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CATALYTIC INVESTIGATION OF Fe-ZSM5 IN THE SELECTIVE CATALYTIC REDUCTION OF NO$_X$ WITH NH$_3$

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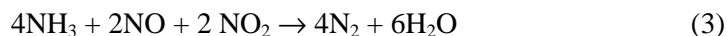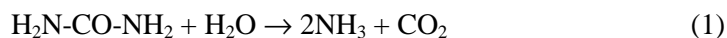Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland

Abstract

Fe-ZSM5 coated on a cordierite monolith was characterized and tested in the selective reduction of nitrogen oxides (NO$_x$) with ammonia. More than 70% of the NO$_x$ were converted at T $\geq$ 350 °C if only NO was present in the feed. For equimolar amounts of NO and NO$_2$ in the feed, NO$_x$ conversions of over 90% were reached for T = 200-450°C. Hydrothermal ageing of Fe-ZSM5 resulted in a small loss in NO$_x$ conversion and enhanced N$_2$O formation.

Keywords: Fe-ZSM5, DeNOx, monolith, SCR, selective catalytic reduction, ammonia

INTRODUCTION

The selective catalytic reduction of NO$_x$ with urea (urea SCR) is the currently favored NO$_x$ abatement technique for mobile heavy-duty diesel engines [1]. Urea is used, because it is a safe and non-toxic storage compound for ammonia (reaction 1), which is the actual reducing agent in the SCR reactions:

$$H_2N\text{-}CO\text{-}NH_2 + H_2O \rightarrow 2NH_3 + CO_2 \qquad (1)$$

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \qquad (2)$$

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

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Reaction 2 is the so-called standard SCR reaction, implying a 1:1 stoichiometry for ammonia and NO and the consumption of oxygen. The SCR reaction can be accelerated by using equimolar amounts of NO and NO_2 in the reaction mixture (reaction 3), called fast SCR reaction. V_2O_5/WO_3-TiO_2 catalysts are commonly used for this process, due to their high activity at low ammonia slip [2, 3]. Fe-ZSM5 is regarded as a potential alternative to the established vanadia based catalysts, because it functions at temperatures up to 600°C, the risk to emit volatile vanadyl species is avoided and no disposal problems occur. Although some literature is available about ammonia SCR on Fe-ZSM5 powders [4-7], not much is known about the SCR activity of Fe-ZSM5 coated on a monolith.

In the present paper, we report on Fe-ZSM5 prepared by solid-state ion exchange and coated on cordierite monolith. The active material was characterized and the catalytic properties of the freshly prepared as well as the hydrothermally treated catalyst were investigated, focusing on realistic test conditions.

EXPERIMENTAL

Fe-ZSM5 was prepared by the solid-state ion exchange method from H-ZSM5 of module (Si/Al ratio) 28 (supplied by Umicore AG, Germany) and $FeCl_2 \cdot 4H_2O$ [8]. The Fe-ZSM5 powder was coated on a cordierite monolith by the following method: the slurry was prepared by suspending 0.5 g of the zeolite in 2 cm^3 of 0.5 M $Al(NO_3)_3 \cdot 9H_2O$ solution. Successive immersions of the cordierite monolith in the suspension were performed to achieve the desired zeolite loading. After each immersion, air was softly blown through the channels in order to eliminate excess suspension and to achieve a uniform layer on the surface. The coated monolith was finally dried at RT for 2 h and then calcined at 500°C for 5 h. The weight of the cordierite was determined before and after immersion, in order to control the amount of zeolite loaded on the monolith.

Specification of the coated monolith: cordierite volume = 7.5 cm^3, cell density = 400 cpsi, catalyst loading (active mass) = 0.82 g (0.170 mol). ICP-AES: Si/Al = 28, Fe = 11.4 wt.%, Fe/Al = 2.3. X-ray diffraction patterns were recorded with a Philips X`Pert powder diffractometer with FeKα radiation. Measurements were carried out in the 2θ range 0-70° using a step size of 0.05°. Peak identification was performed with the "Powder Diffraction File™" from ICDD.

The coated Fe-ZSM5 monolith was hydrothermally aged for 50 h at 650°C in 5% water and 10% oxygen in nitrogen.

The setup of the test apparatus has been described in [9]. The composition of diesel exhaust gas was approximated by a model feed gas containing 10% O_2, 5% H_2O, 1000 ppm of NO and N_2. NH_3 was added in the range 100-1000 ppm. In the case of fast SCR, the NO as well as the NO_2 concentration was 500 ppm. The gas hourly space velocity (GHSV = volumetric gas flow/catalyst volume) was 52,000 h^{-1}, representative of typical operative conditions with automotive diesel exhaust.

The concentrations of NO, NO_2, N_2O, NH_3 and H_2O in the gas phase were analyzed by HR-FTIR spectroscopy (Nicolet Magna IR 560, OMNIC QuantPad software) through a heated multiple pass gas cell.

RESULTS AND DISCUSSION

The XRD patterns in Fig. 1 show an unchanged MFI structure for the Fe-ZSM5 powder after solid-state ion exchange and calcination, compared to the parent H-ZSM5. However, the ion exchange process resulted in the additional formation of Fe_2O_3 in the hematite phase ($2\theta = 42.22$ and 45.36).
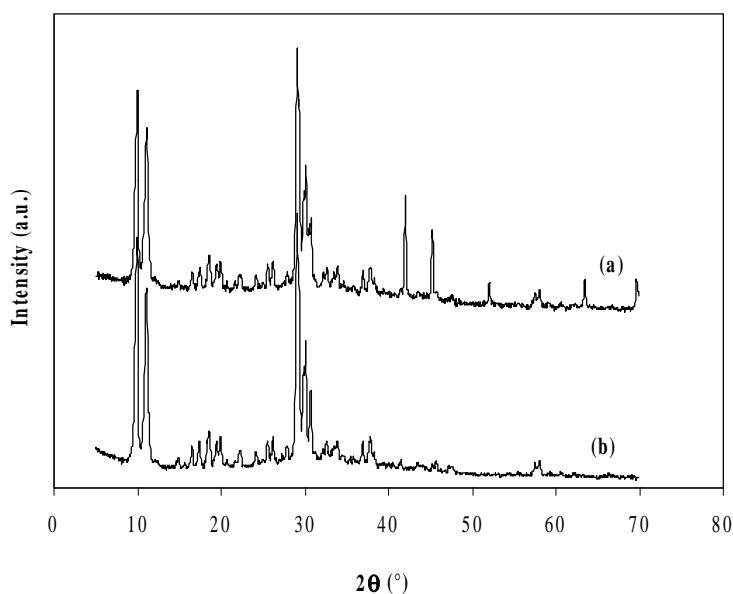

Fig. 1. XRD patterns of (a) Fe-ZSM5 and (b) H-ZSM5 (base material)

The practical application of the SCR process for the exhaust gas treatment of mobile Diesel engines calls for a high NO_x conversion (DeNOx) and simultaneously for a low slip of ammonia through the catalyst. An ammonia emission of 10 ppm in average is generally accepted for exhaust gas treatment techniques, which necessitates a dosage control for adding the right amount of ammonia relating to the NO_x concentration and the activity of the catalyst at a given temperature. The stoichiometric ratio α represents the ratio between moles of nitrogen added as reducing agent and the moles of NO_x contained in the feed, *e.g.* ammonia as reducing agent: $\alpha = NH_{3,in}/NO_{x,in}$.

The conventional measurement of DeNOx *vs* temperature at constant α in the laboratory is thus not sufficient, since the varying α in real systems is not considered. Only the stepwise increase of the dosing ratio from $\alpha = 0$-1.2 for each given temperature and the measurement of the resulting emissions gives a full picture of the catalyst performance. From these data obtained for the fresh and aged Fe-ZSM5 monolith under standard SCR conditions, the DeNOx values were calculated, according to DeNOx = $(NO_{x,in}-NO_{x,out})/NO_{x,in}$ [%]. For the fresh Fe-ZSM5 monolith the plot of the ammonia slip *vs* DeNOx shows curve
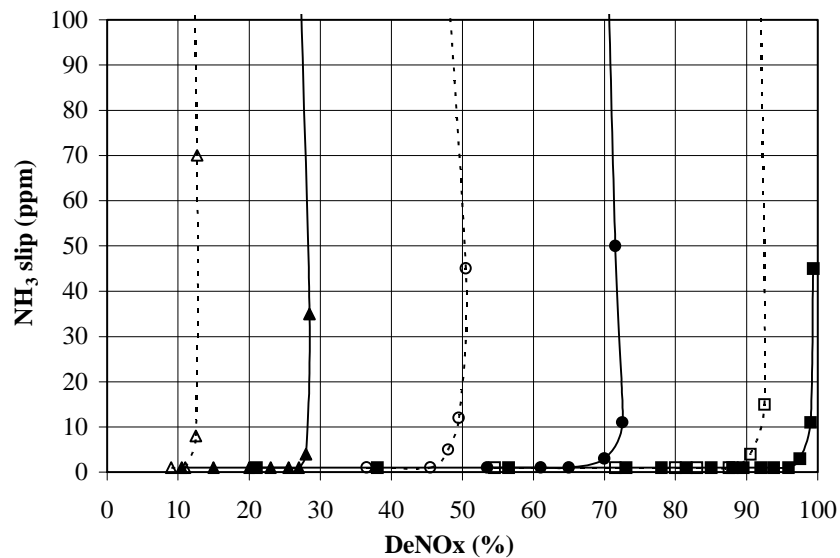

Fig. 2. NH_3 slip through the catalyst *vs* DeNOx of fresh Fe-ZSM5 coated on cordierite under standard SCR conditions (NO_{in} = 1000 ppm). ($\triangle$) 200°C, ($\blacktriangle$) 250°C, ($\circ$) 300°C, ($\bullet$) 350°C, ($\square$) 400°C, ($\blacksquare$) 450°C

curve shapes typical for a well suited SCR catalyst (Fig. 2). High NO_x conversions are reached with negligible ammonia slip up to the maximum activity of the catalyst at each given temperature. Only if ammonia is overdosed the excess is slipping through the catalyst. It is discernible from Fig. 2 that the steep part of the curves are slightly bent backward, indicating an inhibition of the SCR reaction by ammonia.
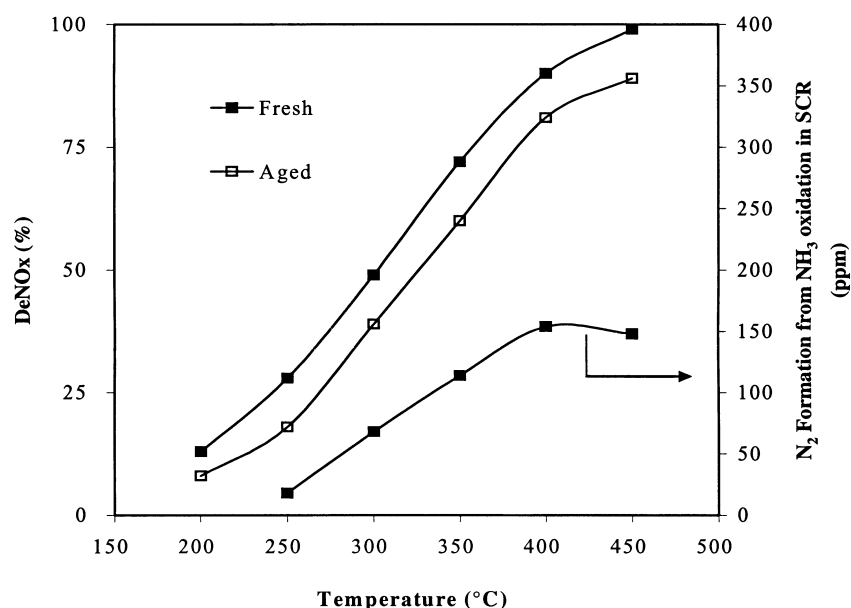

Fig. 3. DeNOx activity of fresh (■) and aged (□) Fe-ZSM5 and N_2 formed from NH_3 oxidation at 10 ppm ammonia slip

The direct oxidation of NH_3 by O_2 in the exhaust gas to N_2 ($NH_{3,ox}$) was calculated as difference between the totally consumed NH_3 ($NH_{3,cons} = NH_{3,out} - NH_{3,in}$) and the NH_3 needed for the SCR reaction ($NH_{3,SCR} = NH_{3,in} - DeNOx/100 \cdot NO_{x,in}$). From the DeNOx values and the NH_3 oxidation of fresh and aged catalyst the results at 10 ppm NH_3 slip were selected and plotted *vs* temperature in Fig. 3. The DeNOx activity is steadily increasing from 200–450°C, reaching $\geq$ 90% for T $\geq$ 400°C. Aging of the catalyst resulted in an absolute decrease of the NO_x conversion of ~ 10% over the entire temperature range, proving the good hydrothermal stability of the catalyst. No N_2O could be detected at all temperatures for both the fresh and the aged catalyst. N_2 formed by NH_3 oxidation was increasing with temperature till T $\leq$ 400°C. Calculating

the ratio of reaction rates $NH_{3,ox}/NH_{3,SCR}$ for each temperature revealed that a nearly constant fraction of about 12% of the consumed ammonia is oxidized to nitrogen and about 88% is going into the SCR reaction.
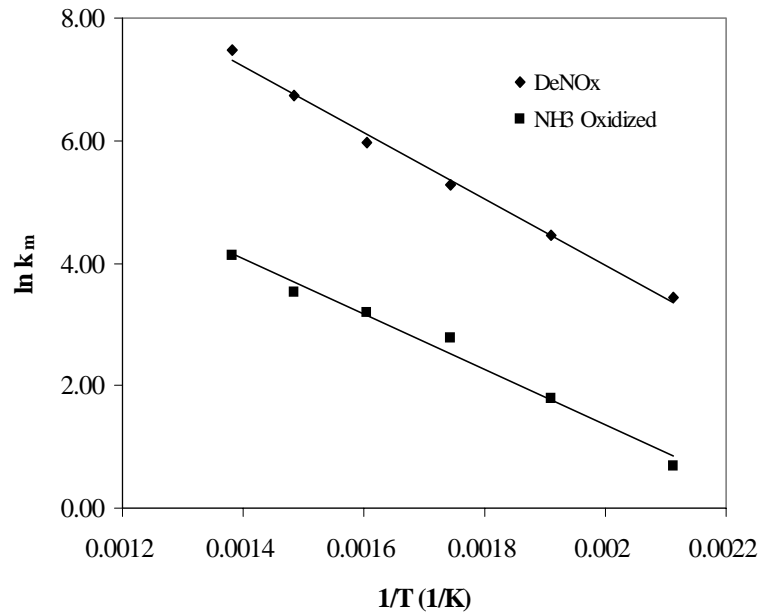

Fig. 4. Arrhenius plot of DeNOx activity (♦) under standard SCR conditions and NH_3 oxidation (■)

For a kinetic analysis of SCR reaction and ammonia oxidation, the DeNOx results from Fig. 3 were evaluated in form of an Arrhenius plot (Fig. 4), complemented with data from a separate experiment, in which only direct NH_3 oxidation was investigated ($NH_{3,in}$ = 1000 ppm, $NO_{x,in}$ = 0). For this aim, the measured NO_x conversions and NH_3 oxidation values were converted into rate constants k_m assuming a first order rate law and applying the equation for a plug flow reactor:

$$k_m = -\frac{V*}{W} \cdot \ln\left(1 - \frac{X}{100}\right)$$

where k_m is the first order rate constant (referred to the catalyst mass) ($cm^3/g\ s$), $V*$ is the gas flow at the actual conditions (cm^3/s), W is the active mass (g) and

X is the conversion (%). From the slope of the regression line in the Arrhenius plot, the activation energy of the SCR reaction was found to be 45 kJ/mol and the pre-exponential factor is 1.7×10^6 cm^3/g s. This activation energy is smaller than the value found by Huang *et al*. for Fe-ZSM5 (54 kJ/mol) [10], but it is close to the value found for Cu-ZSM5 (44 kJ/mol) [11]. The activation energy needed for the direct ammonia oxidation is 38 kJ/mol and the pre-exponential factor is 3.3×10^4 cm^3/g s. The constant ratio of SCR reaction and ammonia oxidation for all temperatures over Fe-ZSM5 was confirmed by the kinetic analysis, revealing similar activation energies and temperature dependencies of the two parallel reactions.
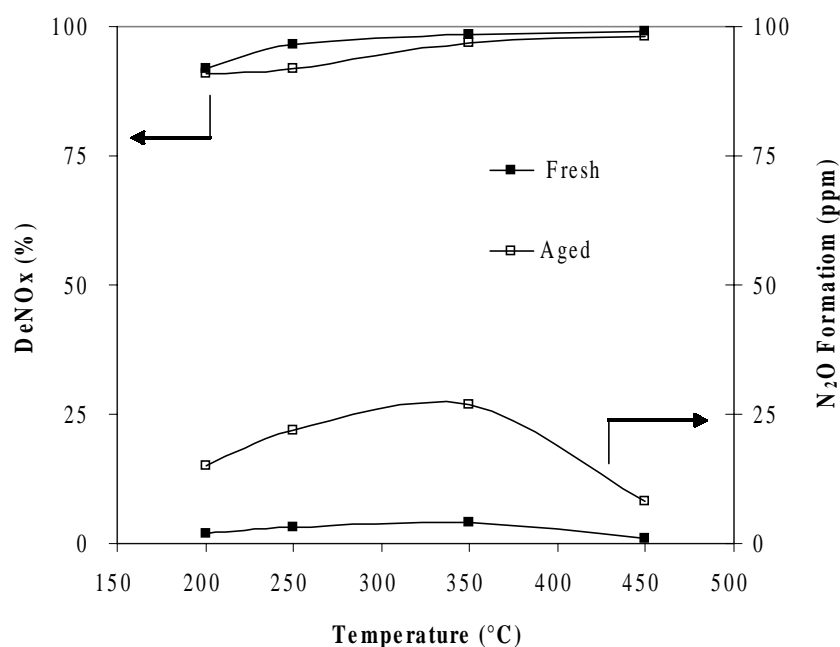

Fig. 5. DeNOx activity and N_2O formation of fresh (■) and aged (□) Fe-ZSM5 coated on cordierite at 10 ppm ammonia slip (NO_{in} = 500 ppm, $NO_{2,in}$ = 500 ppm)

Figure 5 shows the DeNOx activity *vs* temperature at 10 ppm NH_3 slip for the fresh and aged Fe-ZSM5 monolith under fast SCR conditions where equimolar amounts of NO and NO_2 are present in the feed mixture. The DeNOx activity of the fresh catalyst was tremendously enhanced to $\geq$ 90% at T $\geq$ 200°C. Negligible amounts (~ 5 ppm) of N_2O were produced. The NOx conversion was nearly the same for the aged catalyst. The loss in DeNOx

activity was only ~ 3%, but at the same time the production of N_2O was enhanced at all temperatures, the maximum being at $T = 350°C$ (~ 25 ppm). Long *et al*. [12] explained the SCR reaction and the formation of N_2O over Fe-ZSM5 by the postulation of $[NH_4^+]_2NO_2$ as intermediate species, which might react with NO to nitrogen and with NO_2 to nitrogen and N_2O.

CONCLUSIONS

Fe-ZSM5 prepared by solid-state ion exchange is a very active catalyst for the NO reduction with NH_3 under simulated exhausted gas conditions, especially if equimolar amounts of NO and NO_2 are used. However, 12% of the dosed ammonia is always consumed by the oxidation to nitrogen. That implies the necessity of a permanent overdosage of reducing agent if Fe-ZSM5 is chosen as catalyst in a real SCR system. The catalysts remained active even after aging, but the aged catalyst formed N_2O in modest amounts. This has to be regarded critical due to the large greenhouse potential of N_2O. Further investigations are being carried out to identify the Fe sites involved in the SCR reaction and to reveal the influence of Brønsted sites on NO_x conversion.

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