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Isothermal “light-off” during catalytic N_2O decomposition over Fe/ZSM-5

Chimin Sang and Carl R.F. Lund [*]

Chemical Engineering Department, SUNY-Buffalo, Buffalo, NY 14260-4200, USA
E-mail: lund@eng.buffalo.edu

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The catalytic decomposition of N_2O over Fe/ZSM-5 was studied at pressures up to 1 atm. As the partial pressure of N_2O in the feed to a packed bed reactor was varied, the catalytic activity was observed to abruptly increase at inlet partial pressures above some critical value. This abrupt increase in activity was not due to the reaction exotherm, but is believed to be a kinetic phenomenon. In similar experiments where the temperature was varied the activity did not jump to a higher level. The dual levels of activity were observed for several Fe/ZSM-5 catalysts that spanned a range of SiO_2/Al_2O_3 ratios from 30 to 280, irrespective of whether the iron was introduced into the zeolite by ion exchange or by sublimation of iron chloride. When the inlet partial pressure of N_2O to the packed bed reactor was sufficiently high to cause the catalyst to operate in the high activity regime, the high activity state was sustained throughout the catalyst bed, even though the N_2O partial pressure in the latter part of the bed had dropped below the critical level. Microkinetic modeling shows that this kind of behavior is possible in an isothermal catalytic system. The microkinetic model includes two redox cycles. In one cycle the cation oxidation state alternates between Fe^{2+} and Fe^{3+}. In the second, more active redox cycle there is alternation between a surface nitrite and nitrate. The former redox cycle predominates at low partial pressures and the latter at high N_2O partial pressures.

Keywords: nitrous oxide decomposition, Fe/ZSM-5, catalyst activation

1. Introduction

The decomposition of nitrous oxide has been examined over a variety of catalysts. Cation-exchanged zeolites, including many based upon the zeolite ZSM-5, are among the systems that have been studied for this reaction [1–5]. Research in this area was previously reviewed by Kapteijn et al. [6], who also recently reported on a detailed examination of the reaction kinetics over zeolite-based catalyst systems [7]. The reaction has been studied independently, but it is also important as one of the processes that occurs during selective catalytic reduction (SCR) of nitrogen oxides [8–12] and as the source of a unique form of surface oxygen that can be used in the selective oxidation or hydroxylation of organic substrates including benzene and methane [13–16]. It appears that most previous kinetics studies of the decomposition reaction have been conducted with relatively low partial pressures of nitrous oxide, as would likely be encountered in an emission treatment situation. This letter is a preliminary report of an unusual kinetic phenomenon that was observed during the study of the decomposition of nitrous oxide at substantially higher partial pressures (up to 1 atm). Specifically, it reports the observation, upon increasing the reactant partial pressure, of a dramatic increase in catalytic activity of Fe/ZSM-5 for nitrous oxide decomposition similar to that observed when a catalyst “lights-off” thermally, but in this case the system is isothermal.

2. Experimental

The ZSM-5 from which catalysts were prepared was obtained from Zeolyst International in the ammonium cation form. The starting materials were specified by the supplier to contain silica and alumina in the ratios of 30, 50, 80, and 280. To convert the supplied material to the H-exchanged form, a measured amount (typically 10–50 g) was placed in a crucible inside a muffle furnace. The furnace temperature was ramped from room temperature to 120 °C at a rate of $1\,^\circ\mathrm{C\,min^{-1}}$ and then held at 120 °C for 2 h to allow adsorbed water to desorb. The furnace temperature was then ramped from 120 °C at $1\,^\circ\mathrm{C\,min^{-1}}$ to 600 °C and held at that temperature for 18 h. This procedure is expected to cause the ammonium exchange cations to decompose, giving off ammonia and leaving a proton as the exchange cation (H-ZSM-5).

Iron was introduced into the H-ZSM-5 in two ways. One was a conventional ion-exchange method, similar to that used to prepare other Fe/ZSM-5 catalysts for N_2O decomposition [7]. Typically, 1 g of H-ZSM-5, 0.6 g of ferrous sulfate (Fisher) and 1 l of doubly deionized water were mixed and vigorously stirred at 75 °C overnight. The product slurry was filtered using GF/A glass microfiber filter paper (Whatman Laboratory) and a Buchner vacuum filtration apparatus. The filtrate was next washed with a copious amount of doubly deionized water. Finally, the filter cake was dried under vacuum at 100 °C for at least 2 h and calcined overnight in air at 600 °C. Two samples were prepared in this manner, one using ZSM-5 with a

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[*] To whom correspondence should be addressed.

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silica/alumina ratio of 30 and the other with a ratio of 280. These will be designated Fe/ZSM-5(30i) and Fe/ZSM-5(280i), where the values in parentheses indicate the silica/alumina ratio and the ion-exchange preparation method.

The second method by which iron was introduced into the zeolite involved sublimation of $FeCl_3$ and was very similar to the procedure described by Chen and Sachtler [17]. First, the ammonium form of the zeolite was converted to H-ZSM-5 as already described. If the H-ZSM-5 was not freshly prepared (i.e., it had been prepared and stored for some time) a measured amount (typically 10–50 g) was again heated to 120 °C and held at 120 °C for 2 h to desorb water that may have been present. The sublimation apparatus was fabricated from two pieces of ca. 19 mm (0.75 inch) OD stainless-steel tubing, one 15 cm and the other 10 cm long, connected using a Swagelok® union. Typically, about 10 g of HZSM-5 were loaded into the 15 cm length of tubing and 5 g of iron(III) chloride (Acros Organics) were loaded into the 10 cm length of tubing. Both ends of each tube were packed with glass wool and the two tubes were connected. The so-assembled tubing was then placed in a vertical tube furnace, and a helium source (high purity grade, Cryogenic Supply) was connected to the end containing the iron chloride. The other end was connected to tubing that directed the exhaust gas through dilute sodium hydroxide solution (to scrub out hydrogen chloride) before venting to a hood. The helium gas flow rate was set at about 100 sccm, and then the furnace temperature was ramped from room temperature to 280 °C at a rate of $2\,°C\,min^{-1}$. The temperature was maintained constant at 280 °C for 1 h before being further ramped to 305 °C. At this temperature, the iron chloride sublimed as evidenced by its eventual condensation in the exhaust tubing. The inlet helium was turned off when the exhaust tubing became completely blocked by condensed iron chloride, and the furnace was allowed to cool down. The tubing assembly was disconnected and the product, showing a uniform yellow color, was taken out. The recovered zeolite was washed with an excessive amount of double-deionized water and then filtered, as described before. The filter cake was dried under vacuum, crushed and calcined again at 800 °C overnight. Samples were prepared in this manner for each of the silica/alumina ratios; the samples will be designated Fe/ZSM-5(30s), Fe/ZSM-5(50s), Fe/ZSM-5(80s), and Fe/ZSM-5(280s), where the values in parentheses indicate the silica/alumina ratio and the sublimation preparation method.

N_2O (Matheson, UHP grade) was used as reactant without further purification. Helium (Cryogenic Supply, high purity grade), used both as the GC carrier gas and as a diluent mixed with the feed gas, was additionally purified by passage through a Supelco carrier gas drying tube, a Supelco carrier gas purifier and a Supelco OMI-2 indicating purifier.

The N_2O decomposition reaction was carried out in a conventional tubular reactor made of Quartz with a 6.4 mm (0.25 in) OD. Typically, 50 mg of catalyst were loaded in the center of the reactor with quartz wool placed above and below and with a type K thermocouple, shielded with quartz glass, placed just below the catalyst bed. This reactor assembly was heated using a tube furnace with automatic temperature control to within ±1 °C of the desired temperature. The flow rates of the feed gases were controlled with VICI model SA202 flow controllers, and the exhaust gas flow rate was measured using a bubble flow meter. The outlet volumetric flow rate changes with conversion due to the change in moles associated with the N_2O decomposition reaction. This effect was properly accounted for in all reactor modeling and analysis. The pressure in the reactor was not regulated and was assumed to be essentially atmospheric. The product composition was determined using an online Varian 1400 gas chromatograph with a thermal conductivity detector. A ten-port Valco switching valve was used to inject samples automatically. The sampled gas was separated on a Hayesep D column and a 5A molecular sieve column using a switching valve to reverse the column sequence during the analysis. Detector response data were collected and analyzed using PeakSimpleII software (SRI) running on a personal computer.

3. Results

Approximately 50 mg of catalyst were loaded into the reactor as described and exposed to a flowing mixture of He and N_2O. The temperature was held constant and the system was allowed to attain a steady state. The inlet flow rates were then adjusted, changing the feed ratio of He and N_2O, but at the same time keeping the total outlet flow rate and the temperature constant. This was repeated many times, thereby spanning the composition range from low nitrous oxide partial pressure to pure N_2O. Each of the catalysts previously described was tested in this manner; the results for Fe/ZSM-5(280s) are shown in figure 1. In this case three constant temperatures were examined (773, 798, and 823 K), and at each temperature two constant outlet volumetric flow rates were maintained (30 and 60 sccm).

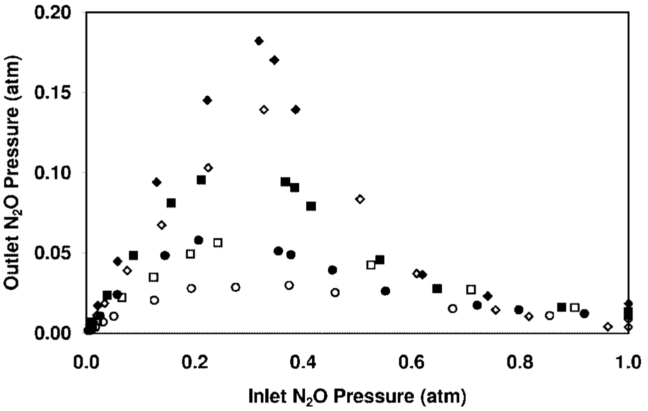


Figure 1. Variation in outlet N_2O partial pressure as a function of inlet partial pressure: (◇, ◆) at 773, (□, ■) at 798, and (○, ●) at 823 K; filled symbols are at an outlet flow rate of 60 sccm and unfilled symbols are at an outlet flow rate of 30 sccm.

Figure 1 shows the measured outlet N_2O partial pressure as a function of the inlet N_2O partial pressure. At an inlet partial pressure of approximately 0.3 atm, the activity of the catalysts increased significantly. This is seen in the figure as a sudden decrease in outlet N_2O partial pressure at inlet partial pressures of ca. 0.3 atm and above. The sequence in which the inlet partial pressure of N_2O was varied in the runs shown in figure 1 was not the same for all runs. In some cases it was increased from low to high, in some cases it was decreased from high to low, and in some cases it was first decreased from near the peak value to low inlet partial pressure, and then returned to the peak value and increased to 1 atm. The behavior was fully reproducible irrespective of the sequence in which the inlet partial pressure was varied.

Most importantly, the data reported for each series in figure 1 are at a constant temperature. The nitrous oxide decomposition reaction is significantly exothermal, and great care was taken in looking for hot spots and other signs of thermal light-off. None was found. When the partial pressure was increased in the range of high catalytic activity, a transient exotherm was indeed indicated by a transient increase in the thermocouple reading taken from within the catalyst bed. However, the temperature always returned to the set point value for the run within a few minutes, and the data reported in the figure were all collected after any brief exotherm had subsided. Replicate experiments using an unshielded thermocouple and varying its position did not reveal any hot spots in the catalyst bed.

To further probe the possibility of thermal light-off, a series of experiments was performed where the feed composition and flow rate were held constant, and the temperature was increased in steps. The results, again for sample Fe/ZSM-5(280s), are shown in figure 2. The filled squares in that figure show the conversion as the temperature was changed in steps from 623 to 848 K, then back in steps to 673 K, and finally up to 873 K in a single step, all using a feed with 5% N_2O in He at a flow rate of 60 sccm. Following each step the temperature was held constant for 1–2 h during which several analyses were made of the reactor outlet. The figure shows every datum collected at every step. Significantly, the figure does not indicate any hysteresis upon stepping the temperature in opposite directions. Figure 2 also shows (as (●)) the results of another experiment done the same way and using the same catalyst, but with a feed of pure N_2O at ca. 1 atm. Again, no hysteresis is observed in the results. If the origins of the jump in activity were thermal, one might expect either to observe a light-off during the temperature cycling or to observe hysteresis. Instead, both figures 1 and 2 suggest that the high activity regime is only attained by increasing the partial pressure of the reactant.

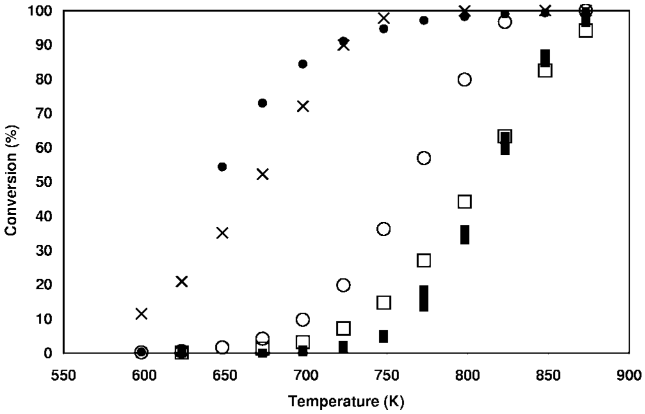
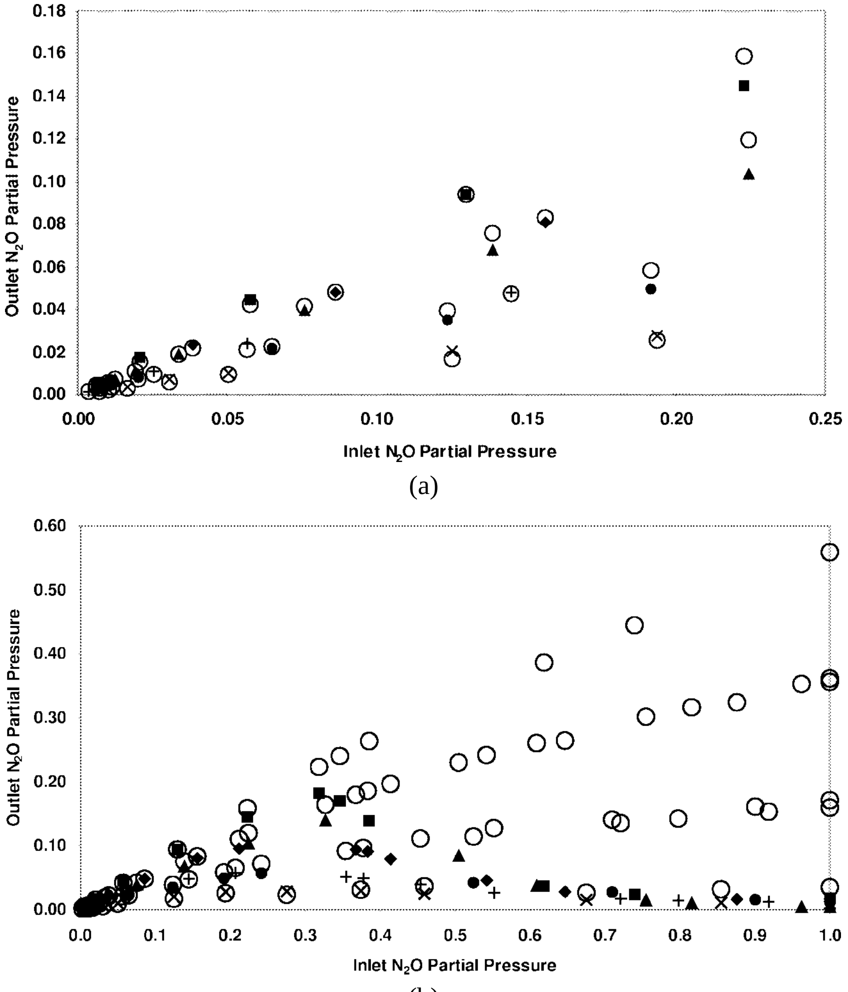


Figure 2. N_2O conversion as the temperature was changed in steps over a range that spanned all possible conversions. Filled symbols are experimental data ((■) 0.05 and (●) 1 atm N_2O). Unfilled symbols are predictions made using the first-order kinetic model that describes the low activity state of the catalyst ((□) 0.05 and (○) 1 atm N_2O). The fit of a separate first-order kinetic model to the 1 atm experiments is also shown as (×).

In previous studies of the decomposition of nitrous oxide over Fe/ZSM-5 and other iron-containing zeolites, it has been observed that the kinetics can be accurately described using a simple two-step Langmuir–Hinshelwood mechanism that simplifies to a first-order rate expression [1,2,7], at least at temperatures below 733 K. Figure 3(a) shows the results of fitting a first-order rate expression to the N_2O decomposition data in the low activity regime. In the fitting process, all data points from figure 1 below (but not including) the point of maximum outlet nitrous oxide partial pressure were included along with all the data for the low pressure run shown in figure 2. The fit is good ($R^2 = 0.98$), giving a pre-exponential factor of 3.4×10^5 mol s^{-1} atm^{-1} g^{-1} and an activation energy of 139 kJ mol^{-1}. The latter value is consistent with other reported studies [6]. The predictions from this fit are also shown in figures 1 and 2 as unfilled symbols. If a diffusion process were rate limiting in the low activity regime, a much lower apparent activation energy would be expected. This suggests that the change in catalyst activity is not caused by a transition from a diffusion limited regime to one where chemical reaction kinetics are controlling. Instead, it appears that chemical reaction kinetics are controlling in both the high and the low activity states.

The first-order rate expression just described could not be used to model the data in the high activity regime. This can be seen in figure 3(b), which shows all the data (not just the low pressure data used for fitting the expression). It is also evident in figure 2 when the predictions for the experiment at 1 atm (○) are compared to the experimental data (●). A separate first-order rate expression therefore was fitted to the data for experiment at 1 atm N_2O pressure (i.e., in the high activity regime). Figure 2 shows the predictions from this fit as well (as ×); it is not particularly good, and an alternative description of the kinetics is offered later in this section. Nonetheless, on the basis of this fit the high activity regime can be characterized using a first-order rate expression with a pre-exponential factor of 8.6×10^2 mol s^{-1} atm^{-1} g^{-1} and an activation energy of 88.5 kJ mol^{-1}.

The conversion observed with Fe/ZSM-5(280s) in the high activity state (pure N_2O feed) is shown as a function



(a)

(b)

Figure 3. Fit of a first-order rate expression to the low pressure data for N_2O decomposition, (a) showing only the data used in the fit and (b) the full data set. (○) represent the fit, all other symbols represent the experimental data ((■) 773 K, 60 sccm; (▲) 773 K, 30 sccm; (◆) 798 K, 60 sccm; (●) 798 K, 30 sccm; (+) 823 K, 60 sccm; and (×) 823 K, 30 sccm).

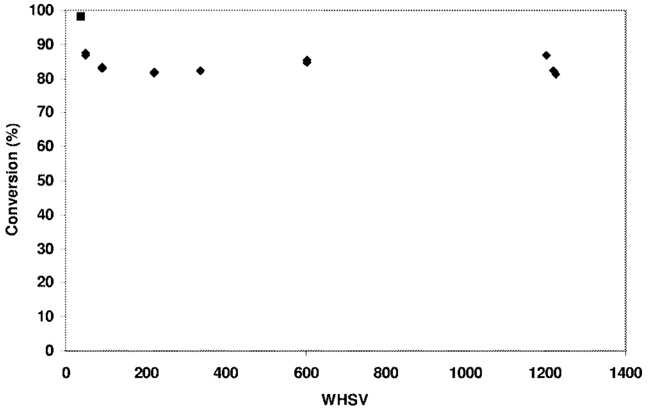


Figure 4. Conversion at 798 K as a function of weight hourly space velocity in the high activity state for Fe/ZSM-5(280s). The datum plotted as (■) is from an experiment using a 50 mg catalyst bed; (◆) are from a run using 3.8 mg of catalyst.

of weight hourly space velocity (WHSV) in figure 4. The results appear unreasonable at first, in that the conversion is less than 100%, yet it does not change with space velocity. However, a very small amount of catalyst was utilized in this run, and it is believed that as a consequence, there was some bypassing of the catalyst by the flowing gas. If this is true, then the conversion of the fraction of the gas that contacted the catalyst was apparently constant and therefore must equal 100%. More importantly, a significant rate of homogeneous, gas phase reaction must not have occurred. If gas phase reactions were causing the conversion in the high activity state, then the conversion should either have been equal to 100% at all WHSVs or there should have been a variation in conversion with WHSV.

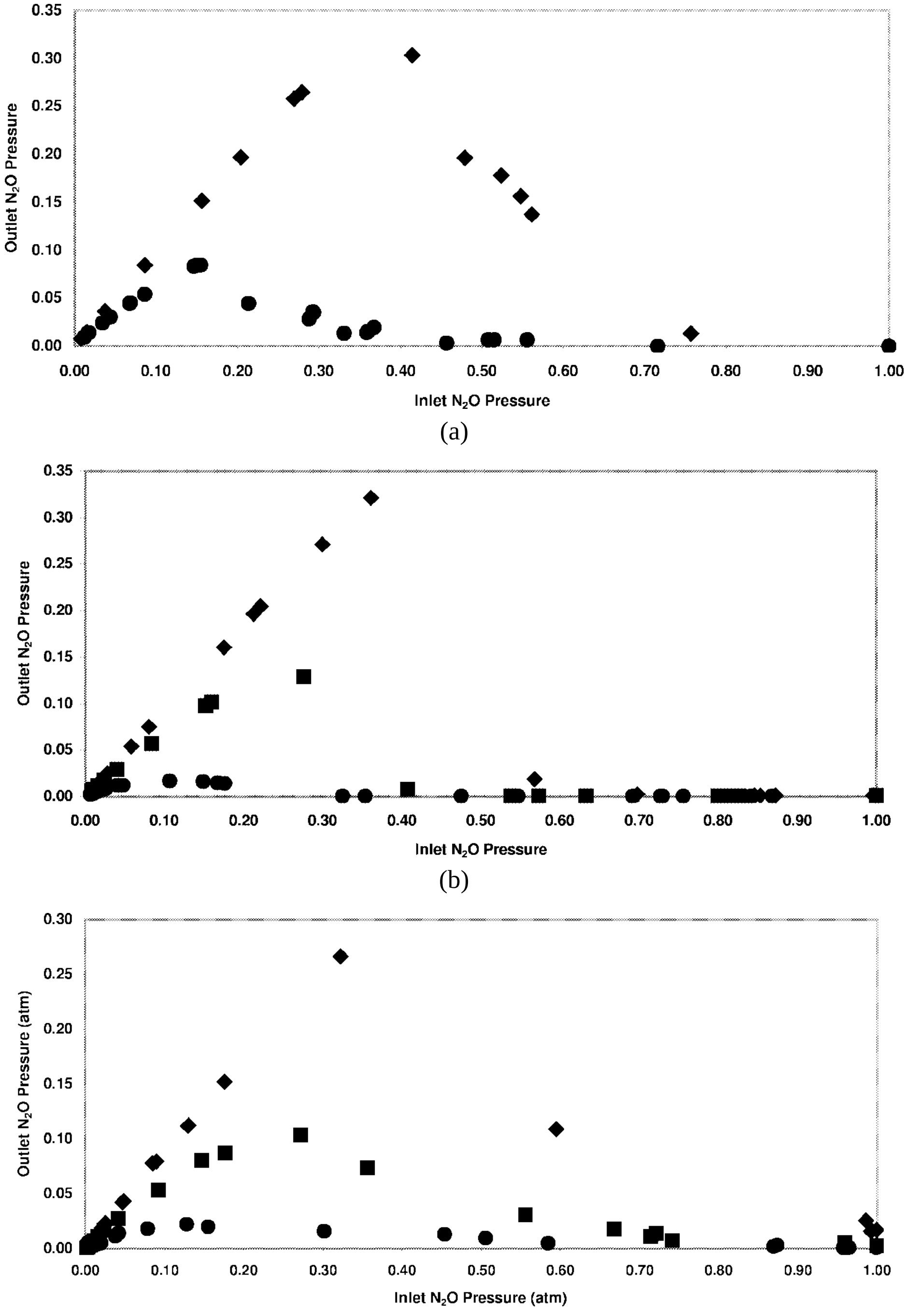
Table 1 compares three experiments performed at 673 K; all used a pure N_2O feed at 1 atm. In the first the reactor was loaded with glass wool as described in section 2, but without any catalyst. In the second the catalyst was H/ZSM-5(30) and in the third the catalyst was Fe/ZSM-5(30s). Significant catalytic activity was only observed in the experiment where the iron-containing zeolite was used.

The effect shown in figure 1 for Fe/ZSM-5(280s) was also observed with each of the other Fe/ZSM-5 catalysts.

Table 1
Control experiments on the decomposition of pure N_2O at 673 K.

Catalyst	N_2O conversion (%)
None	0.24
H/ZSM-5(30)	1.9
Fe/ZSM-5(30s)	100

Figure 5 (a), (b), and (c) shows an abrupt increase in catalytic activity at some critical inlet N_2O partial pressure when using Fe/ZSM-5(80s), Fe/ZSM-5(50s) and Fe/ZSM-5(30s). This series of catalysts have different SiO_2/Al_2O_3 ratios in the zeolites, and consequently different capacities for iron cation exchange. Thus, as the number of iron cations increased, the effect could be observed at higher flow rates, but two levels of activity were clearly evident for all the samples. Similarly, figure 6 (a)

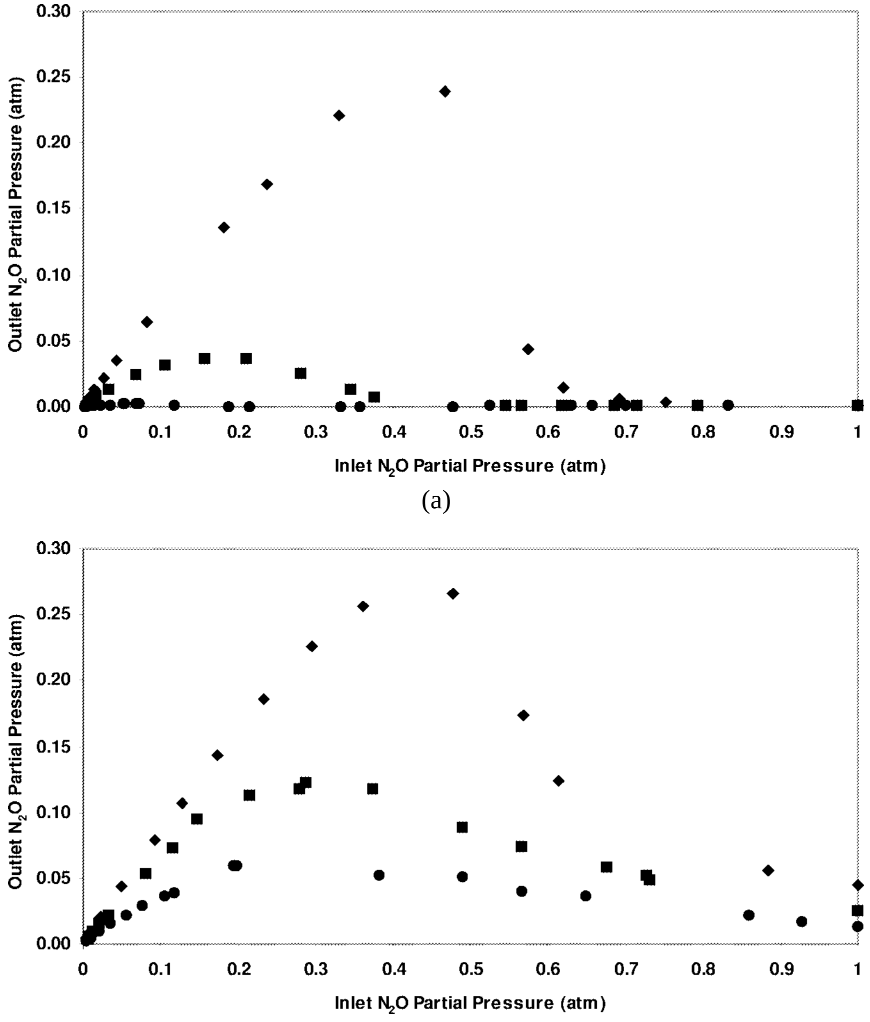


(a)

(b)

(c)

Figure 5. Variation in outlet N_2O partial pressure as a function of inlet partial pressure for catalysts prepared by sublimation using zeolite samples with different silica–alumina ratios ((◆) 673, (■) 698, and (•) 723 K). (a) Fe/ZSM-5(30s) with outlet flow rate of 60 sccm; (b) Fe/ZSM-5(50s) with outlet flow rate of 15 sccm; and (c) Fe/ZSM-5(80s) with outlet flow rate of 12.5 sccm.



(a)

(b)

Figure 6. Variation in outlet N_2O partial pressure as a function of inlet partial pressure for catalysts prepared by ion exchange using zeolite samples with different silica–alumina ratios. (a) Fe/ZSM-5(30i) with outlet flow rate of 12.5 sccm ((◆) 673, (■) 698, and (•) 723 K); (b) Fe/ZSM-5(280i) with outlet flow rate of 30 sccm ((◆) 773, (■) 798, and (•) 823 K).

and (b) shows that the same kind of behavior was observed when the iron was introduced by conventional ion exchange methods instead of sublimation. This is true for the zeolite with the lowest SiO_2/Al_2O_3 ratio, Fe/ZSM-5(30i), and for that with the highest SiO_2/Al_2O_3 ratio, Fe/ZSM-5(280i). Ion exchange generally leads to lower cation loading than sublimation [17–19], and consequently the flow rates are lower and temperatures higher with these samples. Still, the two levels of activity are observed in all cases. Generally, for all the samples the critical inlet partial pressure was between ca. 0.1 and 0.4 atm and for a given catalyst it decreased as the temperature increased.

4. Discussion

Increasing the feed partial pressure of the reactant is expected to increase the rate of reaction. However, for a first-order reaction this still would lead to an increasing outlet partial pressure of N_2O, as is evident in the fits shown in figure 3(b). The maximum in outlet partial pressure that was actually observed is a consequence of increased intrinsic catalytic activity. By comparing the first-order kinetic fits for the low activity and high activity regimes, it can be estimated that the intrinsic catalytic activity increases five-fold upon making the transition from the low activity regime to the high activity regime. That is, after accounting for the effect of the different reactant partial pressures in the two regimes, the higher activity is five times larger than the lower activity per gram.

Kapteijn et al. [7] did not report the kind of phenomenon shown here, for example in figure 1. Their experiments were apparently all performed at low partial pressures of N_2O, and consequently their catalyst was always in the lower activity state. They also performed experiments with added oxygen (up to 100 mbar) and did not see any increase in activity. They did observe a substantial increase in catalytic activity when CO or NO was added to the reactor feed. The increase in activity that they observed is not the same as in the present work, however. When Kapteijn et al. added CO to the feed, the reaction stoichiometry changed so that they were no longer studying N_2O decomposition to N_2 and O_2, but instead they were observing the oxidation of CO by N_2O to produce CO_2 and N_2 in stoichiometric proportions. Similarly, when they added NO, they detected high levels of NO_2, but in this case it appears that two overall reactions were operative: oxidation of NO by N_2O to NO_2 and N_2 along with N_2O decomposition to N_2 and O_2. In sharp contrast, in the work reported here, there were no additives to the reactor feed, and the products were always N_2 and O_2 in a stoichiometric 2 : 1 ratio.

The data for all the catalysts, as typified in figure 1, indicate that there must be some form of communication between the front part of the catalyst bed and the end part of the catalyst bed. This can be understood by first considering a reactor which is being fed N_2O at a partial pressure of 1 atm. Figure 1 shows that the outlet pressure from this reactor is less than 0.02 atm. Thus, if one measured the partial pressure of N_2O at different positions along the length of the catalyst bed starting from the inlet, it would steadily decrease. There then would be a location somewhere within the catalyst bed where the N_2O partial pressure had fallen to a value of 0.3 atm. The data clearly show that in the remaining part of the bed, the catalyst activity remains in the high state because the partial pressure falls to a final value of 0.02 atm. In contrast, when a reactor being fed N_2O at a partial pressure of 0.3 atm is next considered, figure 1 shows that the partial pressure falls to only ca. 0.18 atm by the end of the bed. Thus, in the former case the front end of the bed is apparently able to "communicate" with the back end of the bed and cause it to operate in the high activity regime.

The most likely means of "communication" between the front and back ends of the bed in the high activity state is via a gas phase species. In all the experimental work, the two products were always detected in a stoichiometric 2 N_2 : 1 O_2 ratio, and no other products were observed. As already mentioned, it does not appear likely that the reaction shifts from the surface to the gas phase when the activity changes from the low regime to the high regime. These observations suggest that one or more gas phase species are generated at trace concentrations in the high activity regime, and that the presence of these species causes the catalyst to continue to operate in the high activity state even after the partial pressure of N_2O has fallen below the critical inlet value necessary to generate the high activity state.

In previous studies, the partial pressure in the feed apparently was not sufficiently high to cause the catalyst to operate in the high activity regime. In that work, the kinetic behavior has been described accurately using models derived from the two-step mechanism given in the equations

$$N_2O + * \rightleftharpoons N_2 + O\text{–}* \tag{1}$$

$$N_2O + O\text{–}* \rightleftharpoons N_2 + O_2 + * \tag{2}$$

This two-step mechanism would then be expected to be operative in the present study as well when the inlet partial pressure is below the critical value.

While for some catalysts the product O_2 has been found to inhibit the reaction [6], it is reported to have no effect in the case of Fe/ZSM-5 [7], at least at lower temperatures. Hence, it is not likely that the presence of O_2 alone is responsible for triggering the high activity state. It is more likely that at higher N_2O partial pressures another gas phase species might be produced in small concentration. This is illustrated in equations (3) and (4) which suggests NO as the additional gas phase species,

$$N_2O + O\text{–}* \rightleftharpoons NO + NO\text{–}* \tag{3}$$

$$NO + * \rightleftharpoons NO\text{–}* \tag{4}$$

The generation of NO during the catalytic decomposition of N_2O has precedence. When Cu/ZSM-5 is used as a catalyst, the reaction can be made to undergo isothermal kinetic oscillations [20–23]. Specifically, that catalyst system exhibits steady isothermal oscillations between a state of high catalytic activity and one of lower catalytic activity. During the high activity state NO is experimentally observed in the gas phase. Also, addition of NO to the feed quenches the oscillations and fixes the catalytic system in the high activity state. A model has been suggested to explain the oscillations [24]. In the model, once NO forms, it leads to an accumulation of NO_3 on the catalyst surface. The latter can then decompose producing O_2 and releasing NO. This model cannot explain the present results. The portion of the mechanism involving NO generates O_2, but not N_2. Consequently, it can operate cyclically in a transient mode, but not at steady state.

As already discussed, the gas phase NO must be able to generate high activity sites, even after the N_2O partial pressure has fallen below the critical inlet value. A number of different microkinetic models were developed wherein NO adsorbed to form a more active surface species. Each of these models was able to predict a maximum in the outlet N_2O partial pressure, but none produced a very close agreement with experimental observation. In particular, when compared to the experimental data, these models always predicted a less steep decrease in outlet partial pressure above the maximum and a higher final outlet partial pressure.

Chen et al. [25] observed that the simultaneous exposure of this kind of catalyst to NO and O_2 led to markedly different surface species than exposure to NO alone. Specifically, NO alone simply adsorbed and then desorbed directly during subsequent temperature programming. In contrast, when both NO and O_2 were exposed to the catalyst NO_2 was detected in the gas phase, and upon subsequent thermal desorption, two desorption peaks were observed. Furthermore, NO, NO_2 and O_2 were all detected during the desorption. FTIR suggested the formation of nitro and/or nitrate groups on the surface. These observations indicate that the combined presence of NO and O_2 in the gas phase might lead to high activity sites as suggested in the equations

$$O_2 + NO{-}* \rightleftharpoons NO_3{-}* \tag{5}$$

$$N_2O + NO_3{-}* \rightleftharpoons N_2 + O_2 + NO_2{-}* \tag{6}$$

$$N_2O + NO_2{-}* \rightleftharpoons N_2 + NO_3{-}* \tag{7}$$

Additionally, since the O_2 partial pressure increases along the length of the reactor, this scheme might be expected to lead to a steeper decrease in outlet N_2O partial pressure than the schemes that were considered using only NO to generate high activity sites. Surface nitrogen oxides have also been reported to form during N_2O decomposition over copper-zeolite catalysts [26].

Panov and co-workers [13,14,16] have examined N_2O decomposition over Fe/ZSM-5 catalysts in a batch reactor system. Their data provide additional evidence for the possibility of two different kinds of redox sites. Specifically, they describe a form of surface oxygen that can only be formed by decomposition of nitrous oxide and that exhibits a very high activity in the subsequent oxidation of methane and phenol. Related calculations have been presented [27–29], however, which are claimed to explain the high activity. The sites studied in those calculations did not involve nitro or nitrate species.

The overall mechanism described in equations (1)–(7) provides two catalytic cycles for the decomposition of N_2O. The first cycle is represented by equations (1) and (2) and is predominant at lower inlet N_2O partial pressures. These two steps are consistent with the observed and reported first-order dependence on N_2O partial pressure and absence of inhibition by O_2. The second catalytic cycle is represented by equations (6) and (7). It involves cycling between a surface nitrate and a surface nitrite, and if this mechanism is to explain the experimental observations, then it must predominate at higher N_2O partial pressures. The latter cycle must operate at a higher rate and with a lower apparent activation energy than the other cycle.

The intention of this paper is to report the unusual catalytic behavior that has already been described, but not to establish the mechanism underlying the catalytic phenomena. To do the latter will require much more extensive kinetic studies combined with a battery of other characterization techniques. It does seem appropriate, however, to at least show that a mechanism of the form just described (i.e., equations (1)–(7)) is capable of predicting the isothermal "light-off" of the catalysts. Figure 7 shows the results of fitting a microkinetic model consisting of reactions (1)–(7) to the 60 sccm data from figure 1. The most important point to be made is that the mechanism can provide a very good description of the catalytic activity, capturing both the high activity and the low activity states. It also shows that this kind of behavior is indeed possible in an isothermal reactor.

The mechanistic predictions are consistent with other observations, as well. The seven-step mechanism predicts that greater than 95% of all sites are covered by O at all conditions. It also predicts gas phase NO levels that would be undetectable with the experimental methods used here. While the fit shown in figure 7 is very good, when the data at a 30 sccm flow rate are included, the fit is not nearly as good, as can be seen in figure 8. In particular, at the lower flow rate the onset of the high activity state is predicted at lower inlet partial pressures than experimentally observed. This makes it clear that while the seven-step mechanism of equations (1)–(7) is a promising starting point for further mechanistic investigation, it certainly must be subjected to much more detailed experimental investigation.

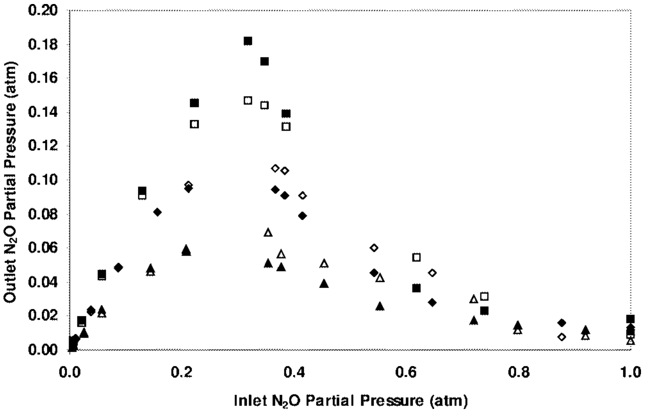


Figure 7. Comparison of seven-reaction microkinetic model (unfilled symbols) to experimental observation (filled symbols) for Fe/ZSM-5(280s) experiments at 60 sccm ((□, ■) 773, (◇, ♦) 798, and (△, ▲) 823 K).

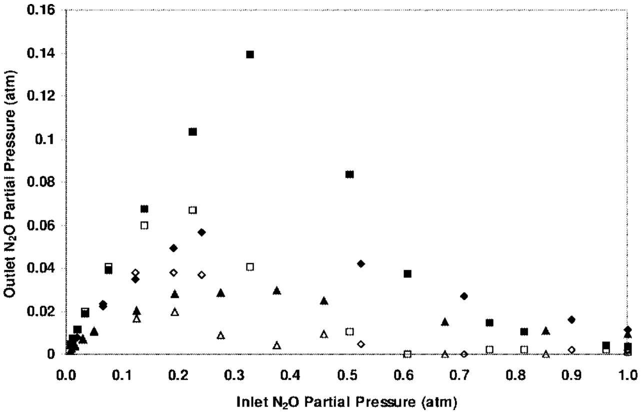


Figure 8. Comparison of seven-reaction microkinetic model (unfilled symbols) to experimental observation (filled symbols) for Fe/ZSM-5(280s) experiments at 30 sccm ((□, ■) 773, (◇, ♦) 798, and (△, ▲) 823 K).

There have been many studies directed at the characterization of the sites that are active for N_2O decomposition and related reactions [1,8,10,18,30–32]. The relative importance of single "naked" cations versus oxo-bridged cation pairs has been considered [17,33]. As the silica/alumina ratio of ZSM-5 increases the probability of forming oxo-bridged cation pairs will decrease as long as the silica and alumina are uniformly distributed within the zeolite framework [34]. The present observation that there are high and low activity sites on catalysts with a broad range of SiO_2/Al_2O_3 ratio and with two different methods of cation addition may eventually provide some additional insight into the nature of the sites. However, before attempting to relate the observations to models for the active sites there must be considerable additional characterization performed on these materials. For this reason, no speculation on the nature of the sites will be offered here.

5. Conclusions

The activity of Fe/ZSM-5 for the decomposition of N_2O increases abruptly when the inlet partial pressure of the reactant is increased above a certain level. Once initiated, this state of greater catalytic activity is sustained even after the partial pressure has fallen below that critical level, suggesting that a minority gas phase species is responsible for generating the higher activity. This effect is seen with ZSM-5 samples with a wide range of SiO_2/Al_2O_3 ratios. The iron exchange cation appears to be required in order to observe the phenomenon, but it is not sensitive to the method used to introduce the iron into the zeolite.

The observations can be explained using a model where trace amounts of NO are produced at higher partial pressures of N_2O. In the model, N_2O decomposes in the low activity state via a redox cycle involving oxidation and reduction of the exchange cation. The model then suggests that once NO has been formed, it can generate nitrite-like and nitrate-like species on the surface. The formation of these species leads to the high activity state wherein N_2O decomposition again occurs through a redox cycle, but in this case one where the nitrite/nitrate species undergo the oxidation and reduction instead of the cation. The latter cycle is more rapid and has a lower activation energy. A microkinetic model was developed using this mechanism and was found to provide a reasonable quantitative fit to some of the data, but additional testing will be required before any firm mechanistic conclusions can be drawn.

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References

[1] J. Leglise, J.O. Petunchi and W.K. Hall, J. Catal. 86 (1984) 392.
[2] C.M. Fu, V.N. Korchak and W.K. Hall, J. Catal. 68 (1981) 166.
[3] M. Rauscher, K. Kesore, R. Monning, W. Schwieger, A. Tissler and T. Turek, Appl. Catal. 184 (1999) 249.
[4] A. Dandekar and M.A. Vannice, Appl. Catal. B 22 (1999) 179.
[5] R.S. da Cruz, A.J.S. Mascarenhas and H.M.C. Andrade, Appl. Catal. B 18 (1998) 223.
[6] F. Kapteijn, J. Rodriguez-Mirasol and J.A. Moulijn, Appl. Catal. B 9 (1996) 25.
[7] F. Kapteijn, G. Marban, J. Rodriguez-Mirasol and J.A. Moulijn, J. Catal. 167 (1997) 256.
[8] G. Centi and F. Vazzana, Catal. Today 53 (1999) 683.
[9] M. Kogel, R. Monnig and T. Turek, J. Catal. 182 (1999) 470.
[10] T.V. Voskoboinikov, H.Y. Chen and W.M.H. Sachtler, Appl. Catal. B 19 (1998) 279.
[11] C. Pophal, T. Yogo, K. Yamada and K. Segawa, Appl. Catal. B 16 (1998) 177.
[12] K. Yamada, C. Pophal and K. Segawa, Micropor. Mesopor. Mater. 21 (1998) 549.
[13] G.I. Panov, A.S. Kharitonov and V.I. Sobolev, Appl. Catal. A 98 (1993) 1.
[14] G.I. Panov, V.I. Sobolev and A.S. Kharitonov, J. Mol. Catal. 61 (1990) 85.
[15] G.I. Panov, G.A. Sheveleva, A.S. Kharitonov, V.N. Romannikov and L.A. Vostrikova, Appl. Catal. A 82 (1992) 31.
[16] V.I. Sobolev, G.I. Panov, A.S. Kharitonov, V.N. Ronannikov, A.M. Volodin and K.G. Ione, J. Catal. 139 (1993) 435.
[17] H.Y. Chen and W.M.H. Sachtler, Catal. Today 42 (1998) 73.
[18] L.J. Lobree, I.-C. Hwang and A.T. Bell, J. Catal. 186 (1999) 242.
[19] P. Marturano, A. Kogelbaur and R. Prins, J. Catal. 190 (2000) 460.
[20] T. Turek, J. Catal. 174 (1998) 98.
[21] T. Turek, Appl. Catal. B 9 (1996) 201.
[22] P. Ciambelli, A.D. Benedetto, R. Pirone and G. Russo, Chem. Eng. Sci. 54 (1999) 2555.
[23] P. Ciambelli, A.D. Benedetto, E. Garufi, R. Pirone and G. Russo, J. Catal. 175 (1998) 161.
[24] T. Ochs and T. Turek, Chem. Eng. Sci. 54 (1999) 4513.
[25] H.-Y. Chen, T. Voskoboinikov and W.M.H. Sachtler, J. Catal. 180 (1998) 171.
[26] M. Shimokawabe, K. Hirano and N. Takezawa, Catal. Today 45 (1998) 117.
[27] M.J. Filatov, A.G. Pelmenschikov and G.M. Zhidomirov, J. Mol. Catal. 80 (1993) 243.
[28] K. Yoshizawa, T. Yumura and T. Yamabe, Bull. Chem. Soc. Jpn. 73 (2000) 29.
[29] A.V. Arbuznikov and G.M. Zhidomirov, Catal. Lett. 40 (1996) 17.
[30] E.-M. El-Malki, R.A. van Santen and W.M.H. Sachtler, J. Phys. Chem. 103 (1999) 4611.
[31] R.L. Garten, W.N. Delgass and M. Boudart, J. Catal. 18 (1970) 90.
[32] L.M. Aparicio, W.K. Hall, S.-M. Fang, M.A. Ulla, W.S. Millman and J.A. Dumesic, J. Catal. 108 (1987) 233.
[33] H.-Y. Chen and W.M.H. Sachtler, Catal. Lett. 50 (1998) 125.
[34] X. Feng and W.K. Hall, Catal. Lett. 46 (1997) 11.