

## Plasmacatalytic low-temperature conversion of $\text{NO}_x$ to $\text{N}_2$ by ammonium-loaded zeolites in a dielectric barrier discharge

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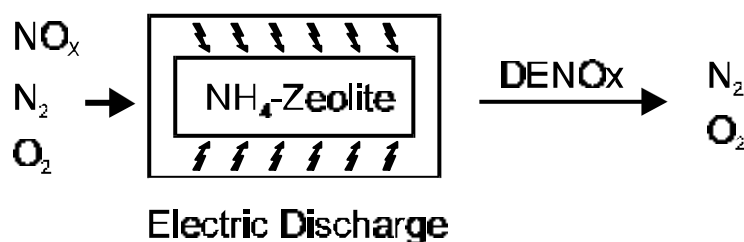
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The direct application of a silent electrical discharge on an ammonium-loaded zeolite as catalyst to remove NO in excess-oxygen results in a synergetic improvement of  $\text{NO}_x$  abatement at temperatures below 373 K.



The selective catalytic reduction (SCR) of NO using the addition of reductants like  $\text{NH}_3$ , urea, hydrocarbons, alcohol's etc. has been studied intensively as a potential method to remove  $\text{NO}_x$  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  $\text{NO}_x$  to  $\text{N}_2$  using  $\text{NH}_4^+$  ions fixed in zeolites as reductant.  $\text{NO}$  is converted in these systems to  $\text{N}_2$  in excess oxygen even at temperatures as low as 373 K. The intermediate oxidation of  $\text{NO}$  to  $\text{NO}_2$  is supposed to be the key step limiting the reaction rate of the reaction sequence. As we will show in this paper, the abatement of  $\text{NO}$  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  $\text{NO}_x$ , 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  $\mu\text{s}$  rise time and a repetition rate up to 115 Hz. The gas composition ( $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{HNO}_x$ ) was determined by an FTIR spectrometer equipped with a long-path (20 m) gas cell (Perkin Elmer) and a  $\text{NO}_x$ -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  $\text{NO}$  in  $\text{N}_2/\text{O}_2$  (5 vol%) on the applied energy both with and without the catalyst. Without the  $\text{NH}_4$ -mordenite,  $\text{NO}$  is partly removed by reactions with the active species from the electric discharge, but at the same time  $\text{NO}_2$  is formed and the overall  $\text{NO}_x$  concentration remains nearly constant. Using the catalyst alone, part of the  $\text{NO}$  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 about 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 significant amount of NO<sub>2</sub> was observed. For comparison it should be noted that the energy input of 20 Wh/m<sup>3</sup> is equivalent to an adiabatic temperature increase of about 70 K.

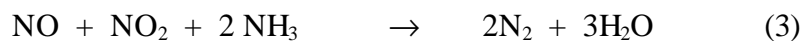
The conversion of NO to N<sub>2</sub> strongly depends on the oxygen concentration in the gas. Fig. 2 shows this dependence again with and without NH<sub>4</sub>-mordenite as catalyst. Whereas the conversion without catalyst declines with increasing oxygen concentration (the NO is converted in NO<sub>2</sub> v.s.), the behaviour in the presence of NH<sub>4</sub>-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<sub>2</sub> 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 before, behind and directly on the catalyst bed. Fig. 3 shows the effect of these combinations on the NO<sub>x</sub> concentration. The application of the DBD behind the catalyst (column 3) converts a part of the remaining NO to NO<sub>2</sub> as should be expected (cf. column 2). If the DBD is applied before the catalyst, the NO<sub>2</sub> 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 produces in an oxygen-containing gas mixture 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<sub>2</sub> (Fig. 3, 1. and 3. columns. In



the presence of  $\text{NH}_4$ -zeolite, however,  $\text{NO}_2$  is removed from the gas stream by the fast catalytic reaction (3) [3], thus preventing the undesirable back conversion (2) of  $\text{NO}_2$  to  $\text{NO}$ .



The ammonia bonded to the zeolite is consumed during the reaction with  $\text{NO}_x$ , leaving the zeolite in the H-form. To maintain the catalytic activity, the zeolite has to be reloaded from time to time with gaseous  $\text{NH}_3$  or by ion exchange. First experiments have demonstrated that this can be done without loss of activity.

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## References

1. for a recent review e.g.:  
R. Burch, *Pure Appl. Chem.*, 1996, **68**, 377 or  
A. Fritz and V. Pitchon, *Applied Catalysis B Environmental*, 1997, **13**, 1-25.
2. M. Richter, B. Parlitz, R. Eckelt and R. Fricke, *J.Chem.Soc., Chem.Commun.*,  
1997, 383-384.
3. M. Richter, R. Eckelt, B. Parlitz and R. Fricke, *Applied Catalysis B  
Environmental*, 1998, **15**, 129-146.
4. B. Eliasson, M. Hirth and U. Kogelschatz, *J. Phys. D: Appl. Phys.*, 1987, **20**, 1421-  
1437.

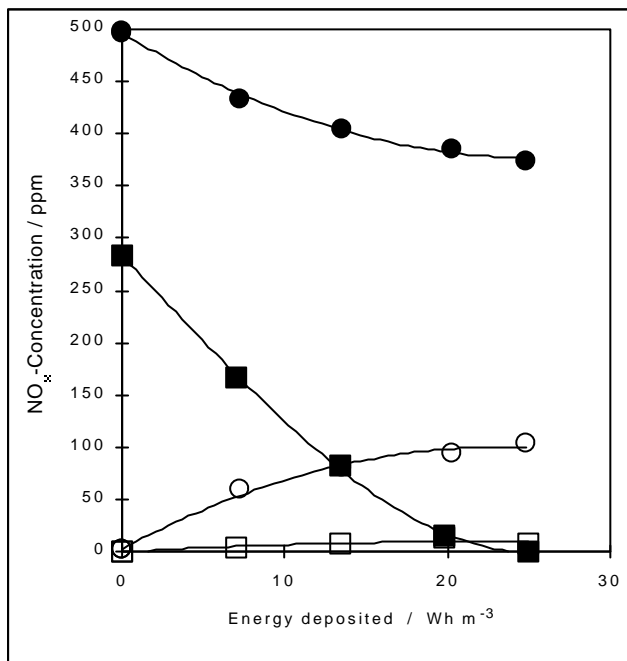


Fig. 1 NO<sub>x</sub> concentration after conversion of 500 ppm NO in N<sub>2</sub>/O<sub>2</sub> (5 vol%) with (■ : NO, □ : NO<sub>2</sub>) and without (● : NO, ○ : NO<sub>2</sub>) NH<sub>4</sub>-mordenite as catalyst at 343 K and GSHV=3000 h<sup>-1</sup> in dependence on the energy of the DBD.

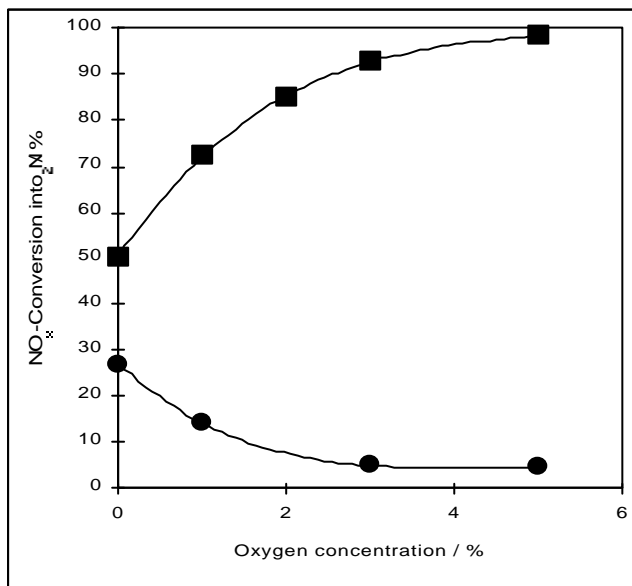


Fig. 2 Conversion of 500 ppm NO into N<sub>2</sub> at DBD (25 Wh/m<sup>3</sup>) without (●) and with (■) NH<sub>4</sub>-mordenite as catalyst at 343 K and GSHV=3000 h<sup>-1</sup>.

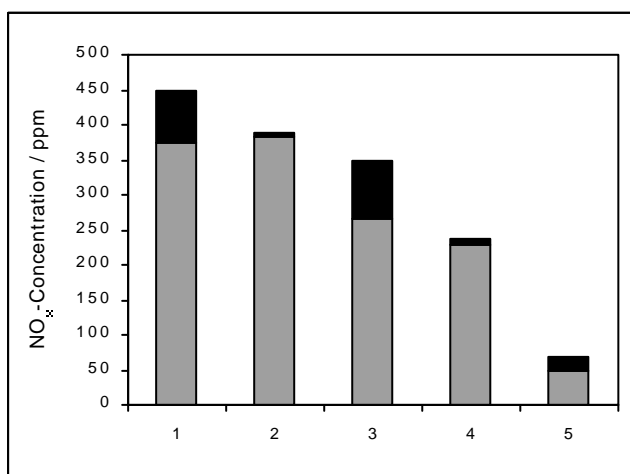


Fig. 3 NO<sub>x</sub> concentration after conversion of 500 ppm NO in N<sub>2</sub>/O<sub>2</sub> (2 vol%) DBD, without catalyst: (1); with NH<sub>4</sub>-mordenite, no DBD: (2); DBD behind the catalyst: (3); DBD before the catalyst: (4); DBD over the catalyst (in-situ): (5). Conditions at the catalyst: 343K, GSHV=3000 h<sup>-1</sup>, DBD: ca. 25 Wh/m<sup>3</sup> NO: hatched, NO<sub>2</sub>: black