

Spontaneous Isothermal Oscillations in N₂O Decomposition over a Cu–ZSM5 Catalyst

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Spontaneous isothermal oscillations of N₂O and O₂ outlet concentrations are observed in N₂O decomposition on an over-exchanged Cu–ZSM5 catalyst. The oscillations are not chaotic but have a kinetic genesis. The oscillating behaviour is established over the pre-reduced catalyst after a transient phase whose duration is reduced with increasing the reactant inlet concentration. The addition of O₂ to the feed reduces the average N₂O conversion and does not substantially affect the frequency and the amplitude of the oscillations up to an O₂/N₂O inlet ratio equal to 10; only at higher inlet ratios do the oscillations disappear. Fourier analysis has revealed that the frequency of the oscillations increases by increasing either the feed flow rate or the N₂O reactor inlet concentration. A reaction mechanism based on the periodic change of the copper oxidation state in the zeolite has been proposed. The mechanism allows us to explain most of the results obtained in different experimental conditions. © 1998 Academic Press

INTRODUCTION

The interest in the control of N₂O polluting emissions, mainly deriving from adipic acid synthesis processes and fluidized bed coal combustion, is related to their potentially disastrous effects on the environment, such as global warming and ozone layer depletion in the stratosphere. As recently reviewed (1), several catalytic systems have been tested for decomposing N₂O into its elements, such as mixed (2) and perovskite-type oxides (3), hydrotalcites (4–6), and metal-exchanged zeolites (6–15). Cu–ZSM5 seems to be very promising for potential applications, as shown by Li and Armor (8). Further interest in studying this reaction on the same catalyst is related to the possible role of N₂O as an intermediate in NO decomposition (16).

During the investigation of over-exchanged Cu–ZSM5 zeolite as catalyst of N₂O decomposition, we discovered a specific feature of this material, i.e. the aptitude to generate

an oscillating behaviour in the rate of N₂O decomposition. We have already reported (11, 12) that, when a gas mixture of nitrous oxide (300 ppm) and helium is fed to a flow reactor loaded with Cu–ZSM5 catalyst, self-sustained isothermal oscillations of N₂O outlet concentration may occur in the range of temperature from 320 to 390°C. Moreover, we have found (12) that the presence of either NO or O₂, fed at a wide range of ratios with respect to N₂O (from 2.5 to 250), lowers the steady-state conversion of N₂O to N₂ and makes the oscillations disappear.

In a parallel investigation, Lintz and Turek (13) found experimental evidences quite similar to our results. By using a different gas mixture (1000 ppm N₂O in N₂) and a Cu–ZSM5 catalyst with different Si/Al ratio (37 instead of 80), they observed the oscillating behaviour in N₂O decomposition by investigating in the range from 400 to 450°C. However, they also obtained experimental results different from ours, such as the formation of the oscillating byproduct NO, and the different effect of NO and O₂ on the oscillations. They reported that the presence of small amounts of NO in the feed (NO/N₂O feeding ratio in the range 0.01–0.1) immediately quenched the oscillations and increased the N₂O decomposition rate, while the addition of high amounts of oxygen (O₂/N₂O feed ratio up to 10) did not significantly change the frequency and the amplitude of oscillations, slightly lowering the average conversion of N₂O to N₂ (13). More recently, Turek (14) has confirmed that the N₂O decomposition rate measured in a gradientless reactor is not affected by the presence of O₂ in the feed in the whole range of temperatures investigated (375–450°C).

It is worthwhile to mention that very few examples of oscillations of monomolecular reactions have been reported in literature (17, 18) while this specific behaviour is common to other bimolecular catalytic reactions, such as CO or NH₃ oxidation over metals, metal oxides, and zeolites (19, 20). Oscillations of the outlet concentration of N₂O were already observed by Hugo (17) over CuO/MgO catalyst, but they were caused by reactor thermal instabilities, due to the different feed composition (100% N₂O).

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In this paper, we have studied the oscillating behaviour occurring in N_2O decomposition rate on an over-exchanged Cu-ZSM5 with a high Si/Al ratio by exploring the influence of several parameters such as catalyst pretreatment, contact time and feed composition. Moreover, a reaction mechanism is provided to account for the observed phenomena.

The interest of this study is related not only to the singleness of the occurrence of a spontaneous isothermal oscillating behaviour in a monomolecular reaction, but also to the possible contribution it may give to unravel the unique role of copper in Cu-ZSM5 zeolites which makes them very active in de- NO_x reactions.

EXPERIMENTAL

Methods

The preparation of Cu-ZSM5 (Si/Al = 80, Cu content = 3.94 wt%) has been previously reported (21, 22). The high content of copper in the catalyst is equivalent to an apparent exchange level of 640% (Cu/Al = 3.2) that we have already explained by assuming that copper ions are present in the zeolite matrix in some hydrated species such as $[Cu_xO_2(OH)_{2x-5}]^+$ (23). We have hypothesized that there exists a distribution of x values in those exchanging cations, with an average value around 3.2, corresponding to the $[Cu]/[Al]$ molar ratio in the catalyst. As an alternative explanation, the possibility that Cu is exchanged not only at protonic sites associated with framework Al sites, but also at defect sites such as nested silanols at Si vacancy defects must be taken into account. Notwithstanding the high copper content, neither X-ray diffraction, UV-visible reflectance spectroscopy, nor combined XPS-Auger characterization (21–23) gives any evidence for the presence of bulk copper oxide species.

The quartz microreactor consists of a 60 cm length tube (i.d. 1.0 cm), in which a porous disc supports the catalyst particles. It is inserted in an electric furnace supplied with three heated and temperature-controlled zones. The temperature is monitored by a chromel–alumel thermocouple, placed into another quartz tube, coaxial and internal to the reactor, along the whole length of the catalytic bed (1–2 cm).

The reactor inlet and outlet gas are analyzed by two continuous analyzers, one for the measurements of NO, NO_2 , and N_2O concentrations (Hartmann & Braunn, URAS 10 E) and another for O_2 concentration (Hartmann & Braunn, MAGNOS 6 G). The gas phase concentration of N_2 is obtained with a gas chromatograph (Hewlett Packard HP 5890, 5 Å molecular sieve column). Before each test, the catalyst has been treated in He (35 N L/h) for 2 h at 550°C to obtain a reduced form of Cu-ZSM5 or in O_2 (6 N L/h) for 45 min at room temperature to stabilize the oxidized form.

RESULTS AND DISCUSSION

In Fig. 1 the concentrations of N_2O and O_2 in the reactor outlet gas are reported as functions of time when a helium gas stream containing N_2O (600 ppm) is fed. The test has been carried out at 344°C with Cu-ZSM5 (200–300 μm particle size) prerduced in flowing He for 2 h at 550°C.

It appears that N_2O and O_2 concentrations begin to oscillate in a quite regular way after about 1 h from the start of the run. It is worthwhile to point out that the axial temperature of the catalytic bed is always constant in the whole experiment (maximum fluctuations ranging within $\pm 0.1^\circ C$). The amplitude of the oscillations of N_2O outlet concentration is roughly 65 ppm, while the main period is about 30 min, i.e. 10^5 times higher than the contact time. On the other hand, the average O_2 concentration is in agreement with the N_2O average consumption. O_2 oscillations exhibit the same frequency and are out of phase with respect to the oscillations of the reactant. Moreover, in the transient phase the system exhibits a peak of N_2O concentration lasting about 1 h and a constant value of O_2 outlet concentration (~ 200 ppm) in the first 30 min. Subsequently, before reaching a dynamic regime, the reactor outlet N_2O concentration has been oscillating around an average increasing value for about 600 min.

During the first half hour of the run, the constant value of O_2 concentration is stoichiometrically in agreement

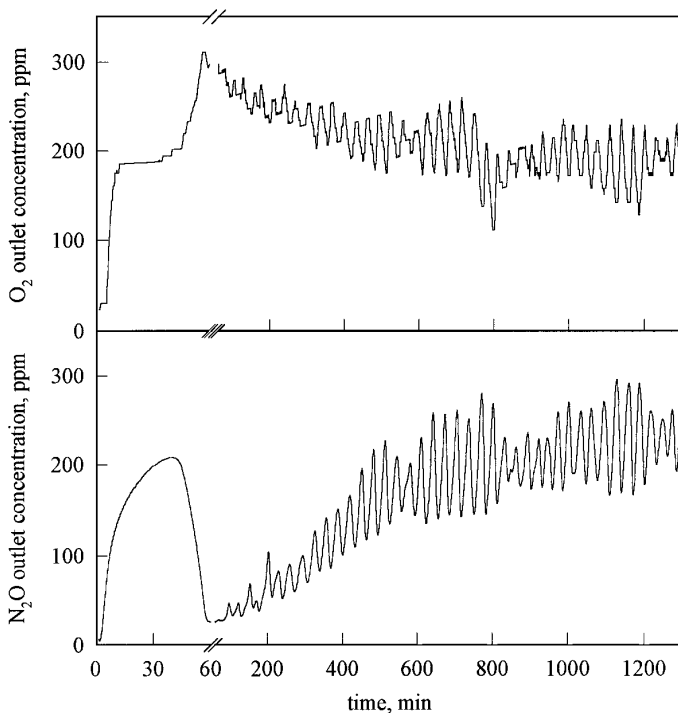


FIG. 1. N_2O and O_2 outlet concentrations as functions of time in N_2O decomposition at 344°C on pre-reduced Cu-ZSM5. Feed: N_2O (600 ppm) in He. $W/F = 0.137$ g s N cm^{-3} .

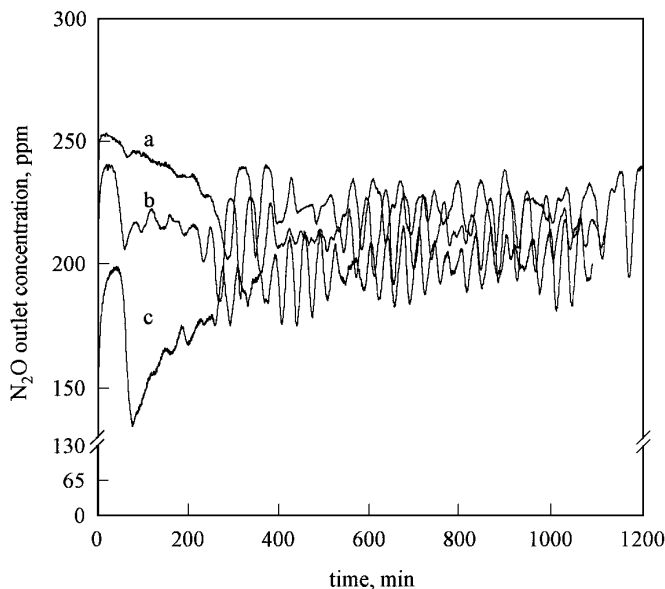
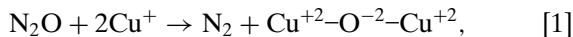


FIG. 2. N₂O outlet concentration as a function of time in N₂O decomposition at 344°C after different Cu-ZSM5 pretreatments: (a) O₂; (b) 4% vol O₂/He mixture; and (c) He. $W/F = 0.038 \text{ g s N cm}^{-3}$. Feed: N₂O (300 ppm) in He.

only with the maximum of N₂O concentration in the peak (~200 ppm, corresponding to 400 ppm of N₂O consumed), while in the remaining run time we measure N₂O and O₂ outlet average concentrations in a strict stoichiometric ratio (O₂/N₂O = 1 : 2). Therefore, it means that the initial consumption of N₂O is higher than that expected from O₂ production. According to the conclusion of a previous study on the redox chemistry of Cu-ZSM5 copper sites in the presence of another nitrogen-containing oxidizing agent, such as NO (23), we relate this phenomenon to the initial reduced state of copper in the catalyst, generated by the helium pretreatment at high temperature. In particular, we propose that a fraction of Cu⁺ ions is re-oxidized to Cu⁺², according to the following stoichiometry:



thus explaining the apparent higher decomposition rate in the initial minutes.

In order to validate the previous assumption, experimental tests on the influence of the initial state of oxidation of the catalyst on the dynamic behaviour of N₂O decomposition rate have been performed. In Fig. 2 the N₂O outlet concentration is reported as a function of time in three different runs carried out in the same experimental conditions, but after different catalyst pretreatment (pure He, 4% vol O₂ in He, pure O₂). The presence of a peak of N₂O concentration in the first 60 min is clearly evident for the pre-reduced catalyst (curve c) but much less for the sample pretreated in O₂/He mixture (curve b), whereas it is absent for the pre-oxidized catalyst (curve a), for which only

the delay until the oscillations start is observed. Moreover, the catalytic activity in the transient phase is strongly affected by the pretreatment, the reduced form of Cu-ZSM5 showing a much more initial consumption of N₂O than the oxidized one. These results strongly support the assumption that the average value of the outlet N₂O concentration (lower in the transient phase with respect to the dynamic regime) should be related to the initial reduced state of copper sites. However, after about 600 min a very similar value of the average N₂O conversion is reached in all cases. As a further confirmation, it appears that the initial activity of the catalyst pretreated with the gas mixture of O₂ in He (curve b) is intermediate with respect to the other two values (curves a and c).

Calculations and experiments have been performed in order to determine the influence of mass transport phenomena on the catalytic behaviour of Cu-ZSM5 in N₂O decomposition. Firstly, transport rate calculations as well as experimental tests have excluded the possibility that the resistance due to external diffusion in the gas phase surrounding the catalyst surface could play a prevailing role on the observed kinetics. Then, in order to evaluate the effect of N₂O intraparticle diffusion, catalytic activity tests with different particle size have been performed. A preliminary set of experiments, performed at 344°C with N₂O inlet concentration of 300 ppm, has shown a negligible dependence of the amplitude of oscillations and of the average N₂O conversion on the catalyst particle size, indicating at this temperature the absence of significant diffusion effects on the chemical kinetics. On the contrary, Fig. 3 reports the results of the experiments carried out at 370°C which show

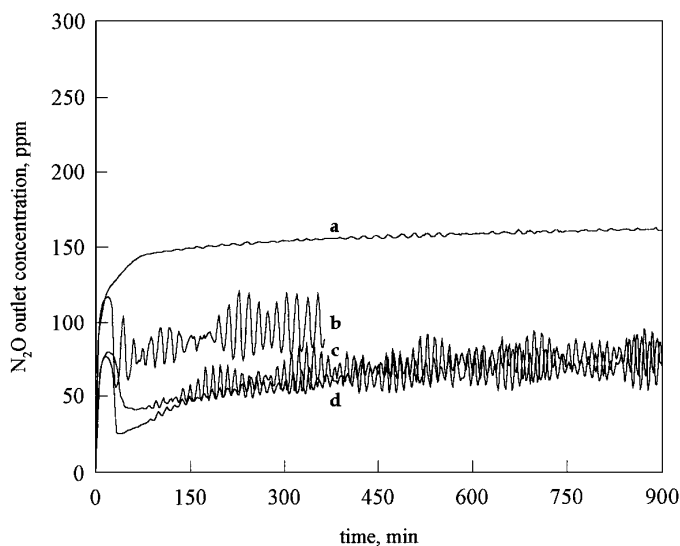


FIG. 3. N₂O outlet concentration as a function of time in N₂O decomposition on Cu-ZSM5 at 370°C with different catalyst particle sizes: (a) >710 μm; (b) 400–710 μm; (c) 300–400 μm; and (d) 200–300 μm. $W/F = 0.038 \text{ g s N cm}^{-3}$. Feed: N₂O (300 ppm) in He.

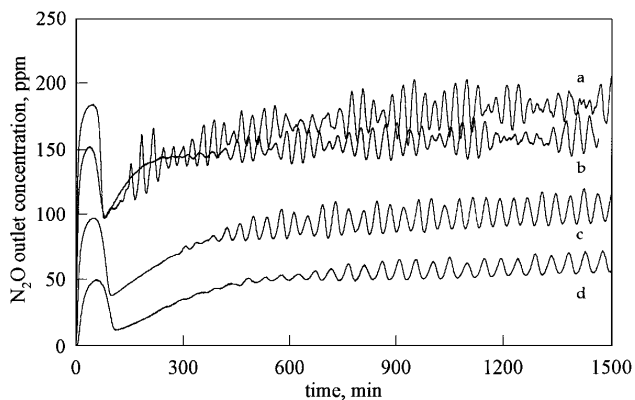


FIG. 4. N_2O outlet concentration as a function of time in N_2O decomposition on Cu-ZSM5 at 344°C and different feed flow rates: (a) 41.0; (b) 31.9; (c) 19.1; and (d) 12.5 N L/h. $W = 0.44$ g. Feed: N_2O (300 ppm) in He.

a meaningful dependence of the catalytic performance on the catalyst particle size.

At 370°C , the average N_2O conversion decreases from 74 to 46% by increasing about four times the average dimension of catalyst particles, indicating the influence of intraparticle diffusion on the reaction kinetics when the particle size is greater than $400\ \mu\text{m}$. It is also observed that the amplitude of oscillations is much lower for the largest values of

particle diameter ($d_p > 710\ \mu\text{m}$). This result, together with the macroscopic isothermicity of the phenomenon, suggests that the oscillating behaviour could have a kinetic genesis, related to a specific reaction mechanism or a catalyst surface transformation, because of the tendency to become less evident in the diffusion-controlled regime.

As some properties of the oscillations may be affected by the contact time, the influence of W/F on the observed oscillating patterns has been investigated, by either changing the gas feed flow rate (F) at constant catalyst load (W) (Figs. 4 and 5) or vice versa (Figs. 6 and 7).

Figure 4 reports the results of four different runs performed at 344°C by keeping constant the amount and the particle size of catalyst ($W = 0.44$ g, $d_p = 300\text{--}400\ \mu\text{m}$) and changing the feed flow rate from 12.5 to 41 N L/h. It appears that the oscillations of N_2O are more and more regular as the contact time is increased, and this eye-perceptible regularity attained at the lowest values of the feed flow rate has been verified by the Fourier analysis performed over the four runs.

Figure 5 reports the power spectra obtained for the oscillations of N_2O outlet concentration shown in Fig. 4. The experimental nature of the curves analysed forces us to assume that only a very small number of frequencies are meaningful. Taking into account the frequencies whose correspondent amplitudes are at least higher than 2 ppm

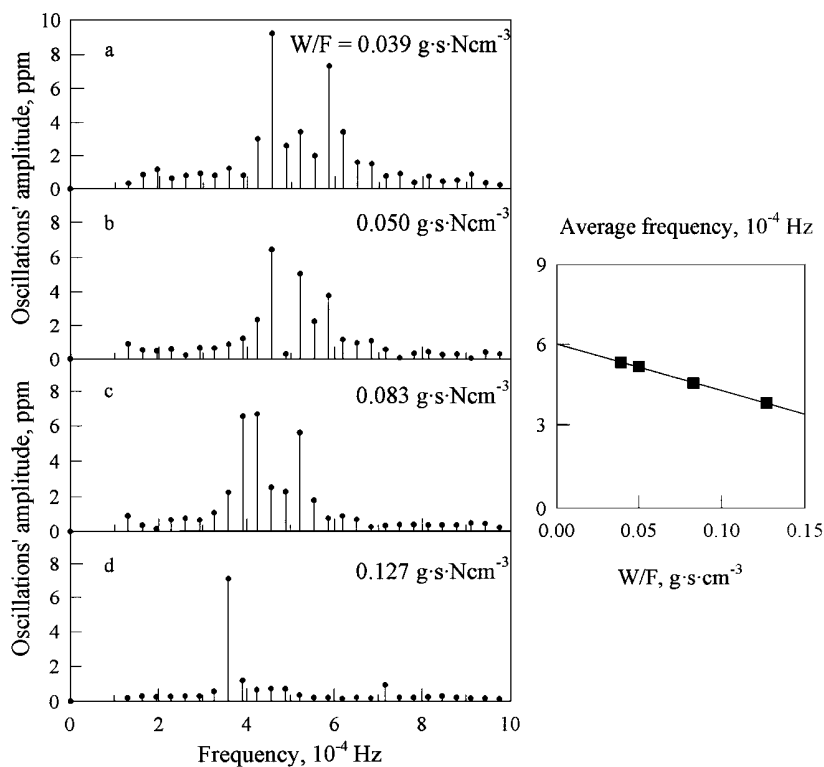


FIG. 5. Fourier power spectra analysis for the oscillations of N_2O concentration at 344°C and different feed flow rates: (a) 41.0; (b) 31.9; (c) 19.1; and (d) 12.5 N L/h. $W = 0.44$ g. Feed: N_2O (300 ppm) in He.

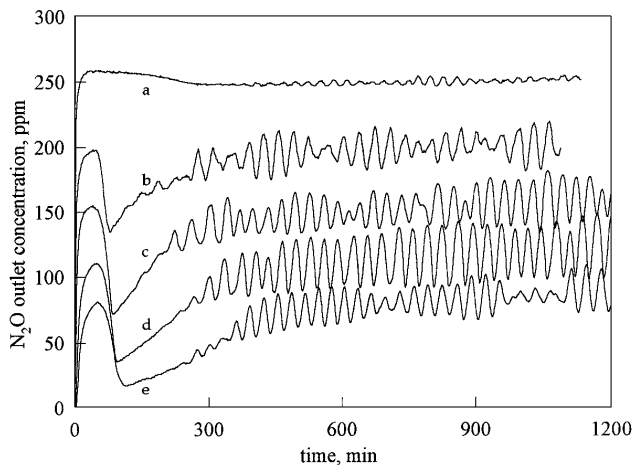


FIG. 6. N₂O outlet concentration as a function of time in N₂O decomposition on Cu-ZSM5 at 344°C and different catalyst loads: (a) $W = 0.18$ g; (b) $W = 0.44$ g; (c) $W = 0.60$ g; (d) $W = 0.80$ g; and (e) $W = 1.0$ g. $F = 42.2$ N L/h. Feed: N₂O (300 ppm) in He.

allows us to identify the observed dynamic regime as not chaotic. This quite small number further tends to decrease by decreasing the gas feed flow rate. Moreover, the average value of the main frequency of the phenomenon linearly

decreases from 5.3 down to 3.8×10^{-4} Hz with decreasing the feed flow rate, suggesting that a significant interaction between the transport of the reactant into the reactor and a nonlinear reaction rate exists.

The effect of the contact time has been also investigated in the same experimental conditions as in Fig. 4, but taking constant the gas feed flow rate (42.2 N L/h) and increasing the catalyst load from 0.18 up to 1.0 g by an average amount of 0.2 g. The results of these experiments, reported in Fig. 6, show a dependence on the contact time quite similar to that previously shown in Fig. 4, as the same average N₂O conversions are attained at the same W/F ratios. Consequently, the effect of mass transfer resistance in the gas phase on the reaction kinetics is negligible. It is also evident that with 0.18 g of Cu-ZSM5 (Fig. 6a) the amplitude of the oscillations is very low, even in the presence of a significant conversion (17%), while it is much higher in the range of catalyst amount from 0.44 to 1.0 g. Moreover, Fig. 6a shows that also the transient phase is different with respect to that exhibited for higher values of W/F (Figs. 6b–e), since the initial peak of N₂O outlet concentration is not present, suggesting that a relevant correlation between the two phenomena may exist.

As can be seen in Fig. 7, Fourier analysis carried out over the five runs reported in Fig. 6 shows that the number of

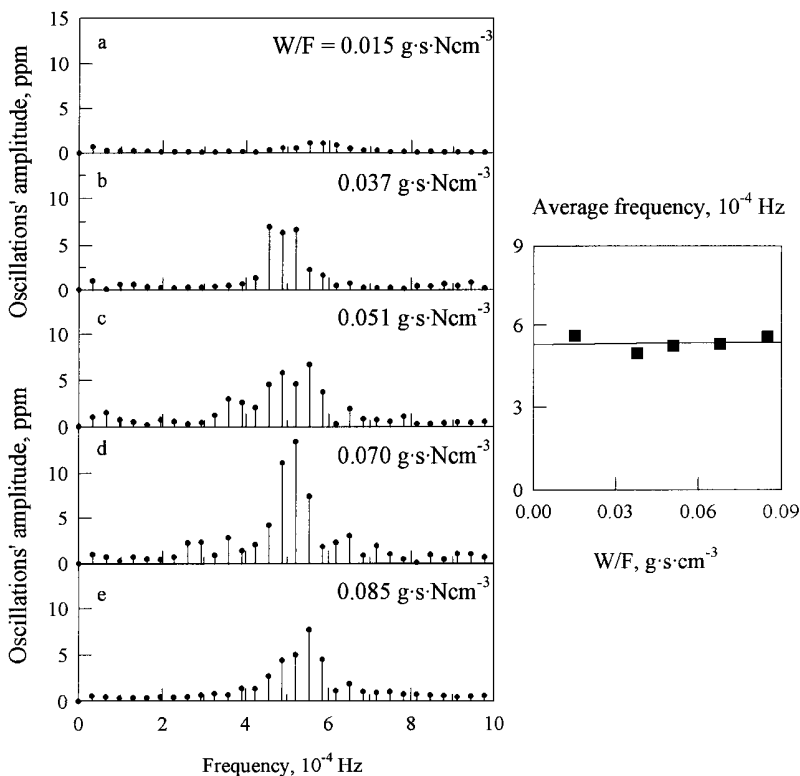


FIG. 7. Fourier power spectra analysis for the oscillations of N₂O concentration at 344°C and different catalyst loads: (a) $W = 0.18$ g; (b) $W = 0.44$ g; (c) $W = 0.60$ g; (d) $W = 0.80$ g; and (e) $W = 1.0$ g. $F = 42.2$ N L/h. Feed: N₂O (300 ppm) in He.

meaningful frequencies of the oscillations decreases with increasing the reactor length, i.e. the contact time, but much less than with increasing the feed flow rate (Fig. 5). Moreover, the power spectra reported in Fig. 7 show a different dependence of the average frequency, that is not affected by the catalyst bed length in all the range of W/F values investigated. This result suggests that increasing the W/F ratio results in enhancing the regularity of the oscillations, while the values of their frequencies are strongly correlated only to the feed flow rate.

We have already reported that the presence of oxygen in the feed influences the activity of the catalyst in N_2O decomposition (12). We have found that at 344°C the presence of 5000 ppm of O_2 in the feed is sufficient to quench the oscillations on the pre-reduced catalyst, while by increasing the inlet O_2 concentration, the average conversion of N_2O to N_2 and O_2 decreases. In contrast, Lintz and Turek (13) observed only a little effect of O_2 on the catalytic activity, and Turek (14) reported that the region of existence of the oscillating behaviour becomes slightly narrower, even in the presence of 12% vol. concentration of oxygen in the feed. The differences between our previous results (11, 12) and those by Lintz and Turek (13, 14) are likely due to the different experimental conditions investigated. In their experiments, the Cu-ZSM5 catalyst has different Si/Al ratio (37) and copper content (2.1 wt%), while a different diluent gas (N_2 instead of He) and a higher N_2O inlet concentration (1000 ppm) have been used. Moreover, a further significant difference is likely to be attributed to the different range of temperatures investigated.

To better understand the phenomenon, we have carried out other experiments with a feed ratio O_2/N_2O lower than that previously involved (0.5–70 instead of 17–170). Oxygen concentration ranging from 150 to 20,000 ppm in the feed was used, the N_2O inlet concentration being 300 ppm. Representative results are reported in Fig. 8 and show that the N_2O outlet concentration oscillates even in the presence of O_2 up to a value of 3,000 ppm inlet concentration (curve d). Only when 5,000 ppm of O_2 are added to the feed (curve e) do the oscillations disappear. Notwithstanding, the average conversion of N_2O decreases with increasing O_2 inlet concentration even at 150 ppm, becoming about 50% lower in the presence of 20,000 ppm O_2 concentration. This behaviour is opposite to that of Fe-ZSM5 zeolite, which shows enhanced activity in the presence of oxygen (24).

It is worth noting that the addition of oxygen to the feed does not change the transient behaviour of the nitrous oxide outlet concentration, except when the O_2 concentration in the feed is 20,000 ppm. The initial peak is still present and its intensity is unchanged with increasing the inlet concentration of O_2 from 0 to 10,000 ppm. In the upper right corner of Fig. 8 it is also shown that, when the oscillations are present, their amplitude and frequency decrease with increasing the O_2 inlet concentration. Note that the values reported refer

to the whole set of O_2 inlet concentration conditions for which the oscillations have been observed.

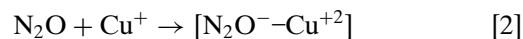
It is worthwhile to recall that we found similar effects as with oxygen addition, by adding nitric oxide to the feed (12). A quite small amount of NO (500 ppm) is enough to give quenching effects comparable to those found at the highest O_2 concentrations in the feed. Moreover, the presence of nitric oxide in the feed resulted not only in preventing the oscillations but also in affecting the transient behaviour of N_2O outlet concentration at the start of the run, being the initial peak of N_2O concentration absent when NO is present in the feed.

The oscillating behaviour of N_2O decomposition is also influenced by the inlet concentration of N_2O , as shown in Fig. 9, where the conversion degree of N_2O is plotted as a function of time for some values of the N_2O inlet concentration investigated.

Figure 9 shows that at the lowest values investigated (curves a and b) the oscillations are not observable, while they are present in the experiments carried out with 300 ppm or higher inlet N_2O concentration. The delay of the oscillations of N_2O decreases with increasing the N_2O inlet concentration. The features of the oscillations are also affected: in particular, the amplitude increases more than linearly by increasing the N_2O inlet concentration. In the right upper corner of Fig. 9, the values of the amplitude and frequency of the oscillations for the whole set of N_2O inlet concentration conditions for which the oscillations have been observed are reported. It appears that both the amplitude and the frequency of the oscillations increase with increasing the N_2O inlet concentration. Since even their ratio increases, it can be concluded that the oscillatory phenomenon seems to be activated at the highest concentrations.

By increasing the N_2O inlet concentration from 100 to 800 ppm, the average N_2O conversion decreases from 80 to 40%, thus showing an apparent reaction order lower than one with respect to N_2O for the average decomposition rate. Turek (14) studied the influence of nitrous oxide concentration on the reaction rate in a gradientless reactor, reporting a first-order dependence on N_2O inlet concentration. Moreover, he reported that the region of existence of oscillations is affected by the reaction temperature, as no oscillations are detected with N_2O inlet concentration lower than 150 ppm at 375°C and lower than 300 ppm at 450°C .

In order to explain the oscillations of the gas phase concentration observed in different experimental conditions, we propose they are related to periodic changes of the state of oxidation of copper in the catalyst, according to the reaction mechanism expressed by the steps reported below:



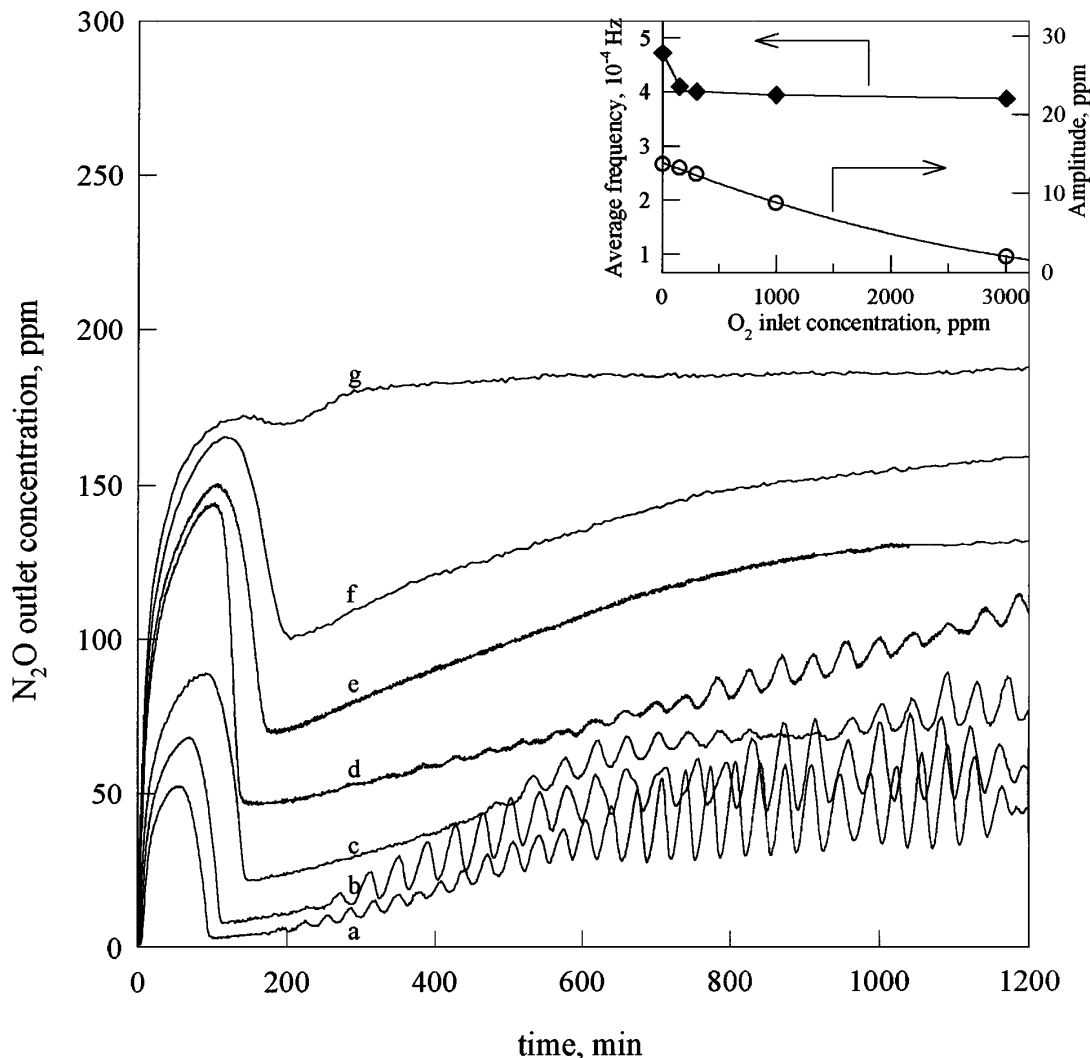
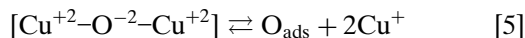
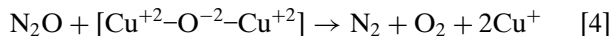


FIG. 8. N₂O outlet concentration as a function of time in N₂O decomposition on Cu-ZSM5 at 344°C and different O₂ inlet concentrations: (a) 0; (b) 150; (c) 1,000; (d) 3,000; (e) 5,000; (f) 10,000; and (g) 20,000 ppm. W/F = 0.137 g s N cm⁻³. Feed: N₂O (300 ppm) in He.



The mechanism in Eqs. [2]–[6] is based on the generally accepted statement that the Cu sites of Cu-ZSM5 can exist in two different oxidation states (Cu⁺² and Cu⁺), depending on the experimental conditions (16, 25–29). Moreover, we have attributed to N₂O the ability of acting as either oxidant or reductant of the catalyst sites. In fact, whereas step [2] describes the adsorption of N₂O on Cu⁺ sites, giving rise to oxidation to Cu⁺², step [4] express the alternative possibility for N₂O of reacting with the oxidized site to produce reduction to Cu⁺ and decomposition into N₂ and O₂. This assumption has been previously reported in (12) and well agrees with those proposed by other authors, in order

to model the N₂O decomposition in the absence of oscillations. Fu *et al.* (7) found that N₂O can reduce Fe⁺³ ions to Fe⁺² and oxidize Fe⁺² back to Fe⁺³ in FeY zeolite. Then, Christopher and Swamy (2), proposing a complete reaction mechanism for N₂O decomposition over a perovskite-type catalyst, assumed N₂O as either oxidant or reductant for the active sites. More recently, Kapteijn *et al.* (15) who have studied this reaction also on Cu-ZSM5, although not detecting any oscillations, have proposed a kinetic model based on a reaction mechanism very similar to ours (12).

It must be noted that while all mechanisms previously proposed (2, 12, 15) are single-site mechanisms, the reaction scheme expressed by the Eqs. [2]–[6] involves two close copper sites. This assumption comes from the usually accepted conclusion concerning over-exchanged Cu-ZSM5. It is known that at high copper loading the catalyst in the oxidised state contains copper pairs such as (Cu⁺²-O⁻²-Cu⁺²)

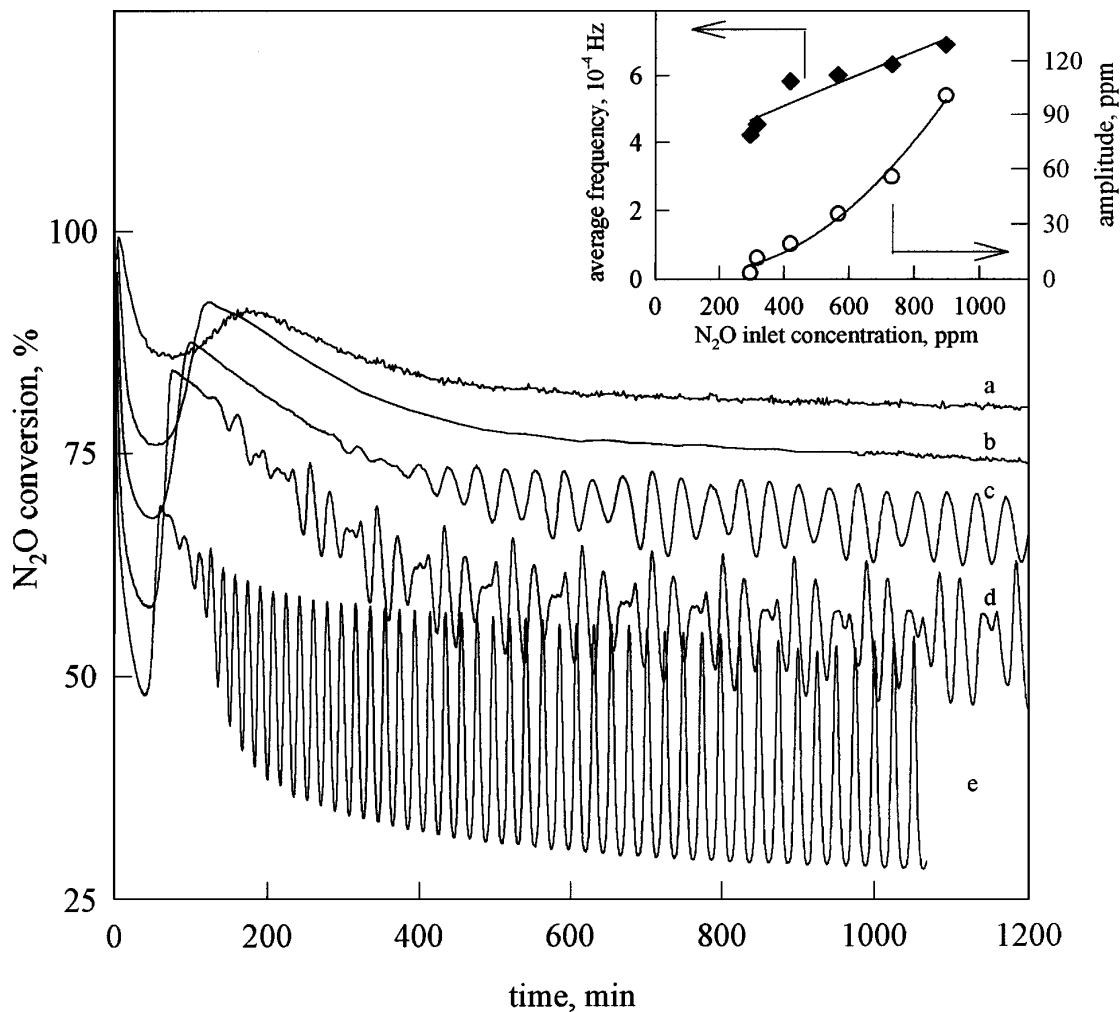


FIG. 9. N_2O conversion as a function of time in N_2O decomposition on Cu-ZSM5 at 344°C and different N_2O inlet concentration: (a) 100; (b) 200; (c) 300; (d) 550; and (e) 800 ppm. $W/F = 0.083 \text{ g s N cm}^{-3}$.

in which extralattice oxygen (ELO) is held bridged between Cu^{+2} ions. It is also known that ELO easily desorbs by just raising the temperature, producing the reduction of copper sites (16, 25–29). Consequently, step [3] between the adsorbate N_2O and a free Cu^+ site is hypothesised to occur in order to produce $(\text{Cu}^{+2}-\text{O}^{-2}-\text{Cu}^{+2})$ sites. Finally, steps [5] and [6] describe the chemical equilibrium between ELO and molecular oxygen. It has been reported that widely separated ELO atoms in Cu-ZSM5 can desorb to form O_2 (30).

The mechanism in Eqs. [2]–[6] can explain most of the experimental results. The oscillations in N_2O decomposition have been attributed to the different reaction rates of N_2O with the oxidized and the reduced copper sites. The transient phase of the reduced catalyst is described by steps [2] and [3], that are equivalent to Eq. [1]. Moreover, it may explain the effects of feed composition on the catalytic behaviour. The significant reduction of N_2O decomposition rate in the presence of O_2 (Fig. 8) is expected

if the reduced sites (Cu^+) are more active than the oxidized ones ($\text{Cu}^{+2}-\text{O}^{-2}-\text{Cu}^{+2}$), since O_2 stabilizes the Cu^{+2} form (step 5). This hypothesis is supported by the results shown in Fig. 2. Moreover, the disappearing of the oscillations, observed when the highest values of O_2 inlet concentration are used, may be attributed to the competition of the step [5] which prevails on the step [2], preventing N_2O to react with the reduced sites.

Concerning the effect of N_2O inlet concentration (Fig. 9), the proposed mechanism may produce a reaction rate less than linearly depending on N_2O concentration. In fact, the formation of increasing amounts of the species $[\text{N}_2\text{O}^--\text{Cu}^{+2}]$ results in the reduction of the total concentration of the catalyst sites Cu^+ and $\text{Cu}^{+2}-\text{O}^{-2}-\text{Cu}^{+2}$.

The interpretation of the effect of contact time on the oscillating behaviour requires to develop a kinetic model based on the reaction mechanism and on the mass balance equations on both solid and gas phase. Preliminary attempts

to model the outlet composition from a plug flow reactor have shown that the reaction mechanism [2]–[6] may produce an oscillating kinetics (31).

CONCLUSIONS

We have studied the oscillating behaviour occurring in N₂O decomposition over a highly over-exchanged Cu-ZSM5 catalyst by exploring a wide range of experimental conditions. It is resulted that a kinetic genesis for the observed oscillations must be considered, because of their isothermal nature and disappearance in diffusion-controlled regime. A specific reaction mechanism involving periodic changes of the copper state of oxidation is able to explain the observed behaviour. Moreover, the long transient phase, observed before the system attains the oscillating regime, is affected by the initial state of oxidation of copper in the catalyst. On the contrary, the dynamic regime is not dependent on the catalyst pretreatment.

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