Possible role of nitrite/nitrate redox cycles in N_2O decomposition and light-off over Fe-ZSM-5

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Surface nitrite/nitrate redox cycles were proposed to explain light-off behavior that was observed during the decomposition of N_2O over Fe-ZSM-5. Further study has demonstrated that while the nitrite/nitrate model can explain the original observations as an isothermal, mechanistic phenomenon, the light-off behavior is thermal, and not a mechanistic effect. Nonetheless, a pathway involving nitrite/nitrate redox cycles appears to be more consistent with experimental observation than the simple two-step pathway involving cation redox cycles. In particular, the nitrite/nitrate pathway can explain the effect of added NO upon the reaction kinetics and the reported isotopic product composition when unlabeled N_2O reacts over an oxygen-labeled catalyst. Further, a nitrite/nitrate pathway is consistent with the steady-state kinetics as well as published thermal desorption and infrared spectroscopic results.

KEY WORDS: Fe-ZSM-5; N_2O decomposition

1. Introduction

It was recently reported by the present authors [1] that the N_2O decomposition reaction “lights off” when the inlet partial pressure of N_2O is increased. This behavior can be seen in figure 1 where the outlet partial pressure of N_2O is plotted against the inlet partial pressure for an atmospheric pressure, plug-flow reactor using Fe-ZSM-5 as the catalyst. The light-off can be seen in the figure as the point where the outlet partial pressure reaches a maximum and starts to decrease with further increase of the inlet partial pressure. This kind of behavior is not uncommon for exothermic reactions like N_2O decomposition, and it most often has thermal origins, i.e., it is evidence for a hot spot in the reactor. This was suspected as the origin of the light-off observed in figure 1, as well. Experiments were performed wherein a thermocouple was moved vertically within the catalyst bed while the reaction was proceeding in the high activity state, and no hot spot was detected. Prior to this, there had been several reports [2–9] that the N_2O decomposition over Cu-ZSM-5 can undergo isothermal oscillations in activity while temperature, pressure and feed composition are all held constant. In addition to these experimental observations, a mechanistic model was developed that fully supported the conclusion that the light-off was isothermal. Specifically, it predicted that the light-off seen in figure 1 can occur in an isothermal reactor; figure 1 shows this prediction along with the experimental data.

In order to explain the light-off behavior with an isothermal reactor, the mechanism given in equations (1) through (7) was postulated. The first two steps by themselves represent the redox cycle that has been used often to explain the N_2O decomposition reaction over ion-exchanged zeolite catalysts [10–13]. Experimentally the reaction is observed to obey first-order kinetics with respect to the N_2O partial pressure and to be unaffected by added N_2 or O_2. If O–$*$ is assumed to be the most abundant surface intermediate, reactions (1) and (2) properly predict this kinetic behavior. The light-off behavior was explained by adding steps (3)–(7). These steps postulate the generation of NO, leading to the formation of a surface nitrate, NO_3–$*$, which then serves as a second kind of redox site. Specifically, it was suggested that once a nitrate was formed, a second redox cycle could become operative wherein the reaction involves cycling between the surface nitrate and a surface nitrite, NO_2–$*$. This second redox cycle is captured in reactions (6) and (7). According to this model, the second redox cycle is not operative at low N_2O feed partial pressures because insufficient NO is

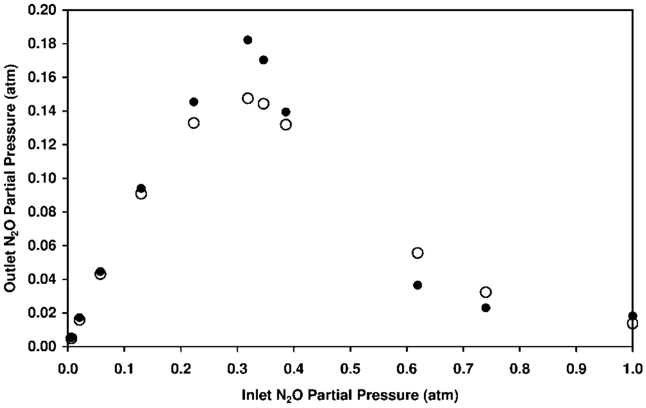

Figure 1. Outlet partial pressure of N_2O as its inlet partial pressure is varied at an apparent temperature of 673 K. The filled symbols represent the experimental data and the unfilled symbols represent the mechanistic prediction for an isothermal reactor.

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generated to sustain it. At higher N_2O feed partial pressures, the second redox cycle quickly becomes operative and then dominant. In this way, the model is able to reproduce the light-off behavior using an isothermal reactor model, as seen in figure 1.

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

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

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

$$NO + * \rightleftharpoons NO{-}* \tag{4}$$

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

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

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

In the absence of experimentally detecting a hot spot, and in light of the reported isothermal oscillations of the reaction over Cu-ZSM-5 combined with this mechanistic model that showed that an isothermal light-off is feasible, the phenomenon and the model were reported [1]. The present communication reports the results of further testing to determine whether such a mechanism is in fact operative. Specifically, the mechanism predicts that if NO and O_2 are present in the feed, then the nitrate surface species can be generated even at low partial pressures of N_2O. The nitrate/nitrite redox cycle should then predominate at all partial pressures, putting the catalyst in the higher activity state at all inlet N_2O partial pressures, and the light-off behavior should not be observed. That is, if NO and O_2 are present in the feed, the mechanistic model predicts that there will not be a maximum in the outlet N_2O partial pressure as the inlet N_2O partial pressure is varied. It will be shown below that this prediction was not confirmed by experiment and that, in fact, the light-off has a thermal origin. However, noting that the simple two-step mechanistic model of equations (1) and (2) cannot explain the kinetic effect of adding NO to the feed, it will be shown that a nitrate/nitrite mechanistic model can explain these effects. The nitrate/nitrite is also consistent with many other experimental observations reported in association with the decomposition of N_2O over Fe-zeolite catalysts, some of which again are not consistent with the simple two-step mechanism.

2. Experimental

The catalysts and methods are the same as reported in the previous study [1]. For present purposes, only one catalyst will be considered. ZSM-5 with a vendor specified silica-to-alumina ratio of 280 was obtained from Zeolyst International in the ammonium-exchanged form. It was converted to the proton-exchanged form by heating first to 393 K and holding for 2 h and then continuing to 873 K and holding there for 18 h. Iron was loaded into the zeolite by sublimation of $FeCl_3$ (Acros Organics) using a procedure very similar to that described by Chen and Sachtler [14]. It was subsequently washed using distilled water and calcined at 1073 K. This catalyst was previously referred to as Fe-ZSM-5(280s), where the terms in parentheses indicate the silica-to-alumina ratio and the sublimation method of preparation.

N_2O decomposition was conducted in a tubular reactor operating at atmospheric pressure. N_2O (Matheson, UHP) and NO (Matheson, CP grade) were used without further purification. O_2 (Matheson, Extra Dry Grade) was passed through activated 5A molecular sieves before use. He (Cryogenic Supply, high purity grade) was further purified using a gas drying tube, a Supelco carrier gas purifier and a Supelco OMI-2 indicating purifier. The reactor consisted of a quartz tube housed inside a computer-controlled tube furnace. In contrast to previous work, two K-type thermocouples were used: one was positioned immediately under the bed of ca. 50 mg of catalyst, while the other was situated above the bed and could be moved vertically. Gas flows to the top of the reactor were controlled using a VICI SA202 flow controller for N_2O and Omega FMA 760 mass flow controllers for the other gases. The composition of the gases leaving the reactor were analyzed using a Varian 1400 gas chromatograph with Haysep D and 5A molecular sieve columns and a thermal conductivity detector. Valve switching to inject samples and to reverse column sequence was controlled using PeakSimple II software (SRI), which also was used to collect and integrate the detector response data.

3. Results

As discussed in section 1, the mechanistic model for isothermal light-off predicts that adding NO and O_2 simultaneously to the feed should eliminate the light-off. Accordingly an experiment was run wherein the total flow from the reactor was fixed at 60 sccm. The feed consisted of 2 sccm O_2, 0.13 sccm NO, a variable flow of N_2O, and He, set to balance the total outlet flow to 60 sccm. In this run, the temperature was read from a single thermocouple positioned just below the catalyst bed, as in the earlier work. The temperature read from this thermocouple was 673 K and the total pressure was atmospheric. The results are shown in figure 2 where it can clearly be seen that a maximum in outlet N_2O partial pressure, characteristic of light-off, is still present. A second run, using 0.32 sccm of NO, showed the same be-

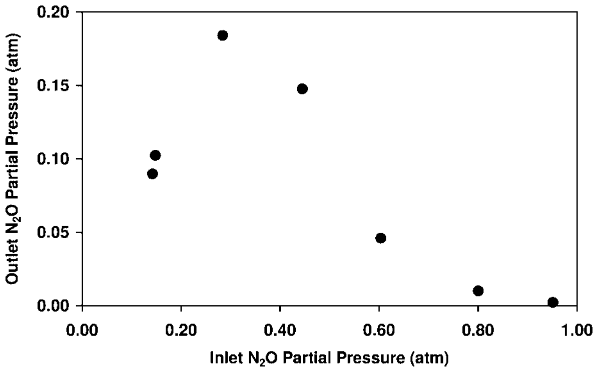

Figure 2. Outlet partial pressure of N_2O as its inlet partial pressure is varied at an apparent temperature of 673 K and with both NO and O_2 added to the feed.

havior. Thus, though the mechanistic model establishes that an isothermal light-off is feasible, this particular model does not apply to the present experimental system. This prompted additional experiments directed toward detecting a hot spot within the reactor.

In the previous experiments to look for a hot spot, a single thermocouple entered from the bottom of the catalyst bed while the catalyst was operating in the lighted-off mode. The vertical position of this thermocouple within the catalyst bed was varied, but no hot spot was observed. In the present study, one thermocouple was fixed immediately below the bed. The reactor was operated in the lighted-off mode and a second thermocouple was introduced from above the bed and slowly moved down toward the top of the bed. Indeed, a hot spot was found at the very top of the bed: the upper thermocouple indicated a temperature as much as 60 K higher than the thermocouple just below the bed (which held constant). If the top thermocouple was subsequently moved so that it was just below the surface of the bed, its reading dropped so that it was essentially the same as the reading of the thermocouple just below the bed. Thus, there was an extremely thin layer at the top of the catalyst bed that had lighted-off while the rest of the bed's temperature was nearly uniform.

Additional experiments were subsequently performed. In all these new experiments, the inlet partial pressure of N_2O was kept below the light-off point and the second thermocouple was used at each point to check the very top of the bed for a hot spot. In all cases included here, the upper thermocouple reading was within 5 K of the expected value indicating that there were no hot spots. Two series of runs were made, one series used a feed with only N_2O and He, and the second series used a feed with N_2O, NO and He. In both series, the total outlet flow rate was held constant at 30 sccm, and in the second series the NO feed rate was also held constant at 0.2 sccm. The N_2O and He flows were varied in order to vary the N_2O partial pressure, keeping the total outlet flow rate constant.

Figure 3 compares the two runs conducted as just described at a temperature of 736 K and 1 atm pressure. It is very clearly seen that the conversion is much greater when NO is present in the feed. A part of the extra conversion may be a result of oxidation of NO to NO_2, but it is not a major part. Specifically, at the highest inlet N_2O partial pressures shown, the total N_2O conversion is $\sim$15% without added NO, while it is $\sim$85% when NO is present in the feed. The complete conversion of the added NO only accounts for $\sim$5% conversion of the N_2O; the remaining 80% is associated with N_2O decomposition.

4. Discussion

N_2O decomposition is catalyzed by a number of different zeolites that contain exchange cations that can have multiple oxidation states, including Fe-ZSM-5 and others. With iron-exchanged zeolites like Fe-ZSM-5 [12] and Fe-mordenite [10] the kinetics are first order with respect to N_2O and zero order with respect to both N_2 and O_2. This kinetic behavior has been explained in terms of a simple two-step mechanism [10–13] given previously in equations (1) and (2). Experimental results indicate that in its active state the catalyst is nearly fully oxidized. That is, the iron cations are predominantly Fe^{3+} and very few "vacant" sites are present on the surface. While this model is consistent with the observed kinetics and the oxidation state of the active form of the catalyst, and while it appears to be widely accepted, it is lacking in several respects.

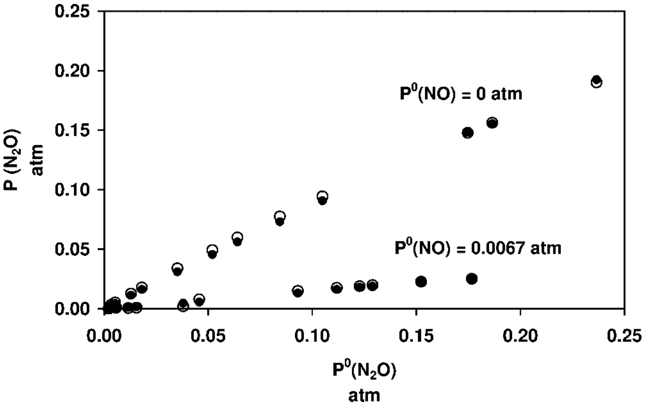

Figure 3. Comparison of the decomposition of N_2O with and without NO added to the feed, showing the outlet partial pressure of N_2O as its inlet partial pressure is varied at a temperature of 736 K and constant outlet flow rate of 30 sccm. The filled symbols represent the experimental data and the unfilled symbols represent a fit of the nitrite/nitrate mechanism to the data.

First, in a zeolite with a very high silica–alumina ratio, the cations are expected to be separated from each other by large distances. In such cases, one of the charges of an Fe^{3+} cation is compensated by the charge on the framework due to the presence of an Al^{3+} in place of a Si^{4+}. The other two charges can then be balanced by an oxygen anion, which would be denoted as $O{-}*$ in the mechanism. It is not immediately clear how such a species can then participate in a reaction like step (2) because this would generate an Fe^{+} species, for which there is no experimental evidence. This is not a problem when the silica–alumina ratio is low, because in that case the iron cations are close enough to each other that an oxo-bridge can form between two cations. A bridging anion compensates one charge of each cation, the charge on the framework compensates a second charge, and, most likely, a hydroxyl group compensates the third charge [14]. When an oxo-bridge exists, then one anion can be removed via a reaction like step (2), and two Fe^{2+} cations are generated. However, Feng and Hall [15] have pointed out that bridge formation in zeolites having Si/Al of 39 or greater will be extremely rare. Catalytic activity for N_2O decomposition has been observed in systems with relative high Si/Al, but this, by itself, does not preclude a two-step mechanism. The two-step mechanism could be operative if the aluminum distribution was non-uniform, if extra iron was present not as exchange cations, or if there was a mechanism by which the iron charge could be accommodated over a longer range (through the framework).

Second, the simple two-step mechanism, equations (1) and (2), does not offer any direct explanation for the present observation that a small amount of NO can cause an increase in the rate of reaction. It is possible that NO could provide a parallel path for generating the reduced site as given in equation (8). However, if only cation redox sites are assumed to exist, this would be a stoichiometric effect. Considering results presented in figure 3, 5% of the N_2O might be consumed very rapidly via equations (1) and (8), but at that point the NO would be fully consumed. The remaining conversion would necessarily proceed via equations (1) and (2). It then is not possible to explain how an additional 75% of the N_2O is converted after the NO is fully consumed whereas only 15% is converted in the absence of any NO. Indeed, Kapteijn et al. studied the decomposition reaction both with and without adding a relatively large amount of NO [12]. In the former situation, the kinetics could be described using the simple two-step mechanistic model, but when large amounts of NO were present in the system, they added an additional pathway to their mechanism. This pathway involved formation of a surface NO_2 species, which then reacted directly with N_2O leading to production of gas phase NO_2.

$$\mathrm{NO} + \mathrm{O}{-}{*} \rightarrow \mathrm{NO_2} + {*} \tag{8}$$

Third, Leglise, Petunchi and Hall [10] conducted the following experiment in an attempt to validate the two-step mechanism. Using Fe-mordenite, they performed an exhaustive isotopic exchange wherein a substantial fraction of the catalyst oxygen was replaced with ^{18}O. The exact amount was estimated to represent 64% of the exchangeable catalyst oxygen, including both extra-framework oxygen ($\mathrm{O}{-}{*}$) and lattice oxygen. They then exposed the catalyst to $N_2{}^{16}O$, expecting that 64% of the first product dioxygen molecules would be $^{16}O^{18}O$ according to the isotopic form of equation (2), given here in equation (9). In fact, the first dioxygen molecules observed were virtually all $^{16}O^{16}O$, and the concentration of $^{16}O^{18}O$ increased slowly from an initial value of zero. This result would appear to disprove the simple two-step mechanism. Leglise et al. suggested that there might have been severe diffusional limitations, or alternatively that only a very small fraction of the exchange cations are active, but that otherwise “it would seem necessary to conclude that the decomposition reaction is unrelated to the redox chemistry.”

$$\mathrm{N_2{}^{16}O} + \mathrm{^{18}O}{-}{*} \rightleftharpoons \mathrm{N_2} + \mathrm{^{16}O^{18}O} + {*} \tag{9}$$

Fourth, during the decomposition of N_2O over Cu-ZSM-5 the catalyst has been reported to undergo isothermal activity oscillations [2–9]. During the high activity phase of the oscillations, NO is detected in the gas phase. This cannot be explained using the simple two-step mechanism, since it does not offer a pathway for NO formation; indeed as already noted, it does not even include NO. Furthermore, if NO, at 900 ppm concentrations, is added to the feed, the isothermal activity oscillations disappear and the catalyst exhibits a steady activity level equal to the high activity phase of the oscillations [8]. This is essentially the same as the first point above.

Finally, it has been reported [16] that following N_2O adsorption, the products evolved during temperature-programmed desorption depend upon whether the desorption is performed in He or in the presence of N_2O. When conducted in the presence of He, an oxygen desorption peak is seen at ca. 623 K. When performed in the presence of N_2O, the desorption spectrum is reported to be nearly the same as that observed following exposure of the catalyst to NO_2 or to both NO and O_2. Chen et al. further report [17] that following NO/O_2 coadsorption, they observed four IR bands. Two of these, those at 1625 and 1570 cm^{-1}, have been assigned to “nitro/nitrate” groups, and they appear to be catalytically important. These surface species have the stoichiometry NO_y, where $y \geqslant 2$.

A nitrite/nitrate redox cycle, similar to that suggested previously, appears to be more consistent with the full body of reported behavior than the simple two-step mechanism that is often used to describe the reaction kinetics. The exact steps comprising such a nitrite/nitrate pathway still need to be experimentally determined. Here, for illustrative purposes, equations (10) through (15) will be used, but again the exact mechanistic steps remain to be determined. (A few of the surface species are written in a somewhat awkward manner here, e.g., $\mathrm{O_2N}$–O–$*$ instead of $\mathrm{NO_3}$–$*$, ON–O–$*$ instead of $\mathrm{NO_2}$–$*$ and N–O–$*$ instead of NO–$*$. This has been done to facilitate subsequent discussion.)

$$\mathrm{N_2O} + \mathrm{O}{-}{*} \rightleftharpoons \mathrm{NO} + \mathrm{N}{-}\mathrm{O}{-}{*} \tag{10}$$

$$\mathrm{N_2O} + \mathrm{N}{-}\mathrm{O}{-}{*} \rightleftharpoons \mathrm{N_2} + \mathrm{ON}{-}\mathrm{O}{-}{*} \tag{11}$$

$$\mathrm{N_2O} + \mathrm{ON}{-}\mathrm{O}{-}{*} \rightleftharpoons \mathrm{N_2} + \mathrm{O_2N}{-}\mathrm{O}{-}{*} \tag{12}$$

$$\mathrm{N_2O} + \mathrm{O_2N}{-}\mathrm{O}{-}{*} \rightleftharpoons \mathrm{N_2} + \mathrm{O_2} + \mathrm{ON}{-}\mathrm{O}{-}{*} \tag{13}$$

$$2\mathrm{NO} + \mathrm{O_2} \rightleftharpoons 2\mathrm{NO_2} \tag{14}$$

$$\mathrm{NO_2} + \mathrm{O}{-}{*} \rightleftharpoons \mathrm{O_2N}{-}\mathrm{O}{-}{*} \tag{15}$$

The nitrite/nitrate mechanism given here does not involve reduction of the cation site. Thus, it may be applied to isolated cations and does not require, nor preclude, the formation of oxo-bridges. It also is capable of describing the kinetics of the reaction. Figure 3 includes the results of fitting this mechanism to the two runs shown in the figure, one where NO has been added to the feed and one where it has not. In both cases, the fit is very good and demonstrates that the mechanism is capable of reproducing the observed first-order behavior with respect to N_2O and the promotional effect of adding NO. In the absence of added NO, the mechanism suggests that most of the surface is covered by O–$*$. There is a relatively small concentration of surface nitrite/nitrate which propagates the reaction via equations (12) and (13). When NO is added to the feed, it is rapidly converted to NO_2 (as seen experimentally). The so-generated NO_2 results in a higher surface concentration of nitrate sites via equation (15), and these sites can then participate in the main redox cycle, equations (12) and (13). The good fit seen in the figure does not prove the mechanism to be true, but it shows convincingly that a nitrite/nitrate redox cycle can reproduce the kinetics both with and without NO. No attempt was made to simulate the reported oscillatory behavior of Cu-ZSM-5, but the nitrite/nitrate mechanism is consistent with the observation of NO during reaction and, as shown, with the promotional effect of NO on the reaction rate.

Perhaps the most compelling argument in favor of the nitrite/nitrate mechanism is its ability to explain the results of Leglise, Petunchi and Hall's [10] isotopic labeling experiment described previously. The most important point is that the original oxygen bound to the cation during the extensive isotopic exchange, ^{18}O in this case, does not need to appear in the product. This is easily seen by rewriting the mechanistic steps in isotopic form, assuming the catalyst to initially contain ^{18}O and the reactant to be $N_2{}^{16}O$ as was true in the experiment. This is done in equations (15)–(20):

$$N_2{}^{16}O + {}^{18}O{-}* \rightleftharpoons N^{16}O + N{-}{}^{18}O{-}* \tag{15}$$

$$N_2{}^{16}O + N{-}{}^{18}O{-}* \rightleftharpoons N_2 + {}^{16}ON{-}{}^{18}O{-}* \tag{16}$$

$$N_2{}^{16}O_2 + {}^{16}ON{-}{}^{18}O{-}* \rightleftharpoons N_2 + {}^{16}O_2N{-}{}^{18}O{-}* \tag{17}$$

$$N_2{}^{16}O + {}^{16}O_2N{-}{}^{18}O{-}* \rightleftharpoons N_2 + {}^{16}O_2 + {}^{16}ON{-}{}^{18}O{-}* \tag{18}$$

$$2N^{16}O + {}^{16}O_2 \rightleftharpoons 2N^{16}O_2 \tag{19}$$

$$N^{16}O_2 + {}^{18}O{-}* \rightleftharpoons {}^{16}O_2N{-}{}^{18}O{-}* \tag{20}$$

The nitrite/nitrate mechanism is thus consistent with Leglise, Petunchi, and Hall's observation that initially only $^{16}O^{16}O$ is produced. The gradual appearance of $^{18}O^{16}O$ would then come about as the oxygen bound to the cation (O–$*$) exchanges with the oxygen bound to the nitrogen. One might expect this to be a slower process, again in agreement with the observation that $^{16}O^{18}O$ was not immediately observed, but that its concentration increased slowly over time.

The critical surface species have been called nitrites and nitrates herein to emphasize the redox nature of the catalytic cycle. At present, the mechanism is nothing more than a proposal, and in particular, structures have not been identified for any of the surface species. In fact, the mechanism can be seen to be consistent with infrared spectroscopic observation of "nitro/nitrate" groups. It is fully consistent with the observation that temperature-programmed desorption profiles are the same whether the catalyst is exposed to NO/O_2 or to NO_2, since in the mechanism, both lead to the same surface species.

A mechanism for the catalytic decomposition of N_2O that involves a nitrite/nitrate redox cycle instead of a cation redox cycle is appealing in several respects. The discussion here has focused upon a few key observations that are difficult to explain in terms of a simple two-step mechanism involving cycling of the cation oxidation state. Key among these are the results of reaction of $N_2{}^{16}O$ with an ^{18}O-enriched catalyst and the promotional effect of adding NO upon the rate of N_2O decomposition. Neither can be easily explained in terms of the simple two-step mechanism, while both can be explained in a straightforward manner in terms of a nitrite/nitrate mechanism.

5. Conclusions

The light-off of N_2O decomposition is not isothermal, and consequently the mechanism that was able to explain it is no longer needed for that purpose. However, the key feature of that mechanism, a redox cycle involving surface nitrites and nitrates, still represents an attractive mechanistic model for N_2O decomposition. Its specific advantages include the following: it can operate on a single isolated exchange cation (cation pairs or bridge structures are not necessary); it is consistent with the observed kinetics of the reaction (first order in N_2O and zero order in N_2 and O_2); it can quantitatively explain the promotional effect seen in the rate of reaction when NO is added to the system; it predicts the correct product isotope distribution when unlabeled N_2O reacts over a catalyst containing labeled oxygen; and it is consistent with spectroscopic and thermal desorption data showing that the same surface species are formed when the catalyst is exposed to N_2O, NO_2 or a mixture of NO and O_2. In the past, the kinetics of decomposition of N_2O have been modeled using a simple two-step mechanism that features a cation redox cycle. The effects of adding NO to the feed then required adding additional reaction pathways. The nitrite/nitrate scheme offers a single framework for explaining the full set of observations.

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