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Selective catalytic reduction of N_2O in industrial emissions containing O_2, H_2O and SO_2: behavior of Fe/ZSM-5 catalysts

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Abstract

The catalytic behavior in N_2O reduction by propane in the presence of O_2, H_2O and SO_2 of Fe/ZSM-5 catalysts prepared by ion exchange and chemical vapour deposition (CVD) is reported. The catalyst prepared by CVD shows a lower dependence of the rate of selective N_2O reduction on the decrease in C_3H_8 to N_2O ratio in the feed and a higher resistance to deactivation by SO_2 in accelerated durability tests with high SO_2 concentration (500 ppm). This catalyst shows stable catalytic behavior in the presence of SO_2 for more than 600 h of time-on-stream. Characterization of the catalysts by UV–VIS–NIR diffuse reflectance indicates that the poor performances of the sample prepared by ion exchange could be related to the presence of highly clustered Fe^{3+} species, in this catalyst. On the other hand, Fe_2O_3 particles are not present in the sample prepared by CVD while mainly isolated Fe^{3+} ions and iron-oxide nanoclusters are present. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Fe/ZSM-5; N_2O reduction; Propane; Iron-oxide nanocluster; Deactivation by SO_2

1. Introduction

The new Osaka agreement on the reduction of greenhouse gas emissions will lead to new legal limits on the emission of N_2O, a powerful greenhouse gas whose tropospheric concentration is continuously increasing [1]. Since it is also emitted in large quantities from natural sources, the stabilization of its tropospheric concentration requires the adoption of efficient technologies for its removal from those emissions which can be effectively controlled, in particular industrial combustion processes (especially of waste) and chemical processes [2,3].

Apart from the specific case of adipic acid production where N_2O concentration is quite high (15–20% or above), current catalysts are not stable and active enough, and the process cannot be applied economically in practical cases [4]. Although several different types of catalysts have been proposed in literature [5–16], none of them tested under practical conditions has proved to possess good activity and stability in N_2O decomposition, when the latter is present in a diluted concentration (typically below 0.1%) in the presence of large concentrations of H_2O, O_2 and other poisoning agents such as SO_2 and NO_x.

Recently, interesting results in the selective reduction of NO with hydrocarbons in the presence of oxygen have been obtained using Fe/ZSM-5 catalysts. Hall et al. [17–19] reported that Fe/ZSM-5 catalysts prepared by ion exchange in an oxygen-free atmosphere (to avoid the oxidation of Fe^{2+} to Fe^{3+} during base-exchange, thus preventing iron-hydroxide precipitation and inhibiting the formation of Brønsted acid sites) are very active in NO reduction with isobutane in the presence of oxygen and, in particular, they show

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stable behavior in the presence of high water concentrations (up to 20%) and/or SO_2 (up to 150 ppm), although at a high temperature (500°C). Joyner and Stockenhuber [20] suggested that the behavior of Fe/ZSM-5 catalysts prepared by conventional ion exchange with iron(III)-nitrate solution could be related to the formation of special iron–oxygen nanoclusters which are stable against reduction.

Chen and Sachtler [21,22] observed that the same high activity and durability, although for a shorter time and in the absence of SO_2, can be obtained preparing Fe/ZSM-5 catalysts by the sublimation of a volatile iron compound into the acid form of the zeolite. The introduction of a second cation such as La^{3+} further promotes the activity, mainly lowering the undesired combustion of the hydrocarbon (isobutane) [22]. Turek et al. [23] reported that Fe/ZSM-5 catalysts can also be used for the simultaneous catalytic reduction of NO and N_2O with propane in the presence of oxygen. Their catalysts were prepared by solid state ion exchange, but no data regarding their stability over a period of time or the effect of water were reported. Segawa et al. [24] used Fe/ZSM-5 catalysts for the selective reduction of N_2O by propene. The catalysts were prepared by ion exchange with a diluted solution of iron(II)-sulphate, but no data on durability were reported.

Therefore, although Fe/ZSM-5 catalysts were shown to possess very interesting properties in the selective catalytic reduction of NO and N_2O by hydrocarbons, no reliable information is available about the exact role of preparation on catalytic behavior, especially in terms of durability in more realistic conditions and in the presence of SO_2. Furthermore, for the specific case of N_2O removal, no data regarding the stability of catalytic behavior were reported. In this specific case, the most critical issues are the stability of catalytic behavior at low reaction temperatures (significantly below those reported in literature for the case of selective NO reduction) and the minimization of the use of the hydrocarbon as selective reductants.

The aim of this work is to compare the behavior of two Fe/ZSM-5 catalysts prepared by ion exchange and chemical vapour deposition (CVD) in terms of the efficiency of the use of hydrocarbons as selective reductants for N_2O and the stability of catalytic behavior at low reaction temperatures (below 500°C) in the presence of oxygen, water and relatively high SO_2 concentrations (up to 500 ppm), in order to help clarify the role of preparation in the behavior of Fe/ZSM-5 catalysts. Propane was chosen as a selective reductant, because this hydrocarbon is much less costly, more widely available and more easily stored than the propene or isobutane used as selective reductants by Segawa et al. [24], Hall et al. [17–19] and Sachtler et al. [21,22], respectively. Furthermore, with respect to methane, it allows much lower reaction temperatures and higher reduction efficiency at a comparable reductant cost, thus lowering operating costs [25].

2. Experimental

2.1. Catalyst preparation

Fe/ZSM-5 samples were prepared by ion exchange and by chemical vapour deposition (CVD) methods, in a similar way to the methods reported by Chen and Sachtler [21]. The parent zeolite for both preparations was the sodium-form of a commercial ZSM-5 sample synthetised with a template-free preparation (SN27 from ALSI-Penta, $SiO_2/Al_2O_3 = 27$). The samples will henceforth be called Fe_{IE}/ZSM-5 and Fe_{CVD}/ZSM-5, respectively.

2.1.1. Preparation of Fe_{IE}/ZSM-5

Two grams of zeolite in ammonium form (obtained from the sodium form by exchange at room temperature with ammonium nitrate aqueous solution) are added to 100 ml of an aqueous solution of Fe^{3+}-salt. The slurry is kept under stirring and reflux for 12 h and then filtered. Two samples were prepared, using different temperatures (25 and 80°C) for the ion exchange. After washing several times with double deionized water, the solid is dried at 150°C overnight and then calcined at 550°C for 6 h, increasing the temperature of the furnace to the final value in about 3 h. The amount of iron in the final catalyst is 1.9% and 5.1% wt (as Fe) (for samples prepared at 25 and 80°C, respectively) and the surface area about 230 m^2/g in both samples. X-ray diffraction analysis does not indicate the presence of crystalline phases other than the zeolite itself.

2.1.2. Preparation of Fe_{CVD}/ZSM-5

Two grams of zeolite in sodium form are loaded in a flow reactor and after elimination of the adsorbed water, heated to 650°C in a flow of air passed through a water saturator kept at room temperature. The zeolite is kept at this temperature for 6 h and then cooled down to room temperature before being extracted from the reactor. The zeolite is then put in a 0.1 N ammonium-acetate aqueous solution and the slurry kept under stirring at room temperature for 1.5 h. After filtration and washing with double deionized water, the zeolite is loaded in a reactor and calcined in a flow of synthetic air at 650°C for 8 h, increasing the temperature up to the final value in about 4 h. After cooling down to room temperature, still in the flow of synthetic air, 0.4 g of $FeCl_3$ are loaded in the reactor before the zeolite bed and separated from it by means of a quartz wool bed. The reactor is then heated up to 300°C in a flow of nitrogen and kept at this temperature for 1 h, after raising the temperature up to the final value at a rate of 10°C/min. Then the catalyst is mixed and the treatment repeated. The uniform deposition of $FeCl_3$ along the catalytic bed can be verified from the presence of a uniform pale-yellow colour. The sample is then removed, washed with double deionized water and dried at 120°C overnight.

The iron content in the final catalyst is 1.1% wt (as Fe) and the surface area 306 m^2/g. As a consequence of the initial pretreatment of the zeolite, the SiO_2/Al_2O_3 ratio increases from an initial value of 27 (parent zeolite) to 34. X-ray diffraction and IR analysis (ratio of the IR bands near to 500 cm^{-1}), however, do not indicate a loss of crystallinity as a consequence of the initial hydrothermal treatment of the zeolite.

2.2. Catalytic tests

Catalytic tests in N_2O reduction in the presence of propane and oxygen were made using a quartz fixed-bed flow reactor loading 0.2 g of zeolite in the form of pellets with a dimension of 40–60 mesh. A total flow (6 l/h) was used corresponding to a gas hourly space–velocity (GHSV) of 18 000 h^{-1}. The typical gas composition for the tests, if not otherwise specified, was 0.05% N_2O, 2% O_2, 3% H_2O, 0.1% C_3H_8 and the remaining helium. The same composition, but with the additional presence of 0.05% SO_2, was used for durability tests.

Analysis of the composition of the inlet and outlet gas streams of the reactor was made using on-line mass quadrupole apparatus, after correction of the mass intensities in order to take multiple fragmentations into account when necessary. The line from the reactor to the mass quadrupole was heated to 150°C to prevent the condensation of the products. Conversion of the reactants (N_2O and C_3H_8) was estimated on a molar basis.

2.3. Catalyst characterization

UV–VIS–NIR diffuse reflectance spectra were measured in air using a Perkin–Elmer Lamda 19 instrument after transformation of reflectivity (R) according to the Kubelka–Munk function: $F(R)=(1-R)^2/2R_\infty$. $BaSO_4$ was used as a reference. Zeolite crystallinity and structure were determined by X-ray diffraction (Philips PW 1710 diffractometer (Cu K_α radiation) and FT–IR (Perkin–Elmer 1750 instrument) analyses. The surface area was determined by the BET method (N_2 adsorption) using Fisons Sorpty 1750 apparatus. Chemical analysis of the samples was made by atomic adsorption spectroscopy using Philips PV9100 apparatus.

3. Results and discussion

3.1. Comparison of catalytic behavior

Fig. 1 shows catalytic behavior in standard conditions (500 ppm N_2O, presence of oxygen and water in the stream) Fe_{IE}/ZSM-5 (the two samples with different iron content are indicated in brackets) and Fe_{CVD}/ZSM-5 samples. Fig. 1(a) shows the conversion of N_2O and Fig. 1(b) the conversion of propane. The conversion of N_2O in all cases is to N_2 only, because no evidence of other nitrogen oxide species was found in any of the range of reaction temperatures. The conversion of propane is mainly to CO_2, with minor formation of carbon monoxide at temperatures below about 350°C. No evidence of the formation of partial oxidation products was found.

The activity curve for N_2O reduction to N_2 of the Fe/ZSM-5 catalysts decreases in CVD (1%) > IE (5%) > IE (2%) order, i.e. it is not proportional to

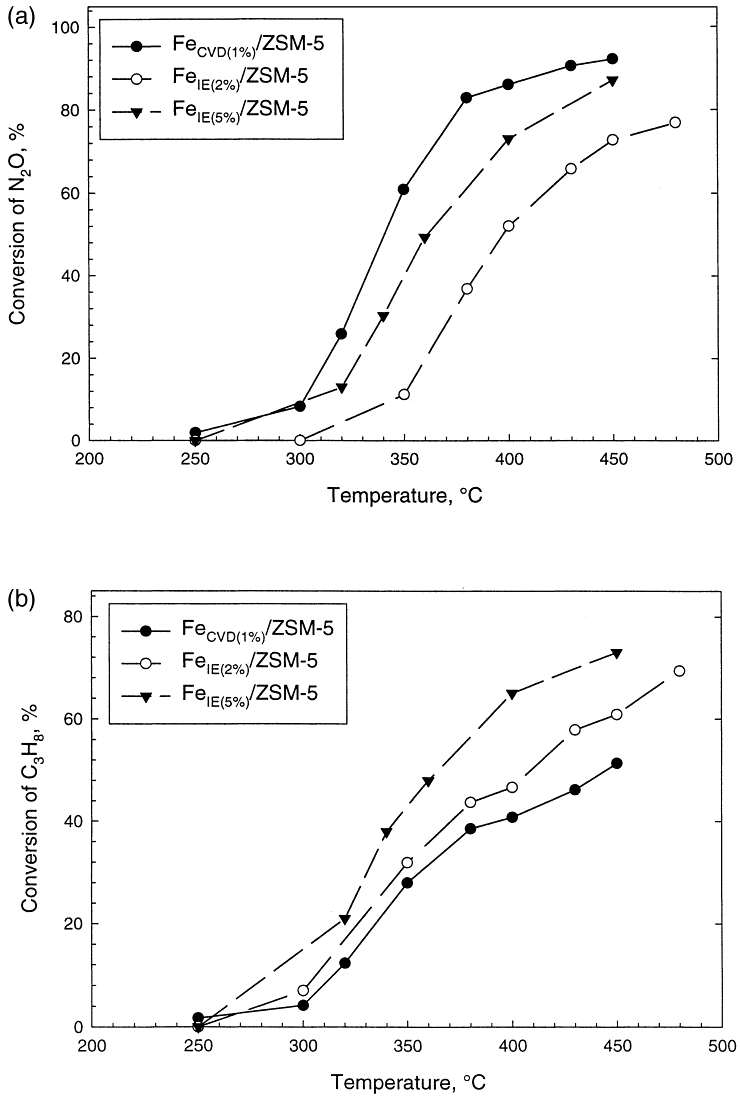

Fig. 1. Conversion of N_2O (a) and of propane (b) as a function of the reaction temperature on $Fe_{IE(2\%)}$/ZSM-5, $Fe_{IE(5\%)}$/ZSM-5 and $Fe_{CVD(1\%)}$/ZSM-5. Experimental conditions: 0.2 g catalyst, 6 l/h total flow of the feed with composition (v/v) 0.05% N_2O, 2% O_2, 3% H_2O, 0.1% C_3H_8, 95.85% He.

the amount of iron in the catalyst. This indicates that the preparation methodology has a major influence in determining the specific activity of the samples. Thus, comparison of the catalytic performances of two samples prepared by these two methods is not possible for samples containing the same amount of iron, because they show different activities and thus the comparison is not homogeneous. For this reason, comparison in the following part of this work will be made between the CVD (1%) and IE (5%) samples which show much more comparable activity curves in N_2O depletion.

It is worth noting that the activity curve for propane oxidation follows an inverse reactivity order with respect to N_2O depletion: IE (5%) > IE (2%) > CVD (1%). The two samples with comparable activity in N_2O depletion (IE-5% and CVD-1%) show significantly different behavior in propane conversion which for $Fe_{IE(5\%)}$/ZSM-5 is about twice that of $Fe_{CVD(1\%)}$/ZSM-5 in all temperature ranges.

3.2. Effect of propane to N_2O ratio

Data reported in Fig. 1 indicate that while the activity of the two zeolites ($Fe_{IE(5\%)}$/ZSM-5 $Fe_{CVD(1\%)}$/ZSM-5) in N_2O reduction is very comparable, their activity in propane conversion is very different. These Fe/ZSM-5 catalysts are much less active in N_2O decomposition. Comparable conversions of N_2O in the absence of propane require reaction temperatures about 100–120°C higher than in the presence of propane. The analogous activity in N_2O reduction, but not in propane conversion, therefore indicates that part of the propane is oxidized by a side reaction which does not affect the selective N_2O reduction mechanism in the presence of propane. Since minimization of this side reaction is necessary to reduce operating costs, the effect of the C_3H_8 to N_2O ratio on the behavior of the two catalysts was analyzed.

Fig. 2 shows the behavior of $Fe_{IE(5\%)}$/ZSM-5 as a function of the C_3H_8/N_2O molar ratio at three reaction temperatures. The three temperatures were selected in order to have conversion values in approximately the 20–80% range and thus obtain more reliable data. The N_2O concentration in these tests was constant (0.05% vol), while that of propane increased.

Fig. 2(a) shows the dependence of the conversion of N_2O on the concentration of N_2O in the feed at different reaction temperatures and Fig. 2(b) shows the dependence of the conversion of propane in the same conditions. The latter is nearly independent of the C_3H_8/N_2O ratio indicating that the rate of propane depletion has a dependence of nearly the first order on the propane concentration (in a fixed-bed reactor such as that used in this work, by applying a plug-flow reactor model it is possible to show that the conversion of a reactant is independent of its concentration only in the case of a first order rate equation). The conversion of N_2O, however, increases linearly with the C_3H_8/N_2O ratio in the 1–3 range. The selective reduction activity of N_2O is thus greatly enhanced by increasing the propane concentration above the molar ratio of 1.0. In the hypothesis of first order kinetics, the rate constant of N_2O depletion about doubles in passing from a C_3H_8/N_2O ratio of 1 to 3.

Fig. 3 shows analogous data obtained for $Fe_{CVD(1\%)}$/ ZSM-5. Behavior is the opposite of that observed for $Fe_{IE(5\%)}$/ZSM-5. The conversion of N_2O is nearly independent of the C_3H_8/N_2O ratio (Fig. 3(a)), while the conversion of propane decreases with the increase of the C_3H_8/N_2O ratio (Fig. 3(b)). The latter fact indicates that the order of reaction for propane depletion in the range investigated is close to zero, in all probability due to a saturation of the active sites for propane conversion. Since the rate of propane conversion does not depend on its concentration in this range, and since unreacted propane is available in all cases, the conversion of N_2O does not depend on the C_3H_8/N_2O ratio (Fig. 3(a)). This indicates, however, that on this catalyst it is possible to use very low amounts of propane as a selective reductant, without affecting the rate of selective N_2O reduction, which is an important beneficial effect in economic terms.

3.3. Durability tests in the presence of SO_2

In line with the findings of Hall et al. [17–19] and Sachtler et al. [21,22], the Fe/ZSM-5 samples used in this work showed high durability in the standard reaction conditions used for the data reported in Fig. 1. However, for this type of stream, other types of catalysts such as supported Rh catalysts active in N_2O decomposition [26] are preferable, because they show similar high durability, but do not require the additional expenses associated with the need to feed a reductant such as propane. However, these catalysts deactivate in the presence of SO_2, a component which is often present in both combustion and chemical processes streams containing N_2O. The advantage of the presence of a selective reductant for N_2O is principally that it enhances the resistance of the catalyst to deactivation by SO_2. The behavior of the two Fe/ZSM-5 catalysts studied in this work in durability tests in the presence of SO_2 in the feedstock was thus analyzed. In order to perform accelerated tests, a high SO_2 concentration was fed (500 ppm) together with the other components (N_2O, propane, oxygen, water). This SO_2 concentration is about one order of magnitude higher than that present in real streams from combustion or chemical processes containing N_2O (about 10–50 ppm) and

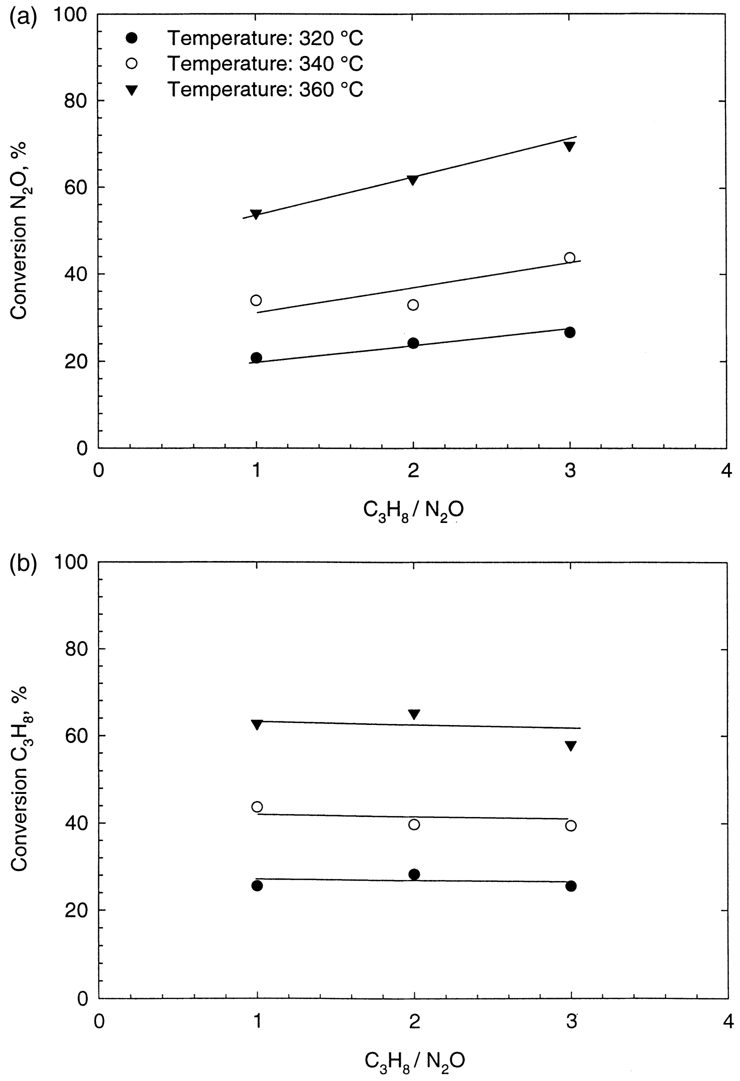

Fig. 2. Effect of the C_3H_8 to N_2O ratio on the conversion of (a) N_2O and (b) propane at 320, 340 and 360°C on $Fe_{IE(5\%)}$/ZSM-5. Experimental conditions as in Fig. 1, but propane concentration in the 0.05–0.15% (v/v) range.

thus gives an indication of the durability of the catalysts under accelerated deactivation conditions. In fact, the total amount of SO_2 passed over the catalyst in 500–600 h of time-on-stream feeding 500 ppm of SO_2 (as in the present tests, see below) corresponds to the total amount of SO_2 'seen' by the catalyst in about 1–2 years of activity under practical conditions of application.

Fig. 4 shows the behavior of the $Fe_{IE(5\%)}$/ZSM-5 catalyst in these durability tests. In these tests, while keeping the feed composition constant, the reaction temperature is increased from 380 to 480°C after some time-on-stream, as outlined in Fig. 4. Therefore, final behavior at the higher temperature is affected by the amount of sulphate stored on the catalyst during the previous time-on-stream at the lower reaction temperatures.

At 380°C very fast deactivation is observed. In a few hours of time-on-stream both the N_2O and propane conversions are about halved, and further deactivation

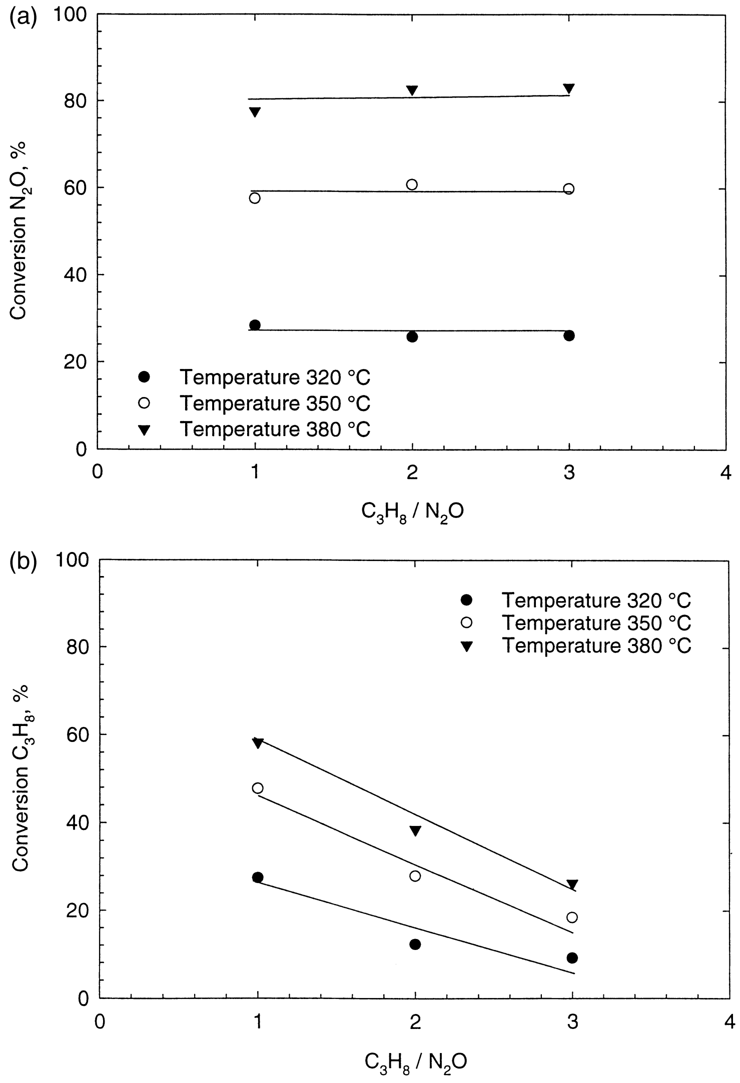

Fig. 3. Effect of the C_3H_8 to N_2O ratio on the conversion of (a) N_2O and (b) propane at 320, 340 and 360°C on $Fe_{CVD(1\%)}$/ZSM-5. Experimental conditions as in Fig. 1, but propane concentration in the 0.05–0.15% (v/v) range.

occurs for longer times up to final conversion values close to 15% after 40 h of time-on-stream. The parallel trend in N_2O and propane conversion is worth noting also for the other further experiments reported in Fig. 4, indicating a parallel inhibition of the conversion of the two reactants. Another remarkable fact is that after the initial fast deactivation in the first hours of reaction, there is near-constant activity up to about 20 h of time-on-stream, after which a further fast reduction occurs. This suggests that different types of iron species are present in the catalyst and are affected differently by the accumulation of sulphur (probably in the form of sulphate species, although the starting iron compound for the ion exchange was already an iron-sulphate compound) on the catalyst.

After about 40 h of time-on-stream, the reaction temperature was increased up to 410°C. An immediate increase in the conversion of N_2O to about 55% and of propane to about 40% was noted, but then the conversion progressively decrease to values of about 35% and

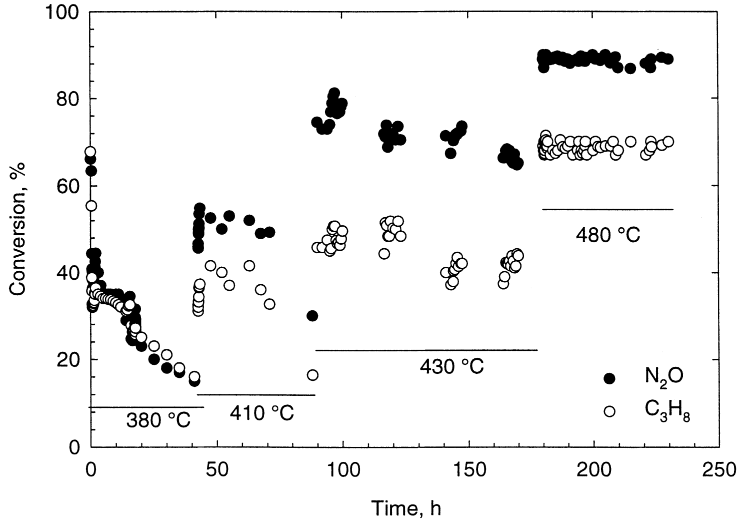

Fig. 4. Accelerated durability tests of $Fe_{IE(5\%)}$/ZSM-5 in the presence of high SO_2 concentration in the feed: conversion of N_2O and propane as a function of the time-on-stream for different consecutive increasing reaction temperatures as reported in the Figure. Experimental conditions: 0.2 g catalyst, 6 l/h total flow of the feed with composition (v/v) 0.05% N_2O, 2% O_2, 3% H_2O, 0.1% C_3H_8, 0,05% SO_2, 94.8% He.

18%, respectively, after 90 h of time-on-stream. When the temperature was subsequently increased to 430°C, the N_2O conversion reached about 80% and that of propane about 50%, but then progressively decreased to 70% and 40%, respectively, after about 180 h of time-on-stream.

It is worth noting that when the temperature is increased, the rate of deactivation progressively decreases. Accordingly, at the higher reaction temperature (480°C), stable catalytic behavior was observed, although with respect to the fresh catalyst (Fig. 1(b)) the activity shifted to temperatures about 60–70°C higher.

The data in Fig. 4 evidence a series of interesting observations:

- The rate of deactivation by SO_2 is a function of the reaction temperature, probably because at the higher temperatures the sulphate species, when formed, are fast reduced by the hydrocarbon.
- Different iron species are present in the catalyst, differently influenced by the deposition of sulphur (probably as sulphate) in the catalyst. Permanent deactivation is caused by this effect, but the catalyst is not completely killed by the SO_2 and at high temperature (480°C) a stable conversion of N_2O close to 90% is possible.
- The effect of SO_2 on catalyst activity is analogous in the N_2O and propane conversions.

Different behavior was detected for $Fe_{CVD(1\%)}$/ZSM-5 (Fig. 5). In this case, even at low temperature (400°C) constant catalytic behavior is observed after an initial decline in activity occurring approximately during the first 100 h of time-on-stream. Then constant activity (conversion of N_2O about 60% and of propane about 20%) was observed up to 600 h of time-on-stream. It should be mentioned that the total amount of SO_2 feed in 600 h in these accelerated durability tests nearly corresponds to the total amount of SO_2 present in about two years of N_2O emissions from industrial waste combustion and chemical processes [1–3] and typically falling in the 20–40 ppm range in terms of SO_2 concentration. Therefore, the data in Fig. 5 indicate the very high resistance of this $Fe_{CVD(1\%)}$/ZSM-5 catalyst towards deactivation by SO_2 and the possibility of its application in commercial processes.

This high resistance towards deactivation by SO_2 is due to the inability of the catalyst to oxidize SO_2 to SO_3 after the initial deactivation step (about first 100 h in Fig. 5). In fact, while chemical analysis of the catalyst after durability tests reveals the presence of sulphate species in the catalyst, analysis of the reactor outlet stream reveals the complete absence of SO_3, as verified by adsorption in NaOH aqueous solution and analysis by ionic chromatography of the presence of sulphate ions in the solution.

If the reaction temperature is increased to about 430°C after durability tests (Fig. 5), the conversion of N_2O increases to above 90% and stable catalytic behavior is observed. Therefore, the 90% N_2O conversion in $Fe_{CVD(1\%)}$/ZSM-5 is reached at temperatures about 50–60°C lower than those necessary for $Fe_{IE(5\%)}$/ZSM-5 after comparable treatment (Fig. 4) and after conditioning in the feedstock containing SO_2, notwithstanding the analogous activity in the fresh samples (Fig. 1) and the smaller amount of iron (about one fifth) in $Fe_{CVD(1\%)}$/ZSM-5 than $Fe_{IE(5\%)}$/ZSM-5.

3.4. UV–VIS–NIR diffuse reflectance characterization of the catalysts

UV–VIS–NIR diffuse reflectance spectra of fresh $Fe_{CVD(1\%)}$/ZSM-5 and $Fe_{IE(5\%)}$/ZSM-5 samples are reported in Fig. 6. The spectra are characterized by two intense bands at 46,500 and 36,000 cm^{-1} due to ligand to metal Fe^{3+} charge transfer in isolated species in distorted octahedral coordination [27–29]. A shoulder is also evident at about 30,000 cm^{-1} which is characteristic of octahedral Fe^{3+} present in small clusters, as observed for clustered Fe^{3+} in hydroxides [30]. This attribution is in agreement with the findings of Joyner and Stockenhuber [20] indicating the presence of iron-oxygen nanoclusters in Fe/ZSM-5 catalysts. Both types of iron species (isolated and clustered octahedral Fe^{3+} species) were observed to form when framework tetrahedral Fe^{3+} ion Fe-silicalite migrates towards extraframework positions as a consequence of thermal treatments [27]. In both $Fe_{CVD(1\%)}$/ZSM-5 and $Fe_{IE(5\%)}$/ZSM-5 samples isolated and clustered octahedral Fe^{3+} species are found, although in the latter the amount is higher in agreement with its higher iron loading. However, in $Fe_{IE(5\%)}$/ZSM-5 additional iron species are also present, as indicated by the evident band at 26,500 cm^{-1} and the shoulder at about 20,000 cm^{-1}. The latter band is characteristic of Fe_2O_3 particles, while the former is observed for example in γ-FeOOH diluted in silica [27]. In both cases, the presence of these bands indicates the appearance of massive oxidic migroaggregates of iron-oxide [27].

In the inset of Fig. 6 the region in 4500–7500 cm^{-1} is also reported. This region is characteristic of the crystalline MFI structure of the zeolite and indicates that the preparation procedure does not alter the zeolite structure or induce loss of crystallinity, in agreement with the X-ray diffraction and IR data mentioned in the experimental part.

In conclusion, UV–VIS–NIR diffuse reflectance spectra indicate that in the $Fe_{IE(5\%)}$/ZSM-5 sample with respect to $Fe_{CVD(1\%)}$/ZSM-5 highly clustered Fe^{3+} species and Fe_2O_3 particles are present together with isolated Fe^{3+} ions and iron-oxide nanoclusters.

3.5. Relationship between nature of iron species and catalytic behavior

A comparison between UV–VIS–NIR diffuse reflectance indications on the nature of iron species present in the two catalysts (Fig. 6) and the data on catalytic behavior (Figs. 1–3) suggests that the side reaction of propane combustion, and thus the different dependence of catalytic behavior on the C_3H_8 to N_2O ratio, can be attributed to the presence of highly clustered Fe^{3+} species and Fe_2O_3 particles in $Fe_{IE(5\%)}$/ZSM-5. In fact, these species were detected to be present in $Fe_{IE(5\%)}$/ZSM-5 and not in $Fe_{CVD(1\%)}$/ZSM-5 by UV–VIS diffuse reflectance spectroscopy. Drawing conclusions about the structure-activity relationship on the basis of the comparison of two samples alone is always risky, but it should be noted that these two samples were carefully selected in order to have comparable activity in N_2O depletion and different activity in propane side oxidation to carbon oxides, and thus to specifically highlight this different catalytic behavior. Nevertheless, this conclusion must be considered a first hypothesis which should be further demonstrated.

By using the same type of approach in the structure-activity relationship, it is possible to suggest that catalytic behavior in the selective reduction of N_2O by propane could instead be related to the presence of isolated Fe^{3+} ions and/or iron-oxide nanoclusters, since these species are present in both samples. It should be noted that catalytic reactivity cannot be related to the intensity of these bands

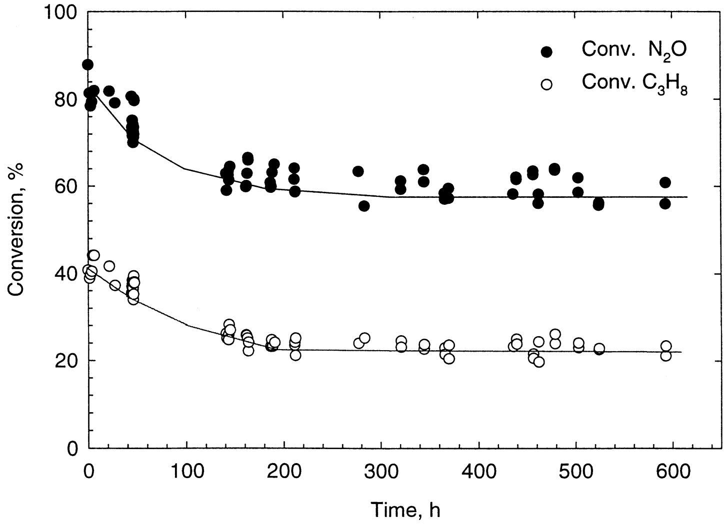

Fig. 5. Accelerated durability tests of $Fe_{CVD(1\%)}$/ZSM-5 in the presence of high SO_2 concentration in the feed: conversion of N_2O and propane as a function of the time-on-stream at 400°C. Experimental conditions as in Fig. 4.

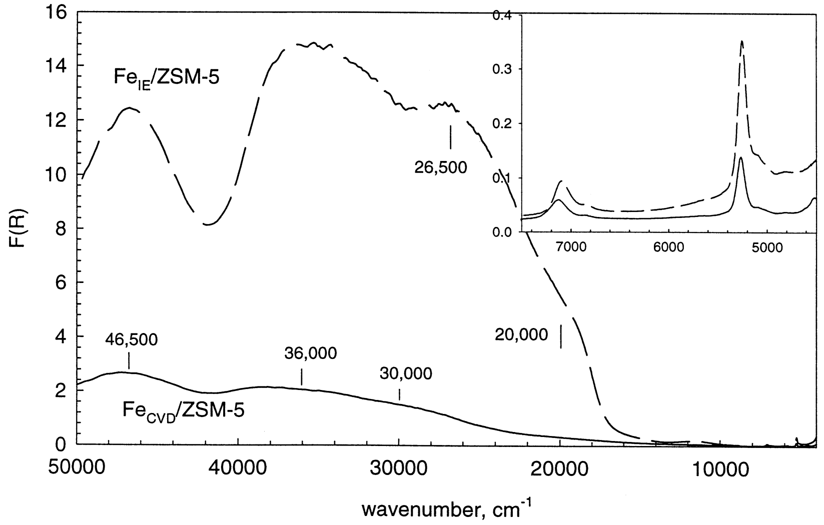

Fig. 6. UV–VIS–NIR diffuse reflectance spectra of $Fe_{IE(5\%)}$/ZSM-5 and $Fe_{CVD(1\%)}$/ZSM-5 in air. In the inset expansion of the spectrum in the 1350–2200 nm region.

in the UV–VIS–NIR diffuse reflectance spectra. In fact, the intensity of these bands is very different in the $Fe_{IE(5\%)}$/ZSM-5 and $Fe_{CVD(1\%)}$/ZSM-5 samples, notwithstanding the analogous reactivity of the fresh samples. Various effects, such as different sensitivity to quenching by gas phase molecules, may influence the intensity of the UV–VIS–NIR diffuse reflectance spectra and thus a quantitative estimation may be not reliable. However, the very great difference in intensity of these bands, while similar catalytic reactivity in selective N_2O reduction is present, suggests that additional factors contribute to or determine catalytic behavior in this reaction.

The presence of different iron species in Fe/ZSM-5 samples also influences their resistance to deactivation by SO_2, as indicated by the results reported in Figs. 4

and 5. As previously discussed for the side oxidation of propane, highly clustered Fe^{3+} species and Fe_2O_3 particles in Fe_{IE}/ZSM-5 probably cause the decreased resistance to deactivation by SO_2, in all likelihood because they catalyze the oxidation of SO_2 to SO_3 and then the formation of iron-sulphate species. This is in agreement with the higher oxidation activity of these species shown by the higher rate of propane side combustion.

On the other hand, isolated or nanoclustered iron species, whose presence is maximized in $Fe_{CVD(1\%)}$/ZSM-5, show a low oxidation activity and both the lower sensitivity of the Fe_{CVD}/ZSM-5 catalyst from the decrease in C_3H_8 to N_2O ratio in the feed (Fig. 3) and its higher resistance to deactivation by SO_2 (Fig. 5). Should be related to this property.

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