# Selective catalytic reduction of $NO_x$ by $NH_3$ on Fe/HBEA zeolite catalysts in oxygen-rich exhaust

Peter Balle, Bastian Geiger, Sven Kureti *

Institut für Technische Chemie und Polymerchemie, Universität Karlsruhe, Kaiserstr. 12, D-76128 Karlsruhe, Germany

## ARTICLE INFO

## ABSTRACT

This paper deals with the systematic study of Fe/HBEA zeolites for the selective catalytic reduction (SCR) of $NO_x$ by $NH_3$ in diesel exhaust. The catalysts are prepared by incipient wetness impregnation of H-BEA zeolite (Si/Al = 12.5). The SCR examinations performed under stationary conditions show that the pattern with a Fe load of 0.25 wt.% (0.25Fe/HBEA) reveals pronounced performance. The turnover frequency at 200 °C indicates superior SCR activity of 0.25Fe/HBEA ($8.5 \times 10^{-3}\,s^{-1}$) as compared to commercial Fe-exchanged BEA ($0.99 \times 10^{-3}\,s^{-1}$) and $V_2O_5/WO_3/TiO_2$ ($1.0 \times 10^{-3}\,s^{-1}$). Based upon powder X-ray diffraction (PXRD), temperature programmed reduction by $H_2$ (HTPR), diffuse reflectance UV–vis spectroscopy (DRUV–VIS) and catalytic data it is concluded that the pronounced performance of 0.25Fe/HBEA is substantiated by its high proportion of isolated Fe oxo sites. Furthermore, isotopic studies show that no association mechanism of $NH_3$ takes place on 0.25Fe/HBEA, i.e. $N_2$ is mainly formed from NO and $NH_3$.

The evaluation of 0.25Fe/HBEA under more practical conditions shows that $H_2O$ decreases the SCR performance, while CO and $CO_2$ do not affect the activity. Contrary, SCR is markedly accelerated in presence of $NO_2$ referring to fast SCR. Moreover, hydrothermal treatment at 550 °C does not change SCR drastically, whereas a clear decline is observed after 800 °C aging.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

Diesel engines with direct fuel injection show the highest efficiency for automotive applications. As a consequence, the low fuel consumption of diesel vehicles leads to reduced production of the greenhouse gas $CO_2$. However, a serious constraint of diesel engines is the emission of nitrogen oxides ($NO_x$) that are involved in various photochemical reactions resulting in the formation of strong irritants, e.g. ozone, as well as acid rain [1]. For the removal of $NO_x$ from the oxygen-rich diesel exhaust the selective catalytic reduction (SCR) and $NO_x$ storage reduction catalysts (NSR) are actually the most favoured techniques. The NSR procedure is based upon periodic adsorption and reduction of $NO_x$ [2–4], whereas the catalysts consist of precious metals, primarily Pt, as well as basic adsorbents, for instance, $Al_2O_3$ and $BaCO_3$. The platinum component supports the oxidation of NO into $NO_2$ that is subsequently stored by the adsorbents. When the storage capacity is reached, rich exhaust conditions are established momentarily by engine management systems. Hereby $NO_x$ desorbs from the substrate and

is reduced by $H_2$, CO and hydrocarbons on the precious metals. Nevertheless, a disadvantage of NSR is the susceptibility of the basic adsorbents to sulfur poisoning [5].

In SCR technique, $NO_x$ is continuously reduced by $NH_3$ on $TiO_2$ supported $WO_3/V_2O_5$ catalysts resulting in the selective formation of nitrogen and water [6–9]. At low temperatures the $NO_x$ reduction is substantially accelerated in presence of $NO_2$ which is called fast SCR [10]. $NO_2$ is formed by oxidation of NO on a Pt pre-catalyst [11]. The required ammonia is produced on board by decomposition and hydrolysis of stored urea in an additional tank. A disadvantage of the SCR procedure is the toxicological concern of the $V_2O_5$ catalyst and therefore its emission should be avoided. However, fracture and abrasion effects have been reported for automotive catalysts leading to significant discharge [12,13]. Furthermore, the volatility of $V_2O_5$ has to be taken into account melting already at 658 °C. In particular, such temperatures are potentially achieved in diesel passenger cars when the SCR catalyst is placed downstream to a particulate filter [14]. In active filter regeneration performed by post-injection of fuel the temperature increases up to 800 °C resulting in drastic loss of activity as well as discharge of $V_2O_5$.

In addition to $V_2O_5$, iron based catalysts are also reported to show high SCR activity, i.e. $Fe_2O_3$ [15–22], Fe containing mixed

* Corresponding author. Tel.: +49 721 608 8090; fax: +49 721 608 2816.
E-mail address: Kureti@ict.uni-karlsruhe.de (S. Kureti).

oxides [23–26] and Fe-exchanged materials [27–31]. A very pronounced performance is found for the Fe-ZSM5 zeolite that has been extensively investigated in the past years [32–44]. Nevertheless, in contrast to the ZSM5 system BEA zeolite has hardly been considered as a carrier for iron oxide [45], whereas some studies have been reported on Fe-exchanged BEA in deN$_2$O [46]. Thus, the objective of the present work is to use BEA zeolite for SCR employing iron oxide as catalytic component. Furthermore, the active sites of the modified Fe/BEA systems and the technical potential of the best material are evaluated. Moreover, some mechanistic investigations are presented for the most effective catalyst.

## 2. Experimental

### 2.1. Preparation and characterisation of the catalysts

A H-BEA zeolite with a molar Si/Al ratio of 12.5 (Süd-Chemie) is modified by iron oxide using the incipient wetness method. The aim of this procedure is to deposit iron oxide on the zeolite surface, whereas a proton exchange is not explicitly intended; for effective ionic exchange other techniques are described [37]. The H-BEA zeolite is impregnated at room temperature by an aqueous solution of Fe(NO$_3$)$_3$ (Merck) with known concentration. For impregnation a defined volume of the solution is taken such that it is completely absorbed. With this technique an accurate load of iron is adjusted as checked by atom absorption spectrometry (AAS 4100, PerkinElmer). The impregnated zeolite is finally calcined in air at 450 °C for 3 h; under these conditions complete decomposition of Fe(NO$_3$)$_3$ into Fe$_2$O$_3$ occurs as proven by thermogravimetry. The load of Fe is established to be 0.02, 0.10, 0.25, 0.50, 1.0, 2.0 and 10 wt.%. The sample code used throughout this work is exemplarily demonstrated for the catalyst with a Fe loading of 0.25 wt.%, i.e. 0.25Fe/HBEA. Furthermore, for reference purposes pure H-BEA as well as a commercially available ion-exchanged Fe-BEA with an exchange degree of ca. 100%. (Si/Al = 20, Zeochem) and V$_2$O$_5$/WO$_3$/TiO$_2$ is used.

The catalysts are characterised by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), X-ray powder diffraction (PXRD), high resolution tramsmission electron microscopy (HRTEM), N$_2$ physisorption, temperature programmed reduction by H$_2$ (HTPR) and diffuse reflectance UV–vis spectroscopy (DRUV–vis).

DRIFTS analyses are performed on a Nicolet 5700 FTIR spectrometer from Thermo Electron equipped with a MCT detector and DRIFTS optics from Specac. The sample is mixed with KBr in the mass ratio of 1:3, heated in Ar flow to 200 °C to remove adsorbed H$_2$O and cooled down to room temperature. Then, the data are recorded, whereas 550 scans are accumulated to a spectrum. Pure KBr is used as background.

The PXRD analyses are performed at room temperature on a D 501 from Siemens with Ni filtered Cu K$\alpha$ radiation. HRTEM pictures are taken with a Philips CM200 FEQ equipped with an EDX detector. N$_2$ physisorption is conducted with a Sorptomatic 1990 from Porotec; the respective N$_2$ isotherm is recorded at −196 °C after pre-treating the sample at 400 °C for 12 h in vacuum ($3 \times 10^{-4}$ mbar).

HTPR is performed on the same bench as for SCR studies (Section 2.2) using a total flow of 100 ml/min (STP). The mass of Fe taken in each HTPR run is 7.0 mg, whereas for the patterns with low Fe contents 5.0 mg (0.50Fe/HBEA and 1.0Fe/HBEA) and 3.5 mg (0.25Fe/HBEA) is employed. Each sample (125–250 μm, vide infra) is pre-treated in nitrogen flow at 300 °C for 15 min to eliminate adsorbed species, e.g. H$_2$O. After cooling down to 50 °C the reaction mixture consisting of 5 vol.% H$_2$ and 95 vol.% N$_2$ is added and then the temperature is linearly increased to 900 °C at the rate of 20 K/min. Temperature is measured directly in front of the sample using a K type thermocouple (TC). The concentration of H$_2$ is continuously measured by TCD (Shimadzu). For specific detection of H$_2$ the water formed during HTPR is removed by passing the reactor effluents through a cold trap (−50 °C).

The UV–vis analyses are performed on a Varian Cary 100 spectrometer with diffuse reflectance optics (DRA-CA-30I). The catalysts are examined at ambient conditions and without dilution, whereas the H-BEA zeolite is used as reference. The spectra are collected in the range from 200 to 850 nm with an instrument resolution of 1 nm, while 14 scans are accumulated to a spectrum. The DRUV–vis spectra are presented in form of the Kubelka Munk function being defined as $F(R) = (1 - R)^2/(2R)$ with $R = R_s/R_r$, where $R_s$ is the reflectance of the sample and $R_r$ is the reflectance of H-BEA [47].

### 2.2. SCR activity studies

The catalytic studies are carried out on a laboratory bench using a synthetic diesel model exhaust. Prior to the investigations, the sample is pressed to pellet with a pressure of 40 MPa, granulated and sieved to a size of 125–250 μm to avoid discharge of catalyst mass. The sample (200 mg) is then packed into the quartz glass tube reactor (i.d. 8 mm), fixed with quartz wool and pre-treated at 500 °C for 30 min under flowing N$_2$. The pre-treatment is performed to remove possible impurities and to obtain reproducible reaction conditions. The temperature is recorded with a K type TC being directly placed in front of and behind the catalyst bed. Throughout the paper the inlet temperature is exclusively presented, whereas the difference of inlet and outlet temperature is always below 10 K; no significant difference in temperature of gas and catalyst is observed as well. After the pre-treatment, the feed is added with a total flow of 500 ml/min (STP) resulting in a space velocity of 50,000 h$^{-1}$. The standard feed consists of 500 ppm NO, 500 ppm NH$_3$, 5 vol.% O$_2$ and N$_2$ as balance. All gases (Air Liquide) are fed from independent mass flow controllers (MKS Instruments). Furthermore, in some experiments CO, H$_2$O and CO$_2$ are dosed as well to evaluate the SCR activity under more practical conditions. The feed is prepared by using two lines. In the first line NO, NH$_3$ and the main part of N$_2$ (400 ml/min) are added, while in the second one O$_2$ (25 ml/min) and the remaining N$_2$ (75 ml/min) are dosed. Both flows are blended ca. 3 cm in front of the quartz glass reactor to avoid formation of NO$_2$. For the investigation of the NO oxidation NH$_3$ is not dosed, while for NH$_3$ oxidation studies NO is not supplied. When water is added a mixture of H$_2$ (25 ml/min), O$_2$ (37 ml/min) and N$_2$ (37 ml/min) is supplied in the second part of the dosing system, whereas the resulting mixture is passed over a commercial Pt containing honeycomb catalyst (90 g$_{Pt}$/ft$^3$, 450 °C) before blended with the co-flow. When a molar NO$_2$/NO$_x$ ratio of 0.25 and 0.50 is adjusted NO is supplied in the second line, where it is partially oxidised by the Pt catalyst; respective NO$_2$ proportion is achieved by adapting the catalyst temperature. A NO$_2$/NO$_x$ ratio of 1 is established by dosing a mixture of NO$_2$ and N$_2$ or Ar (Air Liquide) in the second line without use of the Pt catalyst. CO and CO$_2$ are dosed in the second line. All pipes of the bench made of stainless steel are heated to 150 °C.

In the SCR measurements the temperature is decreased in steps of 50 K from 500 to 150 °C and the reactor effluents are recorded after they reach steady state. The analyses of NO, NO$_2$, N$_2$O, NH$_3$, H$_2$O, CO and CO$_2$ are carried out by a hot measuring FTIR spectrometer (MULTI-GAS Analyzer 2010, MKS Instruments).

The performance of the catalysts is presented in terms of conversion of NO$_x$ ($X$(NO$_x$)) and NH$_3$ ($X$(NH$_3$)) as well as selectivity