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Decomposition of NO and N_2O on Cu-AlTS-1: oscillatory behaviour at full N_2O conversion

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Abstract

Cu-AlTS-1 catalyst was prepared by solid state ion exchange and studied in the NO and N_2O decomposition. Oscillation was observed in a wide range of experimental conditions during the decomposition of N_2O. At full N_2O conversion, oscillations were observed only in the O_2 and NO concentrations the latter being out of phase with respect to O_2 and being originated from the decomposition of an excess oxygen containing nitrito–nitrato-like surface complex. Traces of NO extinguished the oscillations and increased the N_2O conversion if it was below 100%. The NO also plays a key role in the feed back and synchronisation.

Keywords: NO; N_2O; Oscillations; Transients; Zeolite

1. Introduction

The decomposition of NO_x has been considered as an attractive way to remove nitrogen oxides from the exhaust gases of lean burn and diesel engines as they are thermodynamically unstable below 800 °C. In a recent paper, Goralski and Schneider [1] have discussed in detail the thermodynamic limits of decomposition and concluded that NO_x removal based on a thermodynamically equilibrated catalyst under lean exhaust conditions is not practically viable for automotive application. The need to remove N_2O from industrial sources still justifies research in this field. Despite the extensive research work, the mechanism of the reactions is still not understood and there is a lack in analysing the transient behaviour of the Cu containing zeolites. It is obvious that any model set up to explain the steady state behaviour should account for the transients, too.

Transients in NO and N_2O decomposition caused by changes the reaction mixture to inert gas and reverse have been reported [2–4]. We have already dealt with the oscillations in the O_2 concentration of the effluent at full N_2O conversion on Cu-AlTS-1, a titanium containing ZSM-5 type zeolite [4]. The oscillatory behaviour of the N_2O decomposition on high silica Cu-ZSM-5 has been studied by Turek [5–8], Ciambelli et al. [9–12] and Delgass and co-workers [13,14]. In the model proposed first by Ochs and Turek [8], the surface nitrate species played an important role and the oscillations was attributed to the inhibition of their decomposition in the presence of surface

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oxygen. Ciambelli et al. modelled the oscillations by considering a Cu ion redox cycle with coverage dependent activation energies without including surface nitrates.

In the present study, we combine transient kinetic studies with in situ temperature programmed desorption of the intermediates of the NO and N_2O decomposition reaction on Cu-AlTS-1 to find the possible similarities in both reactions. Also the effect of NO on the decomposition of N_2O has been studied.

2. Experimental

The synthesis of the H-AlTS-1 zeolite with $\mathrm{Si/Ti} = 82$ and $\mathrm{Si/Al} = 55$ using propylamine template is detailed elsewhere [2]. The H-AlTS-1 was transformed back into the $NH_4{}^+$ form and Cu was ion exchanged from $CuCl_2{\cdot}2H_2O$ by using solid state ion exchange described in [4]. The ion exchange capacity of the zeolite was 0.29 mmol/g and the Cu exchange was 140% (0.7 Cu per exchange position) resulting in 0.2 mmol Cu/g catalyst. The sample is marked the usual way as Cu-AlTS-1-55-140.

The reactions were performed in a fixed-bed tubular quartz plug flow reactor with 4 mm ID. About 150 mg of the catalyst of the 0.25–0.5 mm sieve fraction was placed between quartz wool plugs. There were four port valves upstream and downstream of the reactor and a bypass line between them to avoid any disturbance of the gas flow when it was switched from Ar to the reaction mixture and for the calibration of the QMS signal. Gas flow rates of 5–80 ml/min were applied. Premixed gases of 1.96 vol.% NO in Ar, 2.01 vol.% N_2O in Ar and pure Ar were further mixed by mass flow controllers. The reaction products were analysed by a Balzers Prisma QMS interfaced to the reactor via a differentially pumped capillary and an orifice to ensure linear response of the signals to the gas phase composition. On measuring the N_2O decomposition, the fragmentation of the parent $m/e = 44$ peak interfered with the NO parent peak at $m/e = 30$ resulting in an uncertainty in the NO concentration when NO was added to N_2O or NO was formed in the reaction. Therefore, instead of NO, the $m/e = 30$ signal is plotted in the figures. The reactor could be temperature programmed to perform in situ TPD and temperature programmed reaction measurements. The heating rate was 10 °C/min during TPD and 2–20 °C/min in other cases.

The catalyst was first heated in 20 ml/min Ar to 600 °C, cooled to 500 °C and contacted with 1.96% NO in argon. This is called as first contact with NO. The temperature was stepwise decreased to 200 °C and the NO conversion as well as the transients in the QMS signal during the ramp were recorded. The NO/Ar was switched for Ar and a TPD was started with final temperatures of 600 °C. The cycle was repeated several times. In some experiments the flow rate and also the NO concentration by dilution with Ar was changed. Isothermal transients on switching from Ar to the reaction mixture and back to Ar have also been measured. Similar measurements were done by the 2.01 vol.% N_2O/Ar mixtures.

3. Results and discussion

In Fig. 1, the transient states during the first contact of the catalysts with NO at 500 °C are shown. It is important to see a delay of 260 s in the O_2 signal and the initial overshoot in the N_2 signal. At 150 s, there is a local maximum in the N_2O and N_2 and a local minimum in the NO signals, respectively. This type of transients could be reproduced only if the catalyst was reduced by hydrogen, CO or used as a three way catalyst under rich gas conditions. In Fig. 2 the transients,

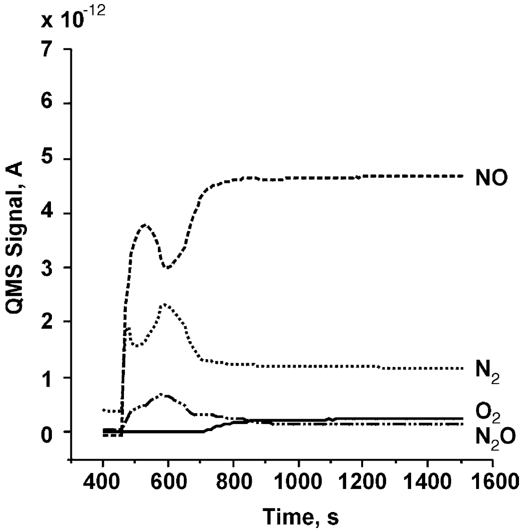

Fig. 1. First contact with NO at 500 °C (20 ml/min gas flow).

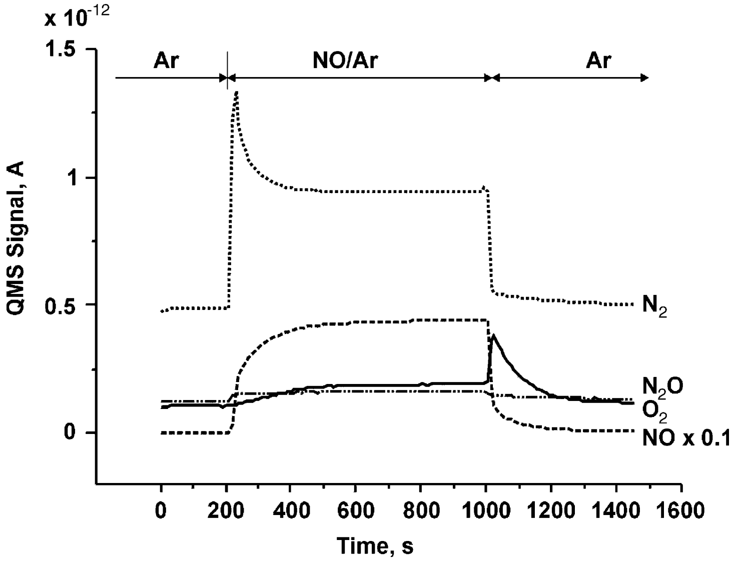

Fig. 2. Isothermal transients on switching Ar → NO → Ar at 400 °C (20 ml/min gas flow).

shown at 400 °C when the catalyst was already used in the NO decomposition reaction, could be reproduced without any additional treatment. In this case, there is also an overshoot in the N_2 signal but only a small delay in the O_2 one, whereas the local minimum and maximum are missing. On switching back to Ar there is a pronounced oxygen peak. In Fig. 3a, the TPD after cooling the catalyst in NO to 200 °C is shown. In Table 1, the quantitative results obtained for the number of moles of NO and O_2 referred to one copper atom, is presented. The amount of N_2O formed during the first contact with the sample was 0.33 N_2O/Cu, or 69 μmol N_2O/g catalyst. The amount of O_2 missing during the initial 260 s is only 18 μmol O_2/g catalyst or 0.09 O_2/Cu.

Table 1
Quantification of TPD and isothermal transients

Process	NO/Cu[a]	O_2/Cu[a]
TPD		
NO	0.17	0.22
N_2O	0.08	0.14
N_2O + NO	0.13	0.18
Isothermal transients reaction mixture → Ar		
NO → Ar	–	0.07
N_2O → Ar	0.07	0.15
N_2O + NO → Ar	0.13	0.16

[a] Moles of NO (O_2) divided by the moles of Cu in the sample.

Comparing these data with those in our previous experiment [2], the solid state ion exchange resulted in similar catalysts as that received by the conventional ion exchange in liquid phase. The amounts of NO and O_2 are substantially less than the amount of copper present in the sample indicating that only a small fraction of the copper is active in the reaction. This also suggests the same mechanism as proposed earlier [15] in which an excess oxygen containing $CuO(O_x)(NO)(NO_2)$ surface complex is the active intermediate in the NO decomposition on Cu-ZSM-5. In the case of Cu-AlTS-1 this surface complex contains slightly more oxygen. Most probably the additional maximum and minimum in the QMS signal during the first contact with NO are in connection with the uptake of this oxygen. As was proposed for Cu-ZSM-5, there is also an irreversible oxidation of some copper species in the catalyst during the first contact with NO. In addition to this, there are copper species, which undergo auto-reduction in Ar and are reversibly re-oxidised in NO as is shown by the nitrogen overshoot in Fig. 2. The conversion of NO has a maximum of 19% at 500 °C in 20 ml/min gas flow [4].

The N_2O decomposition was measured after the NO decomposition, therefore the first contact of the fresh catalyst with N_2O is missing. The catalyst was heated in the usual way in Ar to 600 °C, cooled to 500 °C and the gas flow was switched for 20 ml/min N_2O/Ar.

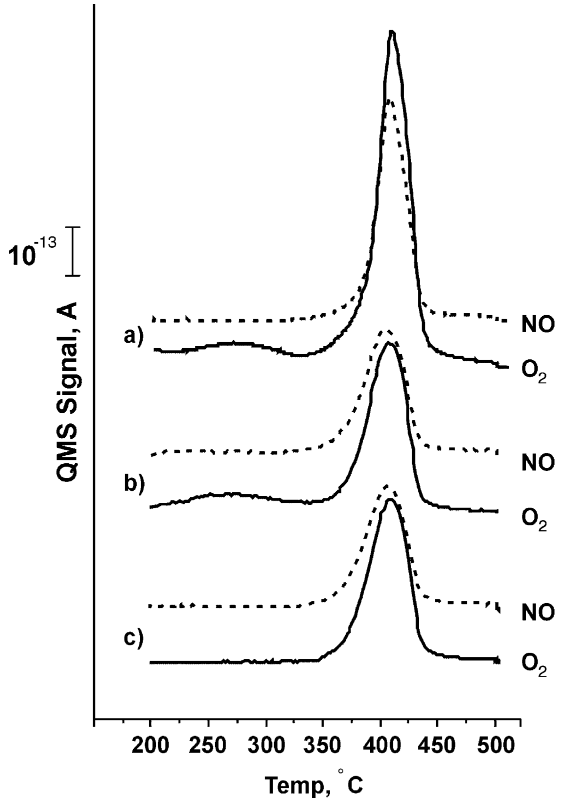

Fig. 3. Temperature programmed desorption into Ar after cooling to 200 °C in the reaction mixture in: (a) NO, (b) $N_2O + NO$, (c) N_2O.

Immediately relaxation type oscillations in the O_2 signal were observed at full N_2O conversion without any changes in the N_2 and N_2O signals as shown in Fig. 4. There are out of phase spikes in the $m/e = 30$ signal which originates only from NO (as no N_2O was there). On decreasing the temperature with a ramp of 2 °C/min the oscillations start also in the N_2O and N_2 signals. The oscillation disappears at about 420 °C, when the conversion drops to about 50%. TPD after cooling in N_2O/Ar to 200 °C is given in Fig. 3c. Similar to the NO TPD only NO and O_2 were detected at about the same temperatures. The only difference is the slightly increased amount of oxygen with respect to NO (see Table 1).

When the heating rate was increased to 10 °C/min, the range of the oscillations shifted to higher temperatures and there was a difference between the up and down ramps due to thermal effects as given in Fig. 5.

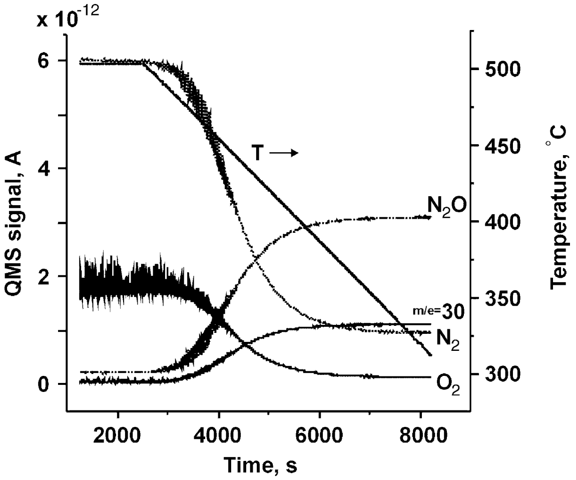

Fig. 4. Oscillations in N_2O decomposition on cooling with 2 °C/min (20 ml/min gas flow).

On stepwise cooling the catalyst from 500 °C (Fig. 6) the oscillations disappear during the ramps together with a temporary increase in the N_2O and a decrease in the N_2 signals when the temperature is stabilised. The oscillations start again with an increase in the O_2 signal. In agreement with Fanson et al. [14], adding of traces of NO to N_2O blocks the oscillations and increases the N_2O conversion as shown in Fig. 7. NO increases the N_2O conversion also at lower temperatures, at which there are no isothermal oscillations as

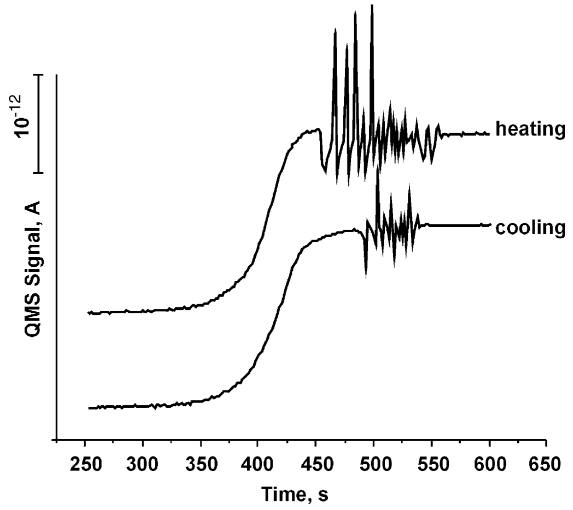

Fig. 5. O_2 oscillations in N_2O decomposition on heating cooling cycle (10 °C/min ramp, 20 ml/min gas flow).

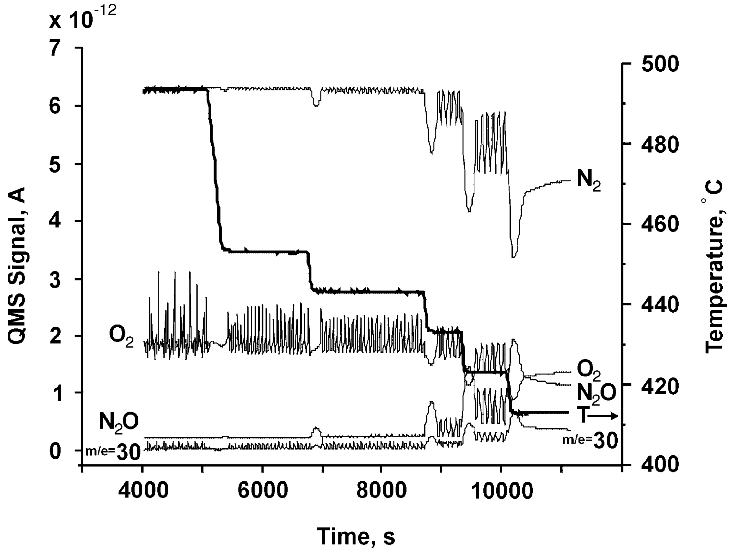

Fig. 6. Isothermal oscillations in N_2O decomposition on stepwise cooling (20 ml/min gas flow).

illustrated in Fig. 8. In that experiment, the catalyst was heated in Ar to 600 °C, cooled to 423 °C and the Ar flow was switched for N_2O/Ar. After the initial transients 0.2% NO was mixed into the N_2O/Ar. At this step, the transients are caused by the disturbance of the flow as the mass flow controllers needed some time to get stabilised (technically it was impossible to use the four way valves for changing the gas composition). TPD after cooling in the N_2O+NO mixture (see Fig. 3b and Table 1) and the isothermal transients on switching to Ar are similar to the NO case, the difference is only in the absolute and in the relative amounts of NO and O_2. The development of the oscillations at 443 °C is demonstrated in Fig. 9. On switching from

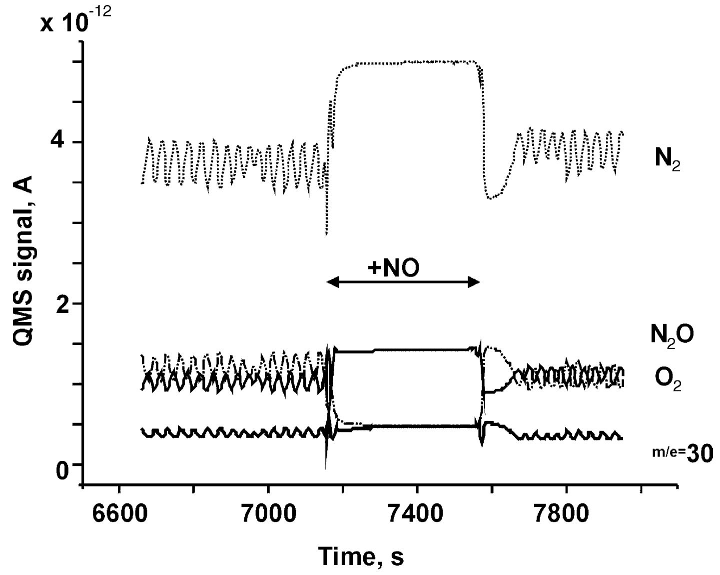

Fig. 7. Effect of NO on the oscillations in N_2O decomposition (80 ml/min gas flow, 443 °C, 0.2 vol.% NO).

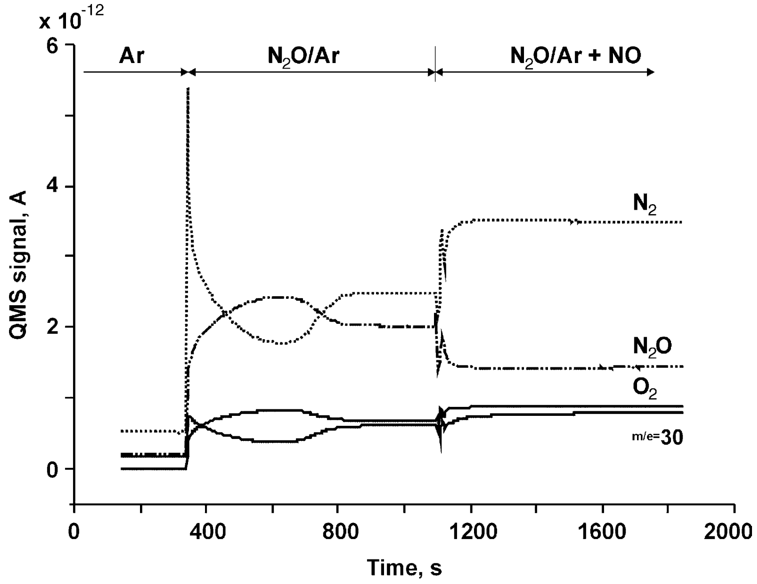

Fig. 8. Stabilisation of the catalyst in N_2O decomposition and effect of NO on conversion (80 ml/min gas flow, 423 °C, 0.2 vol.% NO).

Ar to N_2O/Ar the N_2O conversion decreases in the first 500 s but on the onset of the oscillations it sharply increases. There is an oxygen uptake during the first 50 s as calculated from the mass balance. The $m/e = 30$ signal is a sum of NO and fragments of N_2O; the out of phase peaks are from NO, whereas the in phase ones are fragments. The frequency and the shape of

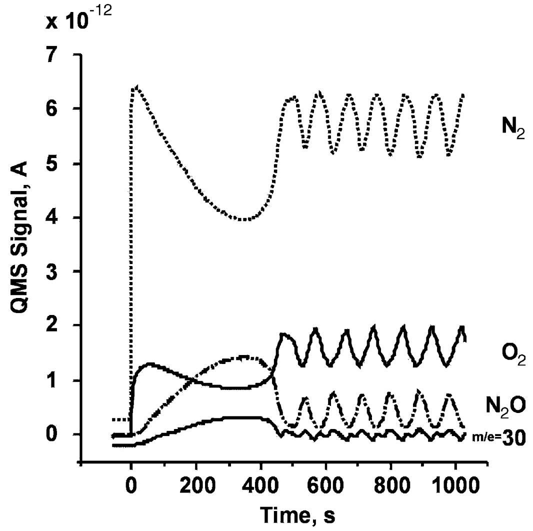

Fig. 9. Development of oscillations at 443 °C.

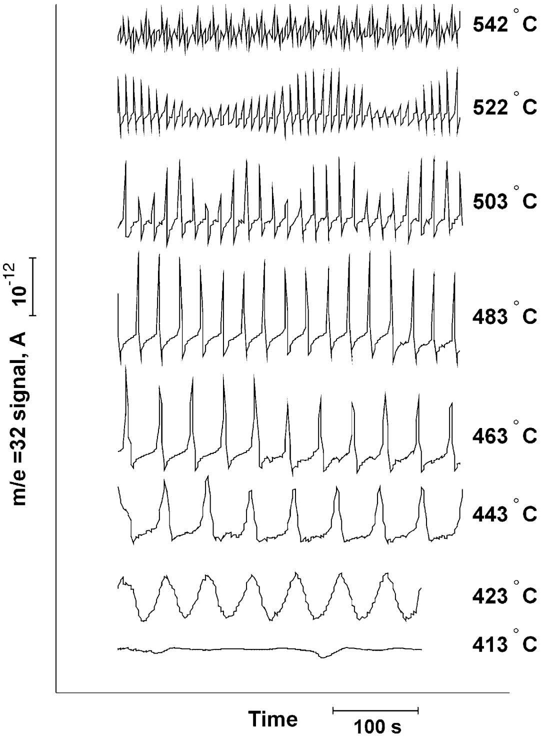

Fig. 10. Effect of the temperature on the oscillations in N_2O decomposition (20 ml/min gas flow).

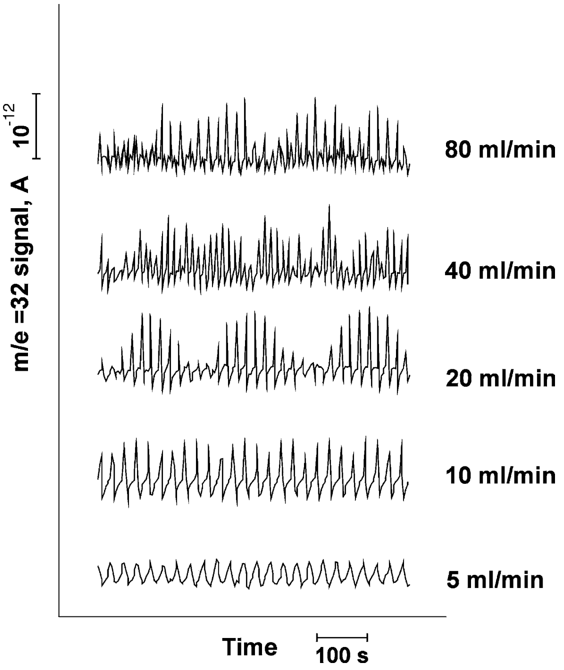

Fig. 11. Effect of the flow rate on the oscillations in N_2O decomposition at 523 °C.

the oscillations depend on the temperature and flow rate as given in Figs. 10 and 11.

The results give further support to our preliminary explanation [4] according to which the active site in the N_2O decomposition is similar to the one active in the NO decomposition, namely, a small fraction of the Cu^{2+} ions with excess oxygen containing nitrito–nitrato species. In contrary to the NO reaction this complex contains slightly more oxygen due to the more oxidative character of the N_2O molecule, which makes the complex sensitive to any change in the reaction conditions. This sensitivity results in a change in its composition, which in turn changes the reaction rate resulting in oscillations. The oscillations in the O_2 signal are a consequence of the change in the oxygen content of the complex. As the temperature is high enough, the lower activity of the remaining complex is enough to maintain full N_2O conversion. It is essential in the explanation of any oscillatory phenomena in flow reactors to find the step and species, which ensure feed back and synchronisation, respectively. We can speculate that in our case the feed back is via the partial formation and decomposition of the oxygen rich surface complex and synchronisation is via gas phase NO originating from the partial decomposition of the complex. The presence of NO from the decomposition of the complex increases the rate of N_2O decomposition and results in an increase in the amount of the surface complex. This is in line with the amounts of 0.002–0.006 NO/Cu and 0.01–0.04 O_2/Cu formed in one oscillation cycle, which are significantly less than the amounts found in TPD and in the isothermal transients. Further work is needed to find a model which describes all the experimental findings as the models proposed [8] fail in our cases.

Acknowledgements

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