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Decomposition of Nitrous Oxide on FeY Zeolite

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The kinetics of N_2O decomposition over Fe(III)Y zeolite between 350 and 650°C are described. With partial pressures of N_2O up to 12%, the decomposition data are represented with reasonable accuracy by $-dN_2O/dt = k_{obs}P_{N_2O}$. The results are consistent with an oxygen transfer redox mechanism in which the rate-determining step is the catalyst reduction by N_2O. Studies were also made using normal reactant ($N_2{}^{16}O$) on the ^{18}O-loaded catalyst. The initial distribution of product oxygen ($^{32}O_2$, $^{34}O_2$, and $^{36}O_2$) was determined by mass spectrometric technique. The experimental results fitted the proposed mechanism but the fraction of $^{32}O_2$ was much higher than expected. This may indicate that a small fraction of the sites is used repetitively. The decomposition of NO was also attempted over the same catalyst. No reaction was detected up to 750°C. This finding suggests that N_2O decomposition reaction is the simplest, most straightforward chemical tool available for studies of the redox chemistry of such systems.

INTRODUCTION

On the basis of his studies of N_2O decomposition over oxides, Winter (*1*, *2*) proposed a general mechanism for this reaction, viz.,

$$N_2O(g) \rightarrow N_2O(ads), \quad (1)$$

$$N_2O(ads) \rightarrow N_2(g) + O(ads), \quad (2)$$

$$2O(ads) \rightarrow O_2(g). \quad (3)$$

The kinetics were generally adequately described by the rate expression

$$\text{Rate} = kP_{N_2O}/(P_{O_2})^{1/2}. \quad (4)$$

Many related papers have appeared in the literature in recent years (see, for example, the reviews (*3*, *4*)). In the development of the kinetics, O(ads) has frequently been assumed to be negatively charged by electron transfer from the surface. This is an unnecessary formalism which we shall ignore. Included are reports on interesting studies of the reaction over several perovskites (*5*), spinel-type solid solutions (*6*), supported metal catalysts (*7*), as well as zeolites (*8*). In many cases, the reaction was investigated in a static recirculation reactor with the pressure change being followed. The experimental data were then analyzed by using the integrated form of Eq. (4), but since a detailed investigation of the kinetics was not always made the validity of this assumption was sometimes questionable.

Recently we reported (*9*) that Fe(II)Y can be oxidized to Fe(III)Y by O_2, NO, or N_2O and the reverse reaction may be accomplished with a reducing gas such as H_2 or CO. The valence state of iron ions varied between +3 and +2, respectively in the two steps. Boudart *et al.* (*10*) had reported that this system acted as an oxygen carrier, one atom of oxygen being added or removed in the redox cycle for every two iron atoms present, a finding which we confirmed (*9*).

In the present work, N_2O and NO decompositions over FeY were studied. The objectives were: (a) to examine in detail the kinetics of these reactions, including the

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effects (if any) of oxygen deactivation; (b) to establish a mechanism based upon the kinetics results, and (c) to confirm the mechanism using tracer techniques.

EXPERIMENTAL

Catalyst and Pretreatment

The FeY zeolite was the same as that used in the earlier work (*9*) where the method for preparation was described and the unit cell composition was given as $Na_{19}Fe(II)_{13}(AlO_2)_{58}(SiO)_{134}$. A 1.0-g sample was treated in a stream of O_2 at 500°C for 16 h, then cooled in He to the first reaction temperature. It was then left in contact with a flowing stream of 3.5% N_2O or NO in He carrier gas for about 2 h before measurements were commenced.

Kinetic Measurements

The continuous-flow, single-pass reactor depicted in Fig. 1 was used for kinetic studies. The system allowed addition of the reaction products, O_2 and/or N_2, to establish their effect on the decomposition rate. The detailed experimental conditions and the procedure for the gas chromatographic analysis have been previously described (*9*). The rates of N_2O decomposition were expressed as the number of micromoles of N_2 formed per second per gram of catalyst; they were calculated from

$$r = \alpha/(W/F_{N_2O}). \qquad (5)$$

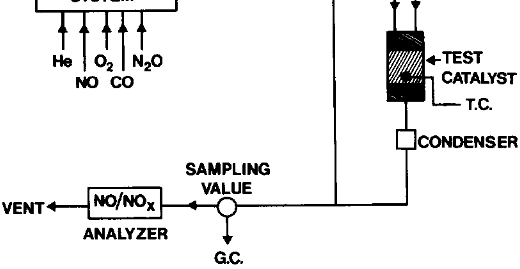

FIG. 1. Schematic diagram of the laboratory flow reactor.

Differential reaction rates were determined from the linear plots of the fractional conversion, α, vs the space velocity, W/F_{N_2O}, where W was the catalyst weight and F_{N_2O} the flow rate. Typically 3.5% N_2O in He at a total flow rate of $\sim 10^2$ cm^3 (NTP) g^{-1} min^{-1} was used and α was calculated from gc data. The product ratio of N_2 to O_2 remained unchanged at 2.0 over the course of an experiment corresponding to the reaction

$$N_2O \rightarrow N_2 + 1/2\ O_2. \qquad (6)$$

Hence, the extent of conversion (α) could be calculated from

$$\alpha = (\%N_2)/[100 - (\%N_2/2)], \qquad (7)$$

where $\%N_2$ denotes the molar percentage of nitrogen in the gas stream leaving the reactor. Under the conditions selected, α never exceeded 15%. A similar calculation could be used to evaluate catalytic rates of NO decomposition (which did not occur).

Isotopic Tracer Studies

$N_2{}^{16}O$ decomposition experiments were carried out over ^{18}O-treated catalysts in an all-glass circulating system in which a known quantity of $N_2{}^{16}O$ was circulated continuously over the zeolite sample. The reaction temperatures ranged from 300 to 500°C and were maintained constant to ±2°C. The progress of the decomposition reaction was monitored by the pressure increase of the system. the isotopic distribution of product oxygen ($^{32}O_2$, $^{34}O_2$, and $^{36}O_2$) was determined by mass spectrometric analysis of samples of the gas phase taken during the run. The exchange rate of ^{18}O between enriched gas-phase O_2 ($\sim$99% ^{18}O) and the ^{16}O-oxidized FeY catalyst was also studied. In both cases, the atomic fraction of ^{18}O, f_{18}, in the gas phase were calculated from

$$f_{18} = (F_{34} + 2F_{36})/2(F_{32} + F_{34} + F_{36}), \qquad (8)$$

where F_{32}, F_{34}, and F_{36} are the molar fractions of $^{32}O_2$, $^{34}O_2$, and $^{36}O_2$, respectively.

RESULTS

NO Decomposition

The NO decomposition was tested over the oxidized FeY catalyst. No reaction was detected up to 750°C. Above 300°C, NO did oxidize the reduced form of the catalyst but only N_2 appeared in the gas phase. Moreover, this reaction stopped after the catalyst became completely oxidized.

N_2O Decomposition, Kinetics

Rates of N_2O decomposition and the product ratios of N_2 to O_2 at four temperatures are listed in Table 1 for the oxidized FeY catalyst. Note that the stoichiometric ratio of 2 for N_2/O_2 was observed over the entire temperature regime. The activity of the catalyst remained very stable over periods of several days. In determining the kinetics, the temperature was varied in a random manner and data could be accurately reproduced on returning to a previously tested temperature.

The effect of N_2O pressure on the rate of decomposition was studied at 500°C over the range of 2 to 12% N_2O in He. In Fig. 2, the N_2 formation rate is plotted versus the partial pressure of N_2O in the feed. A first-order dependence is clearly indicated by the slope of this graph. Furthermore, the addition of O_2 (up to ~10%) to the gas stream had no apparent effect on the decomposition rate. These results established the rate expression as

$$\text{Rate } (N_2 \text{ formation}) = k_{\text{obs}} P_{N_2O}, \quad (9)$$

where k_{obs} is the observed rate constant for this reaction. The apparent activation energy for k_{obs} can be deduced from the data in Table 1. From the Arrhenius plot a value of ~37 ± 2 kcal/mole was calculated for this reaction (Fig. 3).

TABLE 1

N_2O Decomposition over FeY[a]

Temperature (°C)	Product ratio N_2/O_2	N_2 formation rate[b] (μmole/g-cat-sec)
498	2.0	0.054
530	2.0	0.14
621	1.9	1.8
650	1.9	3.5

[a] Gas composition was 3.5% N_2O in He carrier.

[b] These rates may be converted to turnover frequencies by dividing by $2(1.02 \times 10^3$ μmole [Fe]/g-cat). For these it is assumed that each two Fe cations constitute a catalytic site.

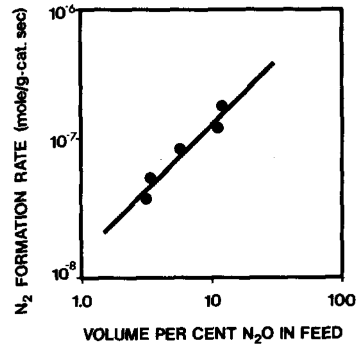

FIG. 2. The change of N_2 formation rate at different inlet concentrations in the decomposition reaction over FeY. The reaction temperature was 500°C. Gas composition = 3.5 to 12% N_2O in He carrier.

Isotopic Tracer Studies

It is not possible to derive a catalytic mechanism with any confidence from kinetic data alone. Under favorable conditions, isotopic tracers can produce a reaction scheme to which the kinetic data must also conform. Thus, an experiment using the normal reactant ($N_2{}^{16}O$) over an ^{18}O-loaded catalyst was attempted. In order to maximize the effect, the reduced catalyst was oxidized and exchanged with $^{36}O_2$ (99.1 at.%) gas several times at 400°C. The final ^{18}O content of the catalyst was calculated to be about 65% of the total exchangeable lattice oxygen at this temperature, which amounts to about 2.4×10^{21} oxygen molecules per gram of catalyst, i.e., between one-third and one-fourth of the total lattice oxygen. This is much larger than the redox capacity (1.5×10^{20} Fe_2O). A small amount of $N_2{}^{16}O$ (~0.5 cm^{3}NTP) was then decom-

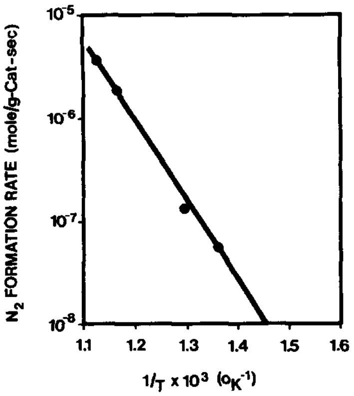

FIG. 3. Arrhenius plot for N_2O decomposition on oxidized FeY. Gas composition = 3.5% N_2O in He carrier.

posed over the ^{18}O-treated FeY at 400°C in recirculating system. The reaction was stopped periodically by freezing out the N_2O with liquid nitrogen. The relative amounts of the species $^{32}O_2$, $^{34}O_2$, and $^{36}O_2$, in the gas-phase product was determined from small aliquots of the remaining gas by mass spectrometry. The experimental results are presented as the first row of data in Table 2. No $^{36}O_2$, was observed. About 80% was $^{32}O_2$ and the remainder was $^{34}O_2$.

DISCUSSION

A reaction scheme for the N_2O decomposition which accounts for all the observed results may be derived as follows. An oxygen transfer redox mechanism is assumed. The chemistry may be written as:

(a) Catalyst reduction:

$$\text{(i) } N_2O + O\text{-(s)} \xrightarrow{k_r} N_2 + O_2 + \square, \quad (10)$$

$$\text{(ii) } 2O\text{-(s)} \xrightarrow{k_r'} O_2 + 2\square \quad (11)$$

and (b) catalyst reoxidation:

$$\text{(iii) } N_2O + \square \xrightarrow{k_0} N_2 + O\text{-(s)}, \quad (12)$$

$$\text{(iv) } O_2 + 2\square \xrightarrow{k_0'} 2O\text{-(s)}, \quad (13)$$

where [□] and O-(s) represent surface vacancies and oxygen-filled sites, respectively.

It was reported previously (9) that N_2O is a more facile oxidizing agent than O_2. The reoxidation became nearly stoichiometric at 300°C when N_2O was used, whereas 500°C was necessary for complete reoxidation with O_2. If Eq. (11) were the main path for O_2 production and the desorption of oxygen occurred by random pairing, then the initial distribution of $^{32}O_2$, $^{34}O_2$, and $^{36}O_2$ could be calculated from the knowledge of the average ^{18}O fraction of the surface, $f_{18} = 0.65$. The expected results are listed in Row 2 of Table 2; it contains a very large $^{36}O_2$ component (42%) which was not observed. On the other hand, if the main source of O_2 is by Eq. (10), the expected result is given in Row 3. It should contain a very large fraction of $^{34}O_2$, but not $^{36}O_2$. This fits the experimental results better than the postulate of Row 2, but the fraction of $^{32}O_2$ is much higher than predicted. This can be accounted for if a (small) fraction of the sites is used repetitively. Furthermore, the decomposition rate was not inhibited by adding O_2 to the feed stream. From these two facts it can be concluded that the catalyst reduction proceeds mainly through Eq. (10).

During the decomposition reaction, the vacancy concentration of the surface, [□], should be very small. Hence the steady-state approximation may be used yielding

$$d[\square]/dt = 0 = k_r P_{N_2O}[O\text{-(s)}] - k_0 P_{N_2O}[\square] - k_0' P_{O_2}[\square]^2. \quad (14)$$

TABLE 2

Oxygen Isotopic Distribution for $N_2{}^{16}O$ Decomposition over ^{18}O-treated FeY at 400°C

No.[a]	f_{18}[b]	O$_2$ (mole%)		
		$^{32}O_2$	$^{34}O_2$	$^{36}O_2$
1	0.65	80	20	—
2	0.65	12	46	42
3	0.65	35	65	—

[a] 1. Experimental result; 2. calculated ratio based on Eq. (11); 3. calculated ratio based on Eq. (10).

[b] f_{18} is the average atomic fraction of ^{18}O-(s).

The conservation of surface oxygen and vacancies gives

$$[\square] + [\text{O-(s)}] = C, \qquad (15)$$

where C is a constant (identified as the oxygen storage capacity of the catalyst). Moreover, since $[\square]$ is small the last term of (14) may be neglected. Combining (14) and (15) yields

$$[\square] = \frac{C(k_r/k_0)}{1 + k_r/k_0} \qquad (16)$$

and

$$[\text{O-(s)}] = \frac{C}{1 + k_r/k_0}. \qquad (17)$$

According to Eqs. (10) and (12), the observed rate of decomposition should be

$$-d(\text{N}_2\text{O})/dt = k_r P_{\text{N}_2\text{O}}[\text{O-(s)}] + k_0 P_{\text{N}_2\text{O}}[\square]. \qquad (18)$$

Substitution of (16) and (17) into (18) gives

$$-d(\text{N}_2\text{O})/dt = 2Ck_r P_{\text{N}_2\text{O}}/[1 + (k_r/k_0)]. \qquad (19)$$

In our previous study (*9*), it was determined that in flow microbalance experiments the catalyst was fully oxidized under reaction conditions. In other words, the vacancy concentration was very small, i.e.,

$$[\text{O-(s)}] \gg [\square]. \qquad (20)$$

From Eqs. (16), (17), and (20), at steady state,

$$\frac{C}{1 + k_r/k_0} \gg \frac{C(k_r/k_0)}{1 + k_r/k_0} \qquad (21)$$

which simplifies to

$$k_r/k_0 \ll 1. \qquad (22)$$

Thus, the rate law for N_2O decomposition may be written as

$$-d(\text{N}_2\text{O})/dt = 2Ck_r P_{\text{N}_2\text{O}}. \qquad (23)$$

The observed rate constant, k_{obs}, may also be identified as

$$k_{\text{obs}} = Ck_r. \qquad (24)$$

In redox reactions, the catalyst can be conceived to function in two extreme ways (*11*). It may either enter into the reaction as an inert template providing a collection of atomic or molecular orbitals of suitable symmetry and energy to hold the reactant molecules, or otherwise it could function as a reversible reactant, being partially reduced and reoxidized in a continuously reversible cycle. The recent treatment of the NO + CO reaction over RhY by Iizuka and Lunsford (*12*) is a good example of the former picture; our earlier studies of FeY, (*9*), appears to be an example of the latter. It is therefore not surprising that the decomposition of N_2O also follows a similar mechanism. The main reaction pathways appear to be via Eqs. (10) and (12) with insignificant contributions from Eqs. (11) and (13). Winter (*1*) mentioned that Eq. (10) could be a possible reaction pathway, but then concluded that desorption of molecular oxygen [Eq. (11)] was probably the main source of O_2 production for his system.

The fact that NO did not decompose on the FeY catalyst also supported the proposed mechanism. Fe(II)Y could be readily oxidized to Fe(III)Y at 500°C, by NO; N_2 was released in this step. No detectable O_2 appeared, either during the oxidation or after this process was complete (when the N_2 disappeared from the gas phase). This result demonstrates that while NO can be used to oxidize the catalyst, just as N_2O at this temperature, catalytic NO decomposition to the elements does not occur. These facts being established, it must be concluded that O_2 cannot be produced at an appreciable rate via Eq. (11). Otherwise the catalytic NO decomposition should occur, just as with N_2O. By the same token, the main pathway for the reduction step most probably is via Eq. (10).

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