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Superior performance of *ex*-framework FeZSM-5 in direct N_2O decomposition in tail-gases from nitric acid plants

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Isomorphous substitution of Fe in the MFI framework and extraction by steaming leads to a highly active and stable catalyst for N_2O decomposition in tail-gas from nitric acid plants.

Nitrous oxide (N_2O) has been identified as a greenhouse gas and a contributor to the destruction of ozone in the stratosphere.[1,2] At present, emission from nitric acid plants is the most important environmentally harmful source of N_2O in the chemical industry, since abatement technologies for the other major industrial source, *i.e.* adipic acid plants, have been successfully developed.[2] The direct catalytic decomposition of N_2O into N_2 and O_2 is an attractive *end-of-pipe* solution to reduce N_2O emissions, but none of the catalysts proposed in the literature show a good activity and stability in N_2O decomposition in the presence of high concentrations of O_2, NO_x and H_2O.[2,3] FeZSM-5 is an interesting system because N_2O conversion shows anomalous behaviour in the presence of these tail-gas components.[4] Different preparation methods have been reported to optimize the catalytic performance of FeZSM-5, not only in N_2O decomposition,[5,6] but also in de-NO_x HC-SCR and selective oxidations.[7–9] In this study, an *ex*-framework FeZSM-5 catalyst is shown to be very active and stable in direct N_2O decomposition in simulated tail-gas from nitric acid plants, compared to FeZSM-5 catalysts prepared by sublimation and (aqueous and solid) ion-exchange methods.

Isomorphously substituted FeZSM-5 was synthesized hydrothermally using TPAOH as the template.[10] The as-synthesized sample was calcined in air at 823 K for 10 h and was converted into the H-form by three consecutive exchanges with a NH_4NO_3 solution (0.1 M) for 12 h and subsequent air calcination at 823 K for 5 h (FeZSM-5*c*). Finally, the catalyst was activated in flowing steam at ambient pressure (water partial pressure of 300 mbar and 30 ml min^{-1} of N_2 flow) at 873 K during 5 h (*ex*-FeZSM-5). Other FeZSM-5 catalysts were prepared by liquid (aqueous) ion-exchange with $Fe(NO_3)_3\cdot 9H_2O$ (*lie*-FeZSM-5) and solid-ion exchange with $FeCl_2\cdot 4H_2O$ (*sie*-FeZSM-5), following standard procedures described in the literature.[5,8] NH_4-ZSM-5 (P&Q Corporation) was used as the support. *Sub*-FeZSM-5 was prepared by sublimation of $FeCl_3$ on H-ZSM-5 (Degussa).[7] The reaction was carried out in a six-flow reactor system,[11] by passing a mixture of N_2O (4.5 mbar), O_2 (70 mbar), NO (1 mbar) and H_2O (15 mbar) in He at a flow rate of 50–100 ml min^{-1} over 50 mg of catalyst (125–200 μm). Total pressure was 3 bar and space velocities (*GHSV*) of 36 000–120 000 h^{-1} were applied. Before reaction, the catalysts were pretreated in He at 723 K for 1 h. The product gases were analyzed with a chemiluminescence NO_x analyzer and by GC equipped with a thermal conductivity detector, using a PoraplotQ column and a Molsieve 5A column.

Table 1 shows the characterization results and the specific activity per mol of iron (turnover frequency, TOF) of the different catalysts. Fig. 1 shows that *sub*-FeZSM-5 and *ex*-FeZSM-5 induce similar absolute N_2O conversion levels in a N_2O–He feed and significantly higher levels than the exchanged catalysts. *sie*-FeZSM-5 is more active than *lie*-FeZSM-5. Calculation of the TOF at 700 K (Table 1) shows that the specific activity per mol of iron is more than 4, 7 and 10 times higher for *ex*-FeZSM-5 than for *sie*-FeZSM-5, *sub*-FeZSM-5 and *lie*-FeZSM-5, respectively. Electron microscopy reveals a very dispersed and homogeneous distribution of FeO_x clusters of 1–2 nm in *ex*-FeZSM-5 (see graphical abstract and Table 1), denoted as micro-aggregates here. The other preparation methods fail to lead to a homogeneous distribution of the iron species in the catalyst, as revealed by the broad FeO_x cluster size distribution indicated in Table 1. Activation of the calcined sample (FeZSM-5*c*) with steam at 873 K is crucial to create active Fe-species in *ex*-FeZSM-5, as can be concluded by comparison of the activity curves of both samples in Fig. 1. The steam treatment induces the migration of iron towards extra-framework positions by cleavage of Si-O-Fe bonds, as revealed by UV–VIS spectroscopy,[10] producing the FeO_x micro-aggregates. This treatment also leads to dealumination of the zeolite framework and formation of a secondary network of larger pores.

The performance of *ex*-FeZSM-5 in different feed mixtures containing N_2O and O_2, NO_x and/or H_2O is shown in Fig. 2. These gases are present in tail-gases from nitric acid plants. *ex*-FeZSM-5 shows a substantial N_2O conversion above 700 K in

Table 1 Data of catalysts used

Catalyst	Si/Al[a]	Fe[a]/wt%	ΔL[b]/nm	10^{-4} TOF[c]/s^{-1}
ex-FeZSM-5	31.3	0.64	1–2	48.6
sie-FeZSM-5	37.5	1.50	5–15	10.5
lie-FeZSM-5	37.5	1.46	7–25	4.7
sub-FeZSM-5	14.0	5.0	3–12	6.5

[a] Determined by ICP-OES and AAS. [b] FeO_x cluster size distribution (determined by TEM). [c] Mol of N_2O converted per mol of Fe ions s^{-1}, determined at 700 K after 1 h time on stream; feed composition: 4.5 mbar N_2O in He, total pressure 3 bar, GHSV = 36 000 h^{-1}.

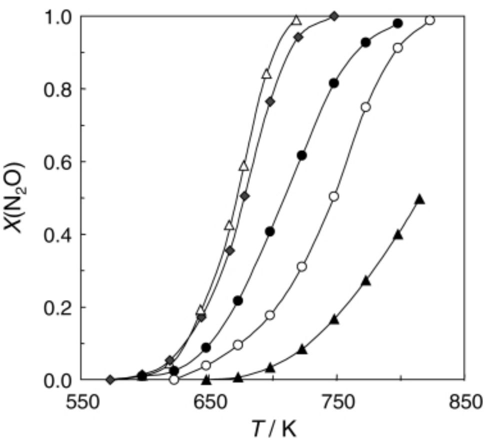

Fig. 1 N_2O conversion as a function of temperature over (◆) *ex*-FeZSM-5, (▲) calcined FeZSM-5*c*, (●) *sie*-FeZSM-5, (○) *lie*-FeZSM-5 and (△) *sub*-FeZSM-5. Feed composition: 4.5 mbarN_2O in He; total pressure 3 bar; GHSV = 36 000 h^{-1}.

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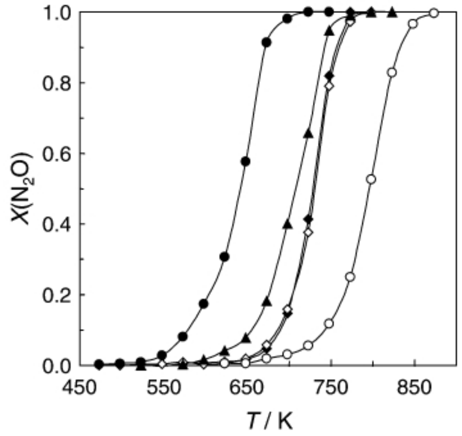

Fig. 2 N_2O conversion as a function of temperature in different feed compositions: (◆) 4.5 mbarN_2O, (◇) 4.5mbarN_2O + 70 mbarO_2, (●) 4.5 mbarN_2O + 1 mbarNO, (○) 4.5 mbarN_2O + 15 mbarH_2O, (▲) 4.5 mbarN_2O + 70 mbarO_2 + 1 mbarNO + 15 mbarH_2O; balance He; total pressure 3 bar; GHSV = 60 000 h^{-1}.

a N_2O–He feed. Addition of O_2 to the feed hardly affects the activity, while NO enhances the reaction rate considerably. Apparently, molecular oxygen does not dissociate over FeZSM-5 and does not compete with N_2O for active sites. NO scavenges adsorbed O* (deposited by N_2O decomposition), forming NO_2 and regenerates the active site. Water severely inhibits the reaction, probably by hydroxylation of the active sites and adsorption in the zeolite channels. Nevertheless, in the complete gas mixture (N_2O + O_2 + NO_x + H_2O), *ex*-FeZSM-5 still shows a significantly higher activity than in N_2O alone. The promoting effect of NO is thus stronger than the inhibition by H_2O. This extraordinary behaviour distinguishes FeZSM-5 from other N_2O decomposition catalysts (usually based on noble metals like Rh or Ru), since these are severely inhibited by NO_x (*via* surface nitrite/nitrate formation) and H_2O.[2,3,12,13] The remarkable behaviour of *ex*-FeZSM-5 is not limited to its activity, but also includes stability. N_2O conversion over *ex*-FeZSM-5 exhibits a remarkable stability in the complete feed mixture at different space velocities, ranging from 36 000 to 120 000 h^{-1} (Fig. 3). *sub*-FeZSM-5 shows slight deactivation at 36 000 h^{-1}. Significant deactivation was observed for the *sie*-FeZSM-5 and *lie*-FeZSM-5 catalysts, further increasing the differences in performance of the catalysts.

The differences in activity and stability of the different FeZSM-5 samples can be related to the preparation method, which lead to different constitutions of the catalysts with respect to dispersion, morphology, and structure of the active sites. A comparison of the FeO_x cluster size and TOF suggests a correlation (Table 1): the TOF increases with decreasing average FeO_x cluster size. The FeO_x micro-aggregates observed by TEM in *ex*-FeZSM-5 represent a large fraction of the total amount of Fe in the sample (*ca*. 70%), as estimated by ^{57}Fe Mössbauer spectroscopy. Sublimation and ion-exchange lead to a significantly lower relative amount of small clusters than the *ex*-framework method. In general, for other FeZSM-5 catalysts, the identification of the active species is difficult, due to the inhomogeneous nature of the catalysts. Isolated Fe^{3+} ions, binuclear and multinuclear complexes, small iron–oxide clusters, and large iron-oxide particles have been identified.[5–10] Large FeO_x particles at the external surface of the zeolite are widely accepted to be inactive in the de-NO_x HC-SCR.[5,7,8] This could also explain the lower activity of ion-exchanged catalysts compared to *ex*-FeZSM-5 in N_2O decomposition. *sub*-FeZSM-5 possesses small FeO_x clusters (*ca*. 3 nm), which may account for the high activity observed, but this catalyst also contains a significant fraction of large FeO_x particles (*ca*. 12 nm). A contribution of other iron species in the zeolites to the N_2O decomposition activity can not be excluded. We are currently further investigating the structure of the active sites in the different samples and the reason for the high stability of the *ex*-framework catalyst. We are also addressing the effect of the pore size distribution and extra framework aluminum formed in the steaming procedure of *ex*-FeZSM-5 on the activity.

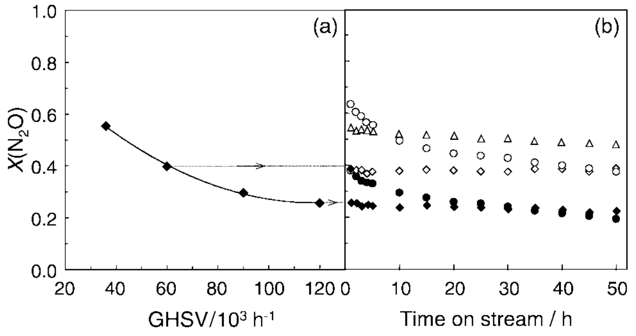

Fig. 3 N_2O conversion as a function of (a) the space velocity (GHSV) over *ex*-FeZSM-5 and (b) time-on-stream over (◇) *ex*-FeZSM-5 (60 000 h^{-1}, 700 K), (◆) *ex*-FeZSM-5 (120 000 h^{-1}, 700 K), (●) *sie*-FeZSM-5 (36 000 h^{-1}, 725 K) (○) *lie*-FeZSM-5 (36 000 h^{-1}, 775 K) and (△) *sub*-FeZSM-5 (36 000 h^{-1}, 700 K). Feed composition: 4.5 mbar N_2O + 70 mbar O_2 + 1 mbar NO + 15 mbar H_2O, balance He. Total pressure 3 bar.

The temperature of the exhaust in nitric acid plants, which ranges from 500 to 773 K depending on the plant operation, is of utmost importance for the feasibility of an *end-of-pipe* catalytic solution. Large modern dual-pressure plants, with tail-gases in the range 723–773 K, contribute to *ca*. 75% of the total N_2O emission. Nitric acid production facilities in the Netherlands (high-temperature tail-gases) contribute to 25 kton y^{-1}, *i.e. ca*. 6% of the global N_2O emission related to nitric acid plants (*ca*. 400 kton y^{-1}).[14] The use of *ex*-FeZSM-5, which shows stable N_2O conversion (> 90%) at 725 K and 60 000 h^{-1}, appears quite viable. This technology can contribute to greenhouse gas abatement in a cost-attractive way, since *ex*-FeZSM-5 does not contain any expensive noble metal. For low temperature tail-gases (500–525 K), typical in low (single or dual)-pressure plants, *ex*-FeZSM-5 would additionally require extra-heat exchange to preheat the feed mixture, or the addition of hydrocarbon as reducing agent.

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