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Isothermal oscillation during N_2O decomposition over Fe- and Fe/Pt-ferrierite: Effect of NO addition

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Abstract

Well-expressed oscillation of the N_2O decomposition over Fe- and Fe/Pt-ferrierite catalysts has been observed, differing both in parameters and conditions from the oscillation behavior described previously for the same reaction over Fe-zeolites. The observed regular oscillation in the N_2O conversion was accompanied by changes in N_2 and O_2 production in a dry N_2O/He gas stream and was quenched reversibly after NO/NO_2 addition. The results were observed in the temperature region of 400–450 °C over Fe/Pt-ferrierite, with periods of 0.5–3.5 min. For Fe-ferrierite, the temperature region for the oscillation behavior was slightly higher (i.e., 450–500 °C. In striking contrast to Fe/Pt-ferrierite, the period of oscillation did not change with temperature over Fe-ferrierite. The patterns of the oscillation over both catalysts were complex and depended on the reaction conditions.

Keywords: Fe-ferrierite; Fe/Pt-ferrierite; N_2O decomposition; Oscillation

1. Introduction

Fe-zeolites have been demonstrated to be efficient catalysts for the decomposition of N_2O [1,2] and concurrent abatement of $NO + N_2O$ [3,4], profiting from the beneficial effect on N_2O decomposition of the presence of NO [5,6]. A synergism for N_2O decomposition between Fe and Ru or Rh, loaded in high-silica zeolites, has been reported previously [7]. Such bimetallic mordenite and ferrierite catalysts have also shown considerable N_2O decomposition activity in the presence of NO.

The mechanism of N_2O decomposition was proposed by Mul et al. [8] and Pérez-Ramírez et al. [9] as a sequence of reaction steps involving direct formation of N_2 molecule and slower formation of an oxygen molecule via primarily formed O_s,

$$N_2O \rightarrow N_2 + O_s, \quad \text{fast}, \tag{1}$$

$$O_s + O_s \rightarrow O_2, \quad \text{slow}, \tag{2}$$

$$O_s + N_2O \rightarrow N_2 + O_2, \tag{3}$$

$$O_s + N_2O \rightarrow 2NO. \tag{4}$$

Step (1) is connected with direct release of molecular nitrogen and oxygen deposition on the active site. It has been proposed that formation of molecular oxygen via pairing of oxygen atoms in step (2) is slow and represents the rate-limiting step [8,9] of the overall reaction. The alternative route to N_2 and O_2 molecules includes interaction of a second N_2O molecule from the gas phase with previously formed O_s (step (3)) [10,11]. Interaction between O_s and N_2O could also produce NO (step (4)), as found by, e.g., Nováková et al. [12,13]. However, the significance of steps (3) and (4) for the final N_2O decomposition rate is not clear.

It has been shown that NO added to the reaction mixture accelerates N_2O decomposition [3–8], simply via the scavenging effect on O_s atoms through the reaction

$$O_s + NO \rightarrow NO_2, \tag{5}$$

or by a mechanism where adsorbed NO could act as a cooperating active site formally mediating two O_s recombinations [12,13].

The gas-phase NO_2 thus produced could be transformed back to NO under assistance of the active site,

$$NO_2 + O_s \rightarrow NO + O_2, \tag{6}$$

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or the NO_2–NO redox cycle could provide for formation of several O_2 molecules. In both cases, both mechanism might explain why one molecule of NO could assist in the decomposition of several N_2O molecules [3–5]. In this connection, the extent of the reaction in step (4) producing NO could play a key role in controlling the main N_2O decomposition reaction. Recently [14], we reported a contribution to mechanism of N_2O decomposition over Fe-zeolites with low iron content by also taking into consideration the distance between isolated Fe ions and the positive role of formation of an electron-acceptor Lewis site. However, in the presence of NO in the feed, both of these effects cease to play an important role for the N_2O decomposition rate.

The complex system of these individual reactions, combined with possible changes in the state of the surface active sites, provides a possible route for complex dynamic behavior of the N_2O decomposition reaction.

Regular changes in the N_2O decomposition rate over metal-loaded zeolites were observed previously by Ciambelli et al. [15–17], Turek et al. [3,18–20], and Fanson et al. [21] for Cu-ZSM-5 and recently by Schay et al. [22,23] for Cu-AlTS-1. However, the oscillation in the N_2O decomposition over Fe-zeolite catalysts has been only recently reported by El-Malki et al. [10,11] over Fe-ZSM-5.

Both Ciambelli et al. [15–17] and Turek et al. [18–20] reported oscillation over overexchanged Cu-ZSM-5 samples, but, as can be illustrated, the proposed conditions and models differed. Ciambelli et al. [15–17] found isothermal oscillation in decomposition of a dry N_2O/He mixture in the temperature range of 323–400 °C. The conversion level was changing by about 10 rel% within a period of about 30 min. Both the N_2O decomposition activity and the oscillation behavior were suppressed by the addition of NO or O_2 [15]. Those authors excluded the possibility that the oscillation could reflect transport phenomena; instead, they attributed it to changes in the reaction kinetics. They proposed a kinetic model [17], explaining the oscillation behavior by periodical changes in the redox state of the Cu-bi-nuclear center, assumed for the active site. The kinetic model was able to closely predict the experimentally observed oscillation and the role of the deposited oxygen. However, it did not take into account the role of NO. Turek et al. [18–20] reported oscillation behavior at temperatures of 375–450 °C. The oscillation period was found to be shorter (i.e., in the range of 7–9 min), but with a strong dependence on temperature, thus increasing to 30 min at lower temperatures. Using transient-response experiments, these authors identified various stages of oscillation and found a correlation between N_2O conversion and periodical changes in the coverage by adsorbed species, namely $–NO_3$ and $–O_s$. The authors suggested an important role of NO in the oscillation mechanism.

The only emergence of an isothermal oscillation over Fe-zeolite in N_2O decomposition has been observed by El-Malki et al. [10,11] over highly loaded Fe-ZSM-5 catalyst. The system behaved in an oscillation manner exclusively using a wet N_2O/He stream and displayed periods of 7–15 min in the temperature range of 450–550 °C. The patterns did not exhibit a sinusoidal character, but rather showed a peak-to-peak shape. They appeared after 2–3 h of reaction time, in the presence of at least of 3% water in the feed. Significantly, the addition of NO or O_2 did not quench the oscillations, but the oscillation period was longer in the presence of NO. The authors concluded that oscillation over Fe-ZSM-5 differed significantly from that observed by previous investigators for Cu-ZSM-5. Based on the need for water in the reaction feed for the oscillating behavior, a mechanistic model was proposed, considering periodic changes in the concentrations of several types of active sites, differing in the number of H_2O ligands and having varying activities for the N_2O decomposition reaction [10]. Nevertheless, they left open the question of which component of the gas-phase reaction mixture might be responsible for synchronization of these oscillations.

It is generally accepted that the oscillatory behavior of the N_2O decomposition found so far does not reflect transport phenomena [15–17], but has some relationship to specific aspects of the reaction kinetics and mechanism [17]. However, the mechanisms considered to date for development of oscillations are disputable.

The positive role of Pt addition in the activity of Fe-ferrierite for N_2O decomposition has been recently noticed [24]. Accordingly, in the present paper, oscillation over both Fe- and Fe/Pt-ferrierite catalysts during N_2O decomposition is presented.

2. Experimental

Parent NaK-ferrierite zeolite, with a composition of Si/Al 8.5, Na 0.47 wt%, and K 1.98 wt%, containing 170 ppm of iron as an impurity, was provided by TOSOH Co. This zeolite was transformed into the NH_4^+-ferrierite form by a conventional ion-exchange procedure using NH_4NO_3 solution. Loading of Fe ions into the zeolite was performed by a technique in which dried NH_4^+-ferrierite was exposed to solution of $FeCl_3$ in acetyl acetone [25,26]. The resulting Fe content was 0.55–1.00 wt%, corresponding to an Fe/Al ratio of 0.06–0.12. The prepared catalysts are designated here as Fe-ferrierite. As checked by Mössbauer analysis of the ^{57}Fe-ferrierite sample prepared by the same procedure, >85% of the present iron was in cationic positions.

The loading of Pt ions into zeolite was achieved by a conventional ion-exchange technique with a 0.001 M solution of $Pt(NH_3)_4Cl_2 \cdot H_2O$ in water, using 25 mL of solution per g of zeolite. The prepared zeolite was then washed and dried at room temperature. The catalyst thus prepared is designated as Pt-ferrierite.

The Fe/Pt-ferrierite sample was prepared using Pt-ferrierite zeolite and introducing Fe in the second step as described above for Fe-ferrierite preparation. The resulting Fe and Pt contents were 1.05 and 0.51 wt%, corresponding to Fe/Al 0.12 and Pt/Al 0.02, respectively. The catalyst is designated as Fe/Pt-ferrierite. It could be anticipated that, in the as-prepared sample, Fe and Pt ions were introduced predominantly into the cationic positions [24–26].

The activity and dynamic behavior of Fe-ferrierite catalyst in N_2O decomposition was studied in a glass flow microreactor with an i.d. of 9 mm. While a reactor inlet was realized via 4-mm-i.d. glass tubing, the reactor outlet was connected via 1.5-mm-i.d. tubing to product analysis, providing for faster detector response.

The components of the reaction mixture were fed using a set of mass-flow controllers (ELMET-CZ) to a mixing line and diluted with a carrier gas, helium. Thus, the resulting flow rate of 100 or 300 $cm^3\ min^{-1}$ was adjusted, corresponding to GHSV of ca. 30,000 or 90,000 h^{-1}, respectively. Sample activation at 450 °C in a flow of pure He or a mixture of O_2 and He, preceded each catalytic experiment.

Rapid measurement of the concentration of each reaction components at the outlet was facilitated via an on-line connected quadrupole mass spectroscope (Balzers QMG420) in the multiple-ion detection mode. The connection of the output of the reactor to the quadrupole mass spectroscope was realized via a jet–separator interface. This interface enabled measurement of all of the components down to low concentration levels, due to a separation effect enriching the He carrier gas in heavy molecules, the fast response of quadrupole mass spectroscope, and the negligible delay in the jet–separator interface. Pressure at the reactor output was typically ~105 kPa. An adjusted portion of the flow from reactor output was fed through a calibrated needle valve into the jet separator, with a pressure of ca. 50 Pa. The enriched mixture was then fed into the ionization part of the mass spectroscope, in which the pressure was typically $\sim 1 \times 10^{-5}$ Pa.

The mass spectroscope was calibrated using pure gases, regarding their fragmentation. This allowed evaluation of the N_2O concentration using the molecular mass (44) and NO_2 using the mass (46). For NO, the mass (30) used was obtained by subtracting parts corresponding to the (30) fragments originating from N_2O and NO_2. The concentrations of NO and NO_2 were registered independently by a chemiluminescence analyzer (VAMET-CZ). Mass (28) was used for N_2 after subtracting the part corresponding to the (28) fragment from N_2O and (32) for O_2. In selected experiments, the on-line analysis of N_2O and NO/NO_2 was performed using an Advance Optima IR analyzer (ABB Co., Germany) and chemiluminescence analyzer (VAMET-CZ), respectively. N_2 and O_2 were checked regularly off-line using a Hewlett-Packard 5890 II gas chromatograph.

Determining the delay in the appearance of N_2 and O_2 after the addition of N_2O (500 Pa) to a Fe-FER (147 mg) freshly activated by evacuation and calcination in oxygen (10^4 Pa at 450 °C) was followed in a batch reactor (total volume, 165 mL). A very small amount of the gas phase was continuously introduced into a quadrupole mass spectroscope (Balzers QMG420) using a needle valve, and the molecular masses (28, 30–34, 36, 44, 46–51) were registered. The decomposition of N_2O and onset of N_2 and O_2 formation were detected at temperatures of 280–400 °C.

3. Results

Fe-ferrierite was active in the N_2O decomposition at temperatures above 350 °C. N_2O was converted into N_2 and O_2 in a strictly stoichiometric ratio, that is, with a N_2/O_2 ratio equal to 2. Pt-ferrierite displayed only negligible activity for N_2O decomposition. Nevertheless, N_2O decomposition was substantially accelerated by adding Pt to the Fe-containing catalyst; thus, the activity of Fe/Pt-ferrierite exhibited a strong synergetic effect of the mutual presence of Pt and Fe in ferrierite.

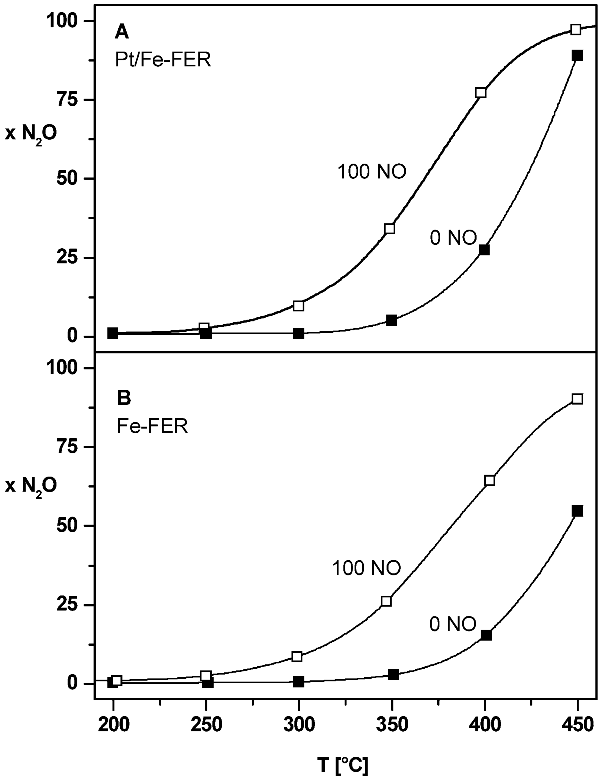

Fig. 1. Dependence of the decomposition of 1000 ppm N_2O on temperature in simple (■) and NO assisted (100 ppm NO added) (□) reactions over Fe/Pt-FER (Fe/Al 0.12; Pt/Al 0.02) (A), and Fe-FER (Fe/Al 0.12) (B). N_2O determined by IR analyzer.

Adding NO further accelerated N_2O decomposition over both Fe and Fe/Pt-ferrierite (see Fig. 1). Depending on the conditions, part of the added NO was oxidized into NO_2, consuming oxygen formed by N_2O decomposition. No evidence of a change in the sum of $NO + NO_2$ concentrations, either due to NO decomposition or through formation of higher nitrogen oxides (N_xO_y), was observed.

The oscillation appeared after several hours of feeding of a dry N_2O/He stream over the catalyst at temperatures of 400–500 °C. This effect is depicted in Fig. 2A for $T = 400\,°C$ and Fe/Pt-ferrierite catalyst. The characteristic period of oscillation in this case was about 180 s, which was ~300 times higher than the contact time.

Changes in the concentrations of N_2O and the produced N_2 and O_2 are depicted in Figs. 2–5, as a function of time, for the N_2O feed in He. No synchronous fluctuation of the temperature of the catalyst layer and composition of the reaction outlet was observed. It should be noted that the oscillation periods are much shorter than those reported by El-Malki et al. [10,11] for Fe-ZSM-5.

For the present experiment, the typical time-on-stream behavior at $T = 400\,°C$ is illustrated, with a higher level of N_2O

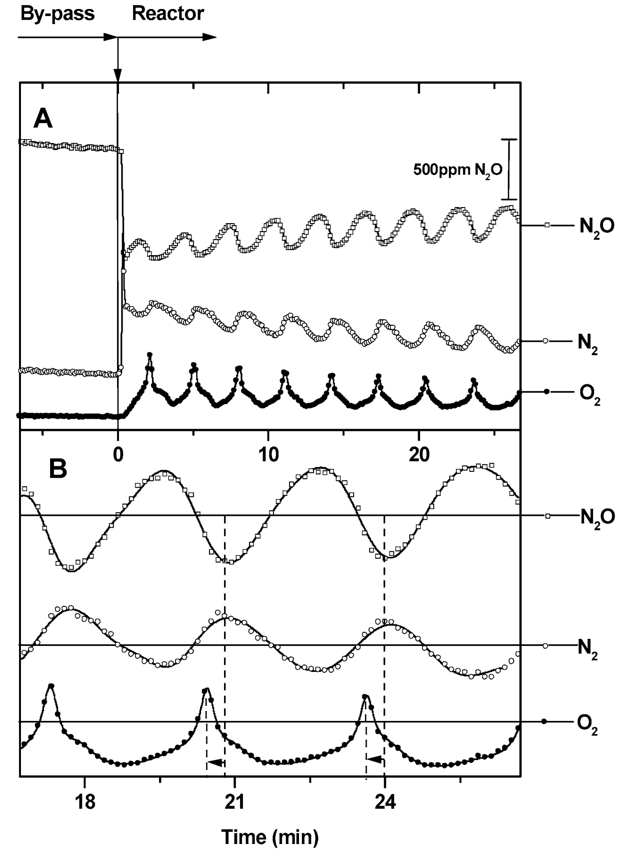

Fig. 2. The MS signals representing outlet concentrations of N_2O (□), N_2 (○) and O_2 (●) as a function of time for feed composition of 1000 ppm N_2O in He and $T = 400\,°C$ over Fe/Pt-FER (Fe/Al 0.12; Pt/Al 0.02) (A), and fitted curves with subtracted background (B).

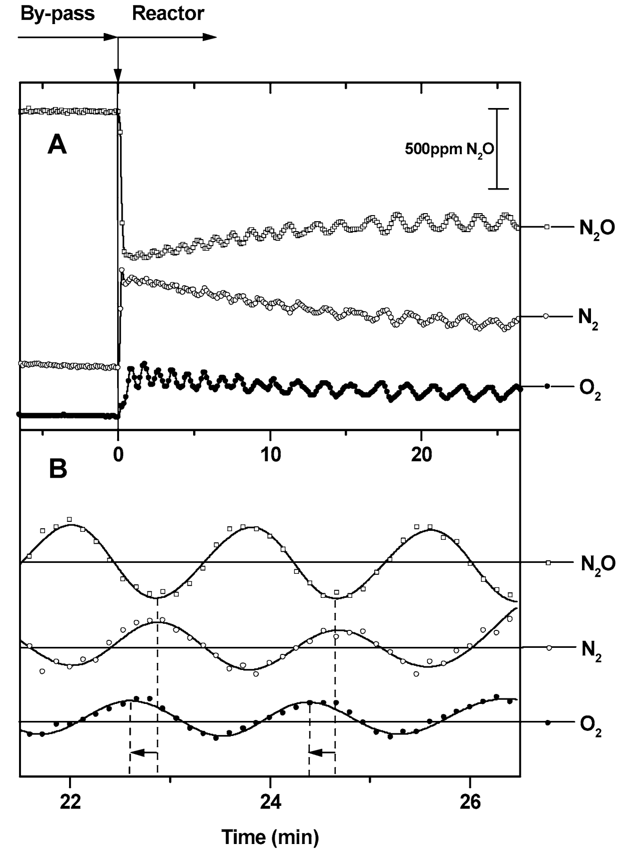

Fig. 3. The MS signals representing outlet concentrations of N_2O (□), N_2 (○) and O_2 (●) as a function of time for feed composition of 1000 ppm N_2O in He and $T = 450\,°C$ over Fe-FER (Fe/Al 0.06) (A), and fitted curves with subtracted background (B).

conversion at the beginning of the experiment (40–50% in the presented case), which then decreased and stabilized over ~20 min to a lower value (here ~25%). The oscillation appeared immediately after the feed introduction and had a regular sinusoidal pattern with an amplitude of ±13% of the conversion. Under constant feed composition and temperature, the oscillations were stable for several hours.

The changes in N_2O and N_2 were exactly in phase (the maxima of the N_2 signal correspond exactly to the minima of the N_2O signal). On the other hand, the maxima of O_2 were slightly shifted compared with N_2O and N_2. Assuming that the oxygen production emerged in advance of the N_2 (see the following discussion), the maximum production of O_2 occurred ~20 s before N_2 and N_2O reached their extremes. Assuming that wave of N_2 forms in advance of O_2, the oxygen production was delayed for about 160 s. For better illustration in Fig. 2B, the monotonic evolution background was subtracted and fitted by a periodical function.

Similar oscillatory behavior was observed with the Fe-ferrierite catalyst. However, the temperature range of oscillatory behavior was shifted to higher temperatures, and, moreover, the period of the steady-state behavior before the oscillation behavior was typically much longer and less predictable for Fe-ferrierite than for Fe/Pt-ferrierite. The character of the oscillation on Fe-ferrierite at $T = 450\,°C$ is illustrated in Fig. 3. The amplitude was only ±3% of N_2O conversion with a period of about 100 s. The amplitude and shape of the oscillation developed gradually and stabilized after ca. 20 min. Other features were similar to those described above for Fe/Pt-ferrierite. As in the previous case, the oxygen wave and the change in N_2O and N_2 concentrations had a phase shift similar to that for Fe-ferrierite.

3.1. Effect of temperature

The change in the oscillation period and pattern with temperature over Fe/Pt-ferrierite is shown in Fig. 4A. The oscillation appears in a relatively narrow temperature range of 400–450 °C. It appears at ~400 °C, and its amplitude gradually increases with increasing temperature up to 420 °C. A further temperature increase then brings a decrease in the amplitude, and changes in N_2O conversion are hardly noticeable at temperatures above 450 °C. With increasing temperature, the period of oscillation grew shorter. Moreover, the oscillation pattern changes with temperature. The shapes of the waves were quite regular in the 400–420 °C region, whereas at slightly higher temperatures, the amplitudes of the waves were periodically changing, with minima of amplitude repeating regularly about every 20 min. This behavior could be tentatively explained by the existence of two superimposed periodic processes with different periods.

In striking contrast to Fe/Pt-ferrierite, no change in the period of the oscillation with temperature was found over Fe-ferrierite.

3.2. Effects of N_2O concentration

The concentration of N_2O in the input was varied in the range of 100–1500 ppm. Its effect on the period of oscillation over Fe/Pt-ferrierite is depicted in Fig. 4B, showing that the oscillation periods decrease regularly with increasing N_2O concentration. The amplitude decreases with decreasing N_2O concentration, whereas their periods are longer. The global variations of the oscillation period with both temperature and N_2O concentration are depicted in Figs. 4C and 4D, respectively.

3.3. Effect of NO addition on oscillation

Although NO addition increased the level of N_2O decomposition over both Fe and Fe/Pt-ferrierite catalysts, at the same time it rapidly extinguished all types of oscillation in the entire temperature range studied (see Fig. 5). The response of the oscillation to the addition and removal of NO from the feed was studied at various temperatures and NO-to-N_2O ratios, also using different NO/NO_2 compositions of the admixture. Fig. 6 shows a typical response to the addition of NO/NO_2 for Fe-ferrierite, showing the results at 400 °C. The transitions between oscillating and stable conversion states are obviously connected with lower and higher conversion levels, responding immediately on NO addition and slowly decreasing after stopping the NO feed into the reaction stream.

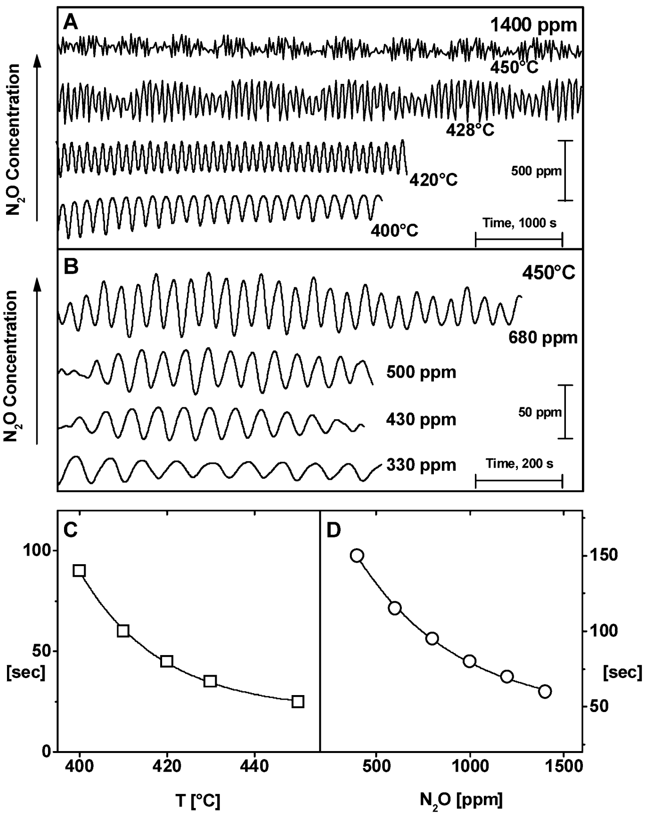

Fig. 4. Changes of the oscillation pattern over Pt/Fe-FER (Fe/Al 0.12; Pt/Al 0.02): (i) with temperature using 1400 ppm N_2O (A); (ii) with concentration of N_2O at temperature of 450 °C (B). N_2O determined by IR analyzer. Summarizations of the changes of the oscillation period with temperature for 1400 ppm of N_2O (□), (C); and with concentration of N_2O at 415 °C (○) over Pt/Fe-FER (D).

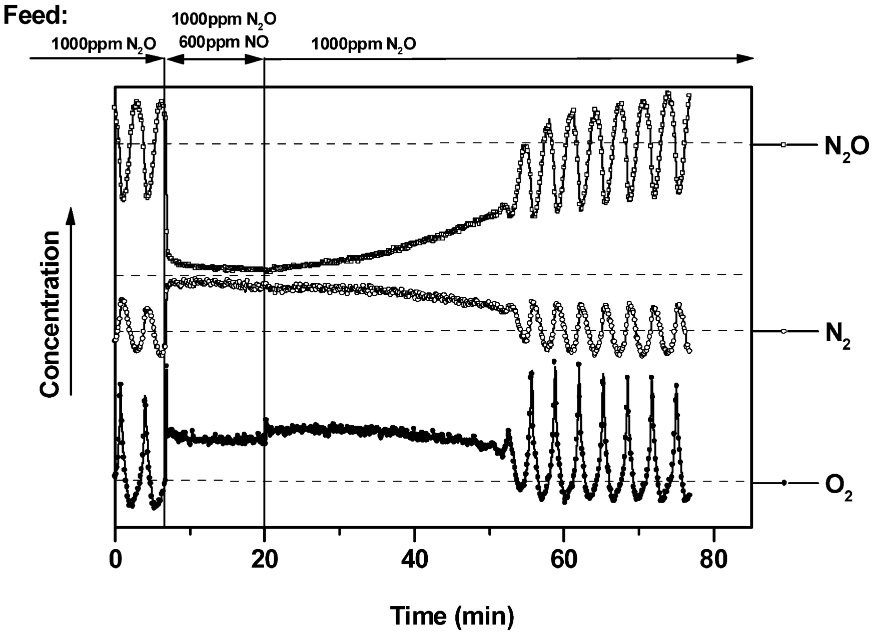

Fig. 5. The MS signals representing outlet concentrations of N_2O (□), N_2 (○) and O_2 (●) as a function of time during the alteration between the simple decomposition (1000 ppm N_2O) and NO assisted regime (1000 ppm N_2O + 600 ppm NO) at $T = 400\,°C$ over Fe/Pt-FER (Fe/Al 0.12; Pt/Al 0.02).

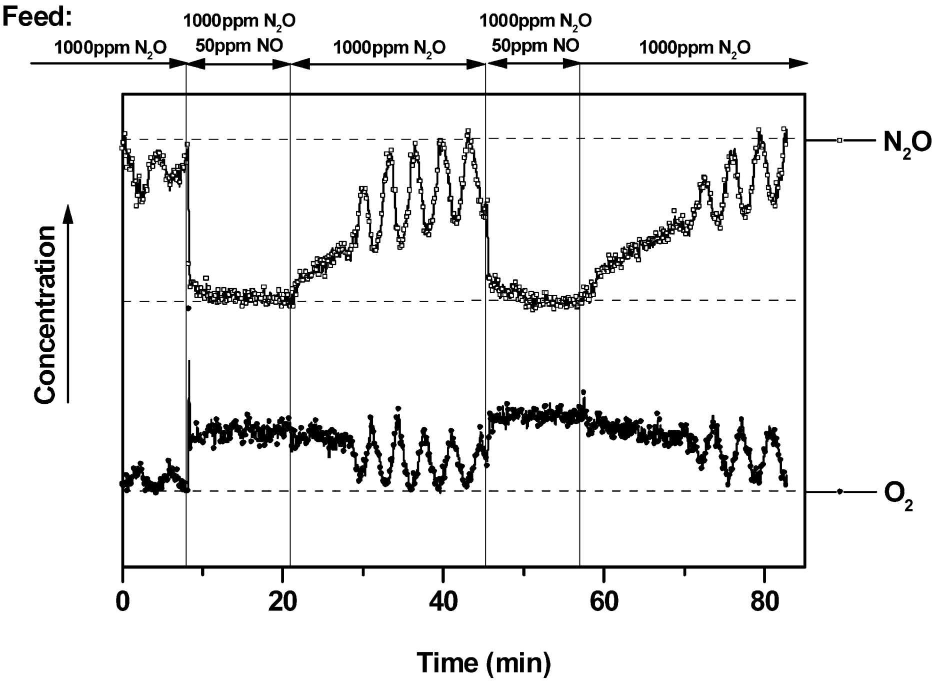

Fig. 6. The MS signals representing outlet concentrations of N_2O (□) and O_2 (●) as a function of time during the alteration between the simple decomposition (1000 ppm N_2O) and NO assisted regime (1000 ppm N_2O + 50 ppm NO) at $T = 400\,^\circ C$ over Fe-FER (Fe/Al 0.06).

The addition of NO immediately decreased the content of N_2O in the reactor outlet; also, the periodic changes in the N_2O as well as N_2 and O_2 ceased, and the system stabilized at the steady-state performance. After the NO co-feeding stopped, the conversion of N_2O slowly decreased and started to oscillate after about 15 min. At the transition region between the steady-state and the oscillation performance, one or more smaller waves before stabilization of the periodic changes could be identified in all three components. The amplitudes of the first waves are very likely below the limits of the experiment.

Once the sustained oscillation was achieved, its parameters were stable for the entire experimental run, that is, for several hours. For both Fe-ferrierite and Fe/Pt-ferrierite, the appearance/disappearance of oscillations was completely reversible and obviously reflected the presence of NO possibly in the adsorbed form on the catalyst surfaces. It was repeatedly found that the time before N_2O decomposition returned to the lower level and began oscillating after ceasing the addition of NO was longer for Fe/Pt-ferrierite.

As shown in additional experiments, a similar effect of oscillation suppression was obtained by co-feeding H_2 or CO (not shown) into the feed even in low concentrations. The addition of these components was associated with increased conversion.

3.4. Delay of the appearance of O_2 after N_2O introduction

To determine the delay in the appearance of gas-phase oxygen after the addition of N_2O over freshly activated Fe-ferrierite, onset of N_2 and O_2 formation was followed at temperatures of 300–400 °C. We found that this delay is strongly temperature-dependent, decreasing from about 180 s at 300 °C to 30 s at 350 °C, and is <10 s for temperatures above 400 °C.

4. Discussion

After a period of steady-state operation in N_2O decomposition, both iron-containing ferrierite catalysts displayed well-expressed spontaneous rate oscillations in this reaction. The conditions for oscillation behavior as well as its parameters differ fundamentally from those reported previously for Fe-ZSM-5 zeolite by El-Malki et al. [10,11]; namely, oscillation appears in a dry N_2O stream and is suppressed by the addition of NO.

The sinusoidal oscillation occurring over Fe-ferrierite was found at lower temperatures than over Fe-ZSM-5 [10,11]. Furthermore, it is characterized by a higher frequency that is temperature-independent, and the oscillation is fully quenched by the addition of NO, whereas a negligible effect of NO on oscillating behavior was found over Fe-ZSM-5. Moreover, in contrast to Fe-ferrierite, the presence of water in the feed was a necessary condition for periodic changes in N_2O conversion over Fe-ZSM-5. All of the aforementioned observations are significant for the claim that the oscillations over Fe-ferrierite and Fe-ZSM-5 are basically different.

El-Malki et al. [10,11] suggested that the structural reasons for periodic activity changes are directly related to changes in the level of hydration of the active site in Fe-ZSM-5. It is proposed that the active sites of Fe-ZSM-5 are Fe···Fe bi-nuclear species or well-defined Fe_xO_y clusters, typical for high concentration levels of iron in the zeolite, whereas the Fe/Al ratio in Fe-ferrierite and Fe/Pt-ferrierite samples reached only 0.06–0.12, and, accordingly, mostly isolated cationic sites should be anticipated along with a negligible amount of Fe_xO_y species, as confirmed by FTIR [24] and Mössbauer spectroscopy [14]. Obviously, the mechanism proposed for Fe-ZSM-5 could be excluded over Fe-ferrierite.

Analysis of the time sequence of N_2 and O_2 is crucial to understanding the nature of the oscillation phenomenon. From the forms of the N_2O, N_2, and O_2 curves (see, e.g., Figs. 2 and 3) could not be directly identified, whether the O_2 wave follows *after* (a shift of about 80 s in Fig. 3) or in *advance* of the N_2 wave (a shift of about 20 s).

In the concentration curves for N_2O and its decomposition products during the transition period between the steady-state and the oscillation performance (Figs. 5 and 6) could be identified one or more of smaller waves before stabilization of the rather stable oscillation behavior. Nevertheless, based on these results, it is hardly possible to indicate whether the N_2O or O_2 wave initiates the oscillation process, because the amplitudes of the first waves are obviously below the limits of the experiment.

The delayed appearance of O_2 in the gas phase compared with that of N_2 after splitting of the N_2O molecule is well established. It has been convincingly explained by the slower process of O_s recombination [27,28], which, as shown previously, includes both the O_s and the framework oxygens [12, 13]. Nevertheless, as shown by the experiments demonstrating the appearance of N_2 and O_2 in the gas phase after introduction of N_2O over the Fe-FER sample, the delay between O_2 and N_2 decreases significantly with increasing temperature. Thus, the delay in the appearance of O_2 appearance after N_2 at temperatures above 400 °C (i.e., at the region of oscillation behavior) is much shorter than the shift of about 80 s observed between the maxima of the periodic changes of N_2 and O_2 over Fe-FER at temperatures above 400 °C (see Fig. 3).

Accordingly, we propose that the O_2 wave formed in advance of the N_2 wave, and thus the oxygen "overproduction" represents the opening step in the development of the oscillation behavior. We further assume that the primary process controlling the periodic changes in oxygen formation would be changes at the surface coverage of the NO_{ads} produced by the reaction (4). This is consistent with the observation showing acceleration of the O_s recombination process after saturation of the surface by NO from the gas phase. (For connections between the NO presence and N_2O decomposition, see also [29,30].) Thus, in the absence of a priori mechanistic and structural reasons for the periodic variations in N_2O decomposition, a new mechanism for such behavior is proposed, connected with buildup and accumulation of adsorbed NO. The reaction (3), predicting the formation of O_2 and N_2 in parallel, could be excluded as a process controlling the present oscillation over Fe-ferrierite, characterized by a stable shift between N_2 and O_2 formation. On the other hand, there exists a potential for a complex interconnection between reaction (4), producing NO, and reaction (2), in which NO plays a role of accelerator. Because the role of NO_{ads} in reaction (2) is probably a local effect, the O_s–NO_{ads} distance on the zeolite surface also should be postulated as an important parameter. Thus, interrelation of reactions (1), (2), and (4) can potentially explain a complex dynamic behavior during the decomposition of N_2O over Fe-ferrierite, which in the specific temperature region could provide the observed oscillating behavior. The role of Pt, positively influencing both the N_2O conversion and the oscillation behavior, is obviously complex, as indicated by the changes in the shapes of the concentration waves of all components.

Thus, the variation in N_2O decomposition rate is directly connected to variation in the surface coverage by the NO_{ads} species. This assumption is also supported by the fact that adding H_2 or CO, which has been shown to block NO_{ads} formation [12,13], also suppresses the oscillation. The same argument could follow from the fact that full saturation of the surface by adding NO to the feed eliminates the role of the reaction (4), and the connected restart of the oscillating behavior is then parallel to the activity decrease after the addition of NO to the feed is stopped.

5. Conclusion

This paper reports oscillation of N_2O decomposition over Fe-ferrierite and Fe/Pt-ferrierite for the first time, and proposes the mechanisms behind this oscillation, including variation in the surface coverage by the NO_{ads} species. The nature of the oscillation is substantially different than that observed previously during N_2O decomposition on either Cu-ZSM-5 or Fe-ZSM-5.

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