SO_2-promoted catalytic N_2O removal over iron zeolites†

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SO_2 promotes the rate of N_2O removal over Fe-zeolites more efficiently than other reducing agents (NH_3) and promoters (NO); the effect of SO_2 as selective reductant is independent of the framework type and composition, preparation method, and iron content, suggesting that its occurrence is not determined by a highly specific iron speciation.

Remarkable progress in the development of catalytic technology for N_2O mitigation in anthropogenic sources has been experienced in recent years. A number of bulk and supported mixed metal oxides and metal-loaded zeolites have been proposed for N_2O decomposition in adipic acid and nitric acid plants.[1–3] Of all catalysts reported, iron-containing zeolites have probably attracted most attention due to their remarkable de-N_2O activity and stability in the presence of O_2, NO_x, and H_2O, *i.e.* typical components in industrial N_2O sources.[3–6] In particular, the positive effect of NO on the rate of direct N_2O decomposition over Fe-ZSM-5, first reported by Kapteijn *et al.*[7] and later studied extensively,[8–11] was decisive for its implementation in nitric acid plants (*e.g.* EnviNOx® process by Uhde). An additional feature of Fe-zeolites is that reducing agents such as hydrocarbons, CO, or NH_3 enable N_2O conversion at significantly lower temperature compared to direct decomposition.[3,5,12,13]

Catalysts for N_2O abatement in SO_2-containing tail gases such as those in (stationary and mobile) combustion processes and some caprolactam plants have not been implemented thus far. In these sources, sulfur dioxide is present in concentrations ranging from 20 to 2000 ppm.[1] Highly active catalysts for direct N_2O decomposition, such as Co-ZSM-5,[7] Cu-ZSM-5,[7,14] Rh/Al_2O_3,[15] calcined Co-Al hydrotalcites with Rh or Pd,[16] Rh/ZrO_2,[17] and Ru/Al_2O_3,[18] are strongly inhibited and/or deactivated by SO_2, through formation of stable surface sulfates. Two studies reported that SO_2 enhances the rate of N_2O decomposition over Fe-ZSM-5 prepared by ion exchange[7] and steam activation.[19] In contrast, Centi *et al.*[17,20] found that SO_2 inhibits the selective catalytic reduction of N_2O with C_3H_8 in the presence of O_2 and H_2O over Fe-ZSM-5 prepared by ion exchange and chemical vapour deposition. Based on these *a priori* equivocal findings, it can be questioned how general is the promoting or inhibiting action by SO_2 on N_2O abatement over iron zeolites.

Prompted by the intriguing results over Fe-ZSM-5 and the urgent demand for sulfur tolerant de-N_2O catalysts, we decided to investigate the N_2O + SO_2 reaction over a large number of iron-containing zeolites. Surprisingly, it has been found that SO_2 accelerates the catalytic removal of N_2O over iron zeolites, independent of the zeolite framework type and composition, preparation method, and iron content. SO_2 acts as a selective reductant for N_2O under excess O_2, being even more efficient than other reducing agents (NH_3) and promoters (NO). These results further magnify the exceptional surface chemistry of iron zeolites in N_2O-related reactions and their significance in environmental catalysis.

The catalysts investigated are listed in Table SI1 of ESI.† Various zeolite structures (ZSM-5, beta, ferrierite, mordenite) with Si/Al ratios of 10–40 and MFI framework compositions (silica, aluminosilicate, and gallosilicate) were considered. Iron was introduced into the microporous hosts using different precursors and preparation routes: hydrothermal synthesis followed by steam activation (st), liquid–ion exchange (lie), chemical vapour deposition (cvd), and incipient wetness (iw). The iron content was in the range 0.017–4.5 wt%. These wide synthetic variations were practised in order to obtain catalysts with different iron speciation. Catalytic performance was measured at ambient pressure in a quartz fixed-bed micro-reactor (9 mm i.d.) using *ca.* 100 mg of sample (sieve fraction 125–300 μm) and a space velocity (SV) of 60 000 ml g^{-1} h^{-1}. Tests were carried out isothermally at 473–873 K using mixtures with N_2O (1.5 mbar), SO_2 (0.2–2.5 mbar), O_2 (20 mbar), NO (1.2 mbar), NH_3 (1.2 mbar), and CH_4 (0.6 mbar), balance He. Reactant and product gases were analyzed by gas chromatography (Agilent 6890N).

The influence of SO_2 on the N_2O conversion over the catalysts is shown in Fig. 1. Rh-ZSM-5 (0.4 wt% Rh) prepared by incipient wetness was taken as a control sample, since it is known that SO_2 inhibits the catalytic N_2O decomposition over rhodium-based catalysts.[15–17] In good correspondence, the N_2O conversion decreased from 100% (open bars) to 62% (solid bars) upon addition of 2.5 mbar SO_2 at 723 K. In contrast, SO_2 boosts the N_2O conversion over all iron-containing zeolites. The N_2O conversion in direct decomposition at 723 K ranged from <5% in Fe-silicalite-st to *ca.* 40% over Fe-ZSM-5-cvd and Fe-ferrierite-lie. These differences are induced by the distinct iron speciation in the samples, which is intimately connected with the particular synthesis method and zeolite host structure. SO_2 increased the de-N_2O activity by 1.5–20 times, depending on the catalyst. The ranking of activity in the absence or presence of SO_2 differs, suggesting

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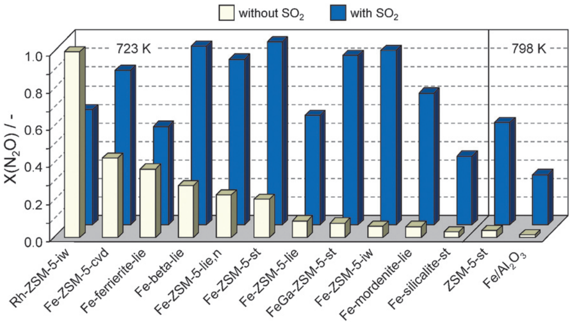

Fig. 1 N_2O conversion over the catalysts in 1.5 mbar N_2O (open bars) and 1.5 mbar N_2O + 2.5 mbar SO_2 in He (solid bars), balance He; P = 1 bar; WHSV = 60 000 ml g^{-1} h^{-1}; T = 723 or 798 K. Details on the catalysts are available in ESI.†

distinct active site requirements in both reactions. For example, Fe-ferrierite-lie is moderately improved by SO_2, while Fe-ZSM-5-st and FeGa-ZSM-5 are greatly promoted. Most of the zeolites display N_2O conversions > 50% in N_2O + SO_2 at 723 K, despite some of them being virtually inactive without SO_2. The impregnated Fe-ZSM-5-iw sample is a remarkable case. As expected, impregnation led to a poorly active N_2O decomposition catalyst due to excessive iron clustering. However, it was one of the most active systems with SO_2. According to these observations, we propose that the reaction of N_2O with SO_2 is not sensitive to a highly specific site structure, *i.e.* a contribution from different iron species can be expected. Due to this, the promotion is a general feature of all the iron-containing zeolites. Interestingly, the positive SO_2 effect was also evidenced in the zeolites without deliberate iron addition. A commercial H-ZSM-5 containing 170 ppm Fe was steam-treated in order to create active iron species.[21] The N_2O conversion over ZSM-5-st at 798 K increased from 5 to 55% upon SO_2 addition (Fig. 1). It can then be inferred that the reaction over few iron sites is largely promoted by sulfur dioxide. The N_2O conversion over Fe/Al_2O_3 (2 wt% Fe) also increased from 2 to 27% in the presence of sulfur dioxide. This result suggests that the beneficial SO_2 effect can be extrapolated to other supported iron catalysts, although experimentation over a wider matrix of non-zeolitic supports is needed to confirm this statement. Blank tests in N_2O + SO_2 mixtures with the empty reactor yielded no N_2O conversion in the temperature range investigated.

Fig. 2 shows N_2O conversion *vs.* temperature profiles over selected Fe-ZSM-5 zeolites in different mixtures. The catalysts displayed significant conversion in direct N_2O decomposition above 650–700 K and was complete at 800–850 K. Addition of 2.5 mbar SO_2 shifted the conversion of N_2O to *ca.* 50–100 K to lower temperature. The shift was more pronounced in the steam-activated zeolites. In order to gain insights into the mechanistic action of SO_2, the N_2O conversion at variable molar SO_2/N_2O ratios was determined over Fe-ZSM-5-st (Fig. 3). The N_2O conversion rapidly increased from 5 to 70% in the presence of 2.5 mbar SO_2 (SO_2/N_2O = 1.7), and then gradually decreased on decreasing the partial SO_2 pressure in the feed mixture. It should be noted that the N_2O conversion at each SO_2/N_2O ratio was stable during several hours, *i.e.* no sign of deactivation was evidenced. Besides, the catalysts rapidly reached steady state upon changing from one ratio to another. By removing SO_2, the N_2O conversion recovered the initial value (open circles). From this test, it can be concluded that SO_2 acts as a reducing agent towards N_2O, according to the tentative reaction $N_2O + SO_2 \rightarrow N_2 + SO_3$. In support of this, O_2 was never detected at the reactor outlet at $SO_2/N_2O \geq 1$. As shown in the inset of Fig. 3, the N_2O conversion increases linearly with the molar SO_2/N_2O ratio up to *ca.* 1, which can be expected from the reaction stoichiometry. The N_2O conversion experiences a plateau at over-stoichiometric SO_2/N_2O ratios. The inverted triangles in Fig. 2 show the N_2O conversion *vs.* temperature profile over Fe-ZSM-5-st at a sub-stoichiometric SO_2/N_2O ratio of 0.4. It can be seen that the N_2O conversion profile shifts from the N_2O reduction by SO_2 to the direct N_2O decomposition ($N_2O \rightarrow N_2 + \frac{1}{2}O_2$) when the reductant is totally oxidised to SO_3 around 700 K. Consequently, above this temperature, the direct decomposition pathway also took place and molecular oxygen was analysed at the reactor outlet. Sulfur trioxide

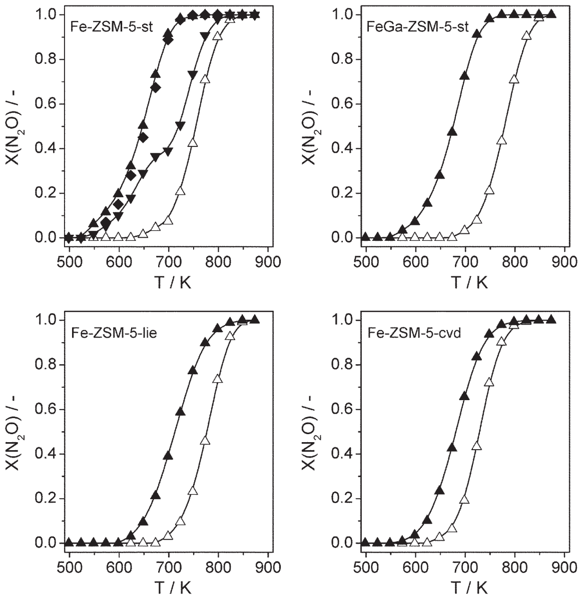

Fig. 2 N_2O conversion *vs.* T over iron-containing ZSM-5 zeolites in (△) 1.5 mbar N_2O, (▼) 1.5 mbar N_2O + 0.6 mbar SO_2, (▲) 1.5 mbar N_2O + 2.5 mbar SO_2, and (◆) 1.5 mbar N_2O + 2.5 mbar SO_2 + 20 mbar O_2; balance He; P = 1 bar; WHSV = 60 000 ml g^{-1} h^{-1}.

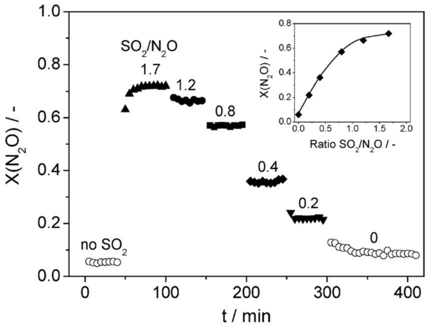

Fig. 3 N_2O conversion *vs.* time over Fe-ZSM-5-st at different SO_2/N_2O ratios. The feed mixtures contained 1.5 mbar N_2O and 0–2.5 mbar SO_2, balance He; T = 698 K; P = 1 bar; SV = 60 000 ml g^{-1} h^{-1}.

formation was supported by condensing the gas at the reactor outlet and adding a 0.2 M $BaNO_3$ aqueous solution. This led to the formation of a precipitate displaying sharp $BaSO_4$ reflections in X-ray diffraction (Fig. SI1 of ESI†). It is put forward that the catalytic reduction of N_2O by SO_2 resembles that by other reducing agents (hydrocarbons, CO, and NH_3)[3] from the viewpoint that adsorbed atomic oxygen species deposited by N_2O decomposition, O*, are effectively scavenged by the reducing agent ($SO_2 + O^* \rightarrow SO_3 + *$), accelerating the reaction rate. This differs from the catalytic nature of the positive effect of nitric oxide on the N_2O decomposition over Fe-zeolites, which requires low NO amounts.[8–11]

Since O_2 is typically present in N_2O-containing tail gases, a key feature of a reducing agent for practical consideration is whether it selectively reacts with nitrous oxide in the presence of excess oxygen. As shown in Fig. 2, addition of 20 mbar O_2 to the $N_2O + SO_2$ mixture does not influence the catalytic behaviour of Fe-ZSM-5-st (compare solid triangles and solid diamonds). In consequence, SO_2 can be designated as a selective reductant for N_2O over Fe-zeolites.

Finally, we have compared the efficiency of SO_2 as selective N_2O reductant with well-known agents able to catalyse N_2O removal over iron zeolites at lower temperature than the direct N_2O decomposition (Fig. 4). Remarkably, SO_2 induces N_2O conversion at lower temperature than NO and NH_3, particularly below 650 K. Methane is the most efficient reductant, achieving the same N_2O conversion as SO_2 at 25–50 K lower temperature. However, the use of hydrocarbons for N_2O reduction in the presence of SO_2 is detrimental. As shown by the crosses in Fig. 4, addition of SO_2 to the $N_2O + O_2 + CH_4$ mixture shifts the conversion to the $N_2O + O_2 + SO_2$ mixture, *i.e.* sulfur dioxide annihilates the reducing effect of the hydrocarbon. This finding agrees with the results by Centi *et al.*,[17,20] who reported inhibition of de-N_2O C_3H_8-SCR by SO_2 over Fe-ZSM-5 catalysts. It can be anticipated that the negative effect of SO_2 applies to other low-temperature reductants such as CO.

In summary, we have shown that catalytic N_2O removal over iron-containing zeolites is greatly enhanced by SO_2, lowering the operating temperature up to 100 K with respect to the direct N_2O decomposition. This result contrasts with the preconceived image of this sulfur compound as a strong inhibitor and/or poison of catalysts for environmental applications, *e.g.* in N_2O abatement over other metals.[7,14–18] A major feature of SO_2 is that it displays a higher de-N_2O efficiency than NO and NH_3 in the presence of excess O_2. It should be remarked that the positive SO_2 action does not require specific synthesis and activation routes of the iron zeolite. Rather, the beneficial effect of SO_2 is independent of zeolite framework type and composition, preparation method, and amount of iron. Based on this generalisation, it does not seem to be unique to a particular iron speciation. The eventual formation of sulfate-type species on the zeolite surface during the $N_2O + SO_2$ reaction and its potential role in the catalytic process require more detailed spectroscopic investigations, which will be undertaken in future work. Our finding has practical implications, as Fe-zeolites become attractive candidates for N_2O abatement in SO_2-containing sources, namely combustion and certain chemical production processes.

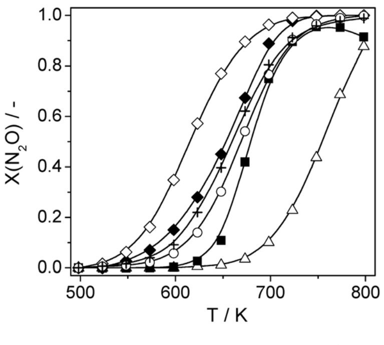

Fig. 4 N_2O conversion *vs.* *T* over Fe-ZSM-5-st in (△) 1.5 mbar N_2O + 20 mbar O_2, (■) 1.5 mbar N_2O + 20 mbar O_2 + 1.2 mbar NH_3, (○) 1.5 mbar N_2O + 20 mbar O_2 + 1.2 mbar NO, (◆) 1.5 mbar N_2O + 20 mbar O_2 + 2.5 mbar SO_2, (◇) 1.5 mbar N_2O + 20 mbar O_2 + 0.6 mbar CH_4, (+) 1.5 mbar N_2O + 20 mbar O_2 + 0.6 mbar CH_4 + 2.5 mbar SO_2, balance He; $P = 1$ bar; SV = 60 000 mL g^{-1} h^{-1}.

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