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Analysis of the structural parameters controlling the temperature window of the process of SCR-NO$_x$ by low paraffins over metal-exchanged zeolites

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Abstract

Catalytic activity of H- and FeH-ferrierite (FER) zeolites with iron content from 50 to 4000 ppm in NO–NO$_2$ equilibration and SCR of NO$_x$ by propane was measured, both in NO$_2$-poor and NO$_2$-rich streams. The activity of FeH-FER in SCR in NO$_2$-poor streams depends strongly on the Fe content; this relationship is valid down to traces of iron, while no such correlation was indicated in NO$_2$-rich streams. This was rationalized by realizing the negligible activity of zeolite protons for NO–NO$_2$ equilibration. Accordingly the SCR activity of H-FER in NO$_2$-poor streams necessitates presence of iron traces. In the NO$_2$–O$_2$–propane mixtures a process in absence of zeolite catalyst initiating propane oxidation and NO$_2$ → NO conversion, but without N$_2$ formation, was evidenced at temperatures over 350 °C. It is suggested that such a radical process participate in characteristic narrow temperature window for NO$_x$ reduction by propane. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic activity; Metal-exchanged zeolites; Nitrogen oxides; SCR-NO$_x$; Temperature windows

1. Introduction

Process of selective catalytic reduction of nitrogen oxides (SCR-NO$_x$) in excess of oxygen by nitrogen containing reductants (e.g. NH$_3$) is one of the most established processes in protection of environment [1]. Utilization of paraffins instead of the environmentally harmful ammonia in oxygen-rich exhaust streams would require accommodation of the catalytic process to the parameters of the pollutant source, namely with respect to temperature, concentration of oxygen and water. Some metal-exchanged zeolites have been shown to be among the candidates for application as catalysts due to their high activity and stable performance in this reaction, including their tolerance to water vapor [2]. Among them Fe species in zeolites seems to exhibit promising catalytic features. Nevertheless, the activity in SCR of NO with increasing temperature displays a typical bell-shaped profile and a severe decrease in utilization of the reductant for SCR reaction at temperatures over 350 °C. Such a temperature profile has been obtained consistently for all Fe zeolites prepared by various preparation routes, either by ion-exchange in solution or by solid state ion-exchange [3] or FeCl$_3$ sublimation [4]. This would represent a serious drawback for practical application of this process for sources where temperature control could be only limited and would demand secondary technical measures for precise temperature control of the catalyst.

The aim of the presentation is to analyze structural parameters of the metal zeolite governing the temperature profile of paraffin selectivity using FeH-ferrierite

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(FER) and NO_x–O_2–propane reaction as a model system. For this analysis FeH-FER with extremely low iron content was used, going thus even below that of the commercial zeolite. As it has been shown recently [5] these systems display the iron ion mostly in one cation site position. Together with high SCR activity thus they make also possible to address a long discussed question of the respective role of acidic protons and metal cations in zeolite in the SCR reaction.

2. Experimental

2.1. Catalyst preparation and characterization

FER was provide by TOSOH (Lot 010812B, Si/Al 8.5, Na/K form, Na 0.47 wt.%, K 1.98 wt.%, Fe 170 ppm) (denoted as FER/C). Laboratory prepared (Si/Al 8.2, Fe 50 ppm) (denoted as FER/P) was prepared using ultra-pure materials [7]. The samples were transformed into NH_4^+ forms by a conventional ion-exchange by NH_4NO_3 solution. FeH-FER sample (4000 ppm Fe) (denoted as FER/Fe) was prepared from NH_4^+ form of sample by TOSOH as described elsewhere [5]. Zeolite composition was obtained by X-ray fluorescence analysis. For evaluation of the siting of Fe at α- and β-cationic sites, the data from [5] were used.

2.2. Catalytic test

The catalytic activities were measured using continuous flow microreactor combined with NO_x/NO chemiluminescence and GC for product analysis. Composition of the inlet streams in SCR test was always the same and consists of 1000 ppm NO_x, 1000 ppm propane and 2.5% O_2, balanced by He to a total flow of 100 ml/min. For experiments with NO_2-poor or NO_2-rich streams, the sequence of O_2 and NO addition in the premixing part situated upstream of the reactor, was reversed and its temperature was varied. Thus, the NO_2/NO_x ratio at the catalyst reactor inlet could be varied between 0.05 and 0.9. The catalysts were calcined at 450 °C in the stream of air for 3 h. Before the catalytic test the catalysts were heated in the stream of He for 4 h and then were stabilized in the reaction mixture at 350 °C until a stable performance in the catalytic test was reached (over 3 h). Then the activity was measured between 150 and 450 °C. The stable activity results for each temperature were reached after about 1 h and, as checked in some cases, the activity was stable for several hours.

3. Results and discussion

Table 1 shows the chemical composition of the FER samples used for the catalytic tests. FER/C sample shows the iron content typical of commercial zeolite samples [6,7]. Addition of a low amount of iron (sample FER/Fe) increased its iron content about 20 times. Using extra-pure preparation procedure (sample FER/P) decreased more than three times the content below that reached in the commercial sample. As it has been already shown [5] in all these samples the prevailing cationic site occupied by Fe ions in the β-site, i.e. in the deformed six-member ring of the eight-ring channel of FER (see e.g. [8]). The concentrations of Brønsted OH groups in FER/P and FER/C are very similar and related to their Si/Al values. Decrease of concentration of OH groups due to iron exchange in FER/Fe compared to FER/C was below 10%.

For empty reactor, i.e. a reactor filled by glass balls, the NO_x conversion was near to zero. NO_x conversion in SCR reaction with propane in NO_2-poor streams displays a strong correlation with iron content (see Fig. 1A). No such correlation of NO_x conversion with Fe content was obtained in experiments with NO_2-rich streams (see Fig. 1B). In the latter experiments the maximum NO_x conversion was equal to that reached for the FER/Fe sample for NO_2-poor streams, i.e. that of about 60–65% at temperatures of 350 °C. In both types of catalytic experiments, a decrease of NO_x conversion at temperatures over 350 °C was found, with the exception of experiments with FER/Fe at NO_2-rich streams (see Fig. 1B, above 400 °C). Selectivity of the SCR process was evaluated by calculating the ratio

Table 1
Chemical composition of FER samples and percentage of population of α- and β-cationic sites

Material	Si/Al	c_{Fe} (ppm)	α/β
FER/P	8.2	50	0/100
FER/C	8.5	170	0/100
FER/Fe	8.5	4000	25/75

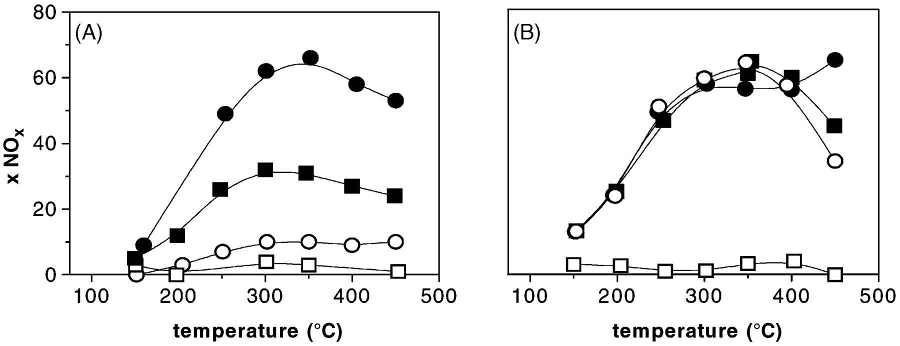


Fig. 1. Temperature dependence of the NO_x conversion in the SCR of NO_x with propane in NO_2-poor ((A) $NO_2/NO_x = 0.05$) and NO_2-rich ((B) $NO_2/NO_x = 0.9$) inlet streams. Conditions: NO_x 1000 ppm; propane 1000 ppm; O_2 2.5%; flow rate 100 ml/min; balance by He. Measured in the absence of a catalyst (□), or with 0.40 g of FER/P (○), FER/C (■), and FER/Fe (●).

of consumption of NO_x and propane by the reaction ($\Delta NO_x/\Delta$propane). This parameter was about 3 and 4 for experiments in NO_2-poor and NO_2-rich streams, respectively. That is above the typical value of 1–1.5 obtained for paraffins over zeolites with Fe/Al $\sim$ 1 [3,9]. We assume that such increase of the process selectivity could be probably assigned namely to the unique structure of the iron sites formed at the low Fe/Al region [5].

Catalytic activity in NO–NO_2 equilibration both in NO_2-poor and NO_2-rich streams displayed a dependence on iron content in the zeolites (see Fig. 2). The composition of NO/NO_2 mixture over FER/Fe sample nearly reached that of the equilibrium, while the FER/P displayed negligible activity in the whole temperature region. The blank experiments with reactor filled with glass balls shown no change of the composition of the inlet stream in the NO_2-poor streams.

These results could be taken as a support for the assumed activity of protonic sites of zeolites in NO_2–propane reaction [10]. Accordingly, it seems that the sole role of Fe cation in such system would be in providing the NO_2 necessary for the reaction of NO_2 with propane. Moreover, and in contradiction to the accepted view, the activity of acidic protons of zeolites in NO–NO_2 equilibration is negligible.

In this respect a decrease in the NO_x conversion and propane conversion increase up to its total consumption (at temperatures over 350 °C) seems to be unjustified for the sample with minimal activity in NO–NO_2 equilibration in experiments with NO_2-rich streams (i.e. for the FER/P sample). It seems that the explanation would necessitate participation of radical processes (see e.g. [11,12]), as could be indicated by analysis of the model experiments illustrated in Fig. 3A and B. Actually, experiments in NO_2-rich streams, and including all components of the NO_x–O_2–propane mixture, have shown a parallel increase in NO–NO_2 equilibration activity and at the same time propane conversion. Nevertheless, significantly, nearly no change in the total NO_x amount was

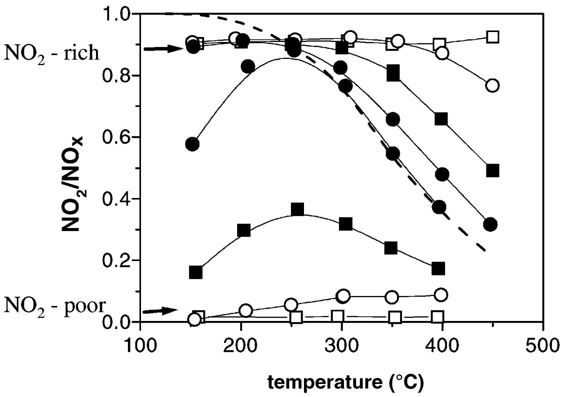


Fig. 2. Temperature dependence of NO_2/NO_x ratio in the NO–NO_2 equilibration in NO_2-poor ($NO_2/NO_x = 0.05$) and NO_2-rich ($NO_2/NO_x = 0.9$) inlet streams. Conditions: NO_x 1000 ppm; O_2 2.5%; flow rate 100 ml/min; balance by He. Measured in the absence of catalyst (□), or with 0.40 g of FER/P (○), FER/C (■), and FER/Fe (●). Dashed line denotes calculated equilibrium composition NO_2/NO_x.

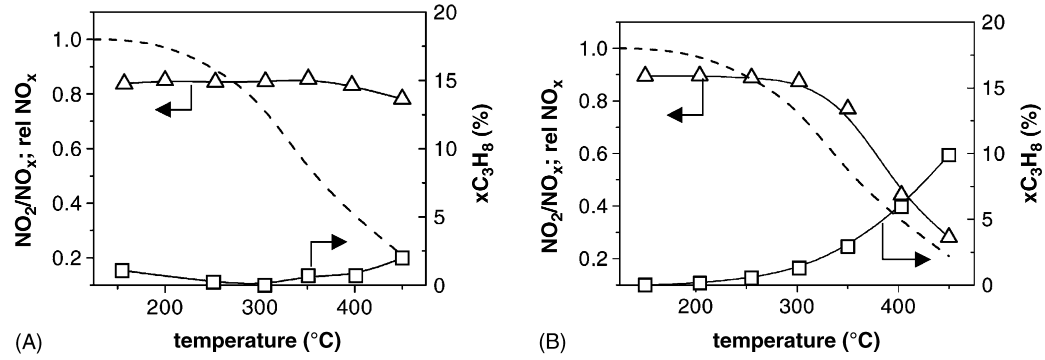


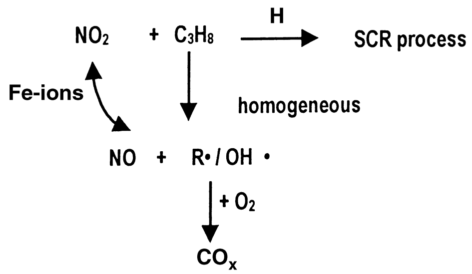
Fig. 3. Temperature dependence of the propane conversion (□), and NO–NO_2 equilibration (expressed as NO_2/NO_x ratio (△)), in NO_2-rich streams over reactor filled by glass balls. Reactions were followed in separated experiments (A), or in a mixed stream (NO_x–O_2–propane) (B). Conditions: NO_x 1000 ppm and/or propane 1000 ppm; O_2 2.5%; NO_2/NO_x 0.9; flow rate 100 ml/min; balance by He. Dashed line denotes calculated equilibrium composition NO_2/NO_x. Under experimental conditions the concentrations of NO_x in the outlet and inlet were identical.

indicated under such conditions. This implies, that the reaction is not the SCR of NO_x by propane, as no N_2 is formed.

By including both these effects illustrated previously, we suggest a tentative generalized scheme for such complex reaction system of SCR of NO_x by propane over H-zeolites with low Fe content (Scheme 1).

It consists of the following steps: (i) NO–NO_2 equilibration provided by iron cation in β-position; (ii) NO_2–propane reaction over active proton of the zeolite, yielding NO_x conversion into N_2; (iii) a radical process bringing consumption of NO_2 and propane but no NO_x conversion to N_2.

It could be speculated that this radical part of the scheme could actually participate in the propane activation for the main process of SCR of NO_x by propane.



Scheme 1.

4. Conclusions

A study of the SCR-NO_x reaction over FeH-FER catalysts with very low iron content, i.e. below the concentration present in the commercial parent FER samples, revealed the extreme activity of iron traces in NO–NO_2 equilibration. On the other hand, and in contradiction to the generally accepted view, only negligible activity for SCR of NO_x by propane in NO_2-poor streams could be assigned to the zeolite acidic protons. This stresses the crucial role of Fe cation for formation of NO_2, as a necessary step for the whole process.

The narrow temperature window for such system seems to be caused by the interconnected radical activation of propane and NO_2 reduction to NO. In such system, provided no other reaction mechanism takes place, the decrease of NO_x conversion and increase of propane conversion up to its full consumption at temperatures over 350 °C, would be inherent to the NO_x–O_2–propane system over FeH-exchanged zeolites.

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