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Nature of active sites in a Fe-Beta catalyst for NO_x selective catalytic reduction by NH_3

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A correlation is observed between the rate of NO_x selective catalytic reduction by NH_3 over Fe-Beta and the number of isolated Fe^{III} species characterised by an ESR signal at $g \approx 4.3$, which is a function of total Fe loading and Si/Al ratio.

The selective catalytic reduction (SCR) of NO_x by ammonia over V–W–TiO_2 catalysts is virtually the only technique for NO_x abatement in an oxidising medium applied in practice (others are modifications of this method, *e.g.*, NO_x SCR by urea).[1–3] Vanadium is hazardous to the environment, and this gives rise to a need for novel NO_x SCR catalysts. Fe zeolites (Fe-ZSM5 and Fe-Beta) represent a promising replacement for V–W–TiO_2 due to high catalytic activity and sufficient stability in the NO_x SCR by ammonia.[4–6]

It is of importance to study factors affecting Fe-zeolite performance in NO_x SCR, the process mechanism and the structure of active sites.[7–9] We observed a correlation of the reaction rate over a Fe-Beta catalyst with a concentration of specific isolated Fe^{III} sites represented by an ESR signal at $g \approx 4.3$[7] for zeolites with different Fe contents, Si/Al ratios and zeolite microcrystal sizes.

Catalysts containing 0.1, 0.3 and 1 wt.% Fe supported on commercial Beta-zeolites (H-form, Tosoh) with Si/Al ratios of 30, 70 and 300 (designated as Beta30, Beta70 and Beta300, respectively) were prepared by incipient-wetness impregnation with a solution of $Fe(NO_3)_3$ followed by drying and calcination at 550 °C in airflow.

The reaction rate was measured in a stainless-steel fixed-bed flow reactor at 225 °C and GHSV = 216000 h^{-1}. The gas contained 7.5% O_2, 10% CO_2, 4% water, 300 ppm of NH_3 and 300 ppm of NO balanced with N_2. For accurate reaction rate evaluation, NO_x and NH_3 conversions were maintained at < 20%. Reaction products were analysed using an Analysis Automation Limited series 440 chemiluminescent NO_x analyzer and a Gasmet FTIR gas analyzer (Temet Instruments Dx-4000n).

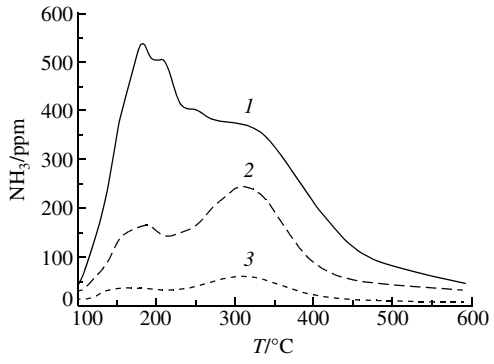

Figure 1 TPD profiles of the Beta-zeolites with Si/Al ratios of (*1*) 30, (*2*) 70 and (*3*) 300.

The acidity of zeolites was evaluated using temperature-programmed desorption of ammonia. A sample of 100 mg (1–2 mm) was placed in a quartz reactor and treated at 520 °C during 1 h in a flow of N_2. After that, the sample was cooled to room temperature, and ammonia was adsorbed (2.8% NH_3 in He, 150 ml min^{-1}) during 30 min. TPD profiles were obtained using the Gasmet FTIR gas analyzer after removal of physically adsorbed ammonia at 90 °C for 30 min in N_2 flow (200 ml min^{-1}) with temperature ramp of 10 K min^{-1}.

The zeolite crystal size was estimated using microphotographs obtained on a JEOL JSM-5300LV scanning electronic microscope.

The ESR spectra were taken in the X-band ($\lambda \cong 3.2$ cm) at –196 °C on a spectrometer equipped with a 4104OR cavity and a co-axial quartz Dewar. The ESR signals were measured in the lack of saturation in the field range 0–3900 G. The signals were recorded at identical magnification from samples of equal weight (0.075 g) evacuated at 90 °C. All ESR intensity data are presented in arbitrary units, which is sufficient for our purpose to monitor relative variations of the concentration of Fe species.

TPD profiles of the used Beta-zeolites are shown in Figure 1 and the amount of acid sites is given in Table 1. TPD spectra comprise two desorption peaks at ~180 and 300–310 °C, which are ascribed by Marques *et al.*[10] and Miyamoto *et al.*[11] to NH_3 desorption from non-acid sites and Brönsted acid sites, respectively. The amount of desorbed ammonia evaluated from the area of the desorption peak at 300–310 °C is in good agreement with a number of acid sites calculated on the basis of Si/Al ratio and varies by an order of magnitude for Beta30 and Beta300.

The SEM photographs of the zeolites are shown in Figure 2. Crystals of Beta30 have a diameter of ~7 μm. Beta300 and Beta70 samples consisted of fine crystals 1 μm in diameter with some amount of aggregates of these crystals of a bigger size for Beta70.

Table 1 Zeolite acidity, microcrystal size and NO_x selective catalytic reduction rate over Fe-Beta.

Zeolite	BAS number/ mmol g^{-1} (obtained using NH_3 TPD)	BAS number/ mmol g^{-1} (calculated from Si/Al ratio)	Average crystallite size/μm	NO_x SCR rate at 225 °C/μmol g_{Cat}^{-1} s^{-1}		
				0.1% Fe	0.3% Fe	1% Fe
Beta30	0.70	0.64	7	7.1	12.4	15.8
Beta70	0.34	0.24	1	4.8	7.7	9.8
Beta300	0.09	0.06	1	2.7	5.1	5.1

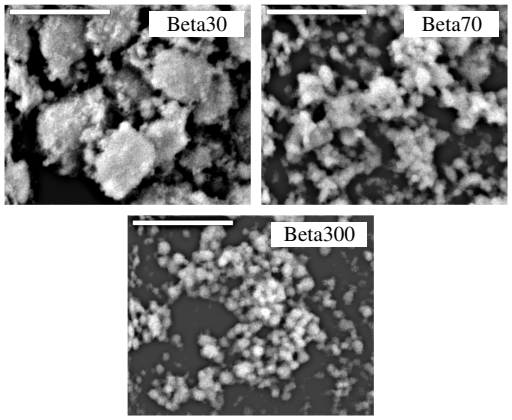

Figure 2 SEM photographs of the Beta-zeolites. White scalebar is 10 μm.

The NO_x reduction rates at 225 °C over the catalysts under study are given in Table 1. Increase in Al content results in an increase in the reaction rate. However, this increase is not directly proportional to the Si/Al ratio. Thus, an increase in Al content by an order of magnitude for Beta30 *vs.* Beta300 is accompanied by an increase in the reaction rate by a factor of 3.

Note that a nonlinear correlation of the reaction rate with the total amount of loaded Fe is observed. The reaction rate increases with increasing Fe content from 0.1 to 1% for Fe-Beta30 and Fe-Beta70 catalysts. On the other hand, an increase in the Fe content of Fe-Beta300 from 0.1 to 0.3% leads to NO_x reduction rate increase; however, further Fe loading does not cause an increase in the reaction rate. Tentatively, this effect may be attributed to a saturation of available cationic positions of Beta300 lattice with Fe^{3+} ions at 0.3% (Fe/Al ≈ 1).[7,12,13]

To verify this assumption, the ESR spectra of the samples were registered. The test samples show two ESR signals: a broad signal at $g \approx 2.2$, which is ascribed to Fe_2O_3 particles, and a signal at 4.3. Relevant parts of the spectra of 1% Fe-Beta30, 1% Fe-Beta70 and 1% Fe-Beta300 are shown in Figure 3. Isolated tetrahedral Fe sites in zeolites can be distinguished and quantified by a signal at $g \approx 4.3$.[7,14] This signal intensity depends on the Si/Al ratio and increases with rising Fe content from 0.1 to 1%.

The correlation between the signal intensity of isolated Fe sites and the NO_x reduction rate is presented in Figure 4. The linear correlation allows us to conclude that a factor determining the rate of NO_x SCR by NH_3 is the number of isolated tetrahedral Fe^{III} sites (or FeO^+ species). Presumably, these are Fe^{III} cations located in zeolite cationic positions.[15]

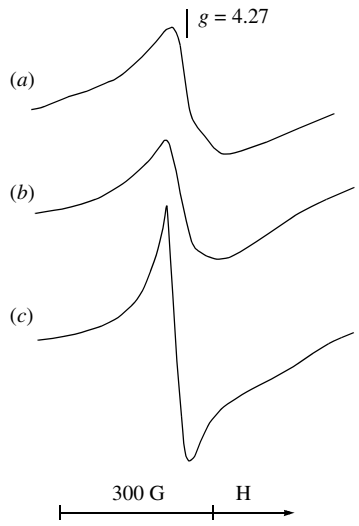

Figure 3 ESR spectra of Fe^{III} species taken at –196 °C: (*a*) 1% Fe-Beta300, (*b*) 1% Fe-Beta70 and (*c*) 1% Fe-Beta30.

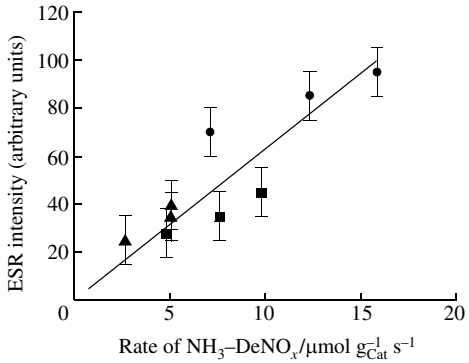

Figure 4 Correlation between ESR signal intensity at $g \approx 4.3$ and NH_3–$DeNO_x$ rate at 225 °C: circles – Beta30, squares – Beta70 and triangles – Beta300.

Note that the reaction rate seems insensitive to crystal size. A comparison of Fe-Beta30 and Fe-Beta70 indicates that observed variations in reaction rate are mostly attributed to a change in the concentration of isolated Fe^{III} sites, while zeolite crystal sizes different by a factor of 4–7 are not a crucial factor affecting the catalyst activity.

The above data allowed us to conclude that the activity of Fe-Beta catalysts in NO_x SCR is determined by a relatively small fraction of isolated tetrahedral Fe^{III} sites, being influenced, in turn, by Fe loading and Si/Al ratio. These results are in agreement with data reported by Schwidder *et al.*,[12] who found that over Fe-ZSM-5 reaction rate in NH_3–$DeNO_x$ correlates with the total Fe content and concentration of isolated Fe^{III}. It is noteworthy that, over Fe-ZSM-5, there is a notable participation of oligomeric Fe species in the overall process.

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