

Impact of Thermal and Chemical Ageing of Fe-BEA SCR Catalyst on NO_x Conversion Performance

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ABSTRACT

Emissions of nitrogen oxides (NO_x) from heavy-duty diesel engines are subject to more stringent environmental legislation. Selective catalytic reduction (SCR) over metal ion-exchanged zeolites is in this connection an efficient method to reduce NO_x. Understanding durability of the SCR catalyst is crucial for correct design of the aftertreatment system. In the present paper, thermal and chemical ageing of Fe-BEA as NH₃-SCR catalyst is studied. Experimental results of hydrothermal ageing, and chemical ageing due to phosphorous and potassium exposure are presented. The catalyst is characterized by flow reactor experiments, nitrogen physisorption, DRIFTS, XRD, and XPS. Based on the experimental results, a multisite kinetic model is developed to describe the activity of the fresh Fe-BEA catalyst. Furthermore, the model can predict deactivation of the catalyst well by decreasing the number of active sites, representing loss of active iron sites due to migration or chemical blockage of the sites. By performing a systematic study of different deactivation mechanisms, a deactivation expression for the active sites can be formulated.

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INTRODUCTION

The increased environmental and legislative demands on reducing NO_x emissions from heavy-duty diesel engines have led to the need for catalytic NO_x reduction technologies. Selective catalytic reduction (SCR) with urea as reductant has been widely introduced in order to reduce NO_x emissions from heavy-duty diesel engines since the introduction of EuroIV/US2010/Japan-NLT legislations. The SCR catalyst can be used as the only catalytic component in the aftertreatment system. However, in the most typical exhaust aftertreatment system configuration for today's state-of-the-art heavy-duty diesel engines, the SCR catalyst is combined with an upstream diesel oxidation catalyst (DOC) and a diesel particulate filter (DPF). The NO_x reduction performance of the SCR catalyst in such a system is quite good, and NO_x conversions above 90-95% are possible to achieve [1]. For a heavy-duty diesel engine application it is however important not only to have high initial NO_x conversion performance, but to maintain the high performance over the lifetime of the vehicle. The catalytic components, including the SCR catalyst, are exposed to high exhaust temperatures and catalytic poisons from the fuel and the lube oil. This exposure can potentially have a detrimental effect on the catalytic activity of the SCR catalyst and the other catalytic components in the system. Decreased catalytic performance may lead to non-optimal tuning of the engine and thus higher fuel consumption and CO₂ emissions. Understanding and

trying to minimize the ageing mechanisms of the SCR catalyst is thus important in order to achieve good performance, low fuel consumption, and low CO₂ emissions of the heavy-duty vehicle.

Several different SCR catalyst materials may be used for NO_x aftertreatment from heavy-duty diesel engines. The main ones are vanadia/titania based catalysts, Fe- or Cu-exchanged zeolites and mixed metal oxides [1]. In the present work, the thermal and chemical ageing of Fe-BEA as SCR catalyst have been studied. In a heavy-duty diesel application, thermal ageing of the SCR catalyst can occur due to high exhaust temperatures from the engine itself, but also and more important, elevated exhaust temperatures may be seen during regeneration of the DPF. The aftertreatment system is exposed to inorganic compounds in the lube oil, typically Ca, Zn, P and S. Exposure of such compounds may also occur from the fuel. Biofuels may contain alkali metals (Na, K) and phosphorous (P). Bartholomew [2] has proposed that hydrothermal deactivation occurs through loss of catalytic surface area due to collapse of the zeolite pores providing the active sites, and loss of support area due to support collapse and crystallite growth. A similar mechanism has been proposed by Brandenberger et al. for hydrothermal deactivation of Fe-ZSM-5 [3].

In the open literature, there are only few studies of chemical deactivation of metal-exchanged zeolites used for NH₃-SCR applications. In these studies the catalysts are exposed to different

high amounts of catalyst poisons. The common conclusion is that the decreased ammonia storage capacity observed upon catalyst poisoning is due to physical or chemical blockage of the adsorption sites.

Chemical deactivation of Fe-BEA has been studied by both Kern et al. [4] and Silver et al. [5]. They used a pseudo-incipient wetness procedure of phosphorous-enriched fuel to study the chemical deactivation by several inorganic components. They both argued that the decreased SCR activity is related to a decreased ammonia storage capacity. However, Kern et al. further discussed that one should not rule out the interaction between the poison and the active metal species in the catalyst which might have a more severe effect on the activity.

In the present work we have studied hydrothermal ageing of Fe-BEA between 600 and 800°C, and chemical poisoning by P and K exposure. In order to study the interaction between the poison and the active iron species, and to avoid any significant decrease in ammonia storage capacity, relatively low amounts of phosphorous and potassium have been used.

Furthermore, Bartholomew [2] has pointed out the need of understanding deactivation mechanisms in order to develop kinetic models to predict deactivation. This is quite important in designing new catalysts and operation conditions when optimizing any catalytic process. Therefore, we have based on the studied deactivation mechanisms developed a multi-site kinetic model, which takes into account changes in the active sites after hydrothermal and chemical deactivation.

EXPERIMENTAL

Hydrothermal Deactivation

An Fe-BEA catalyst described in [6, 7], was hydrothermally aged in an ageing reactor [6], where the hydrothermal treatment was performed between 600-800°C in presence of 5 % H₂O and 6 % O₂ in N₂ as inert gas. A continuous flow-reactor system was used to evaluate the catalytic performance of the deactivated samples compared to fresh samples [6]. The evaluation was done at a space velocity (GHSV) of 28 000 h⁻¹. The samples were further characterized using several techniques; nitrogen physisorption (BET), in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). A detailed description of all experiments performed and conditions used can be found in refs [6-10].

Chemical Deactivation by Phosphorous and Potassium

For the chemical deactivation, phosphorous or potassium were used. H₃PO₄ or KNO₃ were mixed in the water feed before evaporated and mixed with inert gas, which was fed to the ageing reactor. The samples were exposed to phosphorous and potassium at 350°C between 14 and 48 h with a concentration of 10 or 50 ppm for both chemicals, representing 0.21 or 1.05 g/(L×h) H₃PO₄ and 0.21 or 1.05 g/(L×h) KNO₃ [8, 9]. The samples were evaluated in the same type of continuous flow-reactor system as the hydrothermally aged samples and further characterized by TPD of NH₃, NO and NO₂, and by XPS.

Engine Ageing

Ageing Procedure on Engine

Engine ageing of a commercial Fe-zeolite SCR catalyst was performed using a Volvo 13 L heavy-duty diesel engine meeting EPA2010 regulation. The ageing was done in a full system configuration with a DOC and a DPF mounted upstream the SCR catalyst. Two different sets of ageing were performed: 1) Reference ageing using standard low-sulphur diesel fuel and 2) Ageing using 100% biodiesel (FAME).

The ageing sequence consisted of a low-temperature cycle with engine exhaust temperatures between 230-270°C run for 3 hours followed by an excursion to 440°C (full-load operation) for 30 minutes in order to ensure that excessive soot was not accumulated in the filter. This sequence was repeated to accumulate a total of 800 h for the reference ageing and 1000 h for the ageing with biofuel. The same ageing cycle was used for both the reference ageing and the ageing using biodiesel. The standard diesel fuel followed EN590 and had a sulphur level < 10 ppm. The biofuel consisted of 100% FAME and was complying with the EN14214 standard for FAME. Since the fuel was delivered just in time for the test to start, fuel ageing was not considered to be an issue for this test. Table 1 specifies the concentration of catalyst poisons in the engine lube oil used for both reference and biodiesel ageing. Table 2 specifies the concentration of catalyst poisons in the biofuel.

Table 1. Concentration range of chemical poisons in engine lube oil used.

Element	Concentration
Ca	1180-1450 mg/kg
P	900-1140 mg/kg
Zn	990-1250 mg/kg
S	2600-3800 mg/kg

Table 2. Specification of biodiesel fuel used.

Element	Specified concentration	Analyzed concentration
P	< 4 mg/kg	< 1 mg/kg
S	< 10 mg/kg	< 2 mg/kg
Na+K	< 5 mg/kg	< 2 mg/kg
Ca+Mg	< 5 mg/kg	< 2 mg/kg
Sulphated ash	< 200 mg/kg	< 200 mg/kg

Exposure levels in g/L SCR catalyst were calculated assuming all poisons are accumulated in the SCR catalyst. In reality this may not be true since poisons may also accumulate in the upstream DOC and DPF. During the reference ageing, estimated exposure levels of Ca, P, and Zn are low. The levels are in the order of 0.2-0.3 g/L-SCR catalyst. For the ageing with biodiesel, the levels are significantly higher. Estimated exposure level is for Ca+Mg 3.3 g/L-SCR, for P 1.7 g/L-SCR and for Na+K 3.0 g/L-SCR. Since low-sulphur diesel is used for both reference ageing and biofuel ageing, the estimated exposure of sulphur is the same for the two ageing experiments.

Evaluation of Aged Performance on Engine Test Bench

Measurement of catalytic activity before and after engine ageing with reference fuel and biofuel was performed using a Volvo 13 L engine meeting Euro V legislation. The evaluation was done using a stabilized DOC upstream the SCR catalyst. The DOC used for evaluation was not included in the ageing test but only used for evaluating the SCR performance. The reason for this was to ensure a stable level of NO₂ from the DOC, and thus only study the ageing effect on the SCR catalyst and not the additional effect of a potential ageing of the DOC. For the same reason, no DPF was used in the evaluation of the SCR-performance.

NO_x conversion was measured in 7 different engine modes (Table 3). In each engine mode, urea is injected in step-wise increments until NH₃ slip is observed. The NO_x conversion in each point is defined as the maximum NO_x conversion achievable with an NH₃ slip < 10ppm. Details of the corresponding ANR (Ammonia NO_x Ratio) and NH₃ slip are given in Table 4 in Appendix.

Table 3. Engine modes for evaluation of NO_x conversion. Details of SCR inlet temperature and Space velocity for each experiment is given in Table 4 in Appendix.

Engine mode	Average SCR inlet temperature (°C)	Average Space Velocity (h ⁻¹)
A100	436	53 000
C25	250	46 000
C100	390	82 000
B50	341	50 000
A25	266	26 000
B100	401	72 000
B25	270	37 000

RESULTS

Hydrothermal Deactivation

The effect of hydrothermal treatment on the NH₃-SCR activity over Fe-BEA during standard SCR (NO₂/NO_x = 0) is shown in Figure 1. The figure shows the steady-state conversion of NO_x in presence of 400 ppm NO and NH₃, 8 % O₂, 5 % H₂O and inert gas, studied in the continuous flow-reactor. The temperature range is between 150 and 500°C. From the figure it is clear that already after 24 h of hydrothermal treatment, at both temperatures, the SCR activity at lower temperatures (≤ 300°C) has significantly decreased. In figure 2 the deactivation trends for NO_x conversion during SCR conditions at 200 and 250°C are compared for all samples. It can be observed that the deactivation rate is considerably faster during hydrothermal treatment at 700 compared to 600°C. For example the deactivation is more severe after hydrothermal treatment at 700°C for 24 h compared to 600°C for 48 h. Even after treatment at 600°C for 100h, the Fe-BEA catalyst is much less deactivated compared to the sample treated at 700°C for 48 h. Furthermore, at higher temperatures (>300°C), the SCR activity seems to be relatively constant. This can be related to the high reaction rates at those temperatures. A substantial fraction of the catalyst is not used and therefore the deactivation must be severe in order to show similar trends as at lower temperatures.

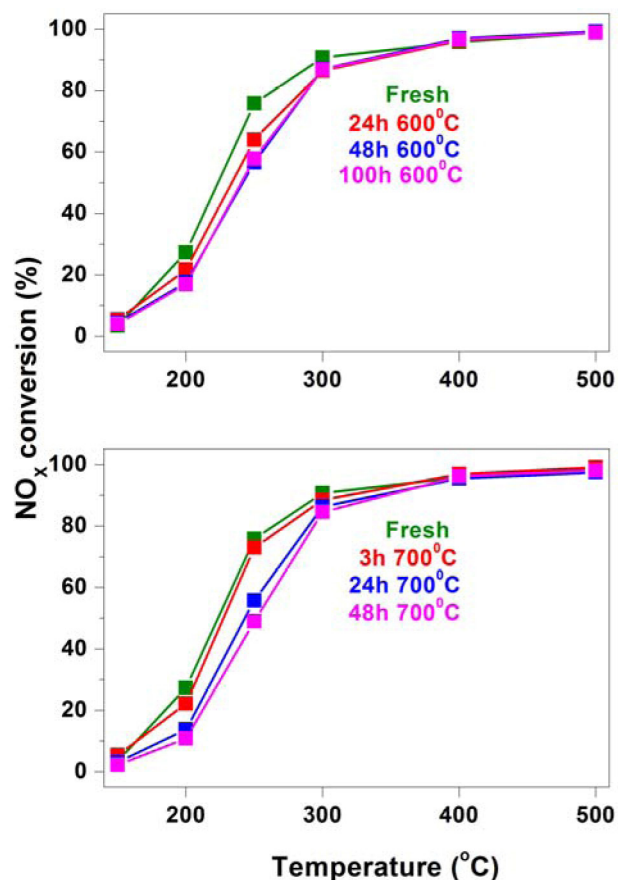


Figure 1. Steady-state NO_x conversion of fresh and hydrothermally treated Fe-BEA samples. Upper panel: Samples treated at 600°C for 24 - 100 h. Lower panel: Samples treated at 700°C for 3 - 48 h. The samples are exposed to 400 ppm NO, 400 ppm NH₃, 8% O₂ and 5% H₂O and the temperature is stepwise increased from 150 to 500°C (150, 200, 250, 300, 400 and 500°C). The total flow rate is 3500 ml/min (GHSV=28 000 h⁻¹).

In situ DRIFT spectroscopy with NO as probe molecule was used to study and follow the dynamics of the different iron species in the catalyst during hydrothermal treatment. Figure 3 shows the results from the DRIFTS measurements. Two distinct peaks can be observed around 1635 and 1880-1870 cm⁻¹. The latter at 1880 cm⁻¹ represents isolated iron species, which could be assigned to monomeric or dimeric iron [10]. The absorption peak around 1870 cm⁻¹ is assigned to smaller iron clusters inside the pores of the zeolite, while the peak at 1635 cm⁻¹ is attributed to larger iron oxide particles located on the external surface of the zeolite [10]. The Fe-BEA samples have been thermally treated in ambient air at 700 and 800°C for 48 h, and compared to a fresh sample. The changes in iron species are schematically shown in Figure 3. The results after thermal treatment at 700°C, shows that isolated species (monomeric and dimeric iron) migrate to form smaller iron clusters inside the pores of the zeolite (represented by the peak shift towards 1870 cm⁻¹). Simultaneously, the intensity of the peak representing larger iron oxide particles on the zeolite surface increases. Furthermore, after a more severe treatment (800°C) the intensity slightly decreases. This can be correlated to a decreased iron surface area due to continuous iron oxide particle growth during thermal treatment.