

## From understanding of redox structures in Fe-zeolites to production of deNOx catalysts

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### Introduction

A progress in the fundamental understanding of the structure of Fe-oxo species and selective formation desired structures is demonstrated on the development of Fe-ZSM-5 and Fe-FER catalysts from laboratory synthesis to production and application in the deN<sub>2</sub>O and NH<sub>3</sub>-SCR-NO<sub>x</sub> processes. The novelty of the approach consists in an insight into mechanism controlling the formation of individual Fe-oxo species depending on the local distribution of charge in the framework of zeolites. The local negative charge balances the counter Fe species and it is a decisive parameter controlling the structure, redox behaviour and catalytic activity. The local negative charge in the framework is controlled by the distribution of aluminium in the framework [1].

### Materials and Methods

ZSM-5 and ferrierite zeolites, both with similar framework aluminium content and significantly different concentration of isolated Al atoms and Al-O-(Si-O)<sub>2</sub>-Al sequences located in one ring were obtained using proper combinations of sources of aluminium and silicon, together with changing synthesis parameters of each zeolites. Al distribution in the framework of ZSM-5 and ferrierite zeolites was analysed using methodology based on the exchange capacity and siting of divalent cations, supplemented by high-resolution <sup>27</sup>Al and <sup>29</sup>Si MAS NMR analysis. Mössbauer, EPR, UV-Vis and FTIR spectroscopy and temperature programmed reduction were used for the analysis of the structure of Fe species. Conversion and selectivity of Fe-ZSM-5 and Fe-FER catalysts in the NH<sub>3</sub>-SCR-NO<sub>x</sub> reaction and catalytic decomposition of N<sub>2</sub>O are reported on both laboratory scale and at pilot NoNOx unit for processing of tens of tons of gases per day.

### Results and Discussion

Fe-cationic species in Fe-ZSM-5 are predominantly represented by bare Fe(II) ions, dinuclear [Fe(II)-O-Fe(II)]<sup>2+</sup> and [Fe(III)-μO<sub>2</sub>-Fe(III)]<sup>2+</sup> and Fe(III)-oxo species of low nuclearity [2,3]. The population of distinct cationic Fe species is largely directed by the local negative charge in the framework of ZSM-5 zeolites. High local negative charge in the framework originating from Al pairs in 6MRs led predominantly to the occurrence of bare Fe(II) and dinuclear Fe(II)-O-Fe(II)<sup>2+</sup> complexes, while a predominant population of single Al atoms caused in a comparable atmosphere a higher occurrence of trivalent Fe(III)-oxo species [2,3]. With NH<sub>3</sub>-SCR-NO<sub>x</sub> in real NO<sub>x</sub> streams from a nitric acid plant, the Fe-oxo species charge-balanced by isolated framework Al atoms in ZSM-5 zeolites are the most active sites exceeding significantly others Fe cationic or Fe oligomer species. In contrast, for nitrous oxide

decomposition, two Fe ions, each balanced by an Al pair in the opposite rings of β-type cationic sites of the framework, are the most active sites.

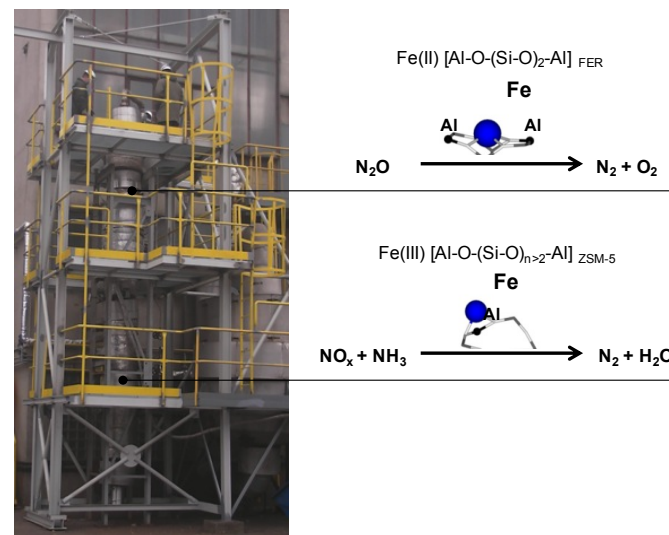


Figure 1. NoNOx pilot unit (catalytic decomposition of N<sub>2</sub>O + NH<sub>3</sub>-SCR-NO<sub>x</sub>) with highly structured Fe-zeolite catalysts with controlled valence and structure of Fe species by local density of aluminium in the zeolite framework. Flow of nitrous gases 500-1000 m<sup>3</sup>.h<sup>-1</sup>, N<sub>2</sub>O decomposition: conversion >99.5% at 420°C, NH<sub>3</sub>-SCR-NO<sub>x</sub>: conversion >99.5% at 200-450°C.

### Significance

These findings show that manipulation of the structure of Fe-cationic species can be achieved by the synthesis of zeolites with different distributions of Al atoms between Al pairs and single Al atoms in the framework. This represents a potential for tailoring of catalytic properties of Fe-zeolite based catalysts for abatement of nitrogen oxides.

### References

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