Plasmacatalytic low-temperature conversion of NO_x to N_2 by ammonium-loaded zeolites in a dielectric barrier discharge

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The direct application of a silent electrical discharge on an ammonium-loaded zeolite as catalyst to remove NO in excess oxygen results in a synergetic improvement of NO_x abatement at temperatures below 373 K.

The selective catalytic reduction (SCR) of NO using the addition of reductants like NH_3, urea, hydrocarbons, alcohols, *etc*. has been studied intensively as a potential method to remove NO_x from exhaust gases with excess oxygen.[1] Depending on the type of catalysts and the reductant used, SCR is effective in a temperature range between 450 and 900 K.

In a recent publication, Richter *et al.*[2,3] have described a catalytic low-temperature conversion of NO_x to N_2 using NH_4^+ ions fixed in zeolites as reductant. NO is converted in these systems to N_2 in excess oxygen even at temperatures as low as 373 K. The intermediate oxidation of NO to NO_2 is believed to be the key step limiting the reaction rate of the reaction sequence. As we will show here, the abatement of NO in oxygen excess can be significantly enhanced further by applying a silent electrical discharge immediately on the ammonium-loaded zeolite as catalysts.

For the experiments a reactor was used that enables a dielectric barrier discharge (DBD) directly on the catalyst bed. A glass tube as dielectric is surrounded by a copper grid as ground electrode and contains an inner electrode, which consists of a rod with equidistant steel discs leaving a gap to the glass tube of 0.5 mm. Between these discs the catalyst can be positioned. As catalyst, a mordenite with a Si : Al ratio of 11 was used in the ammonium form. The mordenite has been shown to be effective in the low temperature conversion of NO_x, but also other zeolites (*e.g.* Y, ZSM-5) could be used.[2,3] The electric discharge was initiated by a high-voltage pulse generator with 20 kV peak voltage, 20 μs rise time and a repetition rate up to 115 Hz. The gas composition (NO, NO_2, N_2O, HNO_x) was determined by an FTIR spectrometer equipped with a long-path (20 m) gas cell (Perkin Elmer) and a NO_x-analyser (ECO-Physics). The energy deposited into the discharge was determined by integrating the voltage–charge traces monitored with a digitising oscilloscope (Tektronics TDS 520 C).

Fig. 1 shows the dependence of the conversion of 500 ppm NO in N_2–O_2 (5 vol%) on the applied energy both with and without the catalyst. Without the NH_4-mordenite, NO is partly removed by reactions with the active species from the electric discharge, but at the same time NO_2 is formed and the overall NO_x concentration remains nearly constant. Using the catalyst alone, part of the NO is removed already without an electric discharge. This is due to the reaction described by Richter *et al.*[3] and also by adsorption phenomena at 343 K. At 373 K *ca.* 400 ppm and at 423 K 450 ppm NO remain in the gas phase without electric discharge. Applying additionally the DBD, a complete conversion of NO without the formation of a significant amount of NO_2 was observed. For comparison it should be noted that the energy input of 20 W h m^{-3} is equivalent to an adiabatic temperature increase of *ca.* 70 K.

The conversion of NO to N_2 strongly depends on the oxygen concentration in the gas. Fig. 2 shows this dependence again with and without NH_4-mordenite as catalyst. Whereas the conversion without catalyst declines with increasing oxygen concentration (the NO is converted to NO_2 *vide supra*), the behaviour in the presence of NH_4-mordenite is just the opposite: The conversion strongly increases with the oxygen content. This is in line with the proposal[3] of the intermediate oxidation of NO to NO_2 as the rate limiting step in the reaction mechanism. The electric discharge obviously promotes this intermediate NO-oxidation, resulting in an enhanced overall reaction rate.

To analyse the influence of the electric discharge in more detail, the local position of the catalyst was varied in order to have the discharge in front of, behind and directly on the catalyst bed. Fig. 3 shows the effect of these combinations on

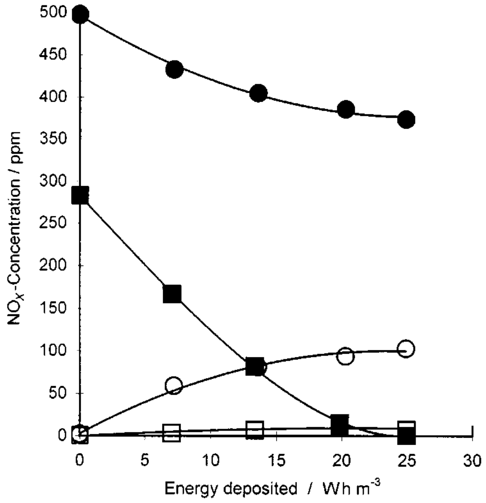

Fig. 1 NO_x concentration after conversion of 500 ppm NO in N_2–O_2 (5 vol%) with (■ : NO, □ : NO_2) and without (● : NO, ○ : NO_2) NH_4-mordenite as catalyst at 343 K and GSHV = 3000 h^{-1}.

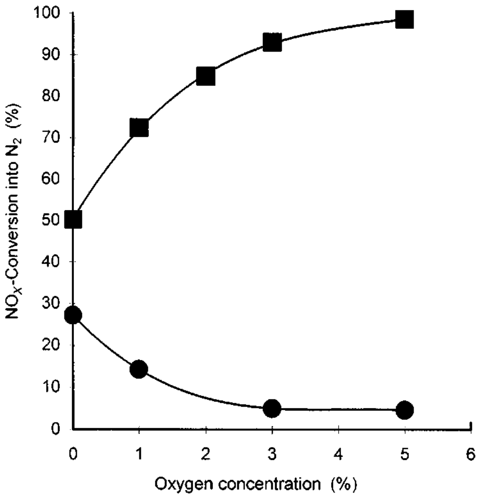

Fig. 2 Conversion of 500 ppm NO into N_2 at DBD (25 W h m^{-3}) without (●) and with (■) NH_4-mordenite as catalyst at 343 K and GSHV = 3000 h^{-1}.

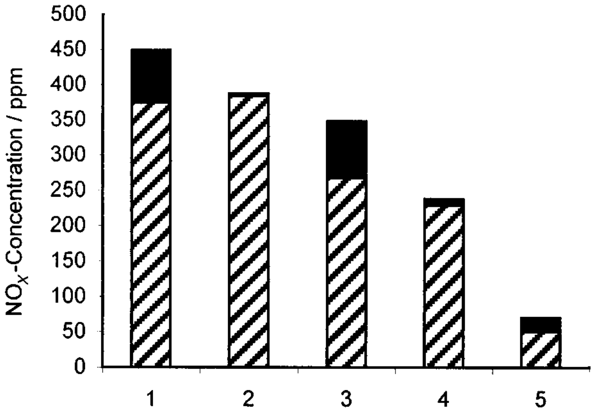

Fig. 3 NO_x concentration after conversion of 500 ppm NO in N_2–O_2 (2 vol%): DBD, without catalyst (1); with NH_4-mordenite, no DBD (2); DBD behind the catalyst (3); DBD in front of the catalyst (4); DBD over the catalyst (*in situ*) (5). Conditions at the catalyst: 343 K, GSHV = 3000 h^{-1}, DBD: *ca.* 25 W h m^{-3}, NO: hatched, NO_2: black.

the NO_x concentration. The application of the DBD behind the catalyst (column 3) converts a part of the remaining NO to NO_2 as should be expected (*cf.* column 2). If the DBD is applied in front of the catalyst, the NO_2 formed in the electric discharge (*cf.* column 1) is converted by the catalyst to nitrogen (column 4). Finally, the *in situ* application of the discharge directly on the catalyst bed results in a synergetic increase of the NO conversion to a degree much higher than the sum of the individual effects (column 5).

This synergy can be explained by the interaction of discharge-induced plasmachemical reactions with the catalysis on the zeolite. A silent electrical discharge in an oxygen-containing gas mixture produces mainly oxygen radicals as active species.[4] Atomic oxygen leads to fast oxidation by the three body reaction (1). In case of the discharge alone without any catalyst, NO removal is limited because of back-reaction (2) and only a part of NO can be converted to NO_2 (Fig. 3, columns 1 and 3). In the presence of NH_4-zeolite, however, NO_2 is removed from the gas stream by the fast catalytic reaction (3),[3] thus preventing the undesirable back conversion (2) of NO_2 to NO.

$$NO + O + M \rightarrow NO_2 + M \qquad (1)$$

$$NO_2 + O \rightarrow NO + O_2 \qquad (2)$$

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

The ammonia bonded to the zeolite is consumed during the reaction with NO_x, leaving the zeolite in the H-form. To maintain the catalytic activity, the zeolite has to be reloaded from time to time with gaseous NH_3 or by ion exchange. Initial experiments have demonstrated that this can be done without loss of activity.

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Notes and references

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