio Forzatti, Isabella Nova and Enrico Tronconi
Politecnico di Milano

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ABSTRACT

Ammonia/urea-SCR is a mature technology, applied worldwide for the control of NO_x emissions in combustion exhausts from thermal power plants, cogeneration units, incinerators and stationary Diesel engines and more recently also from mobile sources. However a greater DeNO_x activity at low temperatures is desired in order to meet more and more restrictive legislations.

In this paper we report transient and steady state data collected over commercial Fe-ZSM-5 and V₂O₅-WO₃/TiO₂ catalysts showing high NO_x reduction efficiencies in the 200 - 350 °C T-range when NO and ammonia react with nitrates, e.g. in the form of an aqueous solution of ammonium nitrate. Under such conditions a new reaction occurs, the so called “Enhanced SCR” reaction,



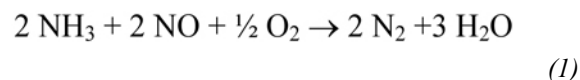
Under the conditions of our experiments the new reaction resulted in total conversion both of the nitrates additives and of ammonia, when they were fed in sub-stoichiometric amounts: thus, the “Enhanced SCR” chemistry is also compatible with limitations on the ammonia slip.

These results open new pathways for low-T NO_x reduction, wherein the amount of boosting agent added to the SCR reactor feed is no longer determined by the activity of the upstream oxidation catalyst, like in the case of NO₂ for the well known Fast SCR reaction, but can be optimally controlled by dosing an aqueous solution of the oxidizing additive (nitrates), possibly by means of the same injection systems currently employed for dosage of ammonia/urea solutions.

INTRODUCTION

The Selective Catalytic Reduction (SCR) is a well known technique used worldwide in order to reduce the nitrogen oxides (NO_x) emissions from stationary and mobile sources [1,2,3,4].

According to the SCR technique, hot exhaust gases containing nitrogen oxides and oxygen are passed over a catalyst in the presence of a reducing agent, generally ammonia or urea, so as to reduce the nitrogen oxides to molecular nitrogen, in line with the so called Standard SCR reaction (1):



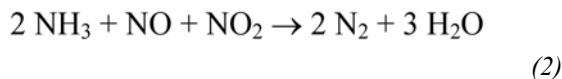
Such a technique is extensively used in stationary applications, particularly in thermal power stations powered with natural gas, coal and combustion oil, gas turbines, industrial boilers, incinerators, chemical plants, stationary Diesel engines, in the cement, glass and steel industry, wherein traditional extruded SCR monolith catalysts made of V₂O₅-WO₃/TiO₂ typically operate at temperatures of 300 to 400°C [1,2].

The SCR technique has been more recently applied to vehicles as well (mobile applications) in order to reduce the nitrogen oxides in the exhaust gases of internal combustion engines operating with excess oxygen such as, for example, Diesel engines, lean-burn spark-ignition engines, such as gasoline direct injection (GDI) engines and compressed natural gas (CNG) engines [3,4]. The SCR technique, and in particular the Standard SCR reaction (1), is however poorly effective at low temperatures, so specifically at the engine start or, also, when traveling on short distances, i.e. when more NO_x are produced.

Accordingly, several methods have been proposed for increasing the SCR activity when the used temperatures are as low as 150°C-200°C.

Electrical heaters have been associated with the SCR converter and with the exhaust input/output pipes in order to quickly raise the temperature of the nitrogen oxides removal system up to the optimal reaction temperature [5,6]. Such systems however imply a high power consumption.

The most commonly used method for improving the SCR catalytic activity in removing nitrogen oxides at low temperatures is that of increasing the NO₂/NO molar ratio in the exhaust gases. In fact, it has been known since the '80s that the kinetics of NO_x reduction with ammonia at low temperature can be promoted by increasing the NO₂ fraction against NO up to a maximum corresponding to an equimolar NO₂/NO ratio [7,8,9]. The reaction between ammonia and nitrogen oxides with the optimal NO₂/NO unit molar ratio, called Fast SCR, proceeds according to the following stoichiometry (2):



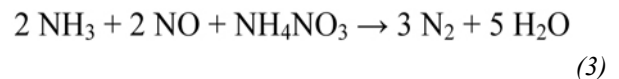
In the case of SCR applications to vehicles, the promoting action associated with NO₂ is achieved by positioning a Diesel Oxidation Catalyst upstream of the onboard SCR unit to partially convert NO to NO₂; however, the DOC is typically based on Pt and/or other Precious Metals, and thus it is particularly expensive. In addition, it is practically impossible to assure a NO₂/NO unit feed ratio for all possible engine operating conditions.

Thus, the only method to efficiently reduce NO_x in mobile applications remains nowadays the implementation of the Fast SCR reaction, which nevertheless implies the installation of an expensive, voluminous and complex to manage pre-oxidation catalyst for the on board generation of NO₂.

An extensive investigation of the chemistry and catalytic mechanism of the NH₃-NO/NO₂ SCR reacting system over commercial V₂O₅-WO₃/TiO₂ and Fe-zeolite catalysts performed in our laboratories [10,11,12,13,14,15,16,17] has revealed that nitrate species are formed in significant amounts onto SCR catalysts when NO₂ is included in the feed stream to the SCR reactor. In the technical and scientific literature, the in situ formation of nitrates, and specifically of ammonium nitrate, was originally regarded as unfavorable. In particular, with reference to zeolite-based catalysts some authors claimed that the ammonium nitrate formation can reduce the catalytic activity [18]. In the case of vanadium-based catalysts, other authors stated that the in situ formation of such compounds is not relevant for the purposes of the

catalytic mechanism and should be avoided, as it inhibits the Fast SCR reaction (2) at low temperature [19].

In the present paper we show that the addition of nitrates to the SCR reactants allows to reduce NO_x more efficiently at low temperatures according to an alternative SCR reaction [20, 21], that we call "Enhanced SCR". This new chemistry involves the selective reduction of NO to N₂ by its reaction with NH₃ and with nitrate species (e.g. supplied in the form of aqueous solutions of ammonium nitrate), as exemplified by



Selected catalytic activity data demonstrating reaction (3) are reported in the following. We will show that the new reaction is associated with a very high DeNO_x efficiency at low temperatures, similar to the Fast SCR activity, even though no NO₂ is fed to the SCR catalyst: accordingly, it can replace reaction (2) in order to boost the NH₃-SCR activity without necessity of pre-oxidizing NO to NO₂.

EXPERIMENTAL

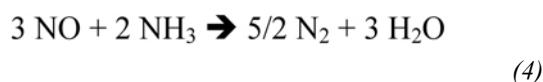
The NO/NH₃/O₂/N₂ SCR reactions were investigated over core samples (about 5 cm³) of commercial Fe-ZSM-5 and V₂O₅-WO₃/TiO₂ SCR monolith catalysts under isothermal steady-state and transient conditions within the 150-450°C T-range. Typical feed concentrations of NO_x and NH₃ were 500-1000 ppm, with 2-10 % O₂ and 1-10 % H₂O v/v, and balance N₂. In addition, aqueous solutions of ammonium nitrate were also dosed to the test reactor by means of a peristaltic pump: such solutions were then vaporized and mixed with the gaseous feed upstream of the SCR catalysts. The space velocity was set to 33000-36000 h⁻¹. Analysis of NO, NH₃, NO₂ in the outlet gases was performed using a UV-analyzer (ABB LIMAS 11HV). Prior to the runs, the catalysts were conditioned in a T-ramp at 10°C/min up to 550°C in 2% O₂ (v/v) and 10% (v/v) H₂O, and keeping them at 550°C for 1 h. Further details on the experimental apparatus and procedures can be found in [14, 22].

RESULTS AND DISCUSSION

Fe-ZSM-5 Washcoated Monolith Catalyst

A commercial Fe-zeolite catalyst was first considered. Figure 1 shows the temporal evolution of the NO, NH₃ and NO₂ outlet concentrations measured over Fe-ZSM-5 during a transient run at 200 °C in which different reactants were added to the feed stream in subsequent steps (ammonia, NO, O₂, NH₄NO₃+ H₂O, respectively).

At the beginning only the N₂ flow was fed to the reactor; then, after around 250 s, 1000 ppm of ammonia were instantaneously fed to the system: the NH₃ outlet concentration showed a dead time, when NH₃ was completely adsorbed onto the catalyst, and then it increased with time, approaching the inlet value of 1000 ppm after ~500 s. At t=950s 1000 ppm of NO were also admitted to the reactor: the ammonia outlet concentration decreased, passed through a minimum and then leveled off to a steady state value close to 980 ppm. Simultaneously the NO outlet concentration increased up to 970 ppm. The steady-state NO concentration, indicating a conversion of about 3%, is consistent with the stoichiometry of the Slow SCR reaction (4),



i.e. the poorly active DeNO_x reaction between NO and NH₃ which prevails on SCR catalysts in the absence of oxygen [16].

At t = 1700 s O₂ (2 % v/v) was added to the reactor feed: both the NO and ammonia concentrations dropped, reaching in a few seconds a new steady state value of about 840 ppm. As expected, the addition of oxygen resulted in the onset of a more significant conversion of NO and NH₃ (about 15%) associated with the Standard SCR reaction (1).

Then, at t = 2200 s the pump started to inject an aqueous solution of ammonium nitrate in the test reactor feed stream, resulting in feed concentrations of 340 ppm NH₄NO₃ and 10 % H₂O v/v. Again, the NO and ammonia outlet concentrations decreased rapidly, both approaching a value of roughly 320 ppm. Such concentrations are in line with the occurrence of reaction (3) with an overall NO conversion of 68%, indicating the complete consumption of the limiting reactant NH₄NO₃. Notably, NO₂ was never detected in significant amounts throughout the whole run, as also evident from Figure 1.

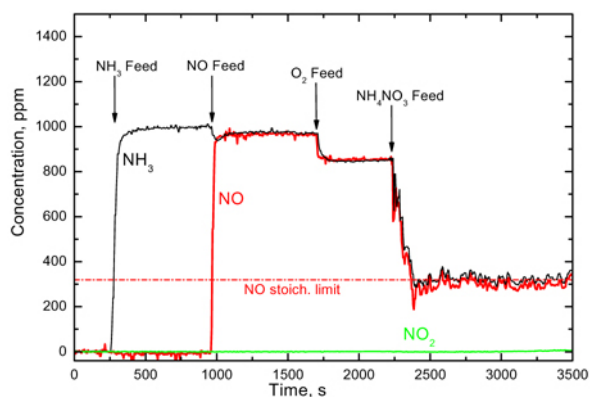


Figure 1. Transient experiment over the Fe-ZSM-5 catalyst at T = 200°C, GHSV = 33,000 h⁻¹. Temporal evolution of NO, NH₃ and NO₂ outlet concentrations upon addition of: a) 2 % v/v O₂ to 1000 ppm NO, 1000 ppm NH₃ in N₂ (at t = 950 sec); b) 340 ppm NH₄NO₃ + 10% H₂O v/v to 1000 ppm NO, 1000 ppm NH₃, 2 % O₂ in N₂ (at t = 2200 sec).

A small delay in the ammonia signal was observed, particularly when ammonium nitrate was also fed to the reactor. Such a behavior, already observed during other experiments, was ascribed to ammonia adsorption onto the lines of the rig and possibly also onto nitrate adsorbed species [12, 18].

Figure 1 clearly indicates that the addition of ammonium nitrate to the NO-NH₃-O₂ reacting system dramatically increased the NO reduction activity at low temperature over the Fe-ZSM-5 catalyst; furthermore, the added NH₄NO₃ itself was totally and selectively converted according to reaction (3).

Figure 2 shows another experiment performed at 206°C over the Fe-zeolite catalyst under transient conditions. In this case 420 ppm of NH₄NO₃ + 1% H₂O v/v were added and removed several times to a feed flow consisting of 1000 ppm NO, 1000 ppm NH₃, 2 % O₂ in N₂.

In the first part of the experiment, besides NO and ammonia, the ammonium nitrate aqueous solution was also added to the feed mixture: indeed, a very high NO conversion, over 80%, was measured already at 206°C, in line with the occurrence of reaction (3) and again indicating essentially total conversion of ammonium nitrate. When at t = 2000s NH₄NO₃ was removed from the feed flow, both the NO and ammonia concentrations increased, slowly recovering the conversion level typical of the Standard SCR reaction (1). Then, after roughly 200 s, the ammonium nitrate solution was again dosed to the reactor, and thus the NO and ammonia outlet concentrations decreased returning, after some oscillations, to the conversion value of 83%. This behavior