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ScienceDirect
Mendeleev Commun., 2014, **24**, 311–312
Mendeleev Communications

Fast and standard selective catalytic reduction in NH_3-$DeNO_x$: pathways discrimination as a key step for the understanding of kinetics

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DOI: 10.1016/j.mencom.2014.09.022

Two methods for distinguishing the fast and standard selective catalytic reduction (SCR) pathways were proposed, and fast SCR activities of Fe-Beta catalysts containing 0.7, 0.2 and 0.02% Fe were compared.

Selective catalytic reduction by ammonia (NH_3-SCR) is one of the most efficient technologies for removing NO_x. However, the efficiency of standard SCR process (1) is insufficient at low temperatures (150–250 °C). A possible solution to this issue is so-called fast SCR reaction (2) known since Kasaoka *et al.*[1(a)] found that the rate of the reaction involving an equimolar NO and NO_2 feed mixture is much higher than that of standard SCR at a low temperature.

$$2NO + 2NH_3 + {}^1/_2O_2 \rightarrow 3H_2O + 2N_2, \quad (1)$$

$$NO + NO_2 + 2NH_3 \rightarrow 3H_2O + 2N_2. \quad (2)$$

Since the first generation of commercial SCR catalysts for mobile applications were vanadia-based catalysts, the fast SCR reaction over powdered and monolithic V_2O_5–WO_3–TiO_2 catalysts was extensively investigated.[1] On the other hand, the next generation of NH_3-SCR catalysts are zeolites promoted by transition metals.[2] These catalysts demonstrate favorable $DeNO_x$ activity in the standard and, especially, fast SCR reactions. The reactivity, mechanism and kinetics of the fast NO/NO_2–NH_3 SCR reaction over zeolite-based catalysts were studied.[3–5] Sjövall *et al.*[6] developed a transient kinetic model for the fast SCR on a Fe-Beta catalyst; however, they did not take into account the standard SCR activity of Fe^{3+} cations[7] and the fact that, in many cases, the fast SCR is an integral part of the overall SCR process. Therefore, this model cannot be used for estimating the quantitative parameters of fast SCR individually. The nature of active sites for fast SCR also remains unclear.

Here, we propose two methods for distinguishing the fast and standard SCR pathways using (1) an under-stoichiometric NO_2/NO mixture (1:3) and (2) 'NO_2 slip' as the criterion of activity. These methods allowed us to compare the efficiency of Fe-Beta catalysts in the fast SCR reaction. Beta zeolite samples with different Fe content were used for evaluation of the role of Fe^{3+} cations in the fast SCR process.[†]

Figure 1(*a*) compares the standard SCR activity of Fe-Beta zeolites with different Fe contents. It is clearly seen that 0.02% Fe-Beta demonstrated negligible activity in the standard SCR, while samples

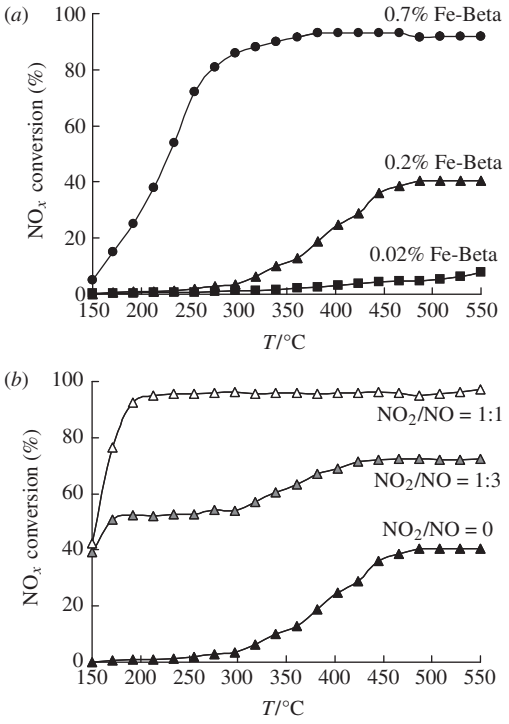

Figure 1 (*a*) Standard SCR performance (NO_2/NO = 0) of Fe-Beta with different Fe contents; (*b*) SCR performance of 0.2% Fe-Beta under the standard SCR, under-stoichiometric and stoichiometric fast SCR conditions. Gas mixture: 500 ppm of NO_x, 530 ppm of NH_3, 10% O_2 and 6% H_2O.

Catalytic tests were carried out in a fixed-bed flow reactor (inner diameter, 4 mm) at a flow rate of 300 ml min^{-1} under GHSV of 270000 h^{-1} (0.040 g of zeolite was diluted by silicon carbide). All the activity data was measured in the TPR mode: the temperature was decreased from 550 to 150 °C at a rate of 2 K min^{-1}. NO_x concentrations (in ppm) were measured on a Gasmet FTIR gas analyzer (Temet Instruments DX-4000) at regular intervals of 5 s; NO_x conversions were calculated from an average of 10 outlet NO_x readings with a temperature step of ~25 °C.

The feed gas contained 10 vol% O_2, 6 vol% H_2O, 530 ppm of NH_3, 500 ppm of NO_x (standard SCR: 0 ppm of NO_2, 500 ppm of NO; the 'stoichiometric' fast SCR 1:1 mixture contained 250 ppm of NO_2 and 250 ppm of NO; the 'under-stoichiometric' fast SCR 1:3 mixture contained 125 ppm of NO_2 and 375 ppm of NO), balanced with N_2. All reactor lines were heated to prevent water vapor condensation and ammonium nitrate deposition.

[†] The commercial samples of 0.2 wt% Fe and 0.7 wt% Fe-Beta were used. The 0.02% Fe-Beta sample was synthesized using Fe-free precursors. All catalysts were calcined in air at 550 °C for 4 h; then, they were pressed, crushed and sieved to yield samples with a particle size of 0.2–0.4 mm. Iron concentrations in the samples were determined by ICP-AES.

with higher Fe loadings provided reasonable NO_x conversions. Thus, the higher was the Fe content, the better standard SCR performance of the catalysts was observed. These results are in a good agreement with the previous data.[7(*b*)]

Fe-Beta zeolites also show high activity in fast SCR reaction [50% NO_2, Figure 1(*b*)]. In order to estimate the activities of samples and to reveal the role of Fe^{3+} cations in the fast SCR we used (1) an 'under-stoichiometric' mixture (NO_2/NO, 1:3) and (2) NO_2 slip as criteria for fast SCR catalytic activity.

As mentioned above, the 0.2% Fe-Beta sample demonstrated reasonable standard SCR activity [NO_2/NO, 0:1, Figure 1(*b*)] at 300–550 °C due to residual Fe^{3+} cations; however, at lower temperatures (150–300 °C), the activity was negligible. When an 'under-stoichiometric' (NO_2/NO, 1:3) mixture was supplied, the fast SCR and standard pathways can be easily discriminated.

(1) Within a temperature range below 300 °C, the SCR process occurs only through the fast SCR pathway. The NO_x conversion does not exceed 50% due to the fast SCR reaction stoichiometry; in other words, the NO_x conversion is limited by the NO_2 concentration in feed gas [equation (1)]. Low conversion below 150–170 °C can be explained by NH_4NO_3 formation.[2]

(2) Within a temperature region above 300 °C, the NO_x conversion increases proportionally to the contribution of the standard SCR activity of 0.2% Fe-Beta.

Under 'stoichiometric' fast SCR conditions [NO_2/NO, 1:1, Figure 1(*b*)], the NO_x conversion on 0.2% Fe-Beta exceeds 95% at $T_{react} > 200$ °C, which makes impossible a discrimination of the standard and fast SCR pathways. Thus, only in the case of 'under-stoichiometric' fast SCR conditions (NO_2/NO, 1:3), the fast and standard SCR pathways are easily distinguished.

In this study, we used an under-stoichiometric mixture in order to evaluate the role of Fe^{3+} cations in the fast SCR process. Figure 2 depicts the temperature dependence of NO_x conversion over Fe-Beta catalysts in an under-stoichiometric mixture (NO_2/NO, 1:3). Evidently, it is difficult to differentiate the standard and fast SCR for 0.7% Fe-Beta, since the contribution of standard SCR to the overall process is significant and ~100% NO_x conversion is achieved at $T_{react} > 200$ °C.

On the other hand, for the catalysts with lower Fe loadings, the standard SCR can be easily distinguished. Over 0.2% Fe-Beta and 0.02% Fe-Beta samples, the NO_x conversion does not exceed 50% at $T_{react} < 300$ °C because the reaction proceeds only *via* fast SCR pathway (2) and conversion is limited by NO_2 concentration in accordance with equation (2).

The increase in NO_x conversion at $T_{react} > 350$ °C over 0.2% Fe-Beta resulted from the contribution of standard SCR. For 0.02% Fe-Beta, the contribution of Standard SCR is negligible, and NO_x conversion is limited by only NO_2 concentration. The marginal decrease in NO_x conversion over 0.02% Fe-Beta at $T_{react} > 400$ °C, can probably be explained by NO_2 decomposition.

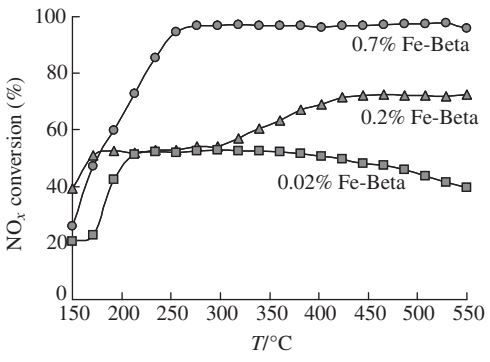

Figure 2 Effect of Fe content on the fast SCR performance of Fe-Beta under under-stoichiometric conditions (NO_2/NO = 1:3). Gas mixture: 125 ppm of NO_2, 375 ppm of NO, 530 ppm of NH_3, 10% O_2 and 6% H_2O.

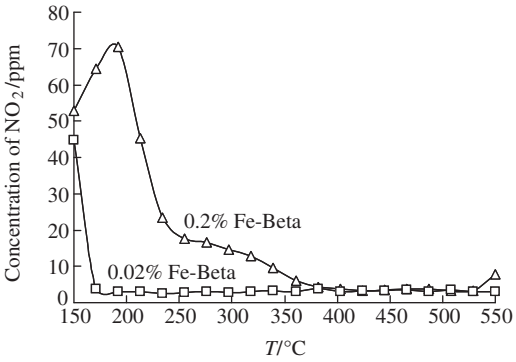

Figure 3 Concentration of NO_2 in the outlet gas during the fast SCR over Fe-Beta with different Fe contents under stoichiometric conditions (NO_2/NO = = 1:1). Gas mixture: 200 ppm of NO_2, 300 ppm of NO, 530 ppm of NH_3, 10% O_2 and 6% H_2O.

It is informative to compare NO_x conversions over 0.2% Fe-Beta and 0.02% Fe-Beta catalysts at $T_{react} = 170–200$ °C where only the fast SCR takes place. This comparison clearly indicates that 0.2% Fe-Beta is evidently more active than 0.02% Fe-Beta indicating a positive role of Fe^{3+} cations in the fast SCR. The data are consistent with the recent results on the decisive role of Fe^{3+} species in ZSM-5 cationic positions in both standard and fast SCR processes.[8,9]

Differences in the fast SCR activities of Fe-Beta catalysts with low Fe loadings (0.2 and 0.02 wt% Fe) were additionally evaluated using residual NO_2 concentrations in the reaction product (*i.e.*, NO_2 slip) as a criterion. Figure 3 shows the temperature dependence of NO_2 slip in the course of the fast SCR (under stoichiometric conditions of NO_2/NO ratio ~1:1).

The difference in NO_2 slips is evident: 0.2% Fe-Beta is significantly more active than 0.02% Fe-Beta in a temperature range of 170–350 °C since an NO_2 slip is observed only at $T_{react} < 170$ °C over 0.2% Fe-Beta. These data suggest a positive role of Fe^{3+} species in the fast SCR reaction.

This work was supported by the Russian Foundation for Basic Research (grant no. 13-03-92711/IND_a) and the Department of Science and Technology, New Delhi (grant no. INT/RUS/RFBR/P-152). A. Mytareva acknowledges the support of Haldor Topsøe A/S in the framework of a Ph.D. student support programme.

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Received: 30th January 2014; Com. 14/4298