



## Journal Article

# Diesel Soot Catalyzes the Selective Catalytic Reduction of NO<sub>x</sub> with NH<sub>3</sub>

**Author(s):**

Mehring, Max; Elsener, Martin; Kröcher, Oliver

**Publication Date:**

2013-05

**Permanent Link:**

<https://doi.org/10.3929/ethz-b-000066471> →

**Originally published in:**

Topics in Catalysis 56(1-8), <http://doi.org/10.1007/s11244-013-9993-5> →

**Rights / License:**

[In Copyright - Non-Commercial Use Permitted](#) →

This page was generated automatically upon download from the [ETH Zurich Research Collection](#). For more information please consult the [Terms of use](#).

# Diesel Soot Catalyzes the Selective Catalytic Reduction of NO<sub>x</sub> with NH<sub>3</sub>

Max Mehring · Martin Elsener · Oliver Kröcher

Published online: 23 February 2013  
© Springer Science+Business Media New York 2013

**Abstract** The catalytic activity of soot samples for the selective catalytic reduction (SCR) of NO<sub>x</sub> with NH<sub>3</sub> was investigated in dependence of the NO<sub>2</sub>, NO and NH<sub>3</sub> concentration in the temperature range between 200 and 350 °C. The highest NO<sub>x</sub> reduction of up to 25 % was measured in the presence of both NO<sub>2</sub> and NO at a GHSV of 35,000 h<sup>-1</sup>. Decreasing space velocities resulted in an increase of the SCR activity. In the absence of NO<sub>2</sub>, NO<sub>x</sub> reduction was not observed. Carbon oxidation and SCR reaction occurred in parallel due to the presence of NO<sub>2</sub> and O<sub>2</sub>, but hardly influenced each other, which suggested that in the NO<sub>x</sub> reduction on soot most probably physisorbed species were involved. The observed stoichiometries indicated the action of the *fast SCR* reaction in the presence of NO and the *NO<sub>2</sub> SCR* reaction in the absence of NO, while the observed gas phase and surface species pointed at reaction steps similar to those on classical SCR catalysts.

**Keywords** Selective catalytic reduction (SCR) · Diesel soot · Soot · Fast SCR · NO<sub>2</sub> SCR

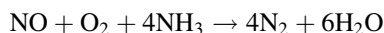
## 1 Introduction

The selective catalytic reduction (SCR) of the nitrogen oxides with ammonia as reducing agent has become the state-of-the-art technology for heavy-duty diesel engines and also for passenger cars [1, 2]. The currently applied catalysts for the SCR process are either vanadia-based catalysts (mostly V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>-TiO<sub>2</sub>) or metal-exchanged zeolites (metals: Fe, Cu) [2]. The toxic and corrosive NH<sub>3</sub>,

which is required in this process, is stored in form of an aqueous solution of the harmless NH<sub>3</sub> precursor compound urea in an extra tank in the vehicle. In dependence on the actual amount of NO<sub>x</sub> in the exhaust gas the urea solution is injected into the exhaust stream, where it thermolyzes and hydrolyzes to NH<sub>3</sub> and CO<sub>2</sub>.

Before SCR was introduced to diesel vehicles, it had already been used for the reduction of NO<sub>x</sub> in stationary applications for several decades [3, 4]. For special low temperature applications at 100–150 °C, activated carbon catalysts were developed for the reduction of NO at space velocities of approx. 2,000 h<sup>-1</sup> in the 1970s and 1980s [5–14]. The up to 80 % conversion reached with these catalysts strongly depends on the carbon type and pre-treatment [8]. Whereas many parameters remain unclear, the amount of acidic surface functional groups on the carbon surface were shown to be important for the adsorption of NH<sub>3</sub> [15–18] and nitrogen embedded in the carbon structure increased the activity [7, 19, 20].

The oxidation of NO with oxygen to NO<sub>2</sub> is assumed to be a prerequisite step for the SCR reaction on soot in presence of NO [5, 20, 21], which takes place at an oxygen-containing surface functional group consisting of an active carbon carrying chemisorbed oxygen [20]. NO adsorbs well on these complexes leading to the formation of NO<sub>2</sub> [20]. It is assumed that NO<sub>2</sub> and NO yield N<sub>2</sub>O<sub>3</sub> [5, 14], which reacts with NH<sub>3</sub> and water to ammonium nitrite (NH<sub>4</sub>NO<sub>2</sub>). The decomposition of NH<sub>4</sub>NO<sub>2</sub> leads directly to nitrogen and water. Based on these reaction steps, an overall reaction equation was formulated, showing the 1:1 NO/NH<sub>3</sub> ratio of the *standard SCR* reaction:



Tighter future emission limits for diesel vehicles will necessitate the application of both diesel particulate filter

M. Mehring · M. Elsener · O. Kröcher (✉)  
Paul Scherrer Institut (PSI), 5232 Villigen, Switzerland  
e-mail: oliver.kroecher@psi.ch

(DPF) and SCR system in the same vehicle. In order to keep exhaust gas aftertreatment compact and simple, new concepts suggest combining both functions in one aftertreatment device, i.e. DPF and SCR catalyst could be placed in the same housing or the DPF could be coated with an SCR catalyst. Consequently, soot,  $\text{NH}_3$  and  $\text{NO}_x$  are present in the same reaction device. It is obvious that the chemistry in such combined DPF-SCR systems has to be understood for a proper reaction design and before such systems can be brought to the market. The above mentioned studies provide valuable information about a possible SCR effect over soot. However, the temperatures were much lower and the space velocities were more than ten times lower, which requires revisiting the SCR reaction over soot under the conditions relevant for diesel exhaust gas aftertreatment.

## 2 Experimental

### 2.1 Catalytic Tests

The SCR tests over diesel soot were performed under isothermal conditions at temperatures between 200 and 350 °C in a heated tubular quartz reactor (length: 650 mm, ID: 49 mm). For the gas analysis the reactor was connected to a FTIR spectrometer (Nicolet Nexus 600) via a heated quartz glass tube. The gas measuring cell had a path length of 2 m and each spectrum was the average of 8 scans at a resolution of 0.5  $\text{cm}^{-1}$ . The soot samples were loaded on 400 cpsi cordierite monoliths by dip coating into a dispersion of soot and isopropyl alcohol (IPA). The loaded monoliths were placed in a sample holder and fitted into the reactor with a ceramic fiber mat to avoid any bypass.  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{NH}_3$ ,  $\text{O}_2$  and  $\text{N}_2$  were provided by a gas mixing unit consisting of six mass flow controllers (Brooks 5850S). Water was generated by controlled hydrogen oxidation over a Pt catalyst (2 % Pt on  $\text{SiO}_2$ ). The base feed gas, which was used for all experiments, consisted of 10 % oxygen and 5 % water with nitrogen as balance at a total flow of 550 or 275 L/h at STP. By variation of both, the total flow and the monoliths size, gas hourly space velocities (GHSV) of 3,000, 9,000, 17,000, 35,000 and 70,000  $\text{h}^{-1}$  were realized. Prior to the actual catalytic tests the soot samples were activated for 25 min with 250 ppm  $\text{NO}_2$  + 250 ppm  $\text{NH}_3$  in the base feed gas. This activation became necessary as preliminary experiments showed that the samples went through a significant activation phase, which reduced the reproducibility. For each temperature a new soot-coated monolith was used. Each experimental series was repeated three to five times and terminated at 50–60 % soot conversion in order to avoid interference by soot limitation.

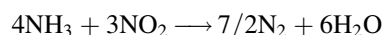
Most experiments were performed with the synthetic soot Printex U from Evonik, supplemented with a limited number of experiments with real diesel soot from heavy-duty diesel engines, complying with old Euro 0 and recent Euro V emission limits. In addition a mixed soot sample collected from several heavy-duty diesel engines was used. The BET surface area of Printex U was 103  $\text{m}^2/\text{g}$ , of the Euro V soot sample 110  $\text{m}^2/\text{g}$ , of the Euro 0 soot sample 132  $\text{m}^2/\text{g}$  and of the mixed soot sample 145  $\text{m}^2/\text{g}$ . Printex U did not contain metals above the detection limits of an ICP-OES analysis. In the Euro V, Euro 0 and the mixed soot sample about 1 % Ca, 1 % Fe beside some Zn, Mg, Na and K could be found (for details refer to [22, 23]). TEM measurements of Printex U and the Euro V soot showed hardly any difference in size and structure of the primary particles between the different samples. However, the Euro V sample might be slightly more amorphous than Printex U.

## 3 Results and Discussion

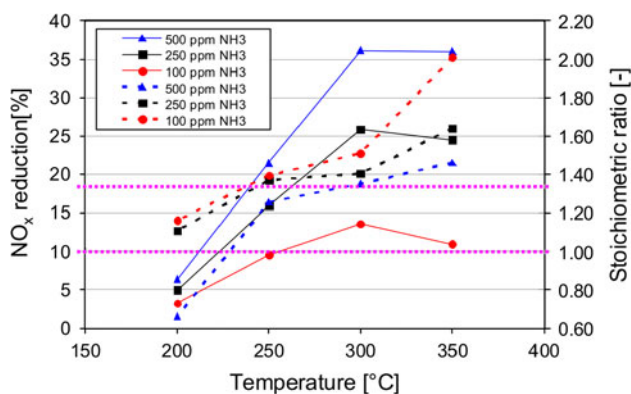
### 3.1 SCR Reaction over Printex U in the Presence of $\text{NO}$ and $\text{NH}_3$

In a preliminary experiment we tested Printex U for its SCR activity under conditions similar to previous studies in the 1980s on activated carbon [5–14, 24]. However, at a GHSV of 3,000  $\text{h}^{-1}$  no  $\text{NO}_x$  reduction activity was observed for Printex U with  $\text{NH}_3$  when  $\text{NO}_x$  was only  $\text{NO}$ . In contrast, considerable  $\text{NO}_x$  reduction could be observed in the presence of  $\text{NO}_2$ . Based on this observation  $\text{NO}_2$  was always added to the feed and only the concentrations of  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{NH}_3$  were varied.

Figure 1 shows the  $\text{NO}_x$  reduction rates over Printex U at temperatures between 200 and 350 °C for varying  $\text{NH}_3$  feed gas concentrations. Beside the  $\text{NO}_x$  reduction, the measured stoichiometry, i.e. the ratio of consumed  $\text{NH}_3$  and consumed  $\text{NO}_x$  is plotted on the secondary y-axis. Under the experimental conditions  $\text{NO}_x$  reduction increased with temperature and reached a plateau up to 36 % at 300 °C. Increasing  $\text{NH}_3$  concentration also resulted in higher  $\text{NO}_x$  reduction rates. It should be noted that up to 80 %  $\text{NO}_x$  conversion was reached when the space velocity was reduced to 3,000  $\text{h}^{-1}$  (results not shown). Regarding the stoichiometric ratios in Fig. 1, between 250 and 300 °C stoichiometric ratios of 1.25–1.50 were found indicating within the measurement error the  $\text{NO}_2$  SCR reaction with a theoretical stoichiometry of 1.33 ( $\text{NH}_3:\text{NO}_2 = 4:3 = 1.33$ ):



At 200 °C, the conversions were too low to reliably determine the stoichiometric ratio. The increasing ratios at



**Fig. 1**  $\text{NO}_x$  reduction and measured stoichiometric ratios ( $=\text{NH}_{3,\text{consumed}}/\text{NO}_{x,\text{consumed}}$ ) over Printex U in dependence of the  $\text{NH}_3$  concentration at a GHSV of  $35,000 \text{ h}^{-1}$ . Base feed + 250 ppm  $\text{NO}_2$  + variable  $\text{NH}_3$  concentrations. Solid lines  $\text{NO}_x$  reduction [%]; dotted lines measured stoichiometric ratios; purple dotted lines calculated stoichiometric ratios of the *fast SCR* and  *$\text{NO}_2$  SCR* reaction

350 °C are caused by the oxidation of  $\text{NH}_3$  to  $\text{N}_2$  and to a small extent to  $\text{NO}$  as well as the formation of  $\text{HNCO}$  and  $\text{HCN}$  from side reactions of  $\text{NH}_3$  with carboxylic surface functional groups.

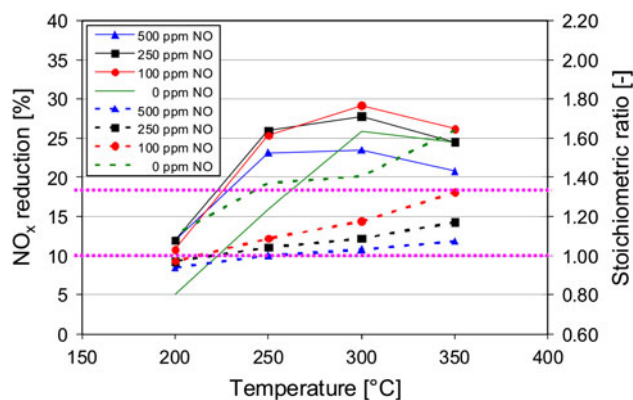
The almost constant  $\text{NO}_x$  reduction above 300 °C is due to a limitation of the reaction by  $\text{NO}_2$ .  $\text{NH}_3$  oxidation is also the reason for the generally higher stoichiometric ratios when the  $\text{NH}_3$  feed gas concentration was increased.

When  $\text{NO}$  was added in varying concentrations to constant amounts of  $\text{NO}_2$  and  $\text{NH}_3$  the  $\text{NO}_x$  reduction rate further increased, as observable in Fig. 2 when comparing the green  $\text{NO}_2/\text{NH}_3$  reference line with the black, red and blue lines, which represent the  $\text{NO}/\text{NO}_2/\text{NH}_3$  mixtures. However, at 300 °C or higher this advantage of the  $\text{NO}/\text{NO}_2$  mixture is less pronounced or the  $\text{NO}_x$  reduction rates even decline below the rates of the  $\text{NO}_2/\text{NH}_3$  reference experiment. The observed stoichiometric ratios decreased with increasing  $\text{NO}$  concentrations, reaching values around 1 for 250 and 500 ppm  $\text{NO}$ , which are in accordance with the stoichiometry of the *fast SCR* reaction [ $\text{NH}_3:\text{NO}_x = 4/(2 + 2) = 1$ ]:



The slightly higher stoichiometry for 100 ppm  $\text{NO}$  can be explained most likely with the occurrence of the *fast SCR* and  *$\text{NO}_2$  SCR* reaction in parallel.

In the presence of 500 ppm  $\text{NO}$ , the observed stoichiometry indicated the occurrence of the rapid *fast SCR* reaction, but the  $\text{NO}_x$  reduction activity seemed to be higher for the  $\text{NO}_2/\text{NH}_3$  reference experiment. In order to understand this effect, please keep in mind that  $\text{NO}_x$  reduction is a relative unit, i.e. although the  $\text{NO}_x$  reduction is nominally lower with  $\text{NO}$  in the feed gas the absolute amount of converted  $\text{NO}_x$  was higher when 500 ppm  $\text{NO} + 250$  ppm



**Fig. 2**  $\text{NO}_x$  reduction and measured stoichiometric ratios ( $=\text{NH}_{3,\text{consumed}}/\text{NO}_{x,\text{consumed}}$ ) over Printex U in dependence of the  $\text{NO}$  concentration at a GHSV of  $35,000 \text{ h}^{-1}$ . Base feed + 250 ppm  $\text{NO}_2$  + 250 ppm  $\text{NH}_3$  + variable  $\text{NO}$  concentrations. Solid lines  $\text{NO}_x$  reduction [%]; dotted lines measured stoichiometric ratios; purple dotted lines stoichiometry of the *fast SCR* and  *$\text{NO}_2$  SCR* reaction

$\text{NO}_2 = 750$  ppm  $\text{NO}_x$  were dosed compared to the reference case with only 250 ppm  $\text{NO}_2 = 250$  ppm  $\text{NO}_x$ . In fact, a detailed analysis of the ongoing reactions, based on the balance of all reactants and products, clearly showed that an almost constant fraction of the  $\text{NO}_2$  was consumed in all experiments for the oxidation of soot and the rest was either consumed in the *fast SCR* or the  *$\text{NO}_2$  SCR* reaction. Since the *fast SCR* is more efficient than the  *$\text{NO}_2$  SCR* reaction, the *fast SCR* reaction run into an  $\text{NO}_2$  deficit and the remaining  $\text{NO}$  could not be converted in the *SCR* reaction as shown in the preliminary experiment.

### 3.2 $\text{NO}_2/\text{NO}/\text{NH}_3$ Reaction Network over Printex U

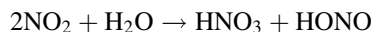
The relationship of  $\text{NO}_x$  reduction reactions and parallel occurring soot oxidation was investigated in detail. Variations of all parameters revealed that the *C*-oxidation rates, calculated on basis of the current amount of remaining carbon, were almost independent of the  $\text{NO}$  and  $\text{NH}_3$  concentration in the feed gas. However, an increase of the  $\text{NO}_2$  concentration led to an expected increase of the *C*-oxidation rate.

Figure 3 exemplarily shows the *C*-oxidation rates during the experiment in Fig. 1, which were hardly influenced by the varying  $\text{NH}_3$  concentrations. The slightly lower oxidation rates at 250–300 °C for 0 and 100 ppm  $\text{NH}_3$  in the feed gas compared to the other concentrations can be explained by the decomposition of nitrile and amide species, which are formed from the reaction of  $\text{NH}_3$  with carboxylic functional groups, as reported in [25]. The decomposition products of these functional groups are  $\text{HCN}$  and  $\text{HNCO}$ , respectively, which were found in traces in our experiments. For details of the involved chemistry please refer to Ref. [22, 23].

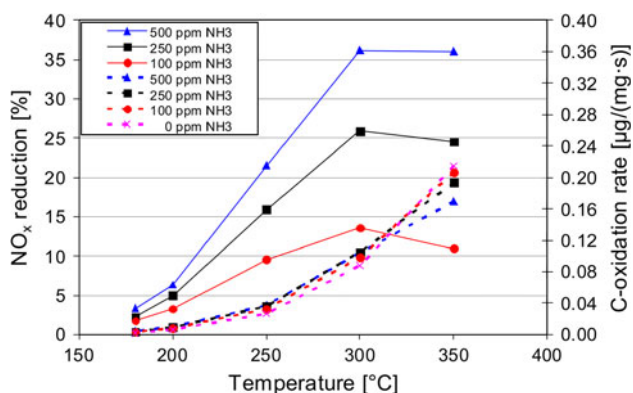


The measured C-oxidation rates for different NH<sub>3</sub>, NO and NO<sub>2</sub> concentrations showed only a minor influence of the SCR conditions on the soot oxidation. This suggested that nitrogen species involved in the SCR process did not affect the decomposition of surface functional groups responsible for the soot oxidation. It can be concluded that the NO<sub>x</sub> surface species involved in the SCR reaction did not form strong bonds with the soot (e.g. surface nitrates and nitrites) and had a more physisorbed nature. Supplementing DRIFTS measurements (results not shown) proved that surface functional groups with chemical C–N and C–O bonds were indeed formed [26–29], but these groups were most probably only involved in soot oxidation and not in the SCR reaction.

Beside the above mentioned main gas components, HCN, HNCO, N<sub>2</sub>O, HNO<sub>3</sub> and HONO (HNO<sub>2</sub>) were detected in concentrations between <1 and 10 ppm during the investigation of the NO<sub>x</sub> reduction over Printex U, which provided valuable information about the mechanisms of SCR reaction, soot oxidation and unselective side reactions. Whereas HCN and HNCO are decomposition products of nitrile and amide surface functional groups, formed upon reaction of NH<sub>3</sub> with carboxylic groups, HNO<sub>3</sub> and HONO (HNO<sub>2</sub>) are typical intermediates of the *fast SCR* and *NO<sub>2</sub> SCR* reaction formed upon disproportionation of NO<sub>2</sub> on the carbon surface in the presence of water [30–32]:



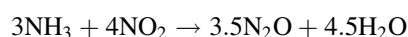
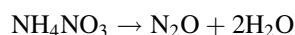
Furthermore, HONO could be generated via hydrogen abstraction from the soot surface by NO<sub>2</sub> as shown in [33] and as it is known from partial oxidation of light organic molecules in the gas phase [34]. HNO<sub>3</sub> and HONO readily react in the presence of NH<sub>3</sub> to ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) and ammonium nitrite (NH<sub>4</sub>NO<sub>2</sub>). These are



**Fig. 3** NO<sub>x</sub> reduction and C-oxidation rates of Printex U during the SCR measurements in dependence of the NH<sub>3</sub> concentration between 200 and 350 °C at a GHSV of 35,000 h<sup>-1</sup>. Base feed + 250 ppm NO<sub>2</sub> + variable NH<sub>3</sub> concentrations. *Solid lines* NO<sub>x</sub> reduction [%]; *dotted lines* C-oxidation rates

the same compounds as the well-known intermediates of the *fast SCR* and *NO<sub>2</sub> SCR* reaction over inorganic SCR catalysts. NH<sub>4</sub>NO<sub>2</sub> is unstable above 60–70 °C and decomposes to N<sub>2</sub>. NH<sub>4</sub>NO<sub>3</sub> has to be reduced in case of the *fast SCR* reaction with NO to NH<sub>4</sub>NO<sub>2</sub>, which again decomposes to N<sub>2</sub>, and in case of the *NO<sub>2</sub> SCR* reaction with NH<sub>3</sub> over several steps to the final SCR product N<sub>2</sub>. Summing up all reaction steps lead to the overall stoichiometries of *fast SCR* and *NO<sub>2</sub> SCR* reaction, respectively.

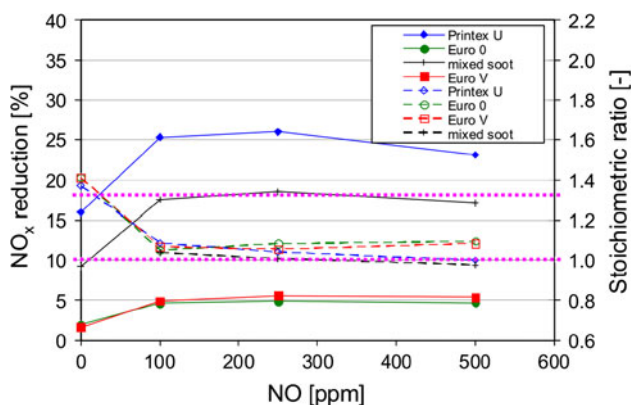
Finally, also the formation of small amounts of N<sub>2</sub>O can be easily explained with this reaction network. N<sub>2</sub>O might be formed as result of the thermal decomposition of the intermediate NH<sub>4</sub>NO<sub>3</sub> or from the oxidation of NH<sub>3</sub>:



### 3.3 SCR Reaction over Diesel Soot in Comparison to Printex U

When selected experiments of the study with Printex U were repeated with the Euro 0, Euro V and mixed diesel soot sample, similar catalytic results were obtained, except the general SCR activity level, which was significantly reduced (Fig. 4). According to correlations in literature between general soot reactivity and surface acidity [9, 15, 16, 35–37], one reason for the high NO<sub>x</sub> reduction rates over Printex U was most probably its high activity to form acidic surface functional groups on the carbon surface upon exposure to NO<sub>2</sub>, which is supported by the observed evolution of higher amounts of HCN and HNCO from Printex U (results not shown). Since the organic carbon content of this soot (i.e. the tar-like soot components) was <1 % the elemental carbon fraction was most likely responsible for the formation of acidic surface functional groups.

The consumption of HNO<sub>3</sub> during SCR on soot according to the above described SCR chemistry was supported by the comparison of the diesel soot samples and Printex U. The diesel soot samples showing lower NO<sub>x</sub> reduction evolved higher amounts of HNO<sub>3</sub>, because it was not consumed in the further SCR process. In addition, higher amounts of HNO<sub>3</sub> evolved from the real diesel soot samples suggesting that the disproportionation of NO<sub>2</sub> to HNO<sub>3</sub> and HONO, which is a prerequisite for the occurrence of the SCR reaction, was most probably not the rate limiting reaction step. This also indicates that the adsorption properties for NH<sub>3</sub> were the critical factor for the SCR reaction over soot in analogy to inorganic SCR catalysts, for which surface acidity is decisive to adsorb NH<sub>3</sub> and consequently reach high activities. This significance of acidic surface functional groups for the adsorption of NH<sub>3</sub>



**Fig. 4** NO<sub>x</sub> reduction and measured stoichiometric ratios ( $=\text{NH}_3\text{,consumed}/\text{NO}_x\text{,consumed}$ ) over Printex U, Euro 0, Euro V soot and the mixed soot sample in dependence of the NO concentration at 250 °C. GHSV: 35,000 h<sup>-1</sup>. Base feed + 250 ppm NO<sub>2</sub> + 250 ppm NH<sub>3</sub> + variable NO concentrations. *Solid lines* NO<sub>x</sub> reduction [%]; *dashed lines* measured stoichiometric ratios; *purple dotted lines* stoichiometric ratios of the *fast SCR* (=1) and *NO<sub>2</sub> SCR* (=1.33) reaction

due to acid–base–interaction [15–18, 38, 39] was confirmed by DRIFTS measurements (results not shown) showing NH<sub>4</sub><sup>+</sup> bands only in the presence of NO<sub>2</sub>, which causes the formation of acidic carboxylic groups on the soot surface.

Considerable amounts of inorganic components have been found in the diesel soot samples by ICP-OES. Regarding the iron-content of approx. 1 % in all samples, the question arises if the soot activity might have been caused by this redox-active component. However, if this assumption is right significantly higher activities would have been expected for the real soot samples compared to the pure Printex U, whereas the opposite was found experimentally. It can be speculated if the alkali metals in the diesel soot samples might have led to the lower NO<sub>x</sub> reduction activity due to their strong basicity, in accordance with findings of Ahmed et al. [40].

#### 4 Conclusions

The investigations of the NO<sub>x</sub> reduction by SCR with NH<sub>3</sub> showed that model and diesel soot samples were able to remove NO<sub>x</sub> in model exhaust gases up to 25 % at 35,000 h<sup>-1</sup>. The presence of NO<sub>2</sub> in the feed gas was a prerequisite for NO<sub>x</sub> reductions, because NO<sub>2</sub> disproportionation was the initial step of the SCR process on soot. Depending on the presence or absence of NO, the *fast SCR* or the *NO<sub>2</sub> SCR* reaction pathway was followed, respectively, which was supported by the observed NH<sub>3</sub>:NO<sub>x</sub> consumptions, the reaction intermediates in the gas phase and the detected surface species.

The obtained results are important for future combined DPF-SCR systems, where urea (or rather NH<sub>3</sub>) and NO<sub>x</sub>

are present together with soot, since significant NO<sub>x</sub> reduction has to be expected in the presence of soot even at high space velocities characteristic for vehicle applications.

#### References

- Busca G, Lietti L, Ramis G, Berti F (1998) Chemical and mechanistic aspects of the selective catalytic reduction of NO<sub>x</sub> by ammonia over oxide catalysts: a review. *Appl Catal B* 18(1–2):1–36
- Kröcher O (2007) Aspects of catalyst development for mobile urea-SCR systems—from vanadia-titania catalysts to metal-exchanged zeolites. *Stud Surf Sci Catal* 171:261–289
- Andersen H, Green W, Steele D (1961) The catalytic treatment of nitric acid plant tail gas. *Ind Eng Chem* 53(3):199–204
- Heck RM (1999) Catalytic abatement of nitrogen oxides-stationary applications. *Catal Today* 53(4):519–523
- Jüntgen H (1986) Activated carbon as catalyst. *Erd Koh Erdg Petr V* 39(12):546–551
- Jüntgen H, Richter E, Knoblauch K, Hoang-Phu T (1988) Catalytic NO<sub>x</sub> reduction by ammonia on carbon catalysts. *Chem Eng Sci* 43(3):419–428
- Jüntgen H, Richter E, Kuhl H (1988) Catalytic activity of carbon catalysts for the reaction of NO<sub>x</sub> with NH<sub>3</sub>. *Fuel* 67(6):775–780
- Knoblauch K, Richter E, Jüntgen H (1981) Application of active coke in processes of SO<sub>2</sub>- and NO<sub>x</sub>-removal from flue gases. *Fuel* 60(9):832–838
- Komatsubara Y, Ida S, Fujitsu H, Mochida I (1984) Catalytic activity of PAN-based active carbon fibre (PAN-ACF) activated with sulphuric acid for reduction of nitric oxide with ammonia. *Fuel* 63(12):1738–1742
- Kusakabe K, Kashima M, Morooka S, Kato Y (1988) Rate of reduction of nitric oxide with ammonia on coke catalysts activated with sulphuric acid. *Fuel* 67(5):714–718
- Mochida I, Ogaki M, Fujitsu H, Komatsubara Y, Ida S (1983) Catalytic activity of coke activated with sulphuric acid for the reduction of nitric oxide. *Fuel* 62(7):867–868
- Mochida I, Ogaki M, Fujitsu H, Komatsubara Y, Ida S (1985) Reduction of nitric oxide with activated PAN fibres. *Fuel* 64(8):1054–1057
- Richter E, Kleinschmidt R, Pilarczyk E, Knoblauch K, Jüntgen H (1985) Thermal desorption of nitrogen oxides from activated carbon. *Thermochim Acta* 85:315–318
- Richter E, Knoblauch K, Jüntgen H (1987) Mechanisms and kinetics of SO<sub>2</sub> adsorption and NO<sub>x</sub> reduction on active coke. *Gas Sep Purif* 1(1):35–43
- Ahmed SN, Baldwin R, Derbyshire F, McEnaney B, Stencel J (1993) Catalytic reduction of nitric oxide over activated carbons. *Fuel* 72(3):287–292
- Ku BJ, Lee JK, Park D, Rhee H-K (1994) Treatment of activated carbon to enhance catalytic activity for reduction of nitric oxide with ammonia. *Ind Eng Chem Res* 33(11):2868–2874
- Martin-Martinez JM, Singoredjo L, Mittelmeijer-Hazeleger M, Kapteijn F, Moulijn JA (1994) Selective catalytic reduction of NO with NH<sub>3</sub> over activated carbons. I: Effect of origin and activation procedure on activity. *Carbon* 32(5):897–904
- Szymanski GS, Grzybek T, Papp H (2004) Influence of nitrogen surface functionalities on the catalytic activity of activated carbon in low temperature SCR of NO<sub>x</sub> with NH<sub>3</sub>. *Catal Today* 90(1–2):51–59
- Grzybek T, Klinik J, Samojeeden B, Suprun V, Papp H (2008) Nitrogen-promoted active carbons as DeNO<sub>x</sub> catalysts: 1. The influence of modification parameters on the structure and catalytic properties. *Catal Today* 137(2–4):228–234

20. Muniz J, Marban G, Fuertes AB (1999) Low temperature selective catalytic reduction of NO over polyarylamide-based carbon fibres. *Appl Catal B* 23(1):25–35
21. Shirahama N, Mochida I, Korai Y, Choi KH, Enjoji T, Shimohara T, Yasutake A (2005) Reaction of NO with urea supported on activated carbons. *Appl Catal B* 57(4):237–245
22. Mehring M (2011) Composition and reactivity analysis of diesel soot with advanced FTIR spectroscopy and a new TG-FTIR system, at the example of the oxidation with O<sub>2</sub>, NO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> and the SCR reaction with NO<sub>x</sub> and NH<sub>3</sub>. Ph.D thesis No. 19993, Zürich
23. Mehring M, Elsener M, Kröcher O (2012) Selective catalytic reduction of NO<sub>x</sub> with ammonia over soot. *ACS Catal* 2(7):1507–1518
24. Kuhl H, Baumann H, Juntgen H, Ehrburger P, Dentzer J, Lahaye J (1989) The importance of active surface area on the NO-reduction with ammonia on carbon catalysts. *Fuel* 68(1):129–130
25. Zawadzki J, Wisniewski M (2003) In situ characterization of interaction of ammonia with carbon surface in oxygen atmosphere. *Carbon* 41(12):2257–2267
26. Azambre B, Collura S, Trichard JM, Weber JV (2006) Nature and thermal stability of adsorbed intermediates formed during the reaction of diesel soot with nitrogen dioxide. *Appl Surf Sci* 253(4):2296–2303
27. Gao X, Liu S, Zhang Y, Luo Z, Ni M, Cen K (2011) Adsorption and reduction of NO<sub>2</sub> over activated carbon at low temperature. *Fuel Process Technol* 92(1):139–146
28. Kirchner U, Scheer V, Vogt R (2000) FTIR spectroscopic investigation of the mechanism and kinetics of the heterogeneous reactions of NO<sub>2</sub> and HNO<sub>3</sub> with soot. *J Phys Chem A* 104(39):8908–8915
29. Shirahama N, Moon SH, Choi KH, Enjoji T, Kawano S, Korai Y, Tanoura M, Mochida I (2002) Mechanistic study on adsorption and reduction of NO<sub>2</sub> over activated carbon fibers. *Carbon* 40(14):2605–2611
30. Akimoto H, Bandow H, Sakamaki F, Inoue G, Hoshino M, Okuda M (1980) Photooxidation of the propylene-NO<sub>x</sub>-air system studied by long-path Fourier transform infrared spectrometry. *Environ Sci Technol* 14(2):172–179
31. Kleffmann J, Becker KH, Wiesen P (1998) Heterogeneous NO<sub>2</sub> conversion processes on acid surfaces: possible atmospheric implications. *Atmos Environ* 32(16):2721–2729
32. Sakamaki F, Shiro H, Akimoto H (1980) Formation of nitrous acid and nitric oxide in the heterogeneous dark reaction of nitrogen dioxide and water vapor in a smog chamber. *Int J Chem Kinet* 15:1013–1029
33. Stadler D, Rossi MJ (2000) The reactivity of NO<sub>2</sub> and HONO on flame soot at ambient temperature: the influence of combustion conditions. *Phys Chem Chem Phys* 2(23):5420–5429
34. Otsuka K, Takahashi R, Amakawa K, Yamanaka I (1998) Partial oxidation of light alkanes by NO<sub>x</sub> in the gas phase. *Catal Today* 45(1–4):23–28
35. Izquierdo MT, Rubio B, Mayoral C, Andrés JM (2001) Modifications to the surface chemistry of low-rank coal-based carbon catalysts to improve flue gas nitric oxide removal. *Appl Catal B* 33(4):315–324
36. Mochida I, Kawano S (1991) Capture of ammonia by active carbon fibers further activated with sulfuric acid. *Ind Eng Chem Res* 30(10):2322–2327
37. Muckenhuber H, Grothe H (2007) A DRIFTS study of the heterogeneous reaction of NO<sub>2</sub> with carbonaceous materials at elevated temperature. *Carbon* 45(2):321–329
38. Lee JK, Park TJ, Park D, Park S (1993) Catalytic activity of chars prepared by fluidized bed pyrolysis for the reduction of nitric oxide with ammonia. *Ind Eng Chem Res* 32(9):1882–1887
39. Singoredjo L, Kapteijn F, Moulijn JA, Martin-Martinez J-M, Boehm H-P (1993) Modified activated carbons for the selective catalytic reduction of NO with NH<sub>3</sub>. *Carbon* 31(1):213–222
40. Ahmed SN, Stencel JM, Derbyshire FJ, Baldwin RM (1993) Activated carbons for the removal of nitric oxide. *Fuel Process Technol* 34(2):123–136