# Feasibility of application of iron zeolites for high-temperature decomposition of $N_2O$ under real conditions of the technology for nitric acid production

**Edyta Tabor**[*], **Galina Sádovská, Milan Bernauer, Petr Sazama, Zdeněk Sobalík**

*J. Heyrovsky Institute of Physical Chemistry of the Czech Academy of Sciences*
*Dolejškova 3, Prague, 182 23, Czech Republic*
**Corresponding author: edyta.tabor@jh-inst.cas.cz*

**Abstract:** *The long-term stabilities of Fe-MFI, Fe-*BEA, and Fe-FER were evaluated to assess their performance as catalysts for high temperature (< 930 °C)* $N_2O$ *decomposition at the presence of* $H_2O$, $O_2$, *and NO. The fresh catalysts contained the following iron forms: isolated Fe(II), mono- and polynuclear Fe(III)-oxo species, or small Fe oxide particles. After 12 days at 800 °C in the stream of* $N_2O$, $O_2$, $H_2O$, *and NO: only FER structure stabilized Fe(II) species; but ZSM-5 and *BEA contained exclusively Fe(III). All fresh catalysts exhibited high* $N_2O$ *conversion at 750-930 °C. Among the aged catalysts, only Fe-FER exhibited high catalytic performance.*

**Keywords:** $N_2O$ decomposition, Fe-zeolite catalysts, long term stability

## 1. Introduction

Nitric acid production represents the largest source of environmentally damaging $N_2O$. One of the solutions for effective $N_2O$ decomposition is the placement of the catalyst layer directly down to ammonia burner, which is the first step in $HNO_3$ production [1-3]. This arrangement requires a stable catalyst working well at high-temperature regime (750 - 930 °C), at a space velocity ~ 350 000 $h^{-1}$ and in a gas mixture containing $N_2O$ (700 - 2 000 ppm) together with 10 % NO, 15 % $H_2O$, and 2 % $O_2$. The primary objective of this paper is to provide an overview of the long-term stability of the catalytic performance for a group of iron zeolites with various framework types. The study was supported by the analysis of both the framework structures and iron species, and enables evaluation of the applicability of iron zeolites in the high-temperature decomposition of $N_2O$ under conditions representative of those involved in $HNO_3$ production.

## 2. Experimental

Three iron zeolites Fe-FER (Si/Al = 9), Fe-ZSM-5 (Si/Al = 12.5), and Fe-*BEA (Si/Al = 12.6) were prepared by the impregnation method using anhydrous solution of $FeCl_3$ in acetylacetone. To prepare the samples for Mössbauer studies isotopically enriched $^{57}FeCl_3$ was used. Aging was performed as follows: the catalysts were exposed for 12 days to gas stream produced by catalytic oxidation of $NH_3$ by air over platinum grid, consisting of 1% $O_2$, 15 % $H_2O$, and 10 % NO in $N_2$ at 800 °C. The structural analysis was performed using XRD, UV-VIS-NIR, FTIR, and Mössbauer spectroscopies. The catalytic activity of both fresh and aged catalysts was measured over a temperature range of 900 to 200 °C. The reaction mixture consisted of 1 000 ppm $N_2O$, 0,5 % NO, 2 % $O_2$, and 10 % $H_2O$ in He, and GHSV of 350 000 $h^{-1}$.

## 3. Results and discussion

The XRD patterns confirmed the resistance of zeolite frameworks to severe treatments, maintaining their structural order and regular periodic arrangement. UV-VIS spectra of fresh Fe-zeolites confirmed the presence of i) isolated $T_d$-coordinated Fe(III) (47 000 $cm^{-1}$), ii) $O_h$-coordinated Fe(III) (40 000 $cm^{-1}$), iii) clustered Fe(III)-oxo species (30 000$cm^{-1}$), and iv) Fe oxides (18 000 $cm^{-1}$). Among them, Fe-FER exhibited high concentration of bridging Fe(III)–oxo complexes and limited amount of both isolated $O_h$-coordinated Fe(III)-oxo ions and iron oxide species. In contrast Fe-*BEA and Fe-MFI exhibited significantly higher concentration of iron oxides particles in comparison with Fe-FER. After aging of Fe-zeolites, the intensity of the charge-transfer bands corresponding to isolated Fe(III)-oxo and oligomers at 30 000 – 50 000 $cm^{-1}$ decreased strongly, indicating the migration of highly dispersed Fe(III) ions, and their agglomeration into Fe oxides as reflected by an increase of the band at 18 000 cm$^{-1}$. For FTIR analysis, NO was used as probe molecule, which detected Fe(II) cations by the formation of mononitrosyl complex visible at 1 872 cm$^{-1}$. Mononitrosil complex was formed on all fresh catalysts, the highest concentration of Fe(II) exhibited Fe-FER. After aging, only FTIR spectrum of Fe-FER showed the typical Fe(II)-NO band [2]. Mössbauer studies of fresh catalysts revealed that Fe-FER contained the highest concentration of Fe(II) species (28 %) in comparison to Fe-MFI and Fe-BEA*, which exhibited Fe(II) concentration below 10 %. After aging Fe-MFI and Fe-BEA* contained exclusively trivalent iron forms. In the case of Fe-FER the concentration of Fe(II) species decreased from 28 to 6% after aging [2]. Summarizing, aging led to transformation of Fe(II) to Fe(III) in all Fe-zeolites (Fig. 1) [3]. Only FER framework well stabilized iron species and part of them after severe conditions of aging was still observed as Fe(II).

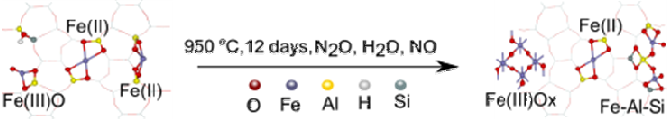

Fig. 1. Changes in the state of Fe species in zeolites during the aging at the conditions similar to those in ammonia burner.

The results of catalytic tests performed both before and after aging are summarized in Fig. 2. The fresh zeolite catalysts showed near-complete conversion of $N_2O$ at temperatures higher than 700 °C and GHSV of 350 000 h$^{-1}$. Nevertheless, after aging the $N_2O$ conversion over Fe-MFI and Fe-*BEA dramatically decreased in contrast to aged Fe-FER, which still exhibited superior catalytic activity [2,3].

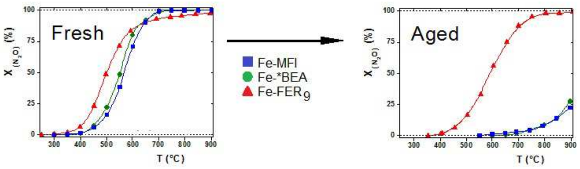

Fig. 2. Catalytic activity of HT-decomposition over fresh and aged Fe-zeolites.

The structure-performance results further support the dominant role of the exposed Fe(II) cations, both before and after exposure to the aging conditions, in the decomposition of $N_2O$. Our results indicate a clear correlation between the catalytic activity and the ability of zeolite structure to stabilized Fe(II) species. Only the Fe(II) coordinated to a local structure with two Al ions in 6MRs was identified as a candidate, which preserved a long term high temperature treatment in the stream of containing $N_2O$, NO, $H_2O$, and $O_2$ [3]. Among studied zeolites structure, the best matrix for stabilization Fe(II) species active in HT-$N_2O$ decomposition served FER framework. Other arrangements were either less stable (including 6MRs in *BEA and MFI), or showed only very low activity (e.g., the products of transformation in MFI and *BEA) [3].

## 3. Conclusions

Zeolite-based iron catalysts have potential for application in the high-temperature decomposition of $N_2O$ under conditions relevant to those used for $HNO_3$ production. Resistance of the catalysts to the effects of long-term exposure to these demanding conditions is directly connected to the stabilization of the local Fe(II) structure and this structure's resulting resistance to transformation into less active iron oxide species. Until now, such a specific local arrangement with the required stability had been found only in the FER zeolite.

References

[1] J. Pérez-Ramírez, Appl. Catal. B. 70 (2007) 31-35.

[2] G. Sádovská, E. Tabor, P. Sazama, M. Lhotka, M. Bernauer, Z. Sobalík, Catal. Commun. 89 (2017) 133-137.

[3] E. Tabor, G. Sádovská, M.Bernauer, P. Sazama, J. Nováková, V. Fíla. T. Kmječ, J. Kohout, K. Závěta, Z. Sobalík, Appl. Catal. B. (2017) https://doi.org/10.1016/j.apcatb.2017.11.014.