Catalysis Letters 30 (1995) 313–318

# Isothermal oscillations in the catalytic decomposition of nitrous oxide over Cu-ZSM-5

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Received 6 October 1994; accepted 2 November 1994

The catalytic decomposition of nitrous oxide was studied on a copper-exchanged ZSM-5 catalyst in the temperature range 648–723 K. Using a mixture of 1000 ppm $N_2O$ in nitrogen, isothermal oscillations both in nitrous oxide and oxygen concentrations occurred, accompanied by formation of small amounts of NO. While the addition of excess oxygen did not significantly change frequency and amplitude of the oscillations, even the presence of small amounts of NO immediately quenched the oscillations. The reacting system then remained in the ignited state at high nitrous oxide conversions.

**Keywords:** nitrous oxide; decomposition; oscillations; Cu-ZSM-5

## 1. Introduction

Oscillations in heterogeneous catalytic systems have been described in numerous reports. The present state-of-the-art has quite recently been reviewed by Schüth et al. [1], Imbihl [2] and Slin'ko and Jaeger [3]. Oscillations are in most cases restricted to bimolecular reactions, the only monomolecular exception observed so far being thermokinetic oscillations in the decomposition of methylamine on noble metal catalysts [4]. The oscillating $N_2O$ decomposition over copper oxide, reported as early as 1968 by Hugo [5], did not originate from the instability of the surface reaction, but was rather due to the instability of the reactor system used under the particular conditions with respect to heat and mass transfer effects [1,3].

Recently, Li and Armor [6,7] have shown that metal exchanged ZSM-5 zeolites are highly active catalysts for the decomposition of nitrous oxide under much milder conditions than previously reported for other catalysts. In the following, we briefly wish to report that isothermal oscillations occur when dilute mixtures of $N_2O$ in nitrogen are contacted with copper exchanged ZSM-5.

## 2. Experimental

The copper exchanged ZSM-5 catalyst was prepared by $Cu^{2+}$ ion-exchange similar to a method proposed by Li and Armor [8]. Elemental analysis of the starting material, Na-ZSM-5 supplied by Bayer, resulted in molar ratios of $Si/Al = 37$ and $Na/Al = 1.1$. 20 g of Na-ZSM-5 dried at 383 K for 16 h were added to 3.5 $\ell$ of an aqueous 0.006 M copper acetate solution at room temperature. After 24 h under vigorous stirring, the product was filtered and the procedure was repeated twice for 14 and 8 h, respectively. The obtained Cu-ZSM-5 was washed by re-suspending in 3.5 $\ell$ of deionized water, filtered, dried for 16 h at 383 K and subsequently calcined in air for 6 h at 823 K. Elemental analysis of the exchanged zeolite gave molar ratios of $Na/Al = 0.1$ and $Cu/Al = 0.80$ corresponding to an apparent $Cu^{2+}$ exchange level of 160%. The calcined zeolite powder was pressed to tablets, crushed and sieved to obtain a fraction of 315–500 μm.

The catalyst (0.25 g) was placed in a pyrex glass tube reactor which was heated electrically. The temperature in the catalyst bed was measured separately using a thermocouple. The gases $N_2O$, NO, $O_2$ and $N_2$ were added via thermal mass flow controllers (Brooks, 5850). The exit concentrations were monitored by means of a magnetic oxygen analyzer (Hartmann and Braun, Magnos 6G) and nondispersive infrared analyzers for $N_2O$ (Perkin Elmer, Spectran 677) and NO (Rosemount, Binos 4). Prior to experiments, the catalyst was pretreated in flowing nitrogen (500 $cm^3/min$, NTP) at 773 K for 1 h. The measurements were then carried out in the temperature range 648–723 K, typically using a gas mixture of 1000 ppm $N_2O$ in nitrogen at a total flow rate of 500 $cm^3/min$ (NTP).

## 3. Results

Fig. 1 depicts the outlet concentrations of oxygen, nitrous oxide and nitric oxide as a function of time when a gas mixture of 1000 ppm $N_2O$ in nitrogen is contacted with Cu-ZSM-5 at 723 K. Irregular oscillations in all concentrations $y_i$ measured can be observed. Minima in the nitrous oxide concentration correspond to maxima in the oxygen concentration as is expected from the stoichiometry of the decomposition reaction. The average oxygen and nitrous oxide concentrations over a period of 45 minutes both amount to a mean nitrous oxide conversion $X_{N_2O}$ of about 90%. On the other hand, the amplitudes in the oxygen concentration are much higher than the corresponding values for $N_2O$. It is interesting that traces of nitric oxide (average concentration $\bar{y}_{NO} = 8$ ppm) are also formed with peaks of NO always emerging when the system is in the state of high conversion.

The temperature in the catalyst bed was constant within ±0.5 K and fluctuations did not follow the pattern of concentration oscillations. Thus the observed oscillations appear to be isothermal.

Fig. 2 illustrates the influence of reaction temperature on the oscillations of

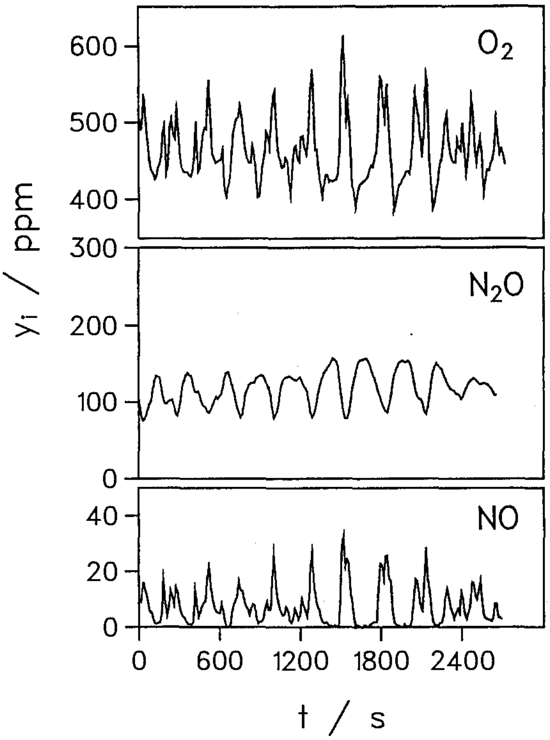

Fig. 1. Outlet concentrations of $O_2$, $N_2O$ and NO as a function of time. 1000 ppm $N_2O$ in $N_2$, $T = 723$ K.

nitrous oxide concentration. The oscillations remain irregular, but it can be clearly seen that the frequency of the oscillations decreases with decreasing temperature. In the whole temperature range studied, the conversions calculated from the nitrous oxide and oxygen balance are in good agreement. In all cases, however, minor amounts of nitric oxide ($\bar{y}_{NO} < 8$ ppm) are formed.

Table 1 summarizes the results obtained using a reaction mixture containing 1000 ppm NO and 1 vol% $O_2$ in nitrogen. The addition of oxygen does not affect amplitude or frequency of the oscillations, but slightly reduces the average nitrous oxide conversion.

In contrast, the presence of only small concentrations of nitric oxide in the reaction mixture markedly influences the behaviour of the system. Fig. 3 compares the oscillations observed using 1000 ppm $N_2O$ in nitrogen at 723 K with results obtained by addition of different amounts of NO. With only 10 ppm nitric oxide at reactor inlet, both frequency of the oscillations and nitrous oxide conversion are significantly increased. When the NO level at reactor inlet is shifted to 20 ppm, the oscillations are quenched and the system remains in a state of high $N_2O$ conversion. Further increase of the NO inlet concentration only slightly enhances the catalyst activity. At 723 K, the system responded in any case within less than five

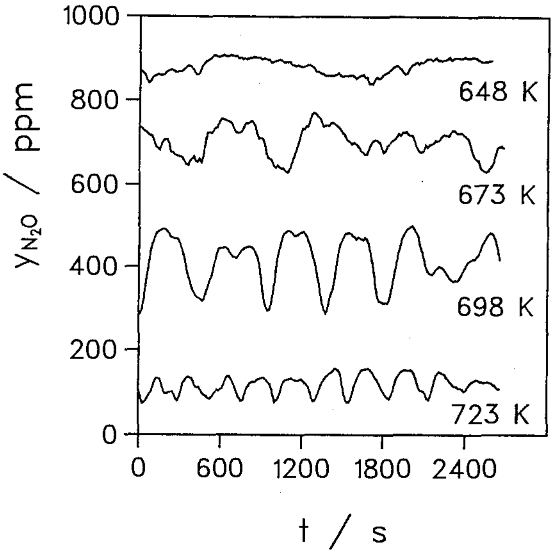

Fig. 2. Effect of reaction temperature on nitrous oxide outlet concentration. Reaction conditions as given in fig. 1.

minutes to rapidly switching on or off the added nitric oxide. Addition of NO as well as an increase of temperature under working conditions resulted in immediate formation of peaks of nitric oxide and oxygen, while no such phenomenon was observed for nitrous oxide. Thus, both NO and $O_2$ seem to be present on the catalyst surface under reaction conditions.

When adding NO to the nitrous oxide/nitrogen mixture at 723 K, inlet and outlet NO concentrations are always very similar, thus NO decomposition does not seem to take place to a considerable extent. This was confirmed by passing a mixture of 100 ppm NO in nitrogen over the catalyst revealing no detectable nitric oxide conversion.

Table 1 also shows results obtained with the mixture of 1000 ppm $N_2O$ and

Table 1
Nitrous oxide conversions (average values in the case of oscillations) for various gas compositions as a function of temperature

| T (K) | $\bar{X}_{N_2O}$ | | $X_{N_2O}$ 1000 ppm $N_2O$ 100 ppm NO |
|---|---|---|---|
| | 1000 ppm $N_2O$ | 1000 ppm $N_2O$ 1 vol% $O_2$ | |
| 648 | 0.13 | 0.13 | 0.27 |
| 673 | 0.32 | 0.29 | 0.58 |
| 698 | 0.61 | 0.56 | 0.85 |
| 723 | 0.90 | 0.82 | 0.98 |

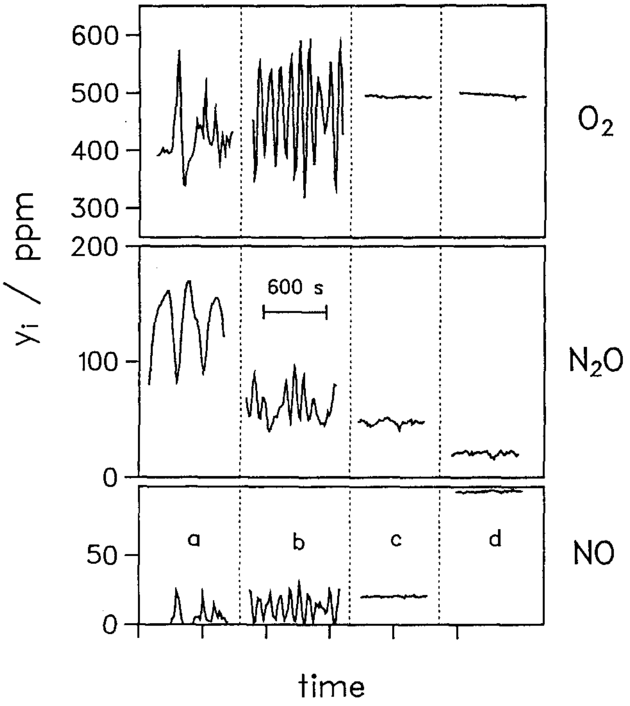

Fig. 3. Influence of NO addition upon the outlet concentrations of $O_2$, $N_2O$ and NO. 1000 ppm NO, $T = 723$ K, (a) no NO added, (b) 10 ppm NO, (c) 20 ppm NO, (d) 100 ppm NO.

100 ppm NO in nitrogen for different temperatures. In the whole temperature range, oscillations are quenched and nitric oxide always has a strong beneficial effect on nitrous oxide conversion.

## 4. Discussion

Isothermal oscillations occur when 1000 ppm $N_2O$ in nitrogen are reacted over copper exchanged ZSM-5 zeolites. As observed in most oscillating systems [1], frequency is decreased with decreasing temperature. The irregular shape of the oscillations is probably due to a limited level of coupling of the individual oscillators in the packed-bed flow reactor [9].

The decomposition of nitrous oxide into the elements,

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

is complicated by the accompanied formation of traces of nitric oxide. Most probably, NO is formed from $N_2O$,

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

This reaction is thermodynamically feasible and has been observed by Riley and Richmond during $N_2O$ decomposition over various oxidic catalysts [10].

Moreover, our experimental results suggest that oscillations in $N_2O$ decomposition are caused by the traces of NO being formed in a side reaction since activity and NO formation peaks always take place simultaneously. On the other hand, if a certain level of nitric oxide concentration in the reaction mixture is reached (20 ppm at 723 K), the system stays, without oscillations, in an "ignited" state of significantly enhanced nitrous oxide conversion.

A model describing the oscillations in the catalytic decomposition over Cu-ZSM-5 cannot be derived based on the present results so far, but there is strong experimental evidence that adsorbed species of both nitric oxide and oxygen are influencing the underlying mechanism. In addition, the rather low frequency of the oscillations suggests that reversible phase transformations in the copper–oxygen system might take place, a possibility which has been discussed earlier [11].

## Acknowledgement

We are indebted to Bayer AG for providing the ZSM-5 used in this study. Helpful discussions with L. Riekert and F. Schüth are also gratefully acknowledged.

## References

[1] F. Schüth, B.E. Henry and L.D. Schmidt, Adv. Catal. 39 (1993) 51.
[2] R. Imbihl, Prog. Surf. Sci. 44 (1993) 185.
[3] M.M. Slin'ko and N.I. Jaeger, in: *Oscillatory Heterogeneous Catalytic Systems*, Studies in Surface Science and Catalysis, Vol. 86 (Elsevier, Amsterdam, 1994).
[4] G.A. Cordonier, F. Schüth and L.D. Schmidt, J. Phys. Chem. 91 (1989) 5374.
[5] P. Hugo, *Proc. 4th Eur. Symp. React. Eng.*, Brussels 1968 (Pergamon, Oxford, 1971) p. 459.
[6] Y. Li and J.N. Armor, Appl. Catal. B 1 (1992) L21.
[7] Y. Li and J.N. Armor, Appl. Catal. B 3 (1993) 55.
[8] Y. Li and J.N. Armor, Appl. Catal. 76 (1991) L1.
[9] J. Rathousky and V. Havlacek, J. Catal. 75 (1982) 122.
[10] B.W. Riley and J.R. Richmond, Catal. Today 17 (1993) 277.
[11] L. Riekert, Ber. Bunsenges. Phys. Chem. 85 (1981) 297.