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N_2O decomposition over Fe/ZSM-5: reversible generation of highly active cationic Fe species

Q. Zhu,[a] E. J. M. Hensen,*[a] B. L. Mojet,[b] J. H. M. C. van Wolput[a] and R. A. van Santen[a]
[a] *Schuit Institute of Catalysis, Laboratory of Inorganic Chemistry and Catalysis, Eindhoven University of Technology, P.O.Box 513, 5600 MB Eindhoven, The Netherlands. E-mail: E.J.M.Hensen@tue.nl*
[b] *Department of Chemical Technology, Catalytic Processes and Materials, University of Twente, P.O.Box 217, 7500 AE Enschede, The Netherlands*

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Fe-oxide species in Fe/ZSM-5 (prepared by chemical vapor deposition of $FeCl_3$)—active in N_2O decomposition—react with zeolite protons during high temperature calcination to give highly active cationic Fe species, this transformation being reversible upon exposure to water vapor at lower temperature.

Despite its low atmospheric concentration, nitrous oxide (N_2O) contributes about 9% to global warming due to its 300 times higher global warming potential compared to CO_2.[1] Fe/ZSM-5 prepared by sublimation of $FeCl_3$ is a promising catalyst for N_2O abatement.[2,3] This catalyst has also been reported to be a potential candidate for the selective catalytic reduction of nitrogen oxides found in automobile exhaust gases.[4,5] One interesting aspect of this system—when applied to decompose nitrous oxide—is the occurrence of isothermal oscillations in the presence of water indicating different catalytically active states.[3,6] Therefore, it is of great interest to study the influence of water on the active sites of the Fe/ZSM-5. We report the transformation of iron species by zeolite acidity or water vapor and their respective roles in N_2O decomposition.

Original Fe/ZSM-5 was prepared by sublimation[4,5] of $FeCl_3$ on HZSM-5 (Si/Al = 19.4, Akzo-Nobel) followed by calcination at 550 °C. The Fe loading is 3.6 wt% (Fe/Al = 0.97). Further treatments of Fe/ZSM-5 included calcination at 700 °C, followed by exposure to 10% water vapor treatment at 500 °C in a repetitive fashion. Each treatment took 3 h. The catalytic N_2O decomposition was carried out in a plug flow reactor with a calibrated on-line mass spectrometer for product quantification. N_2O decomposes stoichiometrically to N_2 and O_2 and neither NO or NO_2 is detected. After some initial deactivation, a steady state is achieved within 1 h. The repetitive treatments were carried out *in situ* between activity measurements.

Infrared spectra of self-supporting 10 mg catalyst wafers were recorded at room temperature on a Bruker IFS113v Fourier Transform IR spectrometer with DTGS detector at a resolution of 4 cm^{-1}. Prior to measurements, the catalyst was pretreated *in situ* at 500 °C for 1 h *in vacuo* (pressure lower than 10^{-6} mbar). Normalization of the overtones of lattice vibration (1870–1950 cm^{-1}) was applied to achieve quantification of Brønsted acid sites.

Fig. 1 shows the relation between reaction temperature and N_2O conversion over Fe/ZSM-5 with various pretreatments. The relatively high temperature calcination (700 °C) treatment of the original Fe/ZSM-5 efficiently increases the activity in N_2O decomposition.[7] Exposure to 10% water vapor at 500 °C lowers the catalytic activity substantially. Repeated treatments show that the behavior is reversible although a small, but significant increase in activity is noted.

Infrared spectra of the various Fe/ZSM-5 catalysts are presented in Fig. 2. The band at 3613 cm^{-1} is the stretching vibration of the Brønsted hydroxyl groups, while the band at 3745 cm^{-1} relates to the vibrations of terminal Si-OH groups.[8] Generally, the band at 3665 cm^{-1} is assigned to the hydroxyl groups connected to extra-lattice aluminium.[9] After the preparation of original Fe/ZSM-5, about 55% Brønsted acid sites of the parent zeolite (not shown) are replaced by cationic Fe species. After high temperature calcination, only around 10% of the Brønsted acid sites remain (Fig. 2B). After the first water treatment, the Brønsted acid sites are restored to about 25% (Fig. 2C). Further high temperature calcination and further water vapor treatment lead to similar disappearance and reappearance of Brønsted acid sites.

The disappearance of Brønsted acid sites might be caused by the removal of framework aluminium. After water vapor treatment, we indeed observe a very small increase of the hydroxyl group that is associated with the extra-framework aluminium (band at 3665 cm^{-1}). This is in line with our earlier observation that significant framework aluminium extraction is only induced by high temperature water treatment.[7] Moreover, high temperature calcination of the parent zeolite HZSM-5 only shows a slight decrease (5%) of Brønsted hydroxyl groups. The recovery of Brønsted acid sites strongly indicates that deal-

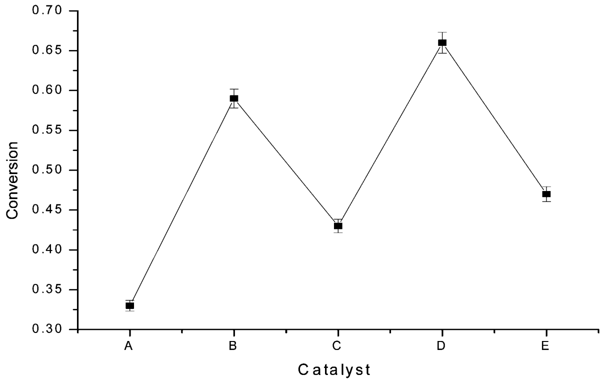

Fig. 1 N_2O decomposition over various Fe/ZSM-5 catalysts (3500 ppm N_2O at GHSV of 24000 h^{-1}, 425 °C). (A) Original Fe/ZSM-5, (B) A after calcination at 700 °C (20% O_2 in He), (C) B after treatment in water vapor at 500 °C (10% H_2O/He), (D) C after calcination at 700 °C (20% O_2 in He), (E) D after treatment in water vapor at 500 °C (10% H_2O/He).

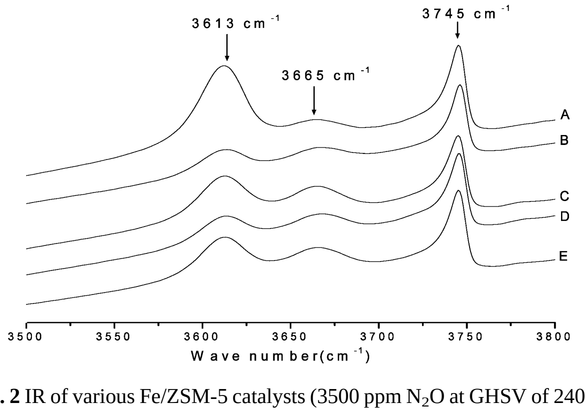

Fig. 2 IR of various Fe/ZSM-5 catalysts (3500 ppm N_2O at GHSV of 24000 h^{-1}, 425 °C). (A) Original Fe/ZSM-5, (B) A after calcination at 700 °C (20% O_2 in He), (C) B after treatment in water vapor at 500 °C (10% H_2O/He), (D) C after calcination at 700 °C (20% O_2 in He), (E) D after treatment in water vapor at 500 °C (10% H_2O/He).

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umination is not of overriding importance. We conclude that the drastic decrease of the number of zeolite protons is induced by their reaction with Fe-oxide species occluded in the zeolite micropores.

The applied preparation method excludes the possibility of Fe at framework positions. Fe species are either present as cationic species counterbalancing the negative charge of zeolite framework or as Fe-oxide clusters. These latter clusters may present themselves as agglomerates at the external surface and as occluded nano-clusters.[7] The nature of both Fe-oxide nanocluster and cationic species is widely debated in the literature.[10–12] For instance, a binuclear Fe species[4,13] based on the active diiron center in methane monooxygenase[14] has been proposed although it is not clear whether it would counterbalance the negative zeolite charge or would be present as a neutral cluster. We capture our results in an oversimplified reaction mechanism [eqn. (1)]

$$\mathrm{Fe}_x\mathrm{O}_y + 2(y-x)\,\mathrm{H}^+ \underset{700\,^\circ\mathrm{C}}{\overset{500\,^\circ\mathrm{C}}{\rightleftarrows}} x\,[\mathrm{FeO}]^+ + (y-x)\,\mathrm{H_2O} \quad (1)$$

where neutral Fe-oxide clusters can react at elevated temperatures with zeolitic protons to cationic Fe species. The specific nature of the proposed species remains to be determined. Upon water treatment cationic Fe species are transformed again in Fe-oxide species, thus explaining the reappearance of Brønsted acid sites. In essence, our results indicate that such cationic species have a much higher activity towards the decomposition of nitrous oxide. It is noteworthy that the Fe-oxide cluster not only react with the bridging hydroxyl groups, but also with the hydroxyl group that is associated with the extra-framework aluminium (Fig. 2C), displaying similar reversible chemistry.

In summary, high temperature calcination can efficiently increase the N_2O decomposition rate over Fe/ZSM-5 prepared by the sublimation method by increasing the number of Fe cationic species upon reaction between Fe-oxide nanoclusters and zeolite protons. Such cationic species can be converted back to Fe-oxide nanoclusters by exposure to water vapor.

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