Exhaust Control

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Enhanced NH_3 Selective Catalytic Reduction for NO_x Abatement

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Nitrogen oxides NO_x, which include NO (nitrogen monoxide), NO_2 (nitrogen dioxide), and N_2O (nitrous oxide), are currently considered to be among the most dangerous air pollutants, as they cause acid rain, contribute to photochemical smog, and have direct harmful effects on human health. For all these reasons, in the last decades NO_x emissions have been regulated in industrialized countries by more and more restrictive legislation.[1] Selective catalytic reduction (SCR) technology is well established and used worldwide to control NO_x emissions from power plants and other stationary sources. A hot exhaust gas is passed over an extruded honeycomb monolith catalyst consisting of V_2O_5–WO_3/TiO_2[2] in the presence of a nitrogenous reductant such as ammonia or urea (an ammonia carrier), which converts NO_x to nitrogen according to the so-called standard SCR reaction (1).

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

Currently NH_3 or urea SCR is also being increasingly employed to reduce NO_x in the exhaust gases of internal combustion engines operated with an excess of air, such as Diesel engines installed in 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 poor activity at low temperatures where most of the NO_x is produced, for example, during cold startup and on traveling short distances. The chosen method to boost the DeNOx activity of SCR catalysts for mobile applications at low temperature is to increase the NO_2/NO molar feed ratio (NO_2 accounts only for few percent of total NO_x in the engine exhaust) and thus promote the fast SCR reaction (2).[3]

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

This is realized in practice by installing a Diesel oxidation catalyst (DOC), typically consisting of precious metals carried on a flow-through honeycomb support, to convert a portion of NO to NO_2 upstream of the SCR converter. Thus, considerable improvements in NO_x conversion are achieved, and the highest DeNOx efficiencies correspond to the NO_2/NO molar ratio of 1/1 associated with reaction (2).[4] However, the oxidation activity of the DOC is strongly dependent on temperature and flow rate of the exhaust gases, so that optimal NO_2/NO feed ratio cannot be guaranteed for all possible engine operating conditions.

Here we reveal that a superior NO conversion efficiency can also be achieved by means of an enhanced SCR reaction[5] involving selective reduction of NO to N_2 by NH_3 and nitrate species such as ammonium nitrate [reaction (3)].

$$2\,NH_3 + 2\,NO + NH_4NO_3 \rightarrow 3\,N_2 + 5\,H_2O \qquad (3)$$

The new reaction has very high DeNOx efficiency at low temperatures, similar to that of fast SCR, even though no NO_2 is fed to the SCR catalyst; accordingly, it can replace reaction (2) in boosting NH_3 SCR activity without the necessity of pre-oxidizing NO.

Figure 1 shows the temporal evolution of the NO, NH_3, and NO_2 outlet concentrations during one run at 205 °C over an Fe-ZSM-5 washcoated monolith catalyst. Initially only equimolar amounts of NH_3 and NO (1000 ppm each) were fed to the catalyst in a nitrogen stream, with negligible conversion. At $t = 1450$ s addition of O_2 (2 vol %) to the reactor feed resulted in the onset of limited conversion of NO and NH_3 (about 15 %) associated with standard SCR reaction (1). At $t = 2800$ s the pump started to inject an aqueous solution of ammonium nitrate into the test-reactor feed stream, resulting in feed concentrations of 340 ppm NH_4NO_3 and 1 vol % H_2O. As a consequence, the outlet NO and NH_3 concentrations dropped rapidly, eventually approaching after a few oscillations the conversion of 68 % predicted from reaction (3) for complete depletion of the limiting reactant NH_4NO_3. Evolution of NO_2 was negligible (< 10 ppm) throughout. Clearly, addition of ammonium nitrate to the reacting NO–NH_3–O_2 system dramatically increases the NO reduction activity at

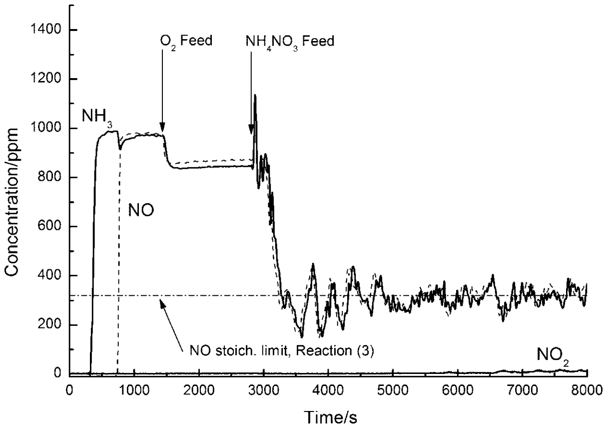

Figure 1. Transient experiment over the Fe-ZSM-5 catalyst at $T = 205$ °C, GHSV = 33 000 h^{-1}. Temporal evolution of NO, NH_3, and NO_2 outlet concentrations on addition of a) 2 vol % O_2 to 1000 ppm NO, 1000 ppm NH_3 in N_2 (at $t = 1450$ s); b) 340 ppm NH_4NO_3 + 1 vol % H_2O to 1000 ppm NO, 1000 ppm NH_3, 2 % O_2 in N_2 (at $t = 2800$ s).

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low temperature over Fe-ZSM-5; furthermore, the added NH_4NO_3 itself is totally and selectively converted according to reaction (3).

The substantial enhancement of the NO_x removal efficiency due to NH_4NO_3 addition as compared to standard SCR was also confirmed at higher temperatures, though it progressively decreased with increasing temperature. Figure 2 shows that when 340 ppm of NH_4NO_3 was added to the reactor feed the steady-state NO conversion remained stable around 68%, that is, the stoichiometric limit of reaction (3), up to 250 °C, and then began to grow slowly with temperature, eventually converging with the NO conversion observed without NH_4NO_3 at high temperature (> 350 °C). This behavior suggests that the promoting action of NH_4NO_3 is most effective at low temperature, but drops off at higher temperature when the catalyst becomes fully active in standard SCR.

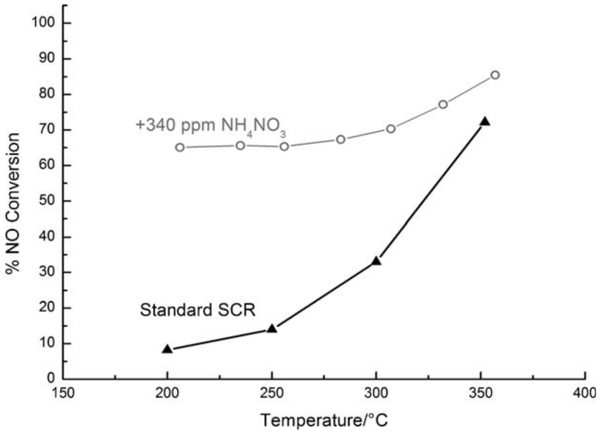

Figure 2. Effect of adding 340 ppm of NH_4NO_3 to the feed stream on the steady-state NO conversion over the Fe-ZSM-5 catalyst as a function of temperature. GHSV = 33 000 h^{-1}. Feed: 1000 ppm NO, 1000 ppm NH_3, 1% H_2O, 2% O_2 in N_2.

To further validate the stoichiometry of reaction (3), runs involving substoichiometric feed contents of both NH_3 (680 ppm) and NH_4NO_3 (340 ppm) with respect to NO (1000 ppm) were also performed. Figure 3 shows steady-state outlet concentrations of NO, NH_3, and NO_2 over Fe-ZSM-5 at different temperatures during such runs. In this case not only was the NO conversion close to the stoichiometric limit at all temperatures, but ammonia emissions were below the detection threshold as well (< 5 ppm), in line with total depletion of both deficient reactants NH_3 and NH_4NO_3 according to reaction (3). This result is also of practical importance, as it shows that, by proper selection of the reactant feed concentrations, reaction (3) can afford enhanced NO reduction efficiencies with negligible ammonia slip.

Enhanced SCR was further examined in a transient experiment at 205 °C at a gas hourly space velocity (GHSV) of 36 000 h^{-1}, wherein the Fe-ZSM-5 catalyst was first exposed to a feed containing 500 ppm NO, 750 ppm NH_3, and 0% O_2 in N_2, to which an aqueous solution of nitric acid corresponding to feeding 250 ppm HNO_3 and 1% H_2O was added in a second stage. In this case a steady-state conversion of both NO and NH_3 close to 90% was observed, consistent with the stoichiometry of reaction (4)

$$3\,NH_3 + 2\,NO + HNO_3 \rightarrow 3\,N_2 + 5\,H_2O \tag{4}$$

which is of course equivalent to reaction (3) when dissociation of NH_4NO_3 to ammonia and nitric acid is considered. Thus, the observed activity enhancement is likely due to the participation of nitrate species in the reaction. The experiment also indicates that oxygen is unnecessary for NO conversion, again in agreement with reaction (3) or (4).

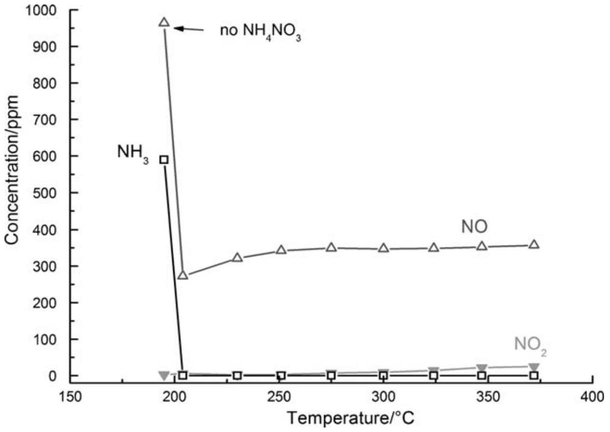

Figure 3. Effect of temperature on the steady-state NO, NH_3 and NO_2 outlet concentrations over the Fe-ZSM-5 catalyst. GHSV = 33 000 h^{-1}. Feed: 1000 ppm NO, 680 ppm NH_3, 340 ppm NH_4NO_3, 1% H_2O, 2% O_2 in N_2.

Finally, reaction (3) was also investigated over a commercial V_2O_5–WO_3/TiO_2 extruded honeycomb catalyst under conditions similar to those adopted for the Fe zeolite catalyst. Figure 4 compares steady-state NO_x conversions measured on feeding 300 or 390 ppm of NH_4NO_3 to those observed in runs with NO_x feeds containing either only NO [standard SCR, reaction (1)] or equimolar amounts of NO and NO_2 [Fast

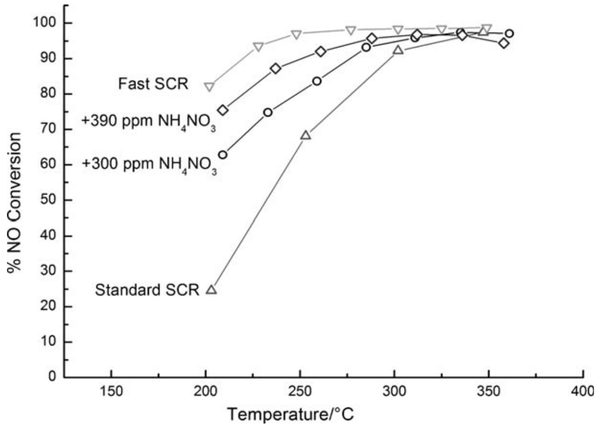

Figure 4. Effect of NH_4NO_3 feed concentration on the steady state NO_x conversion over the V_2O_5–WO_3/TiO_2 catalyst in comparison to standard and fast SCR. GHSV = 33 000 h^{-1}. Feed: 1000 ppm NO_x, 1000 ppm NH_3, 1% H_2O, 2% O_2 in N_2. Standard SCR runs: NO_2/NO_x = 0; fast SCR runs: NO_2/NO_x = 1/2.

SCR, reaction (2)], respectively. The promoting effect of ammonium nitrate on the DeNOx activity compared to standard SCR case was clearly apparent over the V-based catalyst, too. Moreover, Figure 4 shows that the NO_x removal efficiency was limited by the substoichiometric NH_4NO_3 feed content (< 500 ppm), increased with increasing NH_4NO_3 feed concentration, and approached the optimal DeNOx activity of the fast SCR reaction. The observed effect was in fact quite similar to the well-known effect of increasing the NO_2/NO_x feed ratio from 0 to 0.5.[4] Like over the Fe zeolite catalyst, the enhancing effect of ammonium nitrate was most significant at low temperatures, and progressively decreased with increased temperature as total NO_x and NH_3 conversions were approached.

In summary, the transient and stationary data presented here confirm that enhanced SCR reaction (3) has superior NO reduction efficiencies in the temperature range of 200–350 °C over both Fe-ZSM-5 and V_2O_5-WO_3/TiO_2 catalysts, and is accompanied by total conversion both of the nitrate additive and of ammonia when these are fed in substoichiometric amounts. Thus, this chemistry is also compatible with limits on ammonia slip. We emphasize also the selectivity to nitrogen associated with reactions (3) and (4): formation of N_2O was checked by a specific IR analyzer (ABB URAS 15) in a few dedicated runs over a zeolite-based catalyst and found to be comparable to that observed under fast SCR conditions over the same catalyst (ca. 20–40 ppm).

Injecting nitrates to reduce NO_x is apparently paradoxical; nevertheless, our data prove that this is indeed effective for NO_x removal. The enhanced SCR DeNOx activity is in fact similar to that observed in the well-known fast SCR reaction, but in this case nitrate species in aqueous solution rather than gaseous NO_2 are introduced into the feed stream. The role of nitrates as key intermediates in the fast SCR reaction mechanism was recently proposed.[6] In view of the well-known redox nature of the NH_3 SCR catalytic cycle,[7] it is believed that nitrogenous compounds with a high oxidation state can play a strong promoting role in the rate-limiting catalyst reoxidation step.[8] From a fundamental viewpoint, the present results thus offer new perspectives for improved understanding of SCR catalysis, as they establish a correlation between the oxidizing activity of different NH_3 SCR co-reactants (oxygen, nitrogen dioxide, nitrates) and the associated DeNOx activity. Rationalization of such an extended SCR chemistry will likely motivate further significant research in this area.

On the other hand, the present results also have practical implications, as they may open new pathways for NO_x reduction at low temperatures, whereby 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 NO_2 for the fast SCR reaction, but can be optimally controlled by dosing an aqueous solution of the oxidizing additive by means of the same injection systems currently employed for dosage of ammonia/urea solutions. A single aqueous solution containing both the reducing agent (urea) and the oxidizing additive (ammonium nitrate) could be used for this purpose: commercial urea/ammonium nitrate (UAN) solutions are available with suitable compositions. Our data further suggest that this new concept could be applicable to both the current classes of SCR commercial catalysts, namely, V-based systems and metal-exchanged zeolites. Accordingly, the enhanced SCR reaction is suitable to augment the crucial low-temperature DeNOx activity of both SCR converters for Diesel vehicles and modern stationary SCR installations, for example, for energy-efficient incinerators.

Experimental Section

Gaseous $NO/NH_3/O_2/N_2$ mixtures were fed to commercial Fe-ZSM-5 and V_2O_5-WO_3/TiO_2 SCR catalysts in the shape of small 400 CPSI honeycomb monoliths (about 5 cm^3). In addition, aqueous solutions of ammonium nitrate or nitric acid were dosed to the test reactor by means of a peristaltic pump, vaporized, and mixed with the gaseous feed upstream of the SCR catalyst. The concentrations of NO, NH_3, and NO_2 at the reactor outlet were continuously monitored by a UV analyzer (ABB Limas 11-HW).

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