

MÖSSBAUER SPECTROSCOPY STUDY OF THE IRON ACTIVE SITES IN ZEOLITES FOR N₂O DECOMPOSITION

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Iron ferrierites (Fe-FER) are known as catalysts for decomposition of nitrous oxide. It is assumed that Fe-FER – N₂O system could provide the solution for the environmentally relevant problem of eliminating of harmful nitrous oxide that strongly contributes to the greenhouse effect [1-3]. Despite the apparent simplicity of the reaction that takes place during N₂O decomposition over various iron zeolites, mechanistic details of this process have not been completely characterised. It is suggested that the main role in this process play the Fe ions in cationic positions [1,4]. Therefore, this contribution is focused on the identification of Mössbauer parameters of Fe sited in cationic positions, which can be further, apply for determination of the reactivity of Fe species in N₂O decomposition.

A series of Fe-FER with Fe/Al < 0.1 were prepared by impregnation of NH₄-FER by actetylacetone solution of ⁵⁷FeCl₃ [1]. This method makes possible introduction the Fe ions into cationic positions. FTIR and UV-Vis spectroscopy were used to check the location of Fe ions in Fe-FER. Catalytic activity of Fe-FER in N₂O decomposition was carried out in batch reactor. Both the Mössbauer and *in-situ* FTIR spectroscopies were used as main methods for monitoring the nature of Fe species as well as their behavior under oxidized conditions. Mössbauer spectra were acquired under vacuum at RT after: (a) evacuation at 450 °C for 3 h, (b) evacuation at 450 °C for 3 h, followed by O₂ at 450 °C adsorption (c) evacuation at 450 °C for 3 h, followed by adsorption of N₂O at 280 °C. FTIR measurements were performed during the interaction of the evacuated sample (450 °C for 3 h) with N₂O at 280 °C for various interaction times.

Catalytic results have shown that in spite of low Fe loading in FER all samples exhibited high N₂O conversion. UV-Vis and FTIR measurements of evacuated samples confirmed absence of Fe oxide species and location of Fe ions in cationic positions.

By Mössbauer spectroscopy of Fe-FER with low content of iron and well-defined composition the Mössbauer parameters of Fe ions in α and β cationic sites. Moreover, thanks to high sensitivity of the Mössbauer spectroscopy, the two types of β sites (β_1 and β_2) were distinguished. In Fe-FER with Fe/Al lower than 0.036 iron was exclusively present as Fe(II) and located in α and β cationic positions. In the samples with Fe/Al 0.018 and 0.036 the population of β sites was 83 % and 75 %, respectively. At higher iron content (Fe/Al 0.072), Fe(III) was present as well (27 %); Fe(II) ions were equally distributed between α and β sites.

The reactivity of Fe species in Fe-FER was checked by interaction with O₂ or N₂O. Mössbauer spectra of all investigated samples treated by O₂ led to the oxidation of about the same proportion of the Fe cations, i.e. presenting about 20% of the Fe(II) present in the samples. These results clearly suggest that only part of the iron located in cationic positions could be transformed into oxidized form by molecular oxygen. It further confirmed higher resistance of β sites to O₂ oxidation. On the other hand, nearly total transformation of Fe(II) to Fe(III) was observed after oxidation by N₂O at 280 °C. On the Mössbauer spectrum of Fe-FER after N₂O interaction the relaxation component was appeared, which characterized the paramagnetic hyperfine interaction and indicates a change in the microenvironment of Fe species after N₂O treatment. The presence of this component can be assigned to formation of Fe-NO_x species.

Analysis of FTIR spectra after N₂O adsorption at 280 °C showed that after short interaction time Fe-O species are formed. But, with an increasing of interaction time of N₂O with Fe-FER, the amount of Fe(III)-NO_x species increases with simultaneous decreasing of the amount of Fe(III)-O, in agreement with the sequence: Fe(II) → Fe(III)-O → Fe(III)-NO_x.

The studied Fe-FER samples with Fe/Al < 0.1 provide a standard for reliable establishing of Mössbauer parameters of iron cations in α and β cationic positions. Moreover, Mössbauer spectroscopy brings the first experimental support for the presence of two types of β sites in Fe-FER. Recently, based on experimental results (FTIR, UV-VIS, MBS) supported by DFT calculation was shown that iron cations in Fe-FER are preferably located in β cationic positions [1, 5]. It is suggested that part of Fe(II) in β sites is located in adjacent positions across the FER channel. Because the majority of Fe(II) is located in β positions, as evidenced by Mössbauer spectroscopy, it is possible that the observed nitrates are primarily bridged between two Fe(II) ions located in adjacent β positions. Once formed Fe-NO_x species were stable during the subsequent N₂O decomposition and enhanced the reaction rate.

References

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