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Kinetic oscillations during the catalytic decomposition of nitrous oxide

Thomas Turek *

Institut für Chemische Verfahrenstechnik, Technische Universität Clausthal, Leibnizstr. 17, 38678 Clausthal-Zellerfeld, Germany

Abstract

This review summarises experimental and modelling studies concerning the development of kinetic oscillations during the catalytic decomposition of nitrous oxide. Oscillations over Cu-ZSM-5 catalysts have been investigated using several methods and it could be shown that the formation of a strongly adsorbed nitrate formed in side reactions and the interaction of this species with atomic oxygen is responsible for the development of kinetic oscillations. The reaction of nitrous oxide over Fe-ZSM-5 catalysts shows similarities to the observations made with Cu-ZSM-5, but kinetic oscillations occur only in the presence of water vapour. On the other hand, isothermal oscillations observed over precious metal catalysts can be explained by an oxidation/reduction mechanism including the restructuring of the active catalyst surface under reaction conditions.

Keywords: Nitrous oxide; Decomposition; Oscillations; Cu-ZSM-5; Fe-ZSM-5; Rhodium

1. Introduction

In the early nineties it was recognised that nitrous oxide is an important air pollutant because it contributes to the greenhouse effect and the destruction of the stratospheric ozone layer [1]. Thus, considerable research effort was targeted at the development of catalytic processes for nitrous oxide removal. Among the most active catalysts for the decomposition of nitrous oxide are metal-exchanged zeolites as has been shown in pioneering studies by Li and Armor [2,3]. Based on these promising results, several other research groups started to investigate the applicability of zeolite catalysts for N_2O decomposition. Special attention was given at that time to Cu-ZSM-5 catalysts, because this material was also regarded as the most promising system for the hydrocarbon SCR of NO_x from automotive sources. On the other hand, several studies were devoted to rhodium catalysts that also exhibit high activity for nitrous oxide decomposition.

Around 1995, Lintz and Turek in Germany and Ciambelli et al. in Italy discovered independently that isothermal oscillations occur when small concentrations of nitrous oxide were reacted with Cu-ZSM-5 catalysts at temperatures between 325 and 450 °C [4,5]. In contrast to early results reported by Hugo [6], where thermal oscillations were caused by an instability of the reactor system during the highly exothermic decomposition of concentrated N_2O, it could be easily shown that these newly observed oscillations had a kinetic origin. This was rather surprising, because never before kinetic oscillations had been reported for an apparently monomolecular reaction. The present review summarises experimental results and modelling studies concerning the oscillating nitrous oxide decomposition over Cu-ZSM-5 and other copper-exchanged zeolites. Related work obtained with iron-exchanged zeolites and rhodium catalysts is also covered.

2. Oscillations observed with copper-exchanged zeolites

2.1. Kinetic studies using Cu-ZSM-5

Fig. 1 shows examples for the occurrence of oscillations over a Cu-ZSM-5 catalyst in the presence of 1000 ppm N_2O in nitrogen using a gradientless recycle reactor [7].

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* Tel.: +49 5323 72 2184; fax: +49 5323 72 2182.
E-mail address: turek@icvt.tu-clausthal.de.

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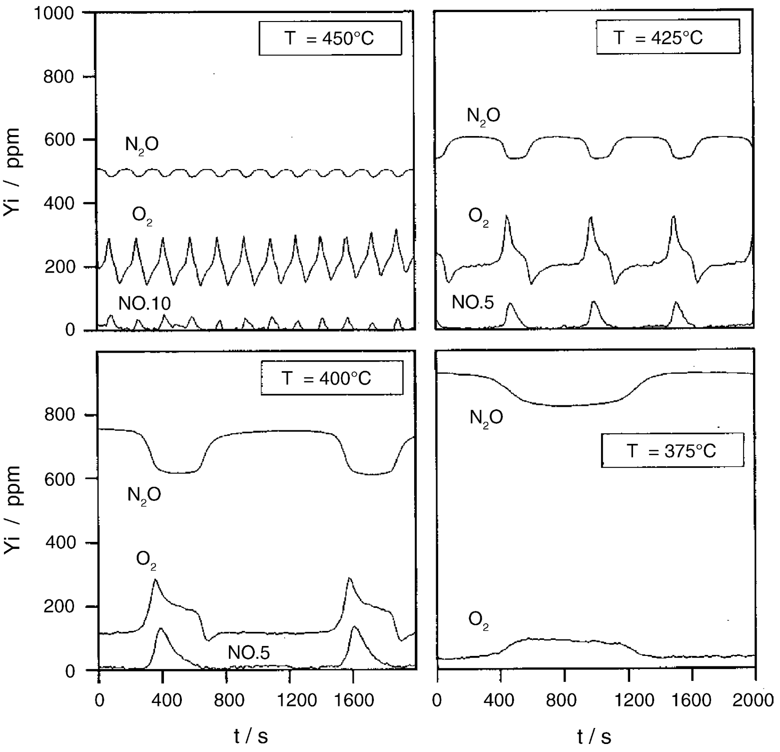

Fig. 1. Mole fractions of N_2O, N_2, and O_2 as a function of time at different temperatures. N_2O inlet mole fraction = 1000 ppm, catalyst mass = 0.227 g, volume flow rate = cm^3/min, NTP (Turek [7], reproduced by permission of Elsevier Science).

The catalyst used was an overexchanged Cu-ZSM-5 zeolite obtained by Bayer with molar ratios of Si/Al = 46 and Cu/Al = 0.80. Variation of the copper content in these catalysts showed that the catalytic activity markedly increased for catalysts with copper ion-exchange levels exceeding 100% (i.e. Cu/Al = 0.5) [8]. Moreover, only overexchanged Cu-ZSM-5 catalysts exhibited sustained oscillations. This activity pattern strongly resembled the picture that was obtained in studies of the NO decomposition over Cu-ZSM-5 [9–12] and it was concluded that most probably the same active sites (Cu^{2+}–O–Cu^{2+} pairs) are involved in both NO and N_2O decomposition.

Fig. 1 reveals that at all temperatures studied, regular fluctuations of the exit N_2O and oxygen concentrations occur. As with many other oscillatory phenomena, the frequency of the oscillations decreases with lower temperature while the amplitude increases. It appears that there are two states of catalytic activity for N_2O decomposition. As can be seen at the reaction temperature of 375 °C, the amounts of N_2O decomposed and O_2 formed correspond to the stoichiometry of the overall reaction (1).

$$2N_2O \rightarrow 2N_2 + O_2 \tag{1}$$

However, overshooting of the oxygen concentration can be observed when the catalyst changes the state of activity at temperatures higher than 375 °C. Additionally, an oxygen uptake occurs at the end of each phase of high decomposition activity. This demonstrates that the catalyst is able to store and release oxygen. Peaks of nitric oxide are also formed in a side reaction which may be written (2),

$$2N_2O \rightarrow 2NO + N_2 \tag{2}$$

with maximum NO concentrations not exceeding 30 ppm at 400 °C.

The observed oscillations must have a kinetic origin, because both thermal effects and any influence of pore diffusion could be excluded. Sustained oscillations occurred with nitrous oxide concentrations as low as 100 ppm at reactor inlet [7]. In that case, the adiabatic temperature rise of the decomposition reaction at complete conversion amounts to less than 0.5 K. Such small temperature excursions are not sufficient to explain the measured fluctuations of the rate of nitrous oxide decomposition with an activation energy of about 100 kJ/mol [7]. On the other hand, Ciambelli et al. have shown by measurements with different catalyst particle sizes (see Fig. 2) that any significant diffusion effects on the observations can be excluded as long as the catalyst particles are sufficiently small [13].

From the results depicted in Fig. 1, it was concluded that nitric oxide or adspecies that decompose to NO in certain phases of the oscillations must play a role in the underlying kinetic mechanism. Measurements with NO addition to the reaction mixture as well as temperature-programmed experiments were used to further evaluate the oscillating N_2O decomposition. When different concentrations of NO were added to N_2O at reactor inlet, it was found that even small amounts were sufficient to quench the oscillations

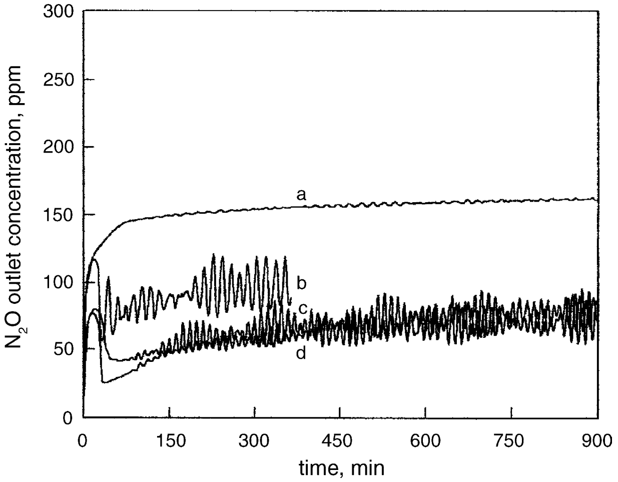

Fig. 2. N_2O outlet concentration as a function of time in N_2O decomposition on Cu-ZSM-5 at 370 °C with different catalyst particle sizes: (a) >710 μm, (b) 400–710 μm, (c) 300–400 μm, and (d) 200–300 μm. W/F = 0.038 g s N cm^{-3}. Feed: N_2O (300 ppm) in He (Ciambelli et al. [13], reproduced by permission of Academic Press).

immediately and to maintain the state of high N_2O decomposition activity [7]. Ciambelli et al. also observed disappearance of the oscillations during experiments at a temperature of 370 °C, although a slightly deactivating effect of the addition of high NO concentrations was observed [5]. In later studies, these authors could confirm the enhancing effect of small amounts of added nitric oxide [14].

Fig. 3 shows the results of transient experiments, in which step-changes of the inlet reactor concentrations were applied during different phases of the oscillations [8]. When about 900 ppm of NO are added to 1000 ppm N_2O in He in the minimum of decomposition activity at 425 °C, the catalyst almost instantaneously reaches the state of high activity while oxygen and also a small amount of NO, as can be seen from a slight overshoot of the NO gas-phase concentration, are desorbed from the catalyst surface. The catalyst then remains in this state without any oscillations, while part of the NO added is oxidised to nitrogen dioxide. On the other hand, the response to addition of NO in the more active state of the catalyst shows that only very small amounts of oxygen and no nitric oxide are released. These findings might be explained by a direct reaction of NO with N_2O (3) that has been also proposed by Kapteijn et al. [15].

$$NO + N_2O \rightarrow N_2 + NO_2 \quad (3)$$

Transient experiments using NO_2 instead of NO [8] revealed that Cu-ZSM-5 is able to catalyse the equilibrium reaction (4), a finding that had been also reported by Ciambelli and coworkers [16].

$$2NO_2 \Leftrightarrow 2NO + O_2 \quad (4)$$

At this stage, it is interesting to remind that Musgrave and Hinshelwood found a remarkably similar scheme in an early investigation of the homogeneous decomposition of N_2O [17]. These authors also found that small amounts of NO were formed in reaction (2), which acted catalytically via reaction (3) to yield an overall enhancement of N_2O decomposition.

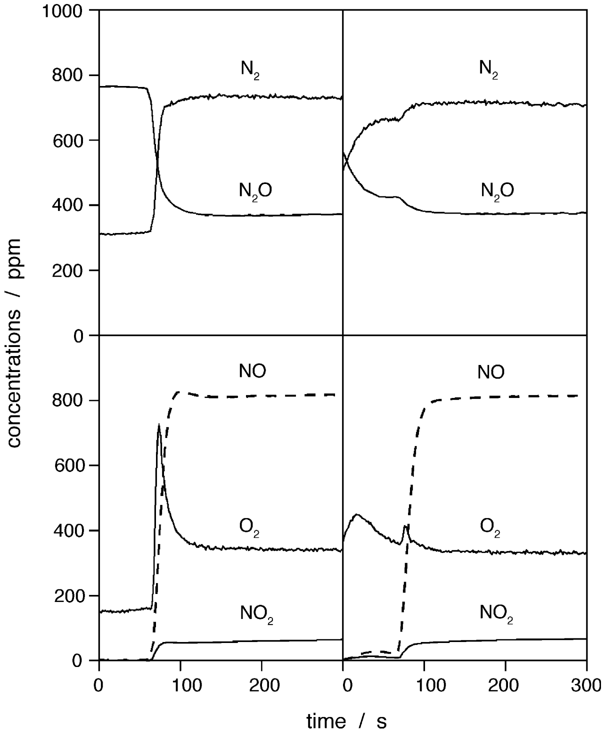

Fig. 3. Response to addition of ca. 900 ppm nitric oxide to the reactant mixture in the minimum (left-hand side) and maximum (right-hand side) of catalytic activity at 698 K. Feed: 1000 ppm N_2O in He (Turek [8], reproduced by permission of Academic Press).

Temperature-programmed experiments were conducted in order to gain insight into the kind of adspecies present under reaction conditions. Fig. 4 shows TPD spectra after adsorption of a stream of 1000 ppm of N_2O, NO, or NO_2 in He at room temperature [8]. While molecular oxygen was not adsorbed in detectable amounts, both NO and N_2O are only rather weakly adsorbed. Desorption of these species is completed far below reaction temperature in N_2O decomposition. On the other hand, nitrogen dioxide is adsorbed in large amounts up to temperatures of ca. 700 K. However, the largest fraction of adpecies formed during exposure to NO_2 is released as NO and O_2 in exactly equimolar amounts at temperatures between 600 and 700 K. It could be therefore concluded that nitrate species are most stable under the conditions of the N_2O decomposition and that these species are most probably involved in the development of oscillations.

2.2. Spectroscopic studies with Cu-ZSM-5

Lauterbach and coworkers studied the isothermal oscillations in the N_2O decomposition using mass spectroscopy and in situ FTIR [18,19]. In the first series of measurements [18], the authors used the same catalyst as Turek et al. (Bayer, Si/Al = 46, Cu/Al = 0.80). The catalyst powder was pressed into an IR transparent wafer of 14 mm

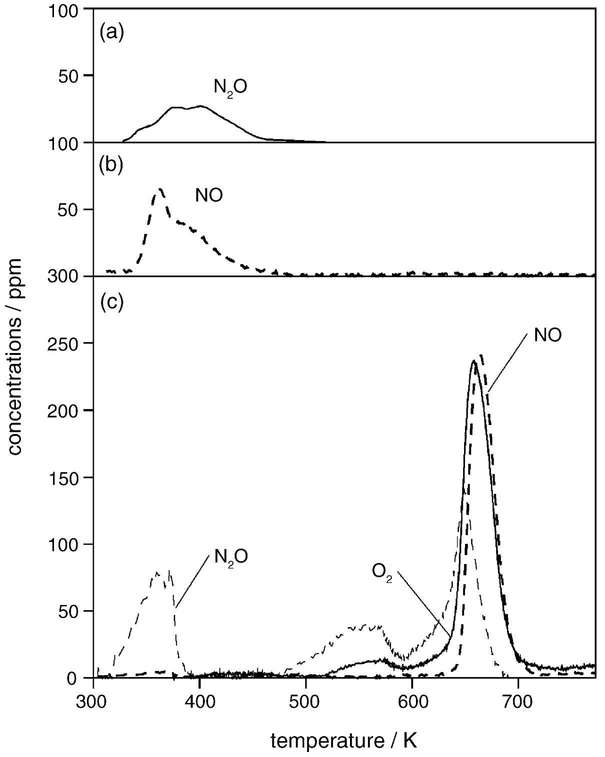

Fig. 4. TPD spectra of adsorbed nitrous oxide (a), nitric oxide (b), and nitrogen dioxide (c) (Turek [8], reproduced by permission of Academic Press).

diameter that was inserted into a flow reactor. Fig. 5 depicts results obtained at a temperature of 460 °C using a flow of 5.0 cm^3/min (STP) pure nitrous oxide at a total pressure of 1.0 Torr. Oscillations of N_2O consumed and nitrogen and oxygen formed with a period of 2–3 min can be clearly observed. In addition to the exit concentrations measured by mass spectrometry, the figure also shows the integrated peaks areas measured at 1624 cm^{-1} as a function of time. The concentrations of the surface species that were attributed to monodentate nitrate bonded to a Cu^{2+} ion, oscillate in a saw-toothed manner. This observation is in excellent agreement with the calculation of the amount of surface nitrates based on the analysis of transient experiments carried out by Ochs and Turek [20].

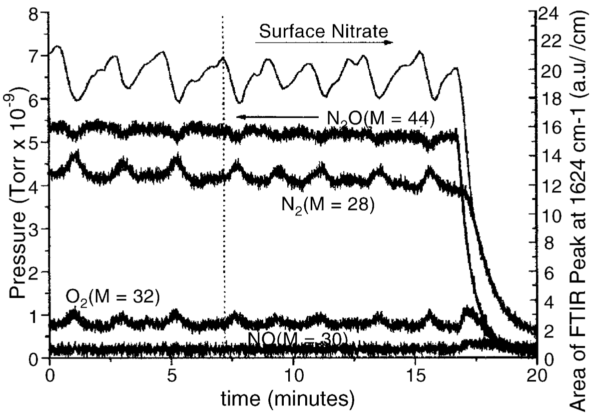

Fig. 5. Isothermal rate oscillations in the decomposition of N_2O as monitored by both FTIR and MS. Reaction conditions are $T = 460$ °C, $p = 1$ Torr, and N_2O flow rate = 5.0 cm^3, STP (Fanson et al. [18], reproduced by permission of Plenum Publishing Corporation).

In a second study, Lauterbach and coworkers used different Cu-ZSM-5 catalysts for their combined kinetic and FTIR studies [19]. Oscillations were observed only using overexchanged copper zeolites. However, some samples with high copper content prepared with a UOP zeolite with Si/Al = 18 did not exhibit any oscillations. It could be shown that a low rate of nitrate formation combined with a low desorption temperature was responsible for the absence of oscillations over these catalysts.

2.3. *Reaction mechanism and mathematical modelling of N_2O decomposition over Cu-ZSM-5*

Ciambelli et al. were the first to propose a mechanistic model describing the development of kinetic oscillations in nitrous oxide decomposition [13,21,22]. Since these authors did not detect any NO as a direct reaction product at the low N_2O concentrations and reaction temperatures employed, the proposed mechanism only includes adsorbed oxygen species, and the gaseous reactants. The following set of reactions was proposed:

$$N_2O + Cu^+ \rightarrow N_2O^- - Cu^{2+} \quad (5)$$

$$N_2O^- - Cu^{2+} + Cu^+ \rightarrow Cu^{2+} - O^{2-} - Cu^{2+} + N_2 \quad (6)$$

$$N_2O + Cu^{2+} - O^{2-} - Cu^{2+} \rightarrow N_2 + O_2 + 2Cu^+ \quad (7)$$

$$Cu^{2+} - O^{2-} - Cu^{2+} \Leftrightarrow O_{ads} + 2Cu^+ \quad (8)$$

$$2O_{ads} \Leftrightarrow O_2 \quad (9)$$

This reaction scheme is based on the assumption that the copper species involved in the reaction are present as reduced (Cu^+) and oxidised state (Cu^{2+}–O^{2-}–Cu^{2+}) and that nitrous oxide is capable of both the oxidation of copper species (5) and their reduction (7). The assumption that monovalent copper is the active site for nitrous oxide decomposition was confirmed by XPS measurements conducted by Chen et al. [23]. These authors also observed oscillations using a catalyst with Si/Al = 50 and Cu/Al = 0.9, although no detailed results were presented.

When the Bendixon criterion [24] is applied to the above reaction scheme, no kinetic oscillations can be predicted, because the trace of the Jacobian matrix is always negative. The authors therefore additionally suggested that the activation energy of step (6), where the bridged copper species is formed, is a linear function of the degree of reduction of the copper species. This assumption is supported by experimental results obtained by Valyon and Hall [10]. With this additional assumption, Ciambelli et al. were successfully able to model self-sustained oscillations of the N_2O decomposition and the oxygen production rate.

Based on the strong experimental evidence that NO formed in a slow side reaction and strongly adsorbed nitrate species play a decisive role in the development of oscillations, Ochs and Turek proposed a different reaction mechanism [20]. The simplest version of the scheme consists of five reactions:

$$N_2O + 2\square \rightarrow O_{ads} + N_2 \quad (10)$$

$$2O_{ads} \rightarrow O_2 + 4\square \quad (11)$$

$$N_2O + O_{ads} \rightarrow 2NO + 2\square \quad (12)$$

$$NO + 2O_{ads} \rightarrow NO_{3,ads} + 3\square \quad (13)$$

$$NO_{3,ads} \rightarrow NO + O_2 + \square \quad (14)$$

According to this proposed mechanism, the catalyst is rapidly deactivated by deposition of atomic oxygen on the active, monovalent copper sites. In agreement with Ciambelli et al., it is assumed that adsorbed oxygen occupies two active copper sites, i.e. a bridged copper species is formed. In a slow side reaction (12) nitric oxide is formed at the expense of adsorbed oxygen. NO quickly reacts to adsorbed nitrate according to reaction (13) and is therefore not observed in the gas phase during the periods of low catalytic decomposition activity. It is furthermore assumed that the nitrate species is only stable as long as sufficient adsorbed oxygen is present on the catalyst surface. If a critical value of the coverage with atomic oxygen is reached, immediate decomposition of nitrate into NO and O_2 occurs. As long as nitric oxide is present in the gas phase, desorption of oxygen is facilitated and the catalyst remains in the state of high decomposition activity. After removal of NO from the reactor, the oscillatory cycle starts again with an uptake of oxygen. With the above reaction mechanism, not only the development of the gas-phase concentrations of N_2O, O_2, N_2, and NO (see Fig. 6) but also the development of the amounts of adspecies determined by transient experiments as well as the desorption kinetics of nitric oxide and oxygen could be described with quite good accuracy.

Ochs and Turek have pointed out that the proposed mechanism is a simplification of the more complex overall chemistry [20]. The additional direct reaction of N_2O with adsorbed oxygen (7) is most probably also possible. Furthermore, the direct reaction of NO with adsorbed oxygen yielding adsorbed nitrate must proceed via intermediates. This was confirmed by Lauterbach and coworkers with their FTIR experiments [19]. During these studies, bands assigned to a monodentate nitrite species could be observed during some measurements.

In conclusion, these studies have developed some basic understanding of the surprisingly complex chemistry of the oscillating decomposition of nitrous oxide over Cu-ZSM-5 catalysts. However, open questions still remain. While there is strong evidence that nitrate species are formed and accumulate on the catalyst surface, it remains unanswered how this species is stabilised at high reaction temperatures and, on the other hand, why it spontaneously decomposes under certain conditions.

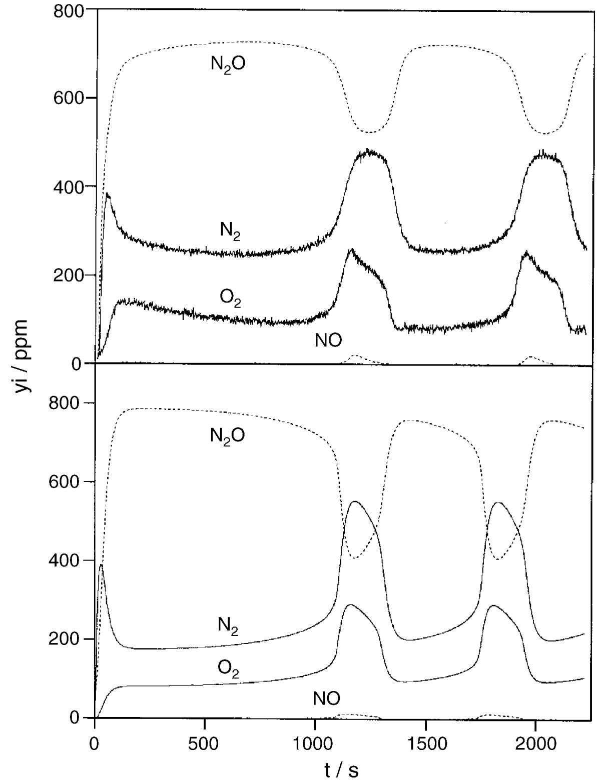

Fig. 6. Comparison of experimental observed (upper part) and calculated (lower part) oscillations in the differential reactor (m = 240 mg, 1000 ppm N_2O, and T = 698 K) (Ochs and Turek [20], reproduced by permission of Elsevier Science).

2.4. Oscillations observed over other copper-exchanged zeolites

Schay and coworkers studied reactions of nitrogen oxides over different copper-exchanged zeolites [25,26]. It was found that Cu-AlTS-1 is a highly active catalyst for N_2O and NO decomposition as well as the hydrocarbon SCR of nitric oxide. During the reaction of nitrous oxide, the catalyst with Si/Ti = 82, Si/Al = 55, and a copper exchange level of 140% exhibited sustained isothermal oscillations. Schay et al. showed in detailed studies employing steady-state and transient kinetic measurements, temperature-programmed experiments as well as in situ FTIR spectroscopy that the reaction mechanisms over Cu-ALTS-1 and Cu-ZSM-5 are identical. The crucial role of the formation of adsorbed nitrate and the decomposition of NO_3 into NO and O_2 could be clearly demonstrated [26].

3. Nitrous oxide decomposition over Fe-ZSM-5

3.1. Role of nitric oxide in N_2O decomposition

Iron-exchanged zeolites have become very popular since these catalysts were shown to have high activity during reactions of nitrogen oxides and apparently better hydrothermal stability than copper-based zeolites. Although no oscillations have been until now observed when diluted mixtures of pure nitrous oxide are contacted with Fe-ZSM-5, it is worth to discuss the similarities of the effect of nitric oxide on the N_2O decomposition over iron and copper ZSM-5 catalysts.

A strong enhancing effect of NO addition during nitrous oxide decomposition over Fe-ZSM-5 was already reported by Kapteijn et al. [15]. It was assumed that strongly adsorbed atomic oxygen reacts with NO to yield nitrogen dioxide according to reaction (3) giving rise to a lower oxygen coverage of the active iron sites and thus to higher decomposition activity. Kögel et al. have shown that the positive effect of NO additions has a catalytic nature, since even traces of NO added are sufficient to strongly increase the nitrous oxide conversions [27].

Sang and Lund, however, have shown that Fe-ZSM-5 catalysts are also able to convert N_2O to small amounts of NO [28]. During experiments with different nitrous oxide inlet pressures it was shown that above a certain level, the catalyst reaches a state of markedly higher decomposition activity. This phenomenon was attributed to the promotional effect of sufficiently high amounts of NO. Sang and Lund proposed a redox cycle involving nitrite and nitrate species to explain their experimental findings [29] that is similar to the reaction scheme proposed by Ochs and Turek [20] for the oscillations during N_2O decomposition over Cu-ZSM-5. However, it was also shown by Sang and Lund that at the high nitrous oxide partial pressures used, an isothermal behaviour of the laboratory reactor no longer could be maintained. It therefore remains unclear whether the observed effect is of kinetic or thermokinetic origin.

A recent study conducted by Renken and coworkers [30] also confirmed that NO can be produced from N_2O using Fe-ZSM-5 catalysts. Upon nitrous oxide addition to a fresh catalyst, the catalytic activity slowly increased with time reaching a steady-state level after some minutes. However, if pulses of NO were added to the reaction mixture, the catalyst immediately exhibited the maximum N_2O decomposition activity.

3.2. Oscillations in the presence of water vapour

Sachtler and coworkers also studied the decomposition of nitrous oxide using Fe-ZSM-5 catalysts [31,32]. When catalyst samples with a high iron content of Fe/Al = 1.0 and a low Si/Al ratio of 14 was used, sustained isothermal oscillations of the N_2O, N_2, and O_2 exit concentrations were observed (Fig. 7). In contrast to copper-exchanged zeolites, the oscillations over Fe-ZSM-5 only occurred in the presence of high concentrations of water vapour. On the other hand, the addition of oxygen or NO did not have a significant effect on the development of oscillations. Although Sachtler and coworkers could show by using FTIR that nitrite and nitrate species were formed under reaction conditions, it appears that the mechanism of the observed oscillations in the presence of water vapour is different from the reaction scheme valid for Cu-ZSM-5.

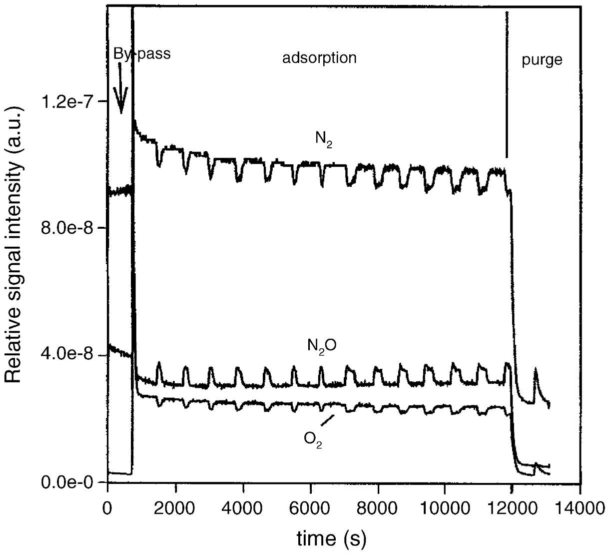

Fig. 7. Outlet concentrations vs. time of N_2O, N_2, and O_2 in N_2O decomposition over Fe/MFI (6.40) at 500 °C, GHSV = 42,000 h^{-1}. Feed: 0.25% N_2O in He and 10% H_2O (Malki et al. [32], reproduced by permission of Academic Press).

4. Oscillations observed over precious metal catalysts

Besides transition metal-exchanged zeolites, precious metal catalysts like rhodium or ruthenium belong to the most active materials for nitrous oxide decomposition in industrial waste gas streams. In a few studies using Rh or Ru catalysts, kinetic oscillations have been observed [33–35]. Centi et al. have presented an extensive study of the nitrous oxide decomposition over rhodium-based catalysts [33,34]. Experiments were carried out over 1 wt.% rhodium supported on zirconia or zirconia–neodymia mixed supports with a feed gas containing N_2O in the presence of realistic concentrations of oxygen and water vapour. Rhodium supported on zirconia–neodymia exhibited sustained oscillations of the N_2O conversion in the temperature range between 320 and 380 °C. Oscillations only occurred in the presence of water vapour. The same effect was observed by Marnellos et al. [35] during measurements with a Ru/Al_2O_3 catalyst at a temperature of 490 °C and gas compositions similar to those used by Centi et al. [33].

Centi et al. proposed a working model to explain the development of oscillations in N_2O decomposition. In a first step, N_2O decomposes on the free sites of the Rh surface, producing strongly adsorbed atomic oxygen. The sticking coefficient for N_2O is assumed to increase with the increase of the oxygen coverage. On one hand, this leads to an increase of the rate constant for N_2O decomposition. On the other hand, the number of available active sites decreases.

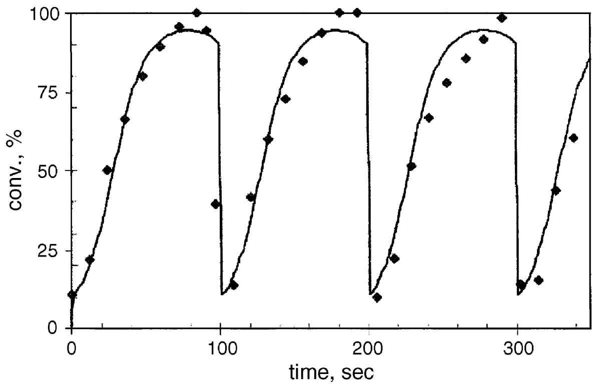

Fig. 8. Experimental data (symbols) and calculated conversion (solid line) at 341 °C for a feed composition of 1% N_2O, 2% H_2O, and 6% O_2 in helium. Rate constants in the kinetic model: $k_1 = 1.35 \times 10^4$, $k_2 = 9.12 \times 10^{10}$, $k_3 = \infty$, and contact time = 0.13 s (Centi et al. [33], reproduced by permission of Academic Press).

Finally, a rapid reconstruction of the Rh particles occurs above a certain concentration of adsorbed oxygen on the Rh surface. This is accompanied by a release of the chemisorbed oxygen and the start of a new oscillation cycle. Using this approach, the following sequence of steps was proposed:

$$N_2O + \Box - k_1 \rightarrow O_{ads} + N_2 \tag{15}$$

$$N_2O + O_{ads} + \Box - k_2 \rightarrow N_2 + 2O_{ads} \tag{16}$$

$$(O_{ads})_n - k_3 \rightarrow \tfrac{n}{2}O_2 \tag{17}$$

where $(O_{ads})_n$ denotes the concentration of chemisorbed oxygen at which rapid release of oxygen caused by surface reconstruction occurs. Fig. 8 shows that a good agreement between experimental results and calculation can be achieved with the above mechanism.

5. Conclusions

The extensive study of different catalysts for the catalytic removal of nitrous oxide in industrial waste gases has yielded some interesting new oscillatory phenomena during this apparently simple reaction. Oscillations of N_2O decomposition over Cu-ZSM-5 have been quite thoroughly investigated. There is general agreement that not only nitrogen and atomic oxygen, but also nitric oxide is a reaction product. This side product is able to accumulate on the active copper sites, most probably as highly stable nitrate. Evidence for the formation of nitrate species was given indirectly by temperature-programmed and transient kinetic experiments, but also directly by using in situ FTIR spectroscopy. The oscillations appear to be caused by the fact that this nitrate species is no longer stable below a certain oxygen coverage of the active sites. In that case, rapid decomposition into nitric oxide and oxygen occurs and the oscillatory cycle starts again.

When Fe-ZSM-5 catalysts are used, many similarities with Cu-ZSM-5, such as the formation of small amounts of NO, the occurrence of adsorbed nitrates and the enhancing effect of NO addition, have been observed. However, no sustained oscillations emerge if diluted N_2O streams are used. On the other hand, the kinetic oscillations over Fe-ZSM-5 in the presence of water vapour appear to be caused by a different mechanism, an explanation for which has not yet been given.

Oscillations observed over precious metal catalysts have been explained successfully by a classical oxidation/reduction mechanism including the restructuring of the active catalyst surface under reaction conditions.

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