# INVESTIGATIONS ON ISOMORPHOUSLY SUBSTITUTED IRON IN Fe-BETA AND Fe-SILICALITE-1

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## ABSTRACT

Fe-Beta and Fe-silicalite-1 samples containing isomorphously substituted iron (~ 1 % at.) were synthesized and characterized by XRD, SEM and Mössbauer spectroscopy, and tested in direct $N_2O$ decomposition. In situ Mössbauer spectroscopy revealed that removal of framework iron to extra-framework positions may occur in a larger extent in Fe-Beta than in Fe-silicalite-1. This behavior is correlated with the catalytic activity observed in the direct decomposition of $N_2O$ where Fe-Beta exhibited better performance.

Keywords: Fe-Beta, Fe-silicalite-1, Mössbauer spectroscopy, $N_2O$ decomposition

## INTRODUCTION

Iron-containing zeolites are known as excellent catalysts for the decomposition of harmful nitrous oxides to nitrogen and oxygen. $N_2O$ is the third largest greenhouse gas contributor to overall global warming, behind carbon dioxide and methane, which attacks ozone in the stratosphere. $N_2O$ emissions are due to agriculture, the production of nylon and nitric acid, and the burning of fossil fuel in internal combustion engines. The preparation method of iron silicates strongly influences the nature and distribution of the resulting iron species, which basically determines the catalyst performance. Iron can be incorporated by isomorphous substitution, ion exchange, and chemical vapor deposition.[1-3] The introduction of iron into the silicate matrix is typically followed by a high-temperature calcination or steam treatment. These treatments are crucial to yield active sites in isomorphously substituted silicates by the extraction of framework iron to extra-framework positions [4].

The present study elaborates on the characterization of isomorphously substituted iron in silicates of BEA and MFI structures. Zeolite beta is a disordered intergrowth of several hypothetical polymorphs, all characterized by a 3D/12-membered ring channel system, whereas silicalite-1 presents a 3D/10-membered ring channel system. Accordingly, the channel dimensions in Beta (0.66 x 0.67 nm and 0.56 x 0.57 nm) are larger than in silicalite-1 (0.53 x 0.56 nm and 0.51 x 0.55 nm). Differences between the two microporous frameworks were compared with regard to crystal structure, morphology and forms of iron species. Mössbauer spectroscopy was used to identify the individual iron forms in the calcined iron silicates treated under various conditions. The performances of these samples in direct $N_2O$ decomposition were also evaluated.

## EXPERIMENTAL

Fe-Beta and Fe-silicalite-1 samples were synthesized using TEAOH and TPAOH as structure directing agents, respectively. The obtained products were calcined at 500ºC for 5 hours in oxygen flow. The X-ray powder diffraction (XRD) patterns were recorded on a PANalytical X'Pert PRO high-resolution diffractometer with Alpha1 configuration using

CuK$_{\alpha 1}$ radiation (1.5406 Å) in the 2θ range from 5 to 35$^o$ 2θ using step 0.034$^o$ and collection time of 100 s per step at fully opened X'Celerator detector. SEM micrographs were obtained by scanning electron microscopy on Zeiss Supra$^{TM}$ 3VP microscope. In situ $^{57}$Fe Mössbauer spectra were collected on calcined Fe-Beta and Fe-silicalite-1 samples after the steps in a sequence of treatments (evacuation at 380°C, and treatments in hydrogen at 360°C, respectively, each treatment lasted for 2 h). Spectra were recorded at ambient temperature in constant acceleration mode. Lorentzian line shapes were used for decomposition, the isomer shift values were related to metallic α-iron. 100 mg of samples were placed into a quartz U-tube reactor (i.d. 4 mm). The samples were heated up in He flow at a heating rate of 10$^o$C / min to 600$^o$C and were activated at the given temperature for 1 hour. Reaction temperature was increased in 50$^o$C steps up to 600$^o$C and the conversion levels were determined at each temperature after the steady state was reached at a given temperature. Finally, the samples were cooled to the lowest reaction temperature (300$^o$C) in He flow. The reaction was initiated by switching from the He flow to a reactant gas mixture containing 1500 ppm $N_2O$ in He. Concentrations of $N_2O$ reactant and $N_2$ and $O_2$ products in the effluent gas from the reactor were continuously monitored by a mass spectrometer (VG ProLab gas analysis system from Thermo-Fisher).

## RESULTS AND DISCUSSION

Pure nanocrystals of Fe-silicalite-1 were prepared by hydrothermal synthesis from clear solution. The pure products crystallized from the gels with the initial pH of 12. Lower amounts of template (lower initial gel pH) were favorable for the formation of amorphous phase as a major phase. Fe-Beta nanoparticles were obtained from viscous solution. Higher amount of iron component increased the crystallization time.

The phase purity of both samples is confirmed by the X-ray powder diffraction data (XRD) in Figure 1. XRD patterns of calcined Fe-Beta and Fe-silicalite-1 show diffraction peaks that correspond to zeolites of BEA and MFI structure, respectively. Reflections due to iron oxides are not observed.
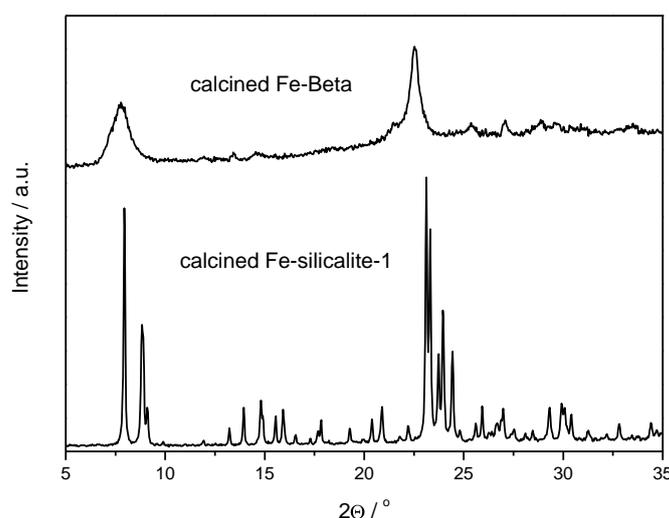


Figure 1: X-ray diffraction patterns of calcined Fe-Beta and Fe-silicalite 1

The morphology of the samples was investigated by SEM microscopy. SEM micrographs (Figure 2) show different morphologies of nanosized particles in both samples. Scanning electron microscopy reveals that Fe-silicalite-1 powders contain nanocrystals with

different shapes, which agglomerate into round and/or angular aggregates, depending on crystallization time, and temperature. On the other hand, different shapes of Fe-Beta were induced by different iron oxidation state in iron components.
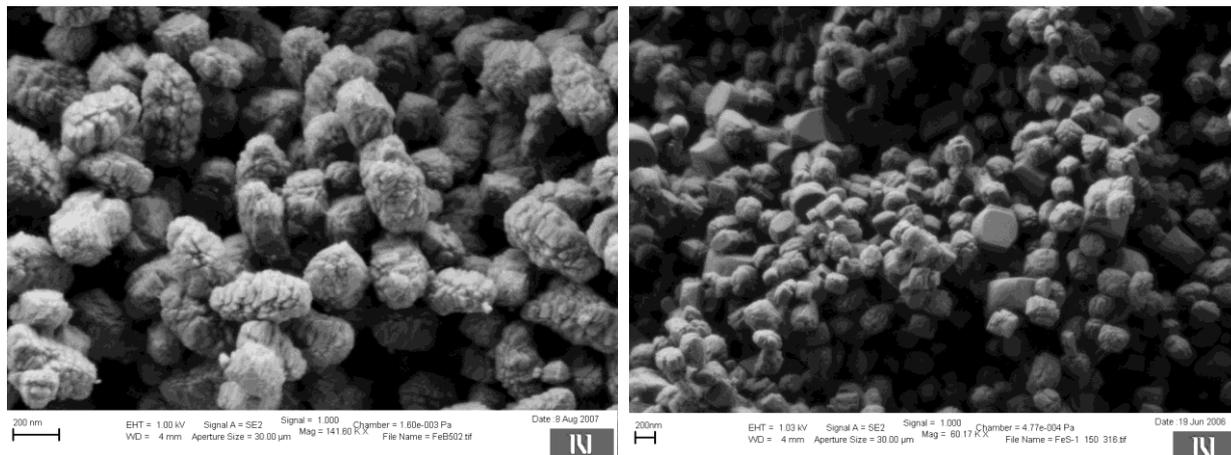


Figure 2: SEM pictures of Fe-Beta (left) and Fe-silicalite-1 (right).
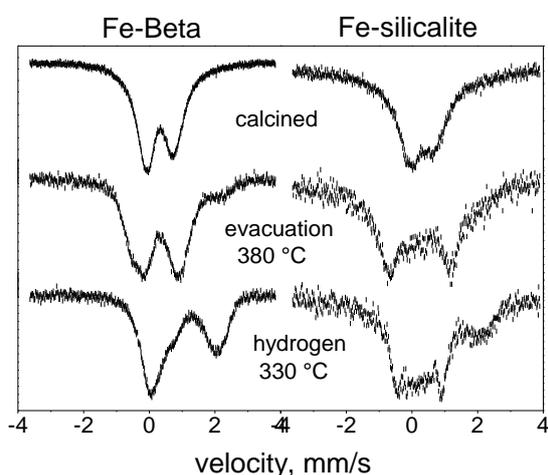


Figure 3: Mössbauer spectra of calcined Fe-Beta and Fe-silicalite-1 samples recorded after each steps in sequence of treatments.

The location and environment of iron in the calcined samples were investigated by in situ Mössbauer spectroscopy under different conditions (see Experimental part). The analysis of in situ Mössbauer spectra (Figure 3) revealed that removal of iron from the isomorphously substituted framework positions proceeded easily in Fe-Beta, whereas this process was less pronounced in Fe-silicalite-1. The $Fe^{3+}$ component with large quadrupole splitting ($1.6 < QS < 1.9$ mm/s) can be assigned to framework substituted tetrahedral ions, whereas reversible $Fe^{3+} \leftrightarrow Fe^{2+}$ redox conversion can mostly be observed on extra-framework ions. The behaviour of the two samples are markedly different:

in Fe-Beta only ca. 1/3 of iron is located in FW tetrahedral sites, whereas in Fe-silicalite c.a 80% of iron occupies FW siting. Reversible $Fe^{3+} \leftrightarrow Fe^{2+}$ conversion can also be observed on both samples. A part of this reversible process may probably proceed only on the extra-framework component of $Fe^{3+}_{framework}$-O-$Fe^{3+/2+}_{extra-framework}$ dinuclear centres, as can be deduced from variations of the quadrupole splittig values [5].

The performance of calcined Fe-Beta and Fe-silicalite-1 samples in direct $N_2O$ decomposition was primarily investigated to support conclusions derived from Mössbauer techniques. In this model reaction, it is well accepted that the nature and distribution of extra-framework iron species determine the $N_2O$ conversion. [3,6,7,] As shown in the conversion versus temperature curves of Figure 4, the activities of the two samples with different particle sizes are different. This difference in the activity can probably be attributed to the more flexible structure of the Fe-Beta and to the more facile relocation of iron to extra-framework positions.
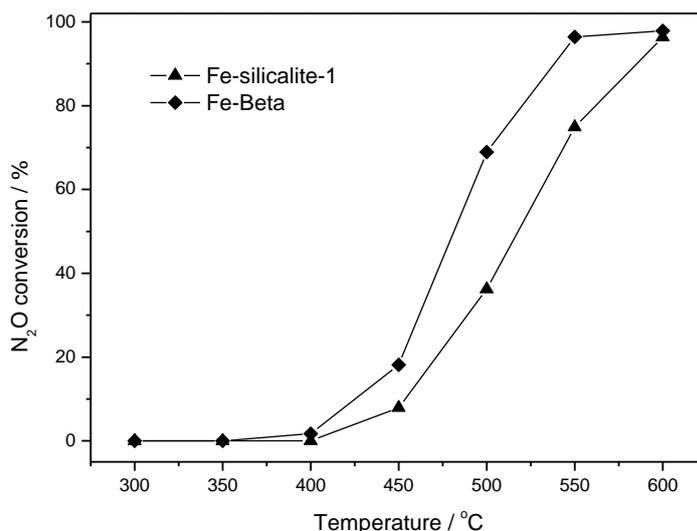
Figure 4: $N_2O$ conversion in the function of the reaction temperature in the direct $N_2O$ decomposition

## CONCLUSION

Iron in isomorphously substituted iron silicates with BEA and MFI structures was characterized by in situ Mössbauer spectroscopy. Results show that larger amount of framework iron species can be easier removed to extraframework positions from Fe-Beta than than from Fe-silicalite-1. Fe-Beta catalyst showed better activity in the direct $N_2O$ decomposition reaction, suggesting that extra-framework iron may play the primary role in the reaction.

## ACKNOWLEDGEMENTS

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