JOURNAL OF CATALYSIS **174,** 98–108 (1998)
ARTICLE NO. CA971941

A Transient Kinetic Study of the Oscillating N_2O Decomposition over Cu–ZSM-5

Thomas Turek

Institut für Chemische Verfahrenstechnik, Universität Karlsruhe (TH) D-76128 Karlsruhe, Germany

Received August 5, 1997; revised October 9, 1997; accepted October 9, 1997

Isothermal oscillations during the catalytic decomposition of nitrous oxide over copper-exchanged ZSM-5 have been studied at 698 K employing mass spectrometry. Catalysts with a copper exchange level greater than 100% are more active for N_2O decomposition and only these samples exhibit sustained oscillations. Two states of the catalysts with different activity toward the formation of N_2 could be identified. Transient experiments by using step changes in nitrous oxide concentration showed that large amounts of adsorbed species are present on the catalyst surface under working conditions. It is proposed that atomic oxygen and nitrate are formed by reaction of nitrous oxide. The amounts of adspecies change during oscillations and mirror the development of gas-phase concentrations. While gas-phase oxygen had no effect on the observed phenomena, addition of NO and other reducing agents such as H_2 and CO resulted in disappearance of the oscillations and maintained the catalyst in the more active state. The results suggest that the active species for nitrous oxide decomposition is monovalent copper and that the periodic oxidation and reduction of active sites is responsible for the development of kinetic oscillations. © 1998 **Academic Press**

INTRODUCTION

Cu–ZSM-5 has now become a model catalyst for the study of several reactions of nitrogen oxides. It is still the most active catalyst for the decomposition of nitric oxide (1) and also exhibits, apart from some precious metal catalysts, the highest activity with respect to decomposition of nitrous oxide (2). An interesting phenomenon with relevance to the mechanism of the above reactions is the development of kinetic oscillations during N_2O decomposition. Lintz and Turek (3, 4) have investigated the region of existence as well as the influence of reactant concentrations on the oscillations. It could be clearly shown that neither thermal effects nor transport resistances are responsible for the observed phenomena. The rate of reaction was first order with respect to N_2O concentration and not affected by oxygen. Small amounts of NO were also formed in a side reaction. Addition of nitric oxide caused quenching of the oscillations and maintained the catalyst in a state of high activity. It was suggested that this effect is caused by stabilizing a reduced oxidation state of the active copper species (4). Ciambelli *et al.* (5) also observed oscillatory behavior during nitrous oxide decomposition using Cu–ZSM-5. These authors found a slightly deactivating effect of both oxygen and nitric oxide. A reaction scheme involving the periodic oxidation and reduction of copper sites by nitrous oxide was proposed by these authors. EPR measurements by Bossmann *et al.* (6) on Cu–ZSM-5 catalysts after cooling down in different states of the oscillations did not show a change of the copper oxidation state, but the existence of EPR silent copper species in Cu–ZSM-5 has to be taken into consideration (7).

Kinetic studies of the N_2O decomposition over various ZSM-5-based catalysts carried out by Kapteijn *et al.* (8–10) did not report on oscillatory phenomena. Steady-state behavior was also observed in investigations by Li and Armor (2), Centi *et al.* (11), and Correa *et al.* (12). Kapteijn *et al.* determined a reaction order of 0.88 with respect to N_2O concentration, a slight inhibition by oxygen, and no effect of added nitric oxide. DRIFTS measurements (8) showed that the Cu–ZSM-5 is oxidized under reaction conditions, and the overall decomposition kinetics were interpreted in the classical manner, as proposed by Leglise *et al.* for N_2O decomposition over iron-exchanged mordenite (13), including reduction and oxidation of copper sites.

The present investigation was undertaken to gain further insight into the oscillatory phenomena. Special attention was paid to the question of whether an underlying redox mechanism results in the development of periodic activity changes. Transient techniques, which have been successfully used to study the decomposition of nitrous oxide over MnO_2 (14) and CaO (15), have been employed.

EXPERIMENTAL

Catalyst Preparation

The Cu–ZSM-5 catalysts were prepared by conventional ion exchange of ZSM-5 (Bayer) in the sodium form. The parent zeolite that has been used in earlier studies (3, 4, 6) was analyzed by ICP and the molar Si/Al ratio was found to

0021-9517/98 $25.00

be 46. The ion exchange was carried out for 24 h using aqueous copper acetate solutions (0.6 to 60 mM) at room temperature. The pH was not adjusted during ion exchange and was in the range between 4.5 (60 mM) and 7.2 (0.6 mM). The copper content of the catalysts was determined by photometric analysis of the solution after ion exchange. Exchange levels were calculated on the common basis that one Cu^{2+} replaces two Na^+. The obtained catalysts were washed by resuspending in deionized water, filtered, dried for 16 h at 383 K, and subsequently calcined in air for 6 h at 823 K. The calcined zeolite powder was pressed, crushed, and sieved to obtain fractions of 315 to 500 μm. Prior to experiments, the catalysts were pretreated for 1 h at 773 K in flowing helium (500 cm^3/min, NTP).

Apparatus and Procedure

The catalysts were placed in a pyrex glass tube reactor which was heated electrically. The temperature in the catalyst bed was measured by use of a thermocouple. A small hole in the heating jacket allowed for the observation of the catalyst color during the experiments. Inlet and exit concentrations were monitored by means of a magnetomechanic oxygen analyzer (Hartmann und Braun, Magnos 6G), nondispersive infrared analyzers for N_2O and NO (Rosemount, Binos 4), and an UV photometer for NO_2 (Rosemount, Binos 5). Furthermore, a Balzers QMS 200 quadrupole mass spectrometer in multiple ion-detection mode was used, which allowed for the analysis of all components including N_2. The vacuum for the mass spectrometer was maintained using a Balzers TPU 100 turbomolecular pump. The gas was introduced into the vacuum system by means of a heated inlet system (Balzers GES 010) consisting of a differentially pumped capillary followed by a stainless steel frit connected to the turbomolecular pump. Certified standard gas mixtures in the concentration range 500 to 1000 ppm in He were used to calibrate the analyzers for the reactants and expected side products. The nitrogen and oxygen mass balance during the experiments was satisfied within ±10%.

All measurements were carried out with 250 mg catalyst at a temperature of 698 K and a total flow rate of 500 cm^3/min (NTP). The gases used were all of >99% purity and mixed with He (99.999%) as inert gas via thermal mass flow controllers (Brooks, 5850) without further purification.

Transient kinetic experiments were carried out by generating step changes of reactant concentrations using a three-way valve. Preliminary experiments in the empty reactor showed that rectangular step functions could be successfully produced. After a step change in the empty reactor, all analyzers reached 90% of the new steady-state concentration within less than 20 s, the only exception being the nitrogen dioxide photometer that exhibited a considerably longer response time (ca. 60 s) due to adsorption of NO_2 in the lines. The amounts of adsorbed species on the catalyst surface during oscillations were determined by replacing the N_2O content in the feed by helium while the gas-phase concentrations down stream of the reactor were analyzed.

The temperature-programmed desorption of reactants was carried out in the following way. Prior to experiments, the catalyst was treated in He at 773 K for 1 h and then cooled to room temperature in flowing He. Reactants (1000 ppm) diluted in He were fed over the catalyst until no further adsorption could be detected. After flushing in pure He, the programmed heating was started from room temperature to 773 K at a rate of 10 K/min while the evolved gases were analyzed.

RESULTS AND DISCUSSION

Influence of Copper Content

The characteristics of the samples prepared by ion exchange in acetate solutions with different concentrations are summarized in Table 1. The influence of copper exchange level on nitrous oxide conversion for 1000 ppm N_2O in He at 698 K is depicted in Fig. 1. In the case of oscillations, the minimum and the maximum conversion, connected by a broken line, are shown. It can be seen that the catalytic activity markedly increases for catalysts with an exchange level of 100% and more. Initially, damped oscillations that extinguished after about 30 min could be observed for the sample with 103% exchange level. The catalysts with higher copper content exhibited sustained oscillations with a period duration of 7 to 9 min.

Interestingly, the first-order rate constant related to the copper content has about the same value for the catalysts between 100 and 200% exchange level (1.7 $m^3/kg_{Cu} \cdot s$ in the maximum and 0.7 $m^3/kg_{Cu} \cdot s$ in the minimum of observed catalytic activity), while this value decreases for the two samples with the highest copper contents. This activity

TABLE 1

Characteristics of the Catalysts Used

Concentration (mM)	Copper content (wt%)	Exchange level (%)	Color
0.6	0.66	60	Green
0.8	0.89	80	Green
1.2	1.14	103	Green
3.0	1.41	126	Green
6.0	1.73	155	Green
6.0[a]	1.97	177	Green-grey
12	2.21	198	Green-grey
30	3.38	303	Brown-grey
60	3.90	350	Brown-grey

[a] Prepared by threefold ion-exchange for 8, 14, and 24 h according to (2).

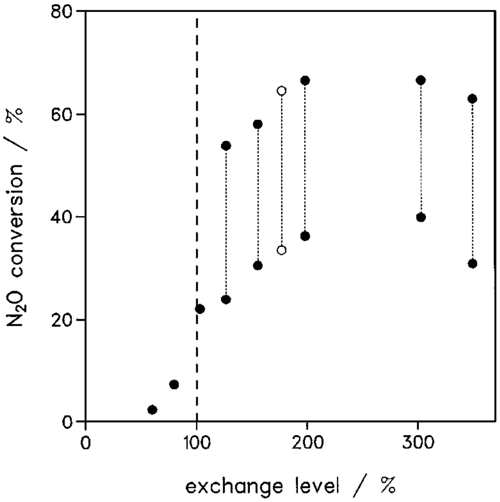

FIG. 1. N$_2$O conversion as a function of copper exchange level. Open circles denote sample prepared by threefold ion exchange.

pattern strongly resembles the picture that was obtained during studies of the decomposition of NO over Cu–ZSM-5 (16–19), where also a distinct enhancement of activity at around 100% exchange level was found. This agreement shows that most probably the same active sites are involved in the decomposition of NO and N$_2$O, which supports the postulated role of nitrous oxide as an intermediate during nitric oxide decomposition (20–22). Generally, the dependence of activity for NO decomposition on copper content is explained by the presence of different copper species in ZSM-5, namely Cu^{2+} with low activity, an easily reducible species (Cu^{2+}–O–Cu^{2+} pairs (7, 22) adjacent to two or Cu^{2+}–OH$^-$ species adjacent to one framework aluminium (23)) that is belived to be the active species, and small copper clusters with again very little contribution to the overall activity. The darker color of the samples with the highest copper content (cf. Table 1) is probably due to the presence of oxidic copper clusters. Thus it appears that the active sites for N$_2$O decomposition are monovalent copper species, which allows rationalizing an ion-exchange capacity of up to 200%, and that these species are also involved in the development of kinetic oscillations.

Sustained Oscillations

The following investigation of the observed oscillations was conducted by using the catalyst prepared by threefold ion exchange, which has been employed in previous studies (3, 4, 6). Figure 2 shows the exit concentrations as a function of time for a feed composition of 1000 ppm nitrous oxide in He as well as the sum of the concentrations of all oxygen and nitrogen containing components. From the concentrations of nitrous oxide and nitrogen it is evident that two states of different catalytic activity can be distinguished. The color of the catalyst is brown-grey in the state of high activity and green-grey, very similar to the color of the fresh catalyst at room temperature, in the state of low activity. The color changes took place simultaneously within about 10 s in the entire fixed bed of catalyst. While the N$_2$O and N$_2$ concentrations approximately correspond to the overall stoichiometry of the decomposition reaction, an oxygen overshoot upon reaching the state of high catalytic activity and a deficit of gas-phase oxygen at the transition from high to low activity can be observed. The mass balance depicted in the lower part of Fig. 2 also clearly shows these deviations from the expected 500 ppm (calculated as O$_2$) oxygen containing species in the gas phase. On the other hand, there are only slight fluctuations in the nitrogen mass balance caused by the desorption of nitric oxide (and traces of nitrogen dioxide) during the phase of maximum activity.

It has been earlier noted (3) that adsorbed species must be present on the catalyst under reaction conditions to explain these phenomena. In order to determine the amount of adspecies quantitatively, transient experiments by switching from 1000 ppm nitrous oxide to pure inert gas were carried out. Figure 3 shows the response to replacing nitrous oxide in the feed by helium during different stages of the oscillations. The N$_2$O concentration (and also the N$_2$ concentration not shown) decreases quickly, corresponding to the response time of the analyzers, which shows that these species are not adsorbed or are only weakly adsorbed under reaction conditions. On the other hand, the desorption

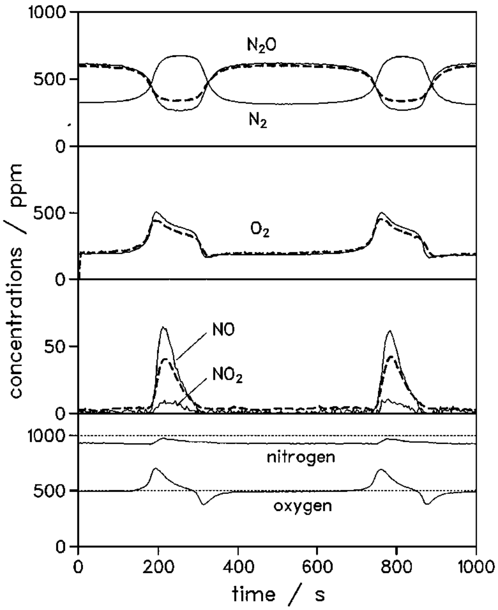

FIG. 2. Outlet concentrations of N$_2$O, N$_2$, O$_2$, NO, and NO$_2$ as a function of time for a feed composition of 1000 ppm N$_2$O in He at $T = 698$ K using the catalyst with 177% copper exchange level. The lower part of the figure shows the mass balance. Solid lines, mass spectrometer; broken lines, magnetomechanic and photometric analyzers.

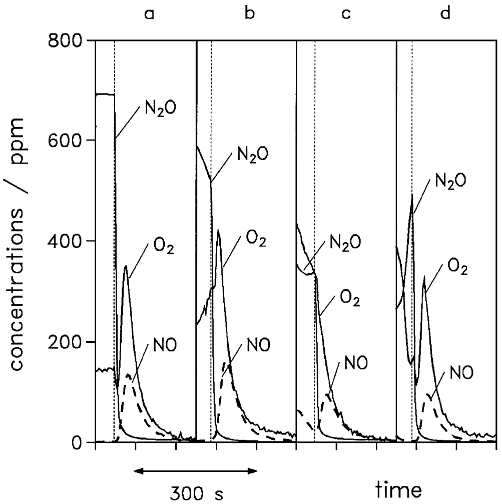

FIG. 3. Exit concentrations of N$_2$O, O$_2$, and NO at 698 K as a function of time after a step change of nitrous oxide inlet concentration from 1000 ppm to zero during different stages of the oscillations (cf. Fig. 4.). (a) Minimum of activity; (b) transition from low to high activity; (c) maximum of activity; (d) transition from high to low activity.

of nitric oxide and oxygen continues to take place for about 3 min. The nitrogen dioxide concentrations were in any case very small and are not shown in this graph. The catalyst displayed always a green-grey color at the end of the transient experiments. After the complete desorption of NO and O$_2$ at 698 K, no further desorption upon heating the catalyst to 773 K could be observed. This result, together with the fact that the catalyst always showed the same initial period after a desorption experiment and subsequent exposure to nitrous oxide, clearly shows that no adspecies are left on the catalyst after the transient experiments.

The amounts of desorbed NO and O$_2$ determined by integration of the concentration response are depicted in Fig. 4 together with an example of undisturbed oscillations. One can see that the amount of desorbed O$_2$ in the state of low activity is constant at around 5×10^{-6} mol, while this value decreases by about a factor of two in the maximum of decomposition activity. This change in oxygen coverage is in good agreement with the oxygen release and uptake that can be determined from the mass balance shown in Fig. 2. The amount of desorbed NO, on the other hand, is in the range 2–3×10^{-6} mol. The amounts of adspecies as a function of time mirror the development of the gas-phase concentrations. Figure 4 reveals that the more active state of the catalyst is characterized by a lower coverage with adsorbed species. Since the catalyst releases oxygen at the transition from low to high activity, it is possible that the more active state of copper is less oxidized. The total copper content in the 250 mg of catalyst used amounts to 77.5×10^{-6} mol, the overexchanged fraction (33.5×10^{-6} mol) of which can be regarded as catalytically active. Thus the maximum total amount of adspecies is only about 25% of the amount of active copper species, but considering that at least part of the oxygen might be present in atomic form as Cu^{2+}–O–Cu^{2+} pairs, the fraction of copper participating in the decomposition reaction might be higher. However, taking into account that the gas-phase composition is changing along the length of the reactor, a quantitative assessment is not possible since the determined amounts of adsorbed species are only integral values.

At this stage it is not clear in which form the desorbed components, O$_2$ and NO, are present on the catalyst. The review by Centi and Perathoner (24) shows that a broad variety of oxygen and nitrogen oxide surface species have been proposed to take part in reactions of nitrogen oxides over Cu–ZSM-5. Indirect information about the adspecies formed during the oscillating N$_2$O decomposition can be obtained from a closer examination of the initial period after the catalyst is contacted with nitrous oxide.

Investigation of the Initial Period

Figure 5 shows a typical example of the initial period after a step change from pure inert gas to 1000 ppm N$_2$O in He. While the lower part of the figure shows the exit gas-phase concentrations, the upper part depicts the development of the amounts of adspecies, which have been determined in the described manner. From the advancement of the nitrogen and nitrous oxide gas-phase concentrations it is obvious that the catalyst is initially in the state of high catalytic activity, but is rapidly deactivated within about 1 min. During this stage, the catalyst takes up oxygen (i.e., copper

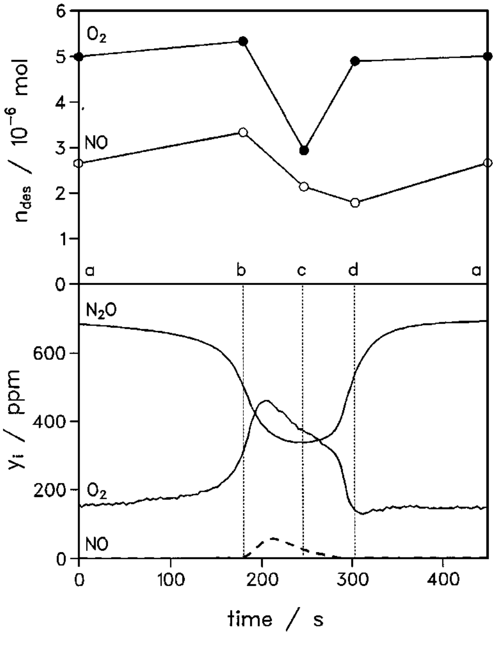

FIG. 4. Desorbed amounts of oxygen and nitric oxide at 698 K. The lower part of the figure shows an example for undisturbed oscillations and the moments of switching from 1000 ppm N$_2$O to pure He.

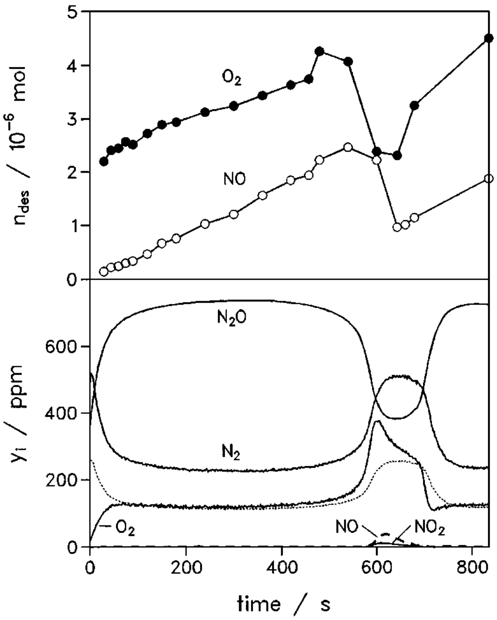

FIG. 5. Desorbed amounts of oxygen and nitric oxide at 698 K. The lower part of the figure shows the undisturbed initial period and the first oscillation. The dotted line denotes $0.5 \cdot y_{N_2}$, i.e., the expected oxygen concentration according to stoichiometry.

is possibly oxidized), which can be seen both from the difference between actual and expected (dotted line) oxygen concentration in the gas-phase and from the amount of desorbed oxygen. After having reached the state of low catalytic activity, the catalyst remains there with little change of the gas-phase concentrations for about 7 min until the first oscillation with the typical pattern (overshoot of oxygen, release of nitric oxide) can be observed. Surprisingly, the amounts of desorbed species significantly increase during this stage. The most striking feature of the development of adsorbed species with time is the linear increase of the O_2 and NO amounts with exactly the same slope. Thus it can be postulated that, after the catalyst has been initially oxidized by reaction with nitrous oxide, a nitrate species is additionally formed with constant rate on the oxidized copper species. This species is decomposed into molecular oxygen and NO, and released together with the initially adsorbed oxygen upon switching to pure inert gas. The formation of nitrate has little effect on the rate of nitrous oxide decomposition during the initial period, but this species is clearly involved in the development of oscillations, i.e., the periodic change between oxidized and less oxidized states of the active species.

It is generally accepted that nitrate species on Cu–ZSM-5 and other zeolite catalysts modified with copper are stable even at high temperatures. Evidence for nitrate formation has been obtained by IR spectra (25–30) and by temperature-programmed desorption of nitrogen oxides (25, 31). Nitrate species have been proposed to be important intermediates in the decomposition of NO (32), the selective catalytic reduction of NO by hydrocarbons (26), and the SCR of NO by ammonia (27). Based on the assumption that the adspecies are present as atomic oxygen O_s and adsorbed nitrate $NO_{3,s}$ before they react to O_2 and NO in the step-change experiments, the desorbed amounts given in Figs. 4 and 5 were recalculated to yield Fig. 6. It appears that the state of high catalytic activity in the N_2O decomposition is almost free of (atomic) oxygen. The development of adsorbed oxygen with time exhibits the typical pattern for relaxation oscillations, whereas the nitrate concentration versus time has a sawtooth-like shape that is caused by a slow rate of formation on the oxidized catalyst and a rapid rate of decomposition on the reduced catalyst. The dynamic interaction of these two intermediates results then in the observed gas-phase concentrations. The development of N_2O and N_2 concentrations can be explained by the two states of activity, while the oxygen concentration as a function of time is further complicated by the decomposition of nitrate into NO and O_2 as well as by the periodic release and uptake of adsorbed oxygen.

Temperature-Programmed Desorption

Supplementary evidence for the possible formation of a nitrate species is gained from the temperature-programmed desorption of reactants. Figure 7 shows TPD spectra after adsorption in a stream of 1000 ppm of N_2O, NO, and NO_2 in He at room temperature. The temperature-programmed desorption spectrum of oxygen is not shown since no detectable O_2 desorption took place. It can be seen that both nitrous and nitric oxide are rather weakly adsorbed and that desorption of these species is completed far below reaction temperature. In contrast to these results, nitrogen dioxide is adsorbed in large amounts. Desorption of NO_2 continues to take place until ca. 700 K, and the major fraction of adsorbed species is released as NO and O_2 between 600 and 700 K in a ratio of exactly 1 : 1. Thus it appears possible that nitrate species that are stable under reaction

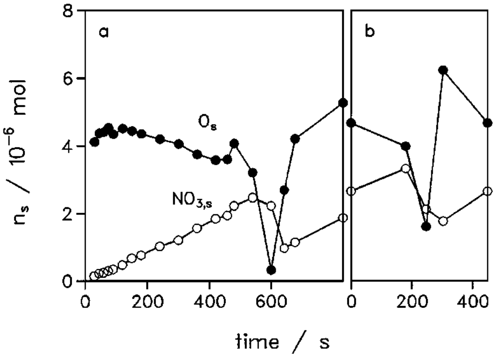

FIG. 6. Amounts of adsorbed atomic oxygen and nitrate species during initial period (a) and for a typical period of oscillations (b).

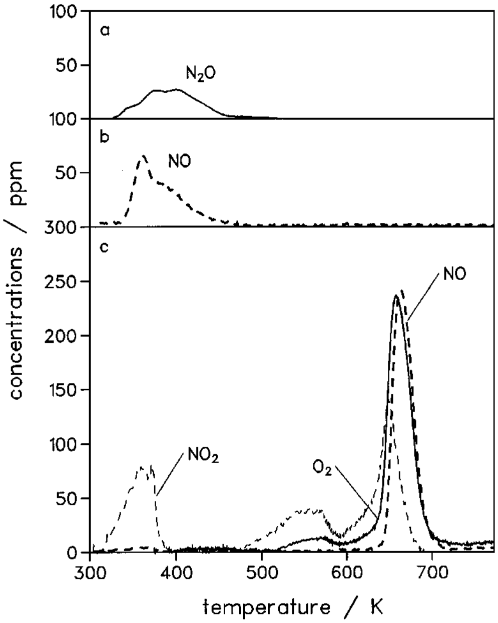

FIG. 7. TPD spectra of adsorbed nitrous oxide (a), nitric oxide (b), and nitrogen dioxide (c).

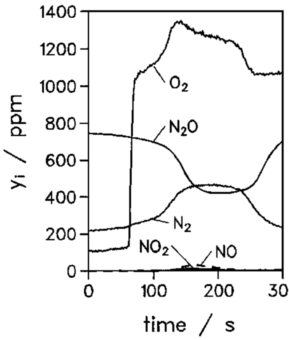

FIG. 8. Response to addition of ca. 900 ppm oxygen to the reactant mixture at the transition of low to high catalytic activity.

conditions even at temperatures up to 698 K are formed on the catalyst used. Moreover, it is evident that nitrogen dioxide (photometrically analyzed) and nitrate are clearly distinguishable species. A careful study of the adsorption properties of Cu–ZSM-5 carried out by Iwamoto and coworkers (33) has also unambiguously shown that a fraction of the adsorbed nitrogen oxides decompose to yield NO and O_2. Thus the assumption by Wang *et al.* (34), that NO desorption during TPD of nitrogen oxides over Cu–ZSM-5 is simply due to fragmentation of desorbed NO_2 in the mass spectrometer, can be excluded.

Addition of Further Components to the Reactant Mixture

In the following series of transient experiments, the response to the introduction or removal of various components during different stages of the oscillations was investigated. Figure 8 depicts the gas-phase concentrations as a function of time for the introduction of 900 ppm of oxygen to the reactant mixture (1000 ppm N_2O in He at reactor inlet). It can be clearly seen that O_2 has essentially no effect on the oscillations. While the N_2O and N_2 concentrations remain unaffected, the oxygen concentration is simply shifted by ca. 900 ppm. The same result was obtained when oxygen was added during different stages of the oscillations. This is in agreement with earlier findings that even the addition of 10% oxygen to 1000 ppm nitrous oxide only slightly affected the development of oscillations (4). On the other hand, Ciambelli *et al.* (5) reported that addition of 0.5% oxygen was sufficient to quench the oscillations observed using 300 ppm N_2O in He at 643 K. A possible reason for this discrepancy could be that the region of existence of the oscillations was found to be rather narrow when a low value of the N_2O inlet concentration is used (4).

In Fig. 9 the effect of adding 900 ppm nitric oxide to the reactant mixture in the two states of catalytic activity is shown. The results upon addition at low activity reveal that the catalyst almost instantaneously reaches the state of high activity while oxygen and a small amount of nitric oxide, as can be seen from a slight overshoot of the NO concentration, are desorbed. The catalyst then remains in this active state with respect to N_2O decomposition, and part of the NO added is converted to nitrogen dioxide. The response to addition of NO in the more active state shows that only very small amounts of oxygen and no nitric oxide

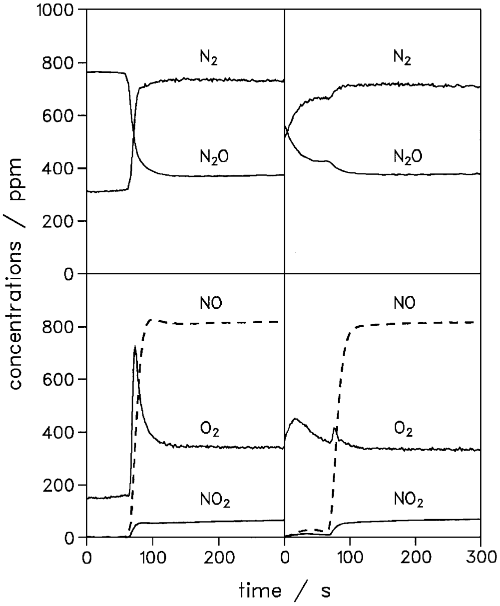

FIG. 9. Response to addition of ca. 900 ppm nitric oxide to the reactant mixture in the minimum (left-hand side) and maximum (right-hand side) of catalytic activity.

are released. It can also be seen that the conversion of N_2O to nitrogen starting from the state of high activity is further enhanced by ca. 50 ppm. As a consequence, about the same amount of nitrogen dioxide is formed. Thus it appears that a direct reaction [1] between N_2O and NO, which has been confirmed by Kapteijn *et al.* (10) over ZSM-5-based catalysts, is responsible for the further increase of nitrous oxide conversion when NO is added:

$$N_2O + NO \rightarrow N_2 + NO_2. \qquad [1]$$

It is interesting to note that Musgrave and Hinshelwood (35), in an early investigation of the homogeneous decomposition of N_2O, found that small amounts of NO were formed in a side reaction, which acted catalytically via Eq. [1], giving rise to an enhancement of the overall nitrous oxide decomposition rate. The presented results confirm earlier findings (4), which showed that the addition of between 10 and 100 ppm NO results in maintaining the state of high catalytic activity for N_2O decomposition in the whole range of temperature studied (648 to 723 K). Again, Ciambelli and co-workers (5) obtained differing results when adding between 500 and 5000 ppm NO at 643 K. The introduction of NO was found to quench the oscillations and to decrease the nitrous oxide conversion. Moreover, this detrimental effect was strongly enhanced by the simultaneous addition of oxygen.

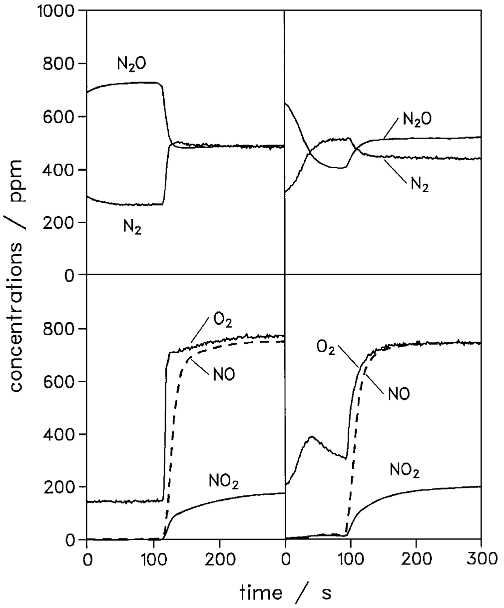

FIG. 10. Response to addition of ca. 900 ppm nitrogen dioxide to the reactant mixture in the state of low (left-hand side) and high (right-hand side) catalytic activity.

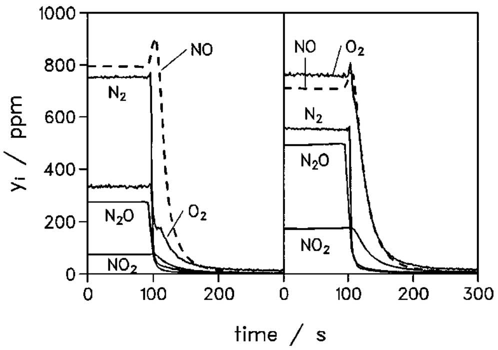

FIG. 11. Response to simultaneous removal of 1000 ppm N_2O/900 ppm NO (left) and of 1000 ppm N_2O/900 ppm NO_2 (right) from the reactant mixture.

An explanation for these contrasting observations could possibly be derived from the experimental results depicted in Fig. 10. The response to addition of 900 ppm NO_2 in the two different states of activity shows that the oscillations are again quenched, but that the catalyst remains in a state below the activity maximum of the undisturbed oscillations. The major fraction of nitrogen dioxide is decomposed into NO and oxygen via the following well-established reaction, which was shown to be very rapid on overexchanged Cu–ZSM-5 (36):

$$2\,NO_2 \rightleftharpoons 2\,NO + O_2. \qquad [2]$$

The equilibrium reaction between NO and NO_2 also offers an explanation for the removal of oxygen from active sites when nitric oxide is present in the gas phase, either added to the reactant mixture or produced via decomposition of nitrates in the course of the N_2O decomposition itself. It could be, as has also been proposed by Kapteijn *et al.* (10), that NO reacts with surface oxygen to form NO_2, which in turn is rapidly decomposed back to NO and O_2, thus giving rise to a catalytic cycle facilitating the desorption of oxygen.

However, the NO_2 concentration after admixture of nitrogen dioxide remains higher than during NO addition (Fig. 9). Since gas-phase oxygen apparently has no effect on the observed phenomena, the difference in the results obtained during NO addition is likely due to the higher nitrogen dioxide level, inhibiting the decomposition activity either by adsorbed NO_2 or by a higher level of nitrates on the catalyst. The responses to the simultaneous removal of both N_2O and the added nitric oxide or nitrogen dioxide (Fig. 11) indicate that the amounts of desorbing species are higher when more nitrogen dioxide is present in the gas phase. If one further takes into account that the equilibrium of reaction [2] is shifted to the left-hand side with decreasing temperature, it is possible that the decrease of nitrous oxide conversion during the experiments of Ciambelli *et al.* (5) were caused by high nitrogen dioxide concentrations present rather than by an intrinsically adverse effect of added NO.

Figures 12 and 13 display the responses to addition of 900 ppm H_2 and CO to the reactant mixture at minimum

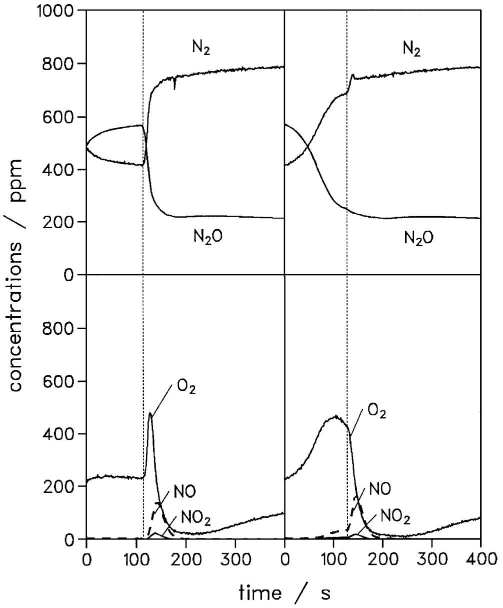

FIG. 12. Response to addition of ca. 900 ppm hydrogen to the reactant mixture in the minimum (left-hand side) and maximum (right-hand side) of catalytic activity.

and maximum of catalytic activity. Admixture of hydrogen has the same effect as nitric oxide. Oxygen, nitric oxide, and traces of nitrogen dioxide are released while the catalyst subsequently remains in the state of high activity. The amounts of desorbed oxygen and nitric oxide are very similar to the respective values during the step changes from 1000 ppm N_2O to pure He. The oxygen concentration after reaching the new steady state is lower than that corresponding to the amount of nitrous oxide converted, which can be explained by the simultaneous oxidation of hydrogen. Given this result, it is surprising that large amounts of oxygen are initially released upon addition of hydrogen in the state of low catalytic activity (Fig. 12, left-hand side). Although the water concentration was not measured, it appears that oxygen desorbs from the catalyst rather than being removed by reaction with H_2.

Admixture of the reducing agent CO (Fig. 13) yields the following results. Again, nitric oxide is desorbed, and at the same time the oscillations are quenched. On the other hand, neither nitrogen dioxide nor oxygen could be detected after addition of CO, while the nitrous oxide conversion was higher than in the state of maximum activity during the undisturbed oscillations. Note that the mass spectrometer signal at 28 amu is due to both nitrogen and unreacted carbon monoxide. Thus it appears that CO is more reactive than H_2 under the conditions used. Carbon monoxide effectively reacts with oxygen and nitrogen dioxide, and also a direct reaction with nitrous oxide takes place.

The effect of adding reductants to the reactant mixture clearly shows that nitric oxide (and even nitrogen dioxide via decomposition into NO and O_2) is also capable of acting as a reducing agent. In all cases, adsorbed oxygen is released and this enables the catalyst to operate with the maximum possible activity during nitrous oxide decomposition. Significant deviations from this state of high activity upon admixture of further reactants only occur if additional reactions have to be considered (carbon monoxide) or the added component is strongly adsorbed, as is possibly the case for nitrogen dioxide.

Pretreatment of the Catalyst

In the following experiments, the initial period of the oscillating N_2O decomposition was investigated pretreating the catalyst with different reactants. Since the previous results have clearly shown that adsorbed species like oxygen and nitrate are not stable when the catalyst is purged in a stream of He, the following strategy was employed. After pretreatment of the catalyst with the desired component for 1 h at 698 K, the integral reactor was bypassed and the composition of the stream was set to 1000 ppm N_2O in He. After 5 min, the gas was lead through the reactor, where the component used for pretreatment, or reaction products thereof, still remained. Figure 14 depicts the initial period and the first oscillation during the decomposition of 1000 ppm nitrous oxide after pretreatment with 1000 ppm NO or NO_2. Pretreatment with nitric oxide results in an initial period very similar to the result obtained after purging in pure inert gas. The only differences are that the catalyst initially remains slightly longer in the state of high activity and that

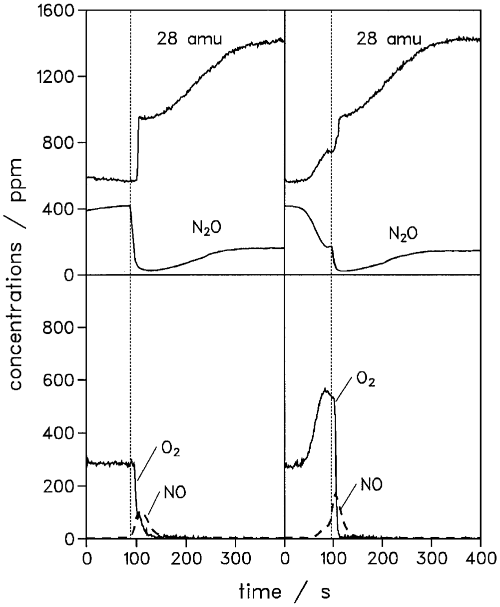

FIG. 13. Response to addition of ca. 900 ppm carbon monoxide to the reactant mixture in the minimum (left-hand side) and maximum (right-hand side) of catalytic activity.

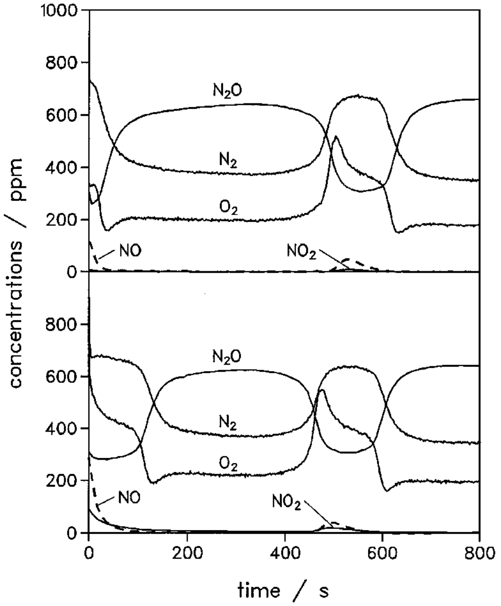

FIG. 14. Exit concentrations as a function of time for a feed composition of 1000 ppm N_2O in He at $T = 698$ K after pretreatment of catalyst with 1000 ppm NO (upper part) and 1000 ppm NO_2 (lower part).

no uptake of oxygen by the catalyst takes place. This might be due to the decomposition of nitric oxide into N_2 and O_2 and subsequent formation of nitrate species while the reactor is being bypassed. It appears that the catalyst starts in a state that is otherwise reached at the end of the first regular oscillation, before the oxygen deficit in the gas phase can be observed.

The pretreatment with 1000 ppm NO_2, on the other hand, results in the formation of a higher amount of adsorbed nitrates than is caused by exposure to nitric oxide. The catalyst consequently starts in the transition state from low to high activity, when normally the oxygen overshoot occurs. The maximum activity is maintained longer, and the initial period after pretreatment with nitrogen dioxide is only as long as the interval between regular oscillations. Both experiments again reveal that the state of high catalytic activity is maintained as long as nitric oxide is present in the gas phase. It is thus possible that the presence or absence of NO synchronizes the oscillations of the active sites. The result after pretreatment in 1000 ppm oxygen is not shown, since no difference to pretreatment in inert gas was observed. This supports that gas-phase oxygen is not capable of interacting with the active copper species.

Figure 15 shows the exit concentrations as a function of time after pretreating the catalyst in 1% CO and 1000 ppm H_2. Dedecek and Wichterlova (23) have shown that exposure of Cu–ZSM-5 to CO gives rise to the formation of Cu^+ without further reduction to copper metal. The higher concentration of 1% was chosen to ensure a complete transformation of the total copper content in the catalyst. The gas-phase concentrations after contacting the catalyst with 1000 ppm N_2O exhibit a behavior remarkably similar to those for the catalyst pretreated in inert gas. The duration of the initial period is slightly longer, but this is most probably caused by the reaction of nitrous oxide with carbon monoxide still remaining in the reactor.

The behavior of the catalyst after treatment with 1000 ppm hydrogen is given in the lower part of Fig. 15. The most important result of this experiment is that the catalyst remains on a lower level of catalytic decomposition activity after regular oscillations have been developed. In contrast to all other experiments, where the average N_2O conversion at the given reaction conditions was found to be around 50%, not more than 30% of nitrous oxide reacted after hydrogen pretreatment. The color of the catalyst was darker than in all other experiments, although color changes during the oscillations still could be observed. Subsequent exposure to oxygen and nitrogen oxides, in an attempt to restore the catalytic activity, did not result in an enhancement of the N_2O conversion. Since the pretreatment of Cu–ZSM-5 with hydrogen was found to transform at least part of the copper to Cu^0 (23), it can be concluded that part of the active copper species has been irreversibly destroyed by reaction with H_2. It has to be noted that no such deactivation could be observed when hydrogen was added under the conditions of the N_2O decomposition reaction (cf. Fig. 12).

Given the results obtained after pretreatment of the catalyst with reducing agents, it appears straightforward to assume that the more active species for the decomposition of nitrous oxide over Cu–ZSM-5 is monovalent copper.

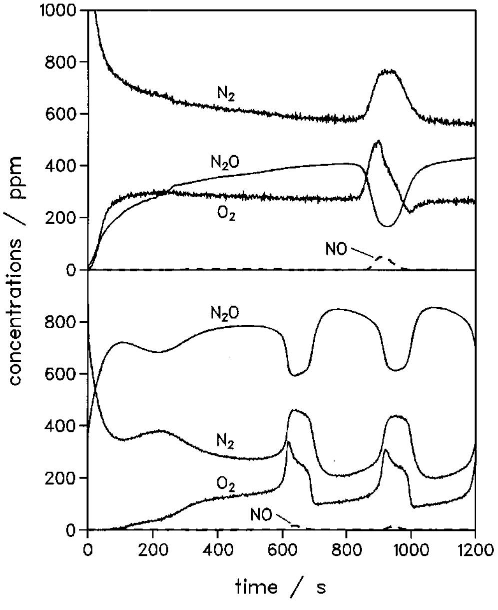

FIG. 15. Exit concentrations as a function of time for a feed composition of 1000 ppm N_2O in He at $T = 698$ K after pretreatment of catalyst with 1% CO (upper part) and 1000 ppm H_2 (lower part).

CONCLUSIONS

It can be summarized that two different states of catalytic activity in the oscillating catalytic decomposition of N_2O can be clearly distinguished. The active state has a lower coverage with oxygen, probably in atomic form, whereas the less active state is accompanied by a higher oxygen coverage. In agreement with the mechanism proposed by Ciambelli *et al.* (5), the active species appears to be Cu^+. Moreover, oscillations as well as appreciable decomposition activity are only observed for catalysts containing "overexchanged" copper, a species that was also found to be essential for the catalytic decomposition of NO. Thus decomposition of NO and N_2O seems to be closely related to and occurs most probably on the same active sites. From the present results it cannot be concluded whether Cu^{2+}–O–Cu^{2+} pairs or other species are involved. However, the active sites are easily reducible and able to release oxygen deposited by reaction of nitrous oxide even upon exposure to inert gas.

In contrast to results by Ciambelli and co-workers, no inhibiting effect of gas-phase oxygen or nitric oxide could be observed in the present investigation. Nitric oxide was rather found to act as a reducing agent and to play a crucial role in the kinetic oscillations. The observed oscillations are caused by a complex interaction of different reactions. The active copper species is initially poisoned by atomic oxygen formed during decomposition of N_2O. Since no evidence for adsorption of nitrous oxide or nitrogen under the conditions used could be found, the first step in the overall reaction might be described as

$$N_2O + \square \rightarrow N_2 + O_s. \qquad [3]$$

After at least part of the active sites have been oxidized, the catalyst reaches the state of low activity, where the overall decomposition rate is also influenced by reactions giving rise to formation of gaseous oxygen. While nitrous oxide itself acts as a reducing agent [4], as has been shown by Kapteijn *et al.* (10), the recombination of atomic oxygen [5] also must be taken into account, since complete desorption of oxygen upon switching to inert gas easily occurred:

$$N_2O + O_s \rightarrow N_2 + O_2 + \square \qquad [4]$$

$$2\,O_s \rightarrow O_2 + 2\square. \qquad [5]$$

The recombination of deposited oxygen is proposed to be irreversible because no effect of O_2 on the observed phenomena could be found. The periodic change between the two states of different catalytic activity is brought about by a simultaneous reaction producing adsorbed nitrates. A mechanistic description of these complex processes is not yet possible, but the development of oscillations can be qualitatively explained. During the state of low catalytic activity, nitrate is formed on the oxidized catalyst with a low rate. After a certain amount of nitrate has been produced, this species starts to decompose into oxygen and NO. Nitric oxide is acting as a powerful reducing agent that facilitates the desorption of oxygen. On the reduced sites, the nitrate species is less stable, which causes further release of NO and maintains the catalyst in the active state for a certain time. However, when the reducing agent is no longer present in the gas phase in sufficient concentrations, the catalyst is rapidly oxidized and reaches again the state of low catalytic activity. The intervals between the more active states are shorter than the initial period, because the catalyst is not completely free of nitrates as at the first exposure to nitrous oxide.

Remaining unanswered questions include the exact role of nitric oxide as reducing agent. While the equilibrium reaction between NO and NO_2 offers a plausible reason, a similar explanation does not hold for the effect of hydrogen, the behavior of which was found to be very similar to nitric oxide. The proposed nitrate intermediate has to be confirmed by further *in situ* measurements. Finally, it is not yet clear why oscillating phenomena occur on some Cu–ZSM-5 catalysts while other samples exhibit steady-state operation in a broad range of conditions. The relationship between Si/Al ratio, as well as synthesis method of the parent ZSM-5 zeolite and the development of oscillations, is under investigation.

ACKNOWLEDGMENTS

This work was supported by Deutsche Bundesstiftung Umwelt and the Fonds der Chemie. Dr. W. Schwieger is gratefully acknowledged for the ICP analysis. Assistance in measurements received from C. Feinauer and M. Rauscher is also gratefully acknowledged.

REFERENCES

1. Iwamoto, M., *Catal. Today* **29**, 29 (1996).
2. Li, Y., and Armor, J. N., *Appl. Catal. B* **1**, L21 (1992).
3. Lintz, H.-G., and Turek, T., *Catal. Lett.* **30**, 313 (1995).
4. Turek, T., *Appl. Catal. B* **9**, 201 (1996).
5. Ciambelli, P., Garufi, E., Pirone, R., Russo, G., and Santagata, F., *Appl. Catal. B* **8**, 333 (1996).
6. Bossmann, S. H., Ottaviani, M. F., and Turek, T., *Ber. Bunsenges. Phys. Chem.* **101**, 978 (1997).
7. Lei, G. D., Adelman, B. J., Sárkány, J., and Sachtler, W. M. H., *Appl. Catal. B* **5**, 245 (1995).
8. Kapteijn, F., Mul, G., Marbán, G., Rodriguez-Mirasol, J., and Moulijn, J. A., *Stud. Surf. Sci. Catal.* **101**, 641 (1996).
9. Kapteijn, F., Rodriguez-Mirasol, J., and Moulijn, J. A., *Appl. Catal. B* **9**, 25 (1996).
10. Kapteijn, F., Marbán, G., Rodriguez-Mirasol, J., and Moulijn, J. A., *J. Catal.* **167**, 256 (1997).
11. Centi, G., Galli, A., Montanari, B., Perathoner, S., and Vaccari, A., *Catal. Today* **35**, 113 (1997).
12. Correa, C. M., Villa, A. L., and Zapata, M., *Catal. Lett.* **38**, 27 (1996).
13. Leglise, J., Petunchi, O., and Hall, W. K., *J. Catal.* **86**, 392 (1984).
14. Kobayashi, H., and Kobayashi, M., *Catal. Rev. Sci. Eng.* **10**, 139 (1974).

15. Nakamura, M., Mitsuhashi, H., and Takezawa, N., *J. Catal.* **138**, 686 (1992).
16. Iwamoto, M., *Stud. Surf. Sci. Catal.* **84**, 1395 (1994).
17. Valyon, J., and Hall, W. K., *Catal. Lett.* **19**, 109 (1993).
18. Moretti, G., *Catal. Lett.* **28**, 143 (1994).
19. Centi, G., Nigro, C., and Perathoner, S., *React. Kinet. Catal. Lett.* **53**, 79 (1994).
20. Pirone, R., Garufi, E., Ciambelli, P., Moretti, G., and Russo, G., *Catal. Lett.* **43**, 255 (1997).
21. Chang, Y.-F., and McCarty, J. G., *J. Catal.* **165**, 1 (1997).
22. Beutel, T., Sárkány, J., Lei, G. D., Yan, J. Y., and Sachtler, W. M. H., *J. Phys. Chem.* **100**, 845 (1995).
23. Dedecek, J., and Wichterlova, B., *J. Phys. Chem.* **98**, 5721 (1994).
24. Centi, G., and Perathoner, S., *Appl. Catal. A* **132**, 179 (1995).
25. Centi, G., and Perathoner, S., *Catal. Today* **29**, 117 (1996).
26. Hadjiivanov, K., Klissurski, D., Ramis, G., and Busca, G., *Appl. Catal. B* **7**, 251 (1996).
27. Komatsu, T., Ogawa, T., and Yashima, T., *J. Phys. Chem.* **99**, 13053 (1995).
28. Shimokawabe, M., Itoh, K., and Takezawa, N., *Catal. Today* **36**, 65 (1997).
29. Aylor, A. W., Larsen, S. C., Reimer, J. A., and Bell, A. T., *J. Catal.* **157**, 592 (1995).
30. Szanyi, J., and Paffett, M. T., *J. Catal.* **164**, 232 (1996).
31. Li, Y., and Armor, J. N., *Appl. Catal.* **76**, L1 (1991).
32. Valyon J., and Hall, W. K., *J. Phys. Chem.* **97**, 1204 (1993).
33. Zhang, W. X., Yahiro, H., Mizuno, N., Izumi, J., and Iwamoto, M., *Langmuir* **9**, 2337 (1993).
34. Wang, Z., Sklyarov, A. V., and Keulks, G. W., *Catal. Today* **33**, 291 (1997).
35. Musgrave, F. F., and Hinshelwood, C. N., *Proc. Roy. Soc. A* **135**, 23 (1932).
36. Pirone, R., Ciambelli, P., Moretti, G., and Russo, G., *Appl. Catal. B* **8**, 197 (1996).