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Catalysis Today 73 (2002) 239–247

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Selective catalytic reduction of NO and NO_2 at low temperatures

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Abstract

The fast SCR reaction using equimolar amounts of NO and NO_2 is a powerful means to enhance the NO_x conversion over a given SCR catalyst. NO_2 fractions in excess of 50% of total NO_x should be avoided because the reaction with NO_2 only is slower than the standard SCR reaction.

At temperatures below 200 °C, due to its negative temperature coefficient, the ammonium nitrate reaction gets increasingly important. Half of each NH_3 and NO_2 react to form dinitrogen and water in analogy to a typical SCR reaction. The other half of NH_3 and NO_2 form ammonium nitrate in close analogy to a NO_x storage-reduction catalyst. Ammonium nitrate tends to deposit in solid or liquid form in the pores of the catalyst and this will lead to its temporary deactivation.

The various reactions have been studied experimentally in the temperature range 150–450 °C for various NO_2/NO_x ratios. The fate of the deposited ammonium nitrate during a later reheating of the catalyst has also been investigated. In the absence of NO, the thermal decomposition yields mainly ammonia and nitric acid. If NO is present, its reaction with nitric acid on the catalyst will cause the formation of NO_2.

Keywords: $DeNO_x$; Selective catalytic reduction; NO; NO_2; SCR

1. Introduction

Diesel engines are outstanding with respect to efficiency and they are therefore the preferred type used in heavy-duty vehicles where high fuel economy is of prime importance. Their disadvantages are however high emissions of nitric oxides and particulates, especially when compared to gasoline engines equipped with a three-way catalyst. In the past few years, considerable improvements were achieved by mere optimization of the combustion chamber and by using higher injection pressures. A well-established trade-off between particulates and nitric oxides impedes the simultaneous reduction of both emissions. Therefore, it is now generally accepted that the forthcoming EURO 4 emission standards proposed for the year 2005 pertaining to HD trucks and buses will be no longer feasible by combustion modifications alone, but will require additional exhaust gas after treatment techniques.

The lean exhaust typical for diesel engines requires special catalytic processes that allow for the preferential reduction of nitrogen oxide besides oxygen. They include HC-SCR [1,2], SCR with N-containing reducing agents [3,4] and the NO_x storage-reduction catalyst [5,6]. Truly selective reduction of NO in the presence of O_2 requires the use of N-containing reducing agents like ammonia or urea.

Urea-SCR has been studied at PSI for more than 10 years, with initial emphasis in the $DeNO_x$ of stationary diesel engines [7,8]. Although these early experiments showed very positive results, an application to mobile diesel engines did not look very promising due to the low space velocities possible with the catalysts available at that time. These were extruded catalysts based on TiO_2–WO_3–V_2O_5 with a maximum cell density of

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0920-5861/02/$ – see front matter
PII: S0920-5861(02)00006-8

100 cpsi allowing for space velocities of 10,000 h^{-1} at the best. It was clear that the volumetric activity of the catalysts had to be improved; the main means to achieve this are an increase of the cell density and intrinsic activity. Although extruded catalysts are now available with 200 and 300 cpsi, the use of coated catalysts allows for even higher cell densities.

Such catalysts are suitable for a mobile $DeNO_x$ system with moderate catalyst volumes if the minimum exhaust temperature is not too low (typically 250 °C). At even lower temperatures, the “fast SCR reaction” offers still further potential to increase the performance of a given SCR catalyst. However, at very low temperatures another reaction will lead to the formation of ammonium nitrate in the catalyst, further complicating the chemistry of an SCR system.

2. Main chemical reactions

2.1. Without formation of ammonium nitrate

Although urea is used in the technical application of the process, our experience has shown that its decomposition into ammonia and carbon dioxide is usually quite fast in a typical $DeNO_x$ system [9]. Therefore, we will restrict our present discussion to ammonia as the selective reducing agent. Due to the fact that NO_x in diesel exhaust consists mainly of NO (>90%), the main SCR reaction is

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

We will subsequently call this reaction “standard SCR”. This reaction is not fully selective to the reduction of NO but also consumes some O_2. The reaction consuming no oxygen is much slower and is therefore not relevant in lean exhaust:

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

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

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

We will further denote this reaction as “fast SCR”. The increase in reaction rate has long been known [10,11] and it is now proposed as an efficient measure to increase the performance of an automotive $DeNO_x$ system. In order to increase the fraction of NO_2 in the exhaust, a strong oxidation catalyst (Pt based) is usually placed upstream of the SCR catalyst. However, any excess of NO_2 will react in the following reaction:

$$4NH_3 + 3NO_2 \rightarrow 3.5N_2 + 6H_2O \qquad (4)$$

Hence, the conversion of NO to NO_2 in the oxidation reactor should not exceed 50% as this will lower the performance of the SCR catalyst.

2.2. With the formation of ammonium nitrate

We will give here a shortened description of the chemistry at very low temperatures. Further details are provided in a previous publication [12]. The formation of ammonium nitrate should be envisaged at $T < 200\,^{\circ}C$ according to the following stoichiometry:

$$2NH_3 + 2NO_2 \rightarrow NH_4NO_3 + N_2 + H_2O \qquad (5)$$

This reaction is well known in the cleanup process of nitric acid production and may lead to the disturbing formation of ammonium nitrate in SCR catalysts [13–15]. It is evident that this reaction may also be considered as a selective $DeNO_x$ reaction and will lead to a NO_x-reduction of at least 50% due to the direct formation of N_2. The ammonium nitrate formed in reaction (5) will deposit as a solid or liquid (melting point = 170 °C) if the product of the partial pressures of NH_3 and HNO_3 exceeds the equilibrium constant K_p of the decomposition reaction:

$$NH_4NO_3(s) \leftrightharpoons NH_3 + HNO_3 \qquad (6)$$

$$K_p = p_{NH_3} p_{HNO_3} \qquad (7)$$

However, the fate of ammonium nitrate formed on a subsequent reheating of the catalyst must be further clarified. The following reactions should be considered for its decomposition:

1) The most often cited decomposition reaction for temperatures up to 260 °C is the decomposition into water and nitrous oxide [16]:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O \qquad (8)$$

2) The explosive decomposition under initial ignition has also been described and yields nitrogen, oxygen and water [16]:

$$2NH_4NO_3 \rightarrow 2N_2 + O_2 + 4H_2O \qquad (9)$$

As will be shown in the Section 3, the following reactions are the most important under typical exhaust gas conditions:

3) The dissociation of ammonium nitrate into NH_3 and HNO_3 according to the reverse reaction (6).
4) In the presence of NO, which is typical for an exhaust gas, nitric acid formed in reaction (6) will react with NO to form NO_2:

$$2HNO_3 + NO \rightarrow 3NO_2 + H_2O \tag{10}$$

Which of the above decomposition reactions contributes the most depends on the exact conditions, especially on temperature and heating rate. The main goal of the present work is to determine the contribution of the various reactions under realistic low temperature SCR conditions.

3. Experimental

Catalysts. The majority of the experiments were performed with a monolithic catalyst. The metallic monolith had a cell density of 600 cells/in.^{2} and a volume of 7.3 cm^3. It had been coated with 1.4 g of a catalyst mixture developed at PSI consisting of ≈3% V_2O_5, 9% WO_3 and TiO_2. Further details on the catalyst preparation have been given in a previous publication [9]. The kinetic experiments described in Section 4.3 were made with a powder sample of the same catalyst ($160 < d < 200\,\mu m$).

Reactor. A tubular glass reactor of 30 mm inner diameter and of about 500 mm length was used. The reactor includes a preheating zone of 150 mm and is heated by two separate heating coils powered by two temperature controls. The kinetic experiments described in Section 4.3 were made in a microreactor of ≈8 mm inner diameter.

Feed gas. The composition of the feed gas used in the experiments was adapted to a typical exhaust gas, i.e. the “base feed” contained 10% oxygen and 5% water, the overall balance being nitrogen. NO, NO_2 and NH_3 were in the range 200–1500 ppm. The feed gas was mixed from gas mixtures of higher concentration using mass flow controllers (Brooks). Water was dosed in liquid form into an electrically heated evaporator. The gas lines to the reactor and from the reactor to the FT-IR spectrometer were heated to 150 °C. More details on the experimental setup including a drawing have been given previously [9,12].

Gas analysis. Multicomponent gas analysis was performed by means of an FT-IR spectrometer (Nicolet Magna IR 560, OMNIC® QuantPad software) equipped with a multiple pass gas cell (Graseby Specac G-2-4-BA-AU, path length 2 m) and a liquid nitrogen cooled MCT detector. The method developed allowed the simultaneous determination of NO, NO_2, N_2O, HNO_3, NH_3 and H_2O.

Calibration for HNO_3. A calibrating gas of ≈300 ppm HNO_3 was prepared by scrubbing a stream of pure nitrogen through a wash bottle containing a solution of 45% nitric acid. The exact concentration was determined by absorbing a measured volume of the calibrating gas into a known excess of alkali and back-titration with acid. The IR adsorption of the calibrating gas was measured in the frequency range 836–917 cm^{-1}. Assuming linear behavior with zero intercept a calibration line was constructed.

4. Results and discussion

4.1. Standard and fast SCR at $T > 200\,^{\circ}C$

The presence of NO_2 has a dramatic effect on the activity of an SCR catalyst at low temperatures. The results of a typical experiment at 200 °C with various ratios of NO_2/NO_x are represented in the performance plot of Fig. 1. This plot is obtained by varying stepwise the addition of NH_3 for the fixed concentration of 1000 ppm NO and measuring the resulting NO_x conversion ($DeNO_x$) and slip (efflux) of NH_3 behind the catalyst.

The strong improvement of the performance with increasing fraction of NO_2 is evident. Due to the fact that in the practical application of the SCR process a high ammonia slip cannot be tolerated, we typically use the $DeNO_x$ at 10 ppm NH_3-slip. It can be seen that this value increases from ≈20% for pure NO to ≈95% for the 1:1 mixture $NO + NO_2$. Expressed in terms of a first order rate law this corresponds to an increase by a factor of ≈13 at these conditions.

The influence of temperature on the standard SCR reaction and the fast SCR reaction is shown in Fig. 2. It can be seen that the increase in NO_x conversion due

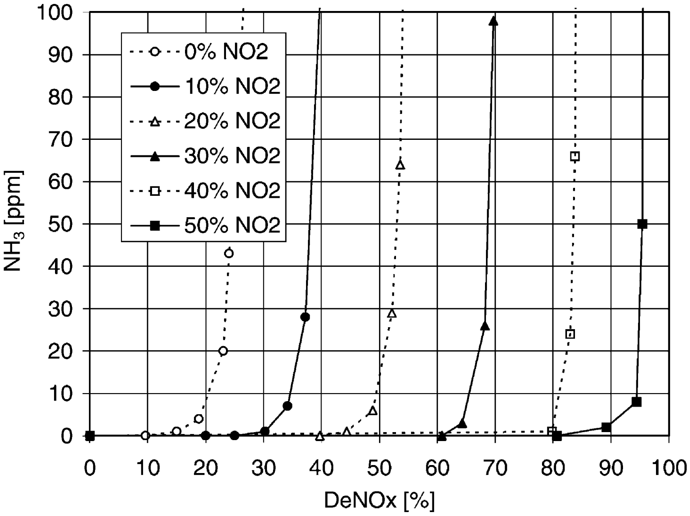

Fig. 1. Performance of monolithic catalyst sample at $T = 200\,^{\circ}C$ for varying ratios of NO_2/NO_x at GHSV = 52,000 h^{-1}. Base feed with 1000 ppm NO_x, NH_3 varied.

to fast SCR is most effective at low temperatures and vanishes at higher temperatures, i.e. about 300–350 °C. The reasons for this behavior will be discussed below in connection with Fig. 6.

Fig. 3 shows the influence of the NO_2/NO_x ratio on NO_x conversion at a fixed temperature of 250 °C. The measured conversion represents the linear combination of the three reactions:

- (1) standard SCR,
- (3) fast SCR,
- (4) SCR with NO_2.

Therefore, at the point of maximum conversion, i.e. 50% NO_2, only the fast SCR reaction takes place. At

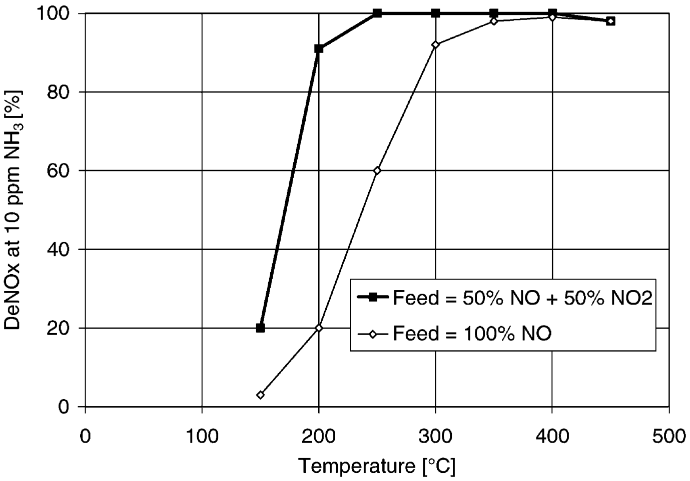

Fig. 2. $DeNO_x$ at 10 ppm NH_3-slip for standard SCR and fast SCR as a function of temperature. GHSV = 52,000 h^{-1}, base feed with 1000 ppm NO_x, NH_3 varied.

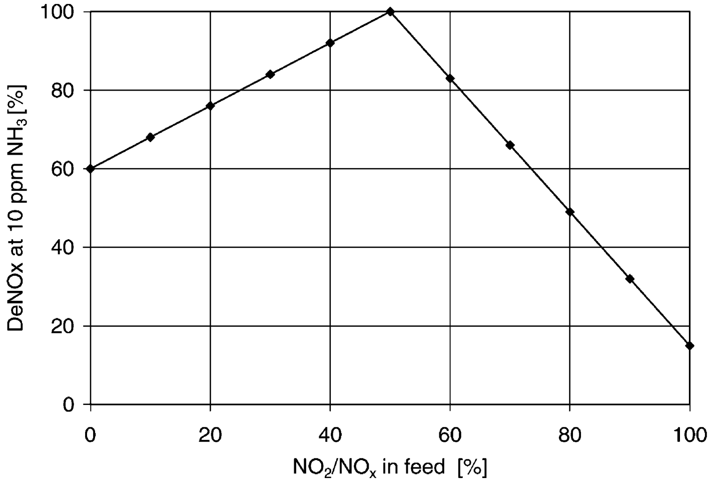

Fig. 3. Influence of the NO_2 fraction on $DeNO_x$ at 250 °C. GHSV = 52,000 h^{-1}, base feed with 1000 ppm NO_x, NH_3 varied.

NO_2 fractions below 50%, both reactions (1) and (3) take place sequentially, the fast SCR reaction consuming first all the available NO_2. Finally, at NO_2 fractions above 50% both reactions (3) and (4) occur sequentially. The higher (negative) slope above 50% NO_2 compared to the (positive) slope below 50% reflects the slower reaction rate of reaction (4) compared to (1).

In conclusion, all results indicate that the optimum NO_2 fraction is 50%, in accordance with the stoichiometry of the fast SCR reaction.

4.2. Experiments at 150 °C

At temperatures below about 200 °C the formation of ammonium nitrate (solid or liquid) according to reaction (5) becomes increasingly important. Previous experiments with a powder sample had shown that the ammonium nitrate reaction is practically the only reaction at 150 °C [12]. This means that only NO_2 and NH_3 will be consumed over the catalyst, whereas NO will pass the catalyst unreacted. On monoliths however the fast SCR reaction (3) consuming also NO is still important at 150 °C. This unexpected difference between powder and monolithic samples has been discussed in detail in a previous paper [12]. The impression is that the ammonium nitrate reaction is not catalyzed by the BET surface, but by the geometric surface which is higher in the case of the powder sample.

The following experiments were made with the goal of elucidating the fate of ammonium nitrate formed by the ammonium nitrate reaction during a subsequent reheating of the catalyst. In the case of an automotive $DeNO_x$ reactor such a reheating occurs during a later load increase of the engine. Ammonium nitrate was synthesized in a first "loading" step on the catalyst using a feed consisting of NH_3 and NO_2 (without NO).

4.2.1. Formation and decomposition of ammonium nitrate in humid conditions

Fig. 4 shows the results of a typical experiment. "Loading" of the monolith sample with ammonium nitrate is performed for 30 min in the humid base feed (5% H_2O, 10% O_2, 1000 ppm NO_2, 1000 ppm NH_3, balance N_2).

During the "loading" period, the outlet concentrations of NO_2 and NH_3 are lower than the inlet values (1000 ppm) and about equal. Half of the missing amounts of both NO_2 and NH_3 form ammonium nitrate in accordance with the 1:1 stoichiometry of reaction (5).

After 30 min, the addition of NH_3 and NO_2 to the feed is terminated and after ≈60 min the reactor is heated up slowly. The decomposition of ammonium nitrate starts soon after the temperature begins to rise. The thermal decomposition yields only ammonia and nitric acid in practically equal amounts. Within the experimental error and taking into consideration the blank adsorption of NH_3, half the amount of each NH_3 and NO_2 dosed during the "loading" step are released in the thermal decomposition experiment

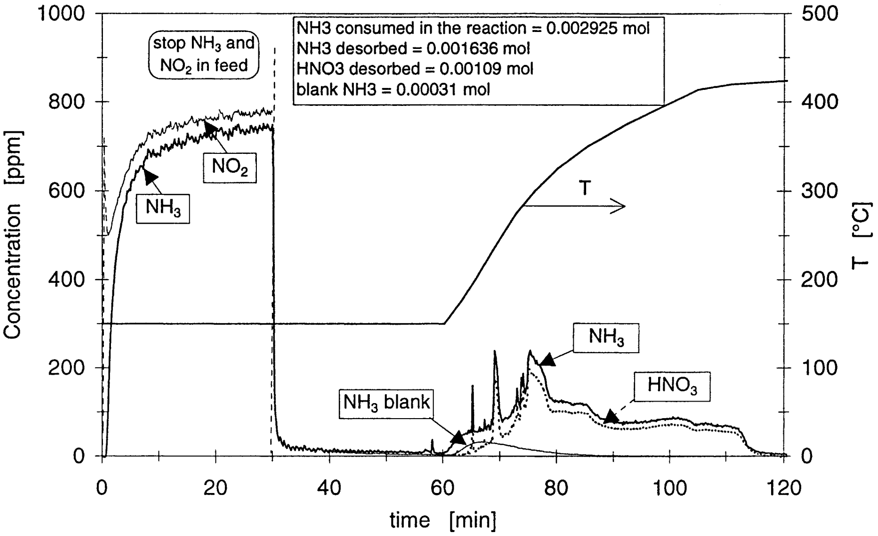

Fig. 4. Efflux of NH_3 and HNO_3 from catalyst during reheating. For details see text.

according to:

$$NH_4NO_3(\text{s or l}) \rightarrow NH_3 + HNO_3 \qquad (6)$$

These quantities of NH_3 and HNO_3 are in agreement with reaction (5), the other half of each NH_3 and NO_2 having formed N_2 and H_2O during the "loading" step. Only a trace of nitrous oxide can be detected during the decomposition. Table 1 resumes the detailed mass balance of this experiment.

Table 1
Mass balance of formation and decomposition of ammonium nitrate (conditions: humid, without NO)

Experimentally measured values	
[1]	NH_3 consumed in reaction (5) = 0.002925 mol
[2]	NH_3 desorbed = 0.001636 mol
[3]	HNO_3 desorbed = 0.00109 mol
[4]	NH_3 blank = 0.000306 mol
Calculated values according to reactions (5) and (6)	
[5]	NH_4NO_3 produced in (5) = 0.5([1] − [4]) = 0.0013095 mol
[6]	NH_3 from NH_4NO_3 according to (6) = [5] = 0.0013095 mol
[7]	HNO_3 from NH_4NO_3 according to (6) = [5] = 0.0013095 mol
[8]	NH_3 desorbed = [6] + [4] = 0.001615 mol; compare with [2]

4.2.2. Formation and decomposition of ammonium nitrate in dry conditions

The observation that virtually no nitrous oxide has been formed in the previous experiment is unexpected. The thermal decomposition of ammonium nitrate is a standard method to produce N_2O in the laboratory [16] and this is in accord with reaction (8). Therefore, we suspected that the presence of water in our experiment would inhibit the decomposition into N_2O and H_2O. The above experiment was therefore repeated under dry conditions, i.e. omitting the 5% water during the "loading" step and during decomposition.

However, the main decomposition products observed were again NH_3 and HNO_3. A small peak of N_2O could be observed, but this amounted to less that 10% of all the nitrogen recovered during the thermal decomposition of ammonium nitrate.

4.2.3. Formation and decomposition of NH_4NO_3 with NO present during decomposition

In this experiment the loading of the catalyst with ammonium nitrate was as described in Section 4.2.1, i.e. in the presence of water (Fig. 5). Ammonia and nitrogen dioxide in the feed were stopped after ≈41 min and 500 ppm NO added instead. A drop in the effluent NO level is immediately observed until ≈70 min with a minimum at ≈55 min. A simultaneous

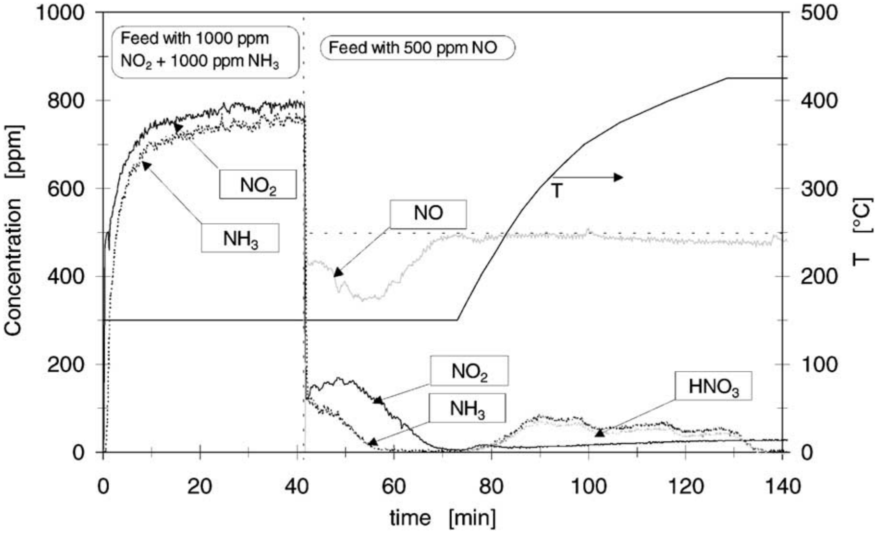

Fig. 5. Efflux of NH_3 and HNO_3 from catalyst during reheating. Decomposition in presence of NO. For details see text.

formation of NO_2 is also seen. Both observations are due to reaction (10), i.e. nitric acid is produced by thermal decomposition of ammonium nitrate which will then react with NO to yield NO_2. Some of this NO_2 will then react with NO and NH_3 in the fast SCR fraction over the catalyst. A mass balance considering reactions (3), (5), (6) and (10) is in quantitative agreement with the integrated values of NO, NO_2, HNO_3 and NH_3 during loading and decomposition.

As may be seen from Fig. 5, only a fraction of the formed ammonium nitrate decomposes according to this complex mechanism. Another fraction decomposes only later during the heating period and here the decomposition yields again NH_3 and HNO_3 in a 1:1 ratio according to reaction (6). We suspect that this second fraction is not deposited on the catalyst, but on the surfaces of the reactor and piping. This suspicion is strengthened from still another experiment where a catalyst without vanadia was used (coating with TiO_2 and WO_3 only). In this case the decomposition at 150 °C in the presence of NO did not lead to the formation of NO_2. Only at rising temperatures (160–250 °C) some depression in NO and formation of NO_2 could be observed. Therefore, we conclude that the reaction (10) is accelerated on a catalyst with redox properties.

The decomposition in the presence of NO comes the closest to the conditions of real exhaust gas. Therefore in a mobile $DeNO_x$ system, we expect at least a partial reduction of nitric acid to nitrogen dioxide. Subsequently, some of this nitrogen dioxide will react with ammonia and NO according to the fast SCR reaction (3).

4.3. Temperature dependence of the four reactions rates

The kinetics of reactions (1), (3), (4) and (5) were investigated in a microreactor at GHSV = 500,000 h^{-1} using the powder sample. The NO_x-conversion ($DeNO_x$) of the following three gas mixtures was measured at different temperatures:

(a) base feed + 1000 ppm NO + 1000 ppm NH_3,
(b) base feed + 500 ppm NO + 500 ppm NO_2 + 1000 ppm NH_3,
(c) base feed + 1000 ppm NO_2 + 1000 ppm NH_3.

The values of conversion found were converted into rate constants k_m assuming a first order rate law and applying the well known equation for a plug flow reactor:

$$k_m = \frac{V^*}{W} \ln(1 - DeNO_x) \qquad (11)$$

where V^* is the gas flow at actual conditions (cm^3/s) and W the catalyst weight (g).

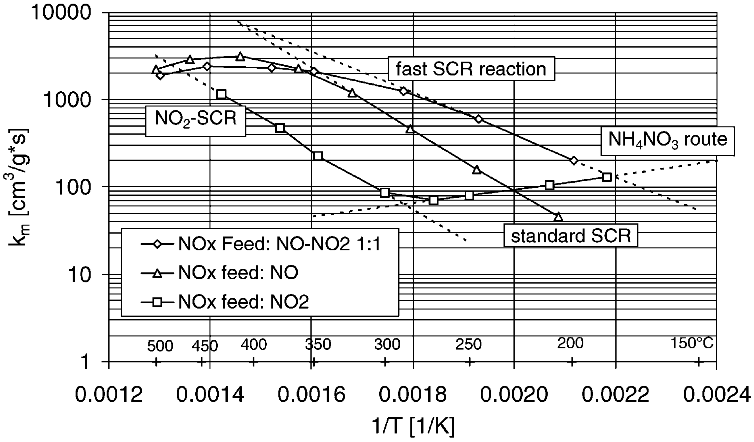

Fig. 6. The rate constants of the four reactions in an Arrhenius plot.

The values of k_m obtained were used in the construction of an Arrhenius plot (Fig. 6). It can be seen that the curves obtained with feeds (a) and (b) show a similar behavior, leveling off and even converging at high temperatures. Feed (a) yields the rate constant of the standard SCR reaction and feed (b) the rate constant for the fast SCR reaction. It is evident that the activation energy of the fast SCR reaction is smaller (≈38 kJ/mol) than that of the standard SCR reaction (≈64 kJ/mol). This causes the difference between the two reaction rates to be more pronounced at the lowest temperatures. At 200 °C this difference amounts to a factor of ≈10.

The behavior of the curve obtained with feed (c) is different, showing a minimum at ≈275 °C. This is due to the fact that this curve is the sum of two reaction rates. At low temperatures the dominant reaction is the ammonium nitrate route represented by reaction (5) with a negative temperature coefficient. At higher temperatures the prevalent reaction is SCR with NO_2 which has a positive temperature coefficient and an activation energy of ≈58 kJ/mol.

5. Conclusions

In the temperature range 200–350 °C the fast SCR reaction with equal amounts of NO and NO_2 shows a much higher rate than the standard SCR reaction. On the other hand, the reaction with pure NO_2 is much slower than the standard SCR reaction. The benefit of utilizing the fast SCR reaction is more pronounced at lower temperatures.

Due to its negative temperature coefficient, the ammonium nitrate reaction shows a different behavior. Its rate increases with decreasing temperature that in turn increases its contribution to the overall conversion. The formation of ammonium nitrate in the pores of the catalyst can cause the temporary deactivation of the catalyst and this limits the practically attainable enhancement of the rate by utilizing NO–NO_2 mixtures. We have shown previously that the practical lower threshold temperature for typical operating conditions with monolithic SCR catalysts is around 180 °C [12].

The thermal decomposition of ammonium nitrate formed previously at low temperatures leads to the formation of ammonia and nitric acid (absence of NO). Nitrous oxide could only be detected under dry conditions in small amounts (<10%). The presence of NO during the thermal decomposition leads to a redox reaction of NO and HNO_3 resulting in the formation of NO_2. Due to the high rate of the fast SCR reaction, this NO_2 can react further with NO and NH_3 on the catalyst.

Acknowledgements

The financial support of the Swiss Federal Office of Energy (BFE) is gratefully acknowledged. We would like to thank the working group GD-Kat of the

Forschungsvereinigung Verbrennungskraftmaschinen (FVV) for valuable discussions.

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