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N_2O decomposition over iron modified zeolites ZSM-5

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Abstract

Fe-ZSM-5 zeolites of different Si/Al ratio prepared by means of ionic exchange from aqueous solution and from solid state were used as catalysts for N_2O decomposition in the range of temperature from 300 to 500 °C. The samples with high iron concentration (3–15 wt.% of Fe), both calcined at 550 and 900 °C, showed very high activity for N_2O decomposition. UV-Vis spectra of iron modified samples have indicated the presence of both the isolated iron species, binuclear complexes and oxide-like phase. Calcination at 900 °C resulted in the formation of binuclear iron species and also enhanced the concentration of oxide phase. From IR spectra of adsorbed N_2O it was concluded that N_2O was bonded to zeolite structure both through the oxygen and nitrogen atoms.

Keywords: Fe-ZSM-5; N_2O decomposition; UV-Vis; FT-IR spectra

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1. Introduction

Different nitrogen oxides have appeared as ingredients of waste gases emitted both from power stations and from industry. Nitrous oxide is mainly formed as a by-product in many industrial processes such as adipic acid and nitric acid production [1]. It has been recently found that N_2O is a very effective oxidant for some oxidation processes resulting in high selectivity towards partly oxidised organic compounds [2–4]. However, consumption of N_2O during the oxidation process has never been 100%, therefore, the decomposition of unreacted N_2O is very important, considering its contribution in greenhouse effect and also some responsibility for ozone layer depletion. Considering the above, the investigations on decomposition of waste nitrous oxide to prevent its emission were extensively developed. Both supported transition and nobel metals, metal oxides [5,6], and transition metals modified zeolites were widely searched as potential catalysts for this reaction. Copper modified zeolites of MFI structure have a long history as a promising catalyst for nitrous and nitric oxides decomposition. However, this catalyst is very sensitive both for water vapours and for SO_x presence in waste gases. The use of iron modified zeolite ZSM-5 (Fe-ZSM-5) resulted in more resistant catalysts. The activity of Fe-ZSM-5 zeolites depended on iron cations concentration, which was related to Si/Al ratio of zeolite matrix and the exchange procedure.

Considering that the Si/Al ratio of zeolite matrix affects the absolute loading of iron ions introduced by ionic exchange, one could expect some influence of Si/Al ratio on the activity of Fe-ZSM-5 samples for the studied reaction. Effect of iron concentration and the thermal treatment of exchanged samples on an ability of Fe-ZSM-5 for N_2O decomposition was also investigated. The interaction of N_2O with active centres present in Fe-ZSM-5 zeolite was observed by means of FT-IR spectroscopy.

2. Experimental

Commercial zeolites ZSM-5, kindly supplied by Süd Chemie (Si/Al ratio = 25, 50, labelled as SCh25 and SCh50 respectively), and by Alsi Penta (Si/Al ratio = 14, 28, labelled as SN27, SN55, SM27 and SM55), were modified with iron cations by means of double ionic exchange from aqueous solution of iron (III) nitrate at 60 °C or by solid state ion-exchange at 550 °C in presence of air using $FeCl_2$ as a source of iron. The samples were calcined at 550 or

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900 °C for 2 h in air. The activity of modified samples for N_2O decomposition was measured in an isothermally operated flow reactor in the temperature range between 300 and 500 °C. A feed gas concentration of 939 ppm N_2O in helium (Linde) and a GHSV $= 30\,000\,h^{-1}$ were chosen as reaction conditions. The samples were characterised by means of XRD patterns (not shown) and diffusion reflectance UV-Vis spectra. ICP analysis was employed to estimate the amount of iron introduced into zeolite during an exchange procedure. FT-IR spectra of N_2O contacted with previously evacuated Fe-ZSM-5 were recorded to show an interaction of N_2O with centres present in modified samples.

3. Results and discussion

Modification of zeolite ZSM-5 with iron cations by means of ionic exchange from aqueous solution and by solid state resulted in different iron loading (Table 1). All of the iron modified zeolites ZSM-5 showed activity for N_2O decomposition starting from 300 °C, however, the activity depended significantly on iron concentration and on the thermal pre-treatment (Figs. 1 and 2). The higher iron loading resulted in a higher activity for N_2O decomposition. This conclusion was in agreement with the earlier report, where it was found that the over exchanged zeolite Fe-ZSM-5 was significantly more active for N_2O decomposition than the near stoichiometric one [7]. Sachtler and coworkers [8] have proved that binuclear iron complexes or the larger iron clusters showed higher activity for N_2O decomposition than the mononuclear centres. According to Joyner and Stockehuber [9] the oxide-like nanoclusters formed during the calcination process showed better activity for NO_x reduction than the isolated iron species. Among the studied samples, Fe-ZSM-5 zeolites prepared by means of ionic exchange from solid state (labelled as Fe-SCh/**S** or Fe-SM/**S**) showed much higher iron concentration (Table 1) when compared to the samples exchanged from aqueous solution (labelled as Fe-SCh/**A** and Fe-SN/**A**). The samples of Fe-SCh/**S** and Fe-SM/**S** containing 3–15 wt.% of iron were able to decompose of N_2O completely in the temperature range of 350–370 °C (Fig. 2), while the decomposition over catalysts with lower iron concentration (0.4–1.4 wt.%) was not completed even at 450 °C (Fig. 1). High temperature calcination (900 °C) of the samples exchanged from aqueous solution (iron concentration 0.4–1.4 wt.%) resulted in lowering of the catalytic activity for N_2O decomposition (Fig. 1). On the other hand, the high temperature calcination of the samples prepared by means of solid state exchange (iron concentration 3–15 wt.%) practically did not influence the catalysts activity (Fig. 2).

Table 1
Iron concentration in modified zeolites ZSM-5, Si/Al ratio, Fe/Al ratio

Symbol of catalyst	Si/Al ratio	Fe (wt.%)	Fe/Al ratio
Fe-SCh25/**A**[a]	25	1.4	0.4
Fe-SCh25/**S**[b]	25	15.0	4.5
Fe-SCh50/**A**[a]	50	0.4	0.24
Fe-SCh50/**S**[b]	50	1.1	0.65
Fe-SN27/**A**[a]	14	2.8	0.29
Fe-SM27/**S**[b]	14	3.0	0.31
Fe-SN55/**A**[a]	28	1.0	0.33
Fe-SM55/**S**[b]	28	1.5	0.5

[a] **A**: after ionic exchange from aqueous solution.

[b] **S**: after solid state ionic exchange.

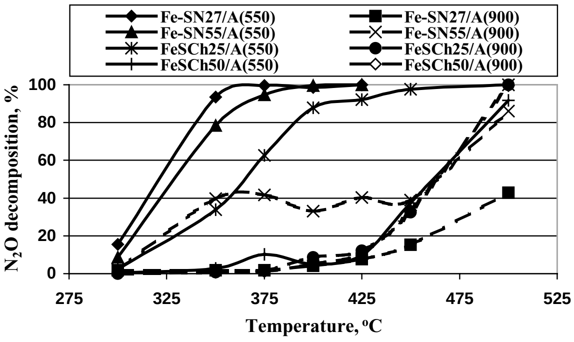

Fig. 1. N_2O decomposition over Fe-ZSM-5 zeolite of SCh and SN series, modified with iron by means of exchange from aqueous solution and calcined at 550 and 900 °C.

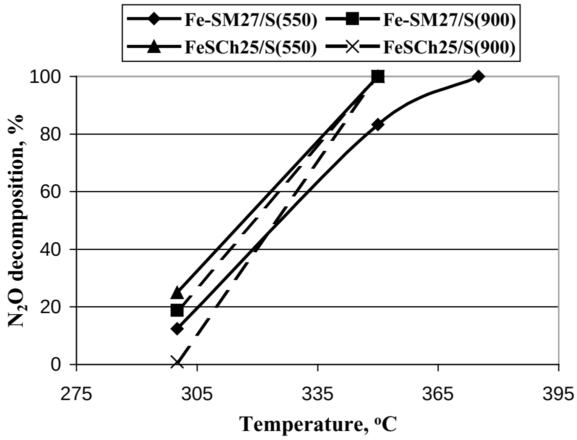

Fig. 2. N_2O decomposition over Fe-ZSM-5 zeolite of SCh and SM series, modified with iron by means of exchange from solid state and calcined at 550 and 900 °C.

From our earlier report based on XPS measurements [10] it was concluded that the high temperature calcination (900 °C) of ZSM-5 zeolite, previously exchanged with iron cations, resulted in the migration of iron cations from the outside zeolite surface into channels with subsequent formation of binuclear iron α-complexes. The last ones were responsible for increasing activity of these samples used for benzene to phenol hydroxylation, carried out in the presence of N_2O as an oxidant [11,12]. According to Sachtler and coworkers [8] and also Peréz-Ramirez et al. [13], binuclear and multinuclear iron clusters play an important role for N_2O decomposition, while monoatomic iron species show rather low activity for this reaction. Panov and cowork-

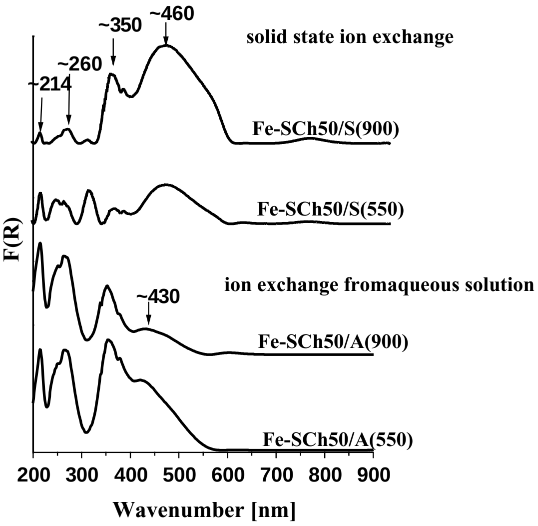

Fig. 3. UV-Vis spectra of Fe-SCh zeolites prepared by means of exchange from aqueous solution and from solid state with following calcination at 550 and 900 °C (Fe-SCh50/**A**—0.4 wt.% of Fe; Fe-SCh50/**S**—1.1 wt.% of Fe).

ers [11] have proved that iron ions present in binuclear α-complexes, active for benzene hydroxylation, operate rather like separate monoatomic entities. It may explain the apparent controversy that the formation of binuclear iron complexes results in lowering activity for N_2O decomposition. High temperature calcination (900 °C) of the samples with low iron concentration (about 1.1 wt.%) resulted in the formation of binuclear α-complexes at the expense of multinuclear complexes, which led to decrease in catalytic activity for N_2O decomposition (Fig. 1). The sample containing very low iron concentration (Fe-SCh50/**A**—0.4 wt.%) showed low activity even after calcination at 550 °C and high temperature treatment (900 °C) did not change this value (Fig. 1). On the other hand, the samples modified by means of solid state exchange, containing high iron concentration (3–15 wt.% of Fe) showed very high activity for N_2O decomposition both after calcination at 550 and 900 °C. It indicated that even after migration part of iron species with subsequent formation of α-iron complexes in zeolite channels, the concentration of multinuclear iron clusters was still high enough to catalyse N_2O decomposition.

The distribution of iron species, which varied both with method of iron introduction (different exchange procedures), and with thermal treatment (550 and 900 °C), might be estimated on the grounds of UV-Vis reflectance spectra (Fig. 3).

UV-Vis reflectance spectra of ZSM-5 zeolite exchanged with iron from aqueous solution (0.4–1.4 wt.% of Fe) and calcined at 550 °C showed the bands at 260–300 nm, attributed to mononuclear iron species [14], as well as a band at 360 nm, which could be described to multinuclear iron clusters. The samples prepared by means of solid state exchange showed additional band in the range of 400–600 nm attributed to the iron oxide phase. Calcination at 900 °C resulted in the increase in the intensity of iron clusters band (∼360 nm) and the band attributed to iron oxide phase (400–600 nm). The bands characteristic of iron oxide phase were mainly recorded for samples prepared by solid state exchange and their intensity increased as a result of calcination at 900 °C. From XRD patterns of iron modified samples both calcined at 550 and 900 °C (the patterns not shown here due to space limitation) one can conclude that the MFI structure was still prevented, however, the intensity of reflexes characteristic of MFI structure decreased for the sample containing 15 wt.% of iron (FeSCh25/**S** both calcined at 550 and 900 °C). Additionally, the low intensity reflexes indicating the presence of iron oxides were recorded in XRD patterns of this sample.

Iron modified zeolites ZSM-5 contain different iron species, which structure and distribution depends on methods of zeolite modification (framework substitution, ionic exchange from aqueous solution, from solid state or by CVD method) as well as on iron concentration and preliminary thermal treatment. According to Sachtler and coworkers [15] high iron loading in zeolite matrix is beneficial for NO_x decomposition while rather low Fe species concentration is required for benzene to phenol hydroxylation with N_2O as an oxidant. Contact of N_2O with Fe-ZSM-5 catalyst resulted in the interaction both with acidic OH groups and with iron complexes. Introduction of N_2O into Fe-ZSM-5 evacuated at 300 °C led to disappearance of IR band at 3612 cm^{-1} characteristic of acidic hydroxyl groups and to the formation of a new broad and strong band with maximum at 3472 cm^{-1} and a weaker one at 3682 cm^{-1}. The silanol OH groups were inert towards N_2O up to 400 °C. The presence of two resonance structures in N_2O ($N{\equiv}N{-}O \Leftrightarrow N{=}N{=}O$) results in the possibility of formation of two adsorbate species with iron cations. One of them should be bonded to iron species through oxygen (N=N–O–Fe) and another one through nitrogen (O=N=N–Fe). These adsorbate structures may be recorded by IR spectra as the bands shifted with regard to N_2O gas modes. The asymmetric stretching vibrations described as N–N bond were recorded in the range of 2200–2300 cm^{-1}, while the symmetric stretching vibrations of N–O bond appeared in the range of 1200–1350 cm^{-1}. N_2O adsorption through oxygen resulted in a weakness of N–O bond and in a strengthen of N–N bond. As a consequence, N–O stretching band (in the region of 1200–1300 cm^{-1}) was red-shifted and asymmetric stretching band (region 2200–2300 cm^{-1}) was blue-shifted.

Interaction of N_2O with Fe-ZSM-5 (calcined previously at 900 °C) in vacuum cell resulted in an appearance of a strong band at about 2220 cm^{-1} (Fig. 4), which was described, according to Fanson et al. [16], to a weak interaction of N_2O with zeolite framework. Contact of N_2O with the samples containing higher iron concentration ($Fe/Al \geq 0.2$) at 200 °C led to the formation of additional, rather weak band, at about 2230 cm^{-1}. According to Rusu and Yates [17], this band should be described to the interaction of transition metal cations with N_2O through the oxygen atom. Analysis of IR bands in the region of N–O bond showed the presence of

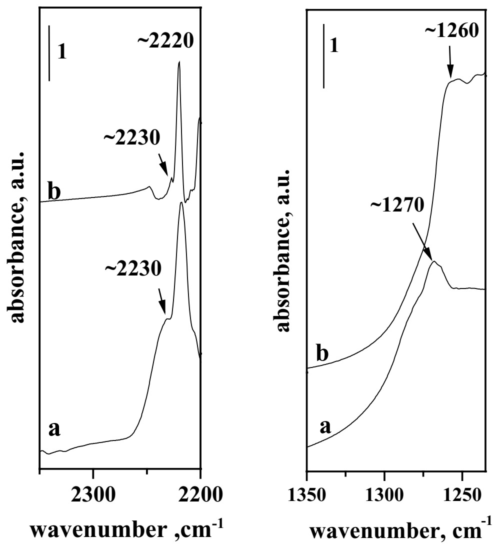

Fig. 4. FT-IR spectra of N_2O adsorbed on Fe-ZSM-5 zeolites (series SCh—line a; series SN—line b) modified with iron by means of exchange from aqueous solution and calcined at 900 °C.

weak bands (at about 1270 cm^{-1}), blue-shifted regarding to N_2O gas phase band (1285 cm^{-1}). The appearance of a pair of bands at about 2230 and 1270 cm^{-1} (Fig. 4) indicated the formation of oxygen bonded adsorptive species of N_2O on iron ions present in Fe-SCh (Fe/Al ratio ≥ 0.2) calcined at 900 °C. According to Isupova et al. [18], the IR band at about 2230 cm^{-1} should be described to the interaction of N_2O with Fe^{2+} species formed in Fe-ZSM-5 zeolite. Formation of Fe^{2+} containing species as a result of Fe^{3+} to Fe^{2+} reduction is favoured by high temperature treatment of iron modified zeolite ZSM-5 and also by high iron concentration [19]. Presence of Fe^{2+} in the samples with Fe/Al ≥ 0.2 calcined at 900 °C was confirmed by the appearance of IR band at about 930 cm^{-1} (Fig. 5). This band was described by Wichterlova and coworkers [20] to Fe^{2+} ions located at cationic position of zeolite ZSM-5. Presence of Fe^{2+} species in the samples under study should also be expected considering their high activity for benzene to phenol hydroxylation [12] and regarding the structure of α-iron complexes (comprising Fe^{2+} ions), required for this reaction [11]. Considering the above, the higher intensity of IR bands related to the interaction of Fe^{2+} ions with N_2O leading to the formation of N=N–O–Fe adsorptive species could be expected. It seems however, that the interaction of N_2O with Fe^{2+} at 200 °C resulted mainly in decomposition of nitrous oxide with O_α formation.

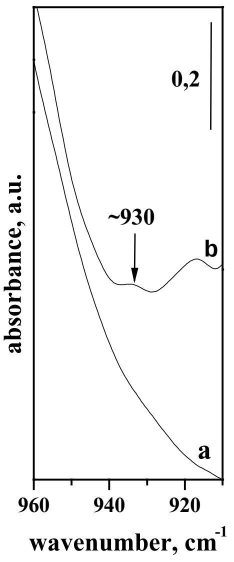

Fig. 5. FT-IR spectra of Fe-SCh50/A zeolite (calcined at 550 °C—line a; calcined at 900 °C—line b) in the region of skeletal vibration; Fe-ZSM-5 evacuated at 300 °C in vacuum cell.

From the results discussed above, one can conclude that the interaction of N_2O with iron modified zeolites, both templated (Fe-SCh) and non-templated (Fe-SM and Fe-SN) ones was strongly influenced by iron concentration. The samples with Fe/Al ratio ≥ 0.20 and calcined at 900 °C, after contact with N_2O, formed the adsorbate species characterised with the pair of bands at about 2230 and 1270 cm^{-1}. The presence of these bands confirmed the formation of oxygen bonded N_2O complexes with iron (II) cations. Additionally, the weak band at about 2250 cm^{-1} (Fig. 4; line b), which may suggest the presence of nitrogen bonded N_2O complexes was also recorded. This band appeared mainly on non-templated Fe-SN catalysts.

4. Conclusions

- Fe-ZSM-5 samples prepared by ionic exchange from aqueous solution and from solid state showed high activity for N_2O decomposition.
- N_2O decomposition over iron modified zeolite ZSM-5 was mainly affected by iron concentration and thermal treatment, which stimulate the formation of multinuclear iron clusters.
- N_2O adsorbed on iron modified zeolite ZSM-5 interacted with acidic OH groups and also with iron cations. Adsorptive N_2O species, oxygen and nitrogen bonded to iron ions, were recorded by IR spectra on all studied catalysts calcined at 900 °C.

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