Role of Oxygen in the Nitrous Oxide/Carbon Reaction

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Received: July 16, 2001; In Final Form: November 20, 2001

An investigation of the role of oxygen in the nitrous oxide/carbon reaction was carried out on various carbon samples (both graphitic and nongraphitic) over a range of temperatures and partial pressures. Previous work reported that oxygen strongly inhibited the nitrous oxide/carbon reaction. Large ratios of O_2/N_2O were used in all previous work. In this work, the O_2/N_2O ratio was kept below 1, and we found that oxygen did not inhibit the rate of the $C + N_2O$ reaction. Instead, the rate of the reaction in the presence of oxygen was essentially that predicted by the two independent reactions, nitrous oxide/carbon and oxygen/carbon, occurring simultaneously. A simple theoretical explanation is given for the observations, both past and present, on the basis of competitive chemisorption of nitrous oxide and oxygen on active sites.

Introduction

Emissions of nitrogen oxides, NO_x, have been a point of considerable interest. The largest sources of NO_x emissions are fossil fuel combustion emissions from both stationary and mobile power generators. Other sources of NO_x include land cultivation and biomass burning.[1] Nitrogen oxides, including nitrous oxide, contribute to atmospheric pollution as they are a major source for acid rain and the depletion of the stratospheric ozone layer.[1−3] As a greenhouse gas, nitrous oxide, in particular, is ca. 300 times more potent in GWP (global warming potential) than CO_2.[4] The ramifications of NO_x emissions on both the environment and human health provide the motivation to control these emissions.

To eliminate or minimize NO_x pollution, it is desirable to catalytically reduce all nitrogen oxides to nitrogen and oxygen.[5] It has been observed in coal combustion processes that nitrogen oxides can further react with carbon to produce nitrogen and other off-gases.[6] One approach currently being investigated is reacting N_2O on carbon to yield nitrogen, carbon monoxide, and carbon dioxide.[1−3,5,6] To effectively pursue this option, it is first necessary to understand the effect of oxygen on the reaction kinetics and the mechanism of NO_x reduction because oxygen is invariably present in emissions containing NO_x. The $C + NO_x$ reaction has been investigated extensively,[1−3,5−30] and two excellent reviews are available.[31,32]

A most intriguing aspect of the $C + NO_x$ reaction is the effect of oxygen.[33] Oxygen has been reported to play opposite roles in the $C + NO$ and $C + N_2O$ reactions. For the $C + NO$ reaction, the effect of O_2 is known to enhance the rate, whereas the opposite has been reported for the $C + N_2O$ reaction. The promoting effect has been reported widely and the phenomenon is reasonably understood, i.e., the presence of O_2 increases surface oxygen complexes and also increases the active sites.[33] The opposite effect for the $C + N_2O$ reaction has been explained by Zhu et al.[33] From molecular orbital calculation results, it

was concluded that the presence of excess surface oxides made the chemisorption of N_2O less stable.[33]

The negative or inhibiting effect of O_2 on the $C + N_2O$ reaction was first reported by Pels.[6] Using a fixed bed of activated carbon (from Norit) and gaseous reaction product analysis, Pels measured the reduction of N_2O in a carrier of N_2 or N_2 mixed with O_2 in the temperature range 500−650 °C. The inlet N_2O concentration was 35−45 ppm, while the additive O_2 concentration was 23%. He reported decreases of approximately 40% in the N_2O reduction rate by the presence of 23% O_2. Noda et al.[3] performed a similar experiment, using a char from a resin and fixed bed TPR (temperature-programmed reaction). Their inlet N_2O concentration was approximately 90 ppm, and two levels of O_2 additives were used: 570 and 5100 ppm. Very large inhibition of the N_2O reduction was observed in the temperature range 600−900 °C, the extent of the inhibition depended on the temperature. A similar inhibition effect was also observed for the same reaction catalyzed by CuO, by Zhu et al.[13] The inhibition was approximately 20% for the $C + N_2O$ reaction using activated carbon doped with CuO. The condition was 0.3% N_2O and 1.5% O_2, at 320 °C.[13]

It is clear that in all three reports of the inhibition of the $C + N_2O$ reaction by O_2, large excesses of O_2 were used. More importantly, all experiments were performed by gas product analyses. In this work, we used a gravimetric method to measure the carbon gasification rates for the reaction, with and without O_2. More importantly, the effects of O_2 with comparable N_2O and O_2 concentrations will be established.

Experimental Section

Materials. Union Carbide SP-1 graphite was used predominantly, because it offers exceptional purity and regular particle geometry consisting of uniform, disk-shaped particles. The SP-1 graphite is essentially single crystalline. The geometry of the sample allows for a straightforward calculation of active sites so that the turnover frequency is easily used to quantify and compare the rate data. Table 1 contains the physical properties of SP-1 graphite.

In addition to the SP-1 graphite sample, Micro 850 graphite (from Asbury Graphite Mills, St. Mary, PA) and Calgon PCB-

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TABLE 1: SP-1 Graphite Physical Properties[2]

BET (m^2/g)	2.01
diameter (μm)	33.00
height (μm)	0.47
basal plane surface area (m^2/g)	1.96
edge plane surface area (m^2/g)	0.06

TABLE 2: Micro 850 Graphite Physical Properties[1]

BET (m^2/g)	15.5
diameter (μm)	4.00
height (μm)	0.06
basal plane surface area (m^2/g)	15.05
edge plane surface area (m^2/g)	0.45

activated carbon were also used. Micro 850 is another high-purity graphitic carbon with consistent disk-shaped particle geometry. The reaction between the Micro 850 and N_2O was studied extensively,[1,2,29] and the data will also be used for comparison in this work. Table 2 contains the physical properties for Micro-850 graphite. Calgon PCB is a granular activated carbon, which was pulverized before testing to allow for a more uniform sample and to better facilitate using a small sample mass. The Calgon PCB-activated carbon is among the activated carbons with the least impurities (at approximately 2 wt %) and had a surface area of approximately 1000 m^2/g.[34]

TGA Experiments. A Cahn 2000 thermogravimetric analyzer was used to measure the rate of carbon gasification by monitoring weight loss. The microbalance had a nominal sensitivity of 0.1 μg.

To minimize the interparticle mass transfer limitation, approximately 5 mg of sample (or nearly a monolayer of particles) was used for each rate measurement. The other experimental conditions (such as gas flowrate) were such that the measured rates were within the regime where the measured rates were the intrinsic rates, without diffusion limitations.[1,2,29] Prior to each run, the sample was degassed at 120 °C for 2 h in pure helium to remove any adsorbed gases. Each sample was then heated to its respective temperature at a ramp rate of 10 °C/min in pure helium. Once steady state was achieved at the reaction temperature, the inert gas was switched to reactant gas. Rate data was collected between 5 and 20% burn-off according to previous observations.[1,2,29] This range of burn-off previously lead to the most accurate and reproducible results.

Experiments were performed at temperatures from 500 to 700 °C and partial pressures of oxygen from 0.005 to 0.03 atm. The partial pressure of N_2O was maintained at 0.05 atm and the total pressure was maintained at 1 atm with helium making up the balance. The total gas flow rate was 200 mL/min for all trials. The rates of reaction of O_2 on carbon and N_2O on carbon were also measured independently to investigate the possibility of additive independent reactions.
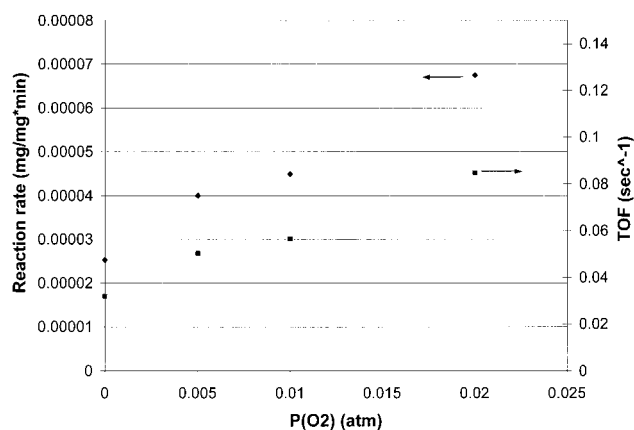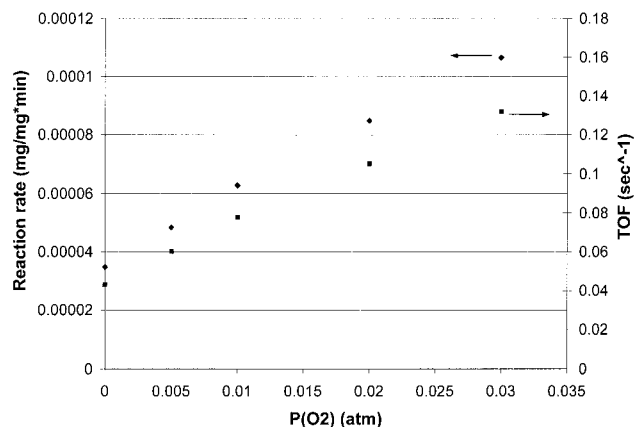
Turnover Frequency. The turnover frequency, TOF, is a meaningful representation of the true reaction rate. Consequently, the TOF has been used extensively to analyze the present data. The TOF was calculated as

$$TOF = \left[\frac{atoms \cdot gasified}{edge \cdot atoms \cdot seconds}\right] = \left[\frac{atoms \cdot gasified/time}{\rho_{1120} \cdot A_2}\right] \quad (1)$$

where ρ_{1120} is the number of active sites per edge surface area and A_2 is the edge surface area.

Results and Discussion

Turnover Frequencies for C + O_2 and C + N_2O Reactions. The TOF of the C + O_2 reaction has been studied extensively on well-defined active sites by electron microscopy in the same

Figure 1. Reaction rates and turnover frequencies of N_2O/SP-1 graphite ($P_{N_2O} = 0.05$ atm) at 500 °C.

Figure 2. Reaction rates and turnover frequencies of N_2O/SP-1 graphite ($P_{N_2O} = 0.05$ atm) at 600 °C.

temperature range as in this work.[35−37] The reaction is approximately first order with respect to the partial pressure of O_2.

The TOF for the C + N_2O reaction on Micro 850 graphite was studied by TGA.[1,29] Similarly, the C + NO reaction was studied using both SP-1 graphite and Micro 850 graphite, also by TGA.[1,2,29] The TOF for the C + NO reaction was considerably higher on the SP-1 graphite than that on Micro 850. A possible reason based on differences on the basal plane surface area was given for the difference in the TOF.[29]

Effect of O_2. The effects of O_2 on the C + N_2O reaction were studied in this work for the three carbon samples: SP-1, Micro 850, and PCB-activated carbon. The results are shown in Figures 1−5. The detailed data for SP-1 at 600 °C are also given in Table 3.

Table 3 shows the TOF rates on SP-1 at 600 °C for pure O_2, pure N_2O, and mixtures of O_2 and N_2O. The concentration of O_2 was varied (at 0.5, 1, and 2%) while that of N_2O was kept constant at 5%. For pure O_2, the data essentially followed the first-order dependence as seen before. With mixtures, no retardation on the total TOF by O_2 was seen. On SP-1 graphite at 600 °C, the total TOF rates were essentially the sum of the independent TOF rates predicted from the pure gas rates. The same results (on the lack of inhibiting oxygen effects) were obtained at 500−700 °C, shown in Figures 1−3.

The oxygen effects on the same reaction on the Micro 850 graphite are shown in Figure 4. For pure N_2O, the TOF was lower than that on the SP-1 graphite, due to different basal plane surface areas, as explained previously.[29] The lack of an inhibiting O_2 effect was again seen on this graphite.
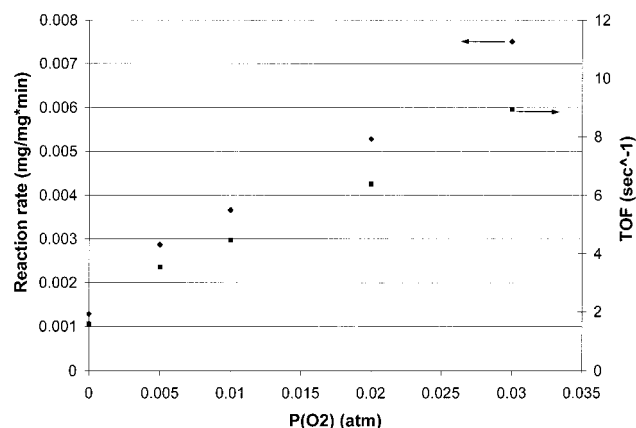
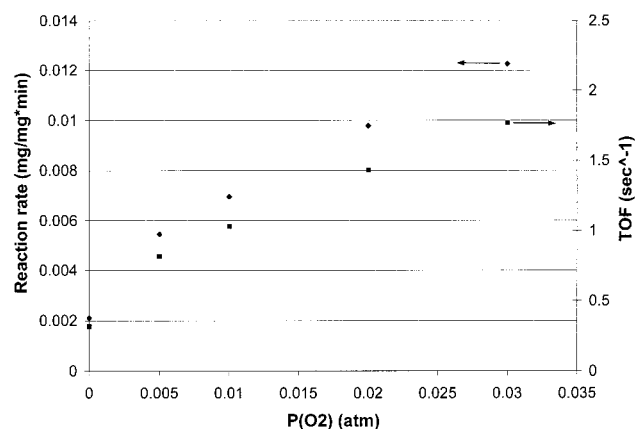**Figure 3.** Reaction rates and turnover frequencies of N_2O/SP-1 graphite ($P_{N_2O} = 0.05$ atm) at 700 °C.

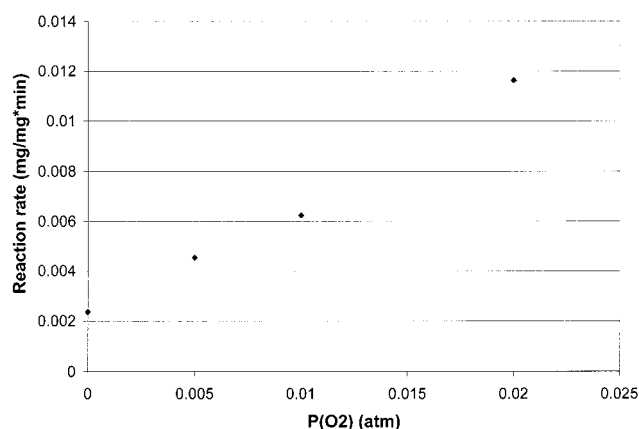**Figure 4.** Reaction rates and turnover frequencies of N_2O/Micro 850 graphite ($P_{N_2O} = 0.05$ atm) at 700 °C.

Figure 5. Reaction rates of N_2O/Calgon PCB-activated carbon ($P_{N_2O} = 0.05$ atm) at 600 °C.

Since the retardation effects of oxygen were reported only on nongraphitic carbons, i.e., activated carbons[6,13] and char,[3] we also used an activated carbon, the PCB carbon. The results on the activated carbon are shown in Figure 5. Again, an inhibiting O_2 effect was absent.

In the work of both Pels[6] and Noda et al.,[3] large retardation effects were reported. With 23% O_2 and 40 ppm N_2O, the retardation was 35% at 540 °C and 46% at 650 °C, in Pels' work.[6] In the work of Noda et al.,[3] only conversions of N_2O from a fixed bed reactor were given. The conversion was 90% with 90 ppm N_2O at 700 °C. With 5100 ppm added oxygen, the conversion decreased to only 31%, corresponding to a very large decrease in the rate.

TABLE 3: N_2O/SP-1 Graphite Rate Data at 600 °C

trial	P_{N_2O} (atm)	P_{O_2} (atm)	measured TOF (s^{-1})	predicted TOF (s^{-1})	deviation
1	0.00	0.005	0.0195		
2	0.00	0.01	0.0292		
3	0.00	0.02	0.0700		
4	0.05	0.00	0.0433		
5	0.05	0.005	0.0601	0.0628	−4%
6	0.05	0.01	0.0779	0.0725	+7%
7	0.05	0.02	0.1053	0.1133	−7%

In both studies by Pels[6] and Noda et al.,[3] large ratios of O_2/N_2O were used. In our work, the ratio was kept below 1. Therefore, the conclusion from this work is that for O_2/N_2O ratios near or below 1, oxygen has no or negligible effects on the C + N_2O reaction.

According to the study by Zhu et al.[33] using molecular orbital theory, NO adsorption is much more thermodynamically favorable than O_2 either on two adjacent edge sites or on single edge sites isolated by semiquinone oxygens. The latter case is very possible in the presence of oxygen. The presence of oxygen in the NO−carbon reaction system can continuously produce a large amount of new active sites due to the formation of epoxy oxygens according to the unified mechanism suggested by Yang and co-workers.[38−40] This is the reason for the enhancement of the NO−carbon reaction by the presence of O_2.

Contrary to NO adsorption, N_2O adsorption is much less favorable compared to O_2 on either consecutive edge sites or isolated edge sites.[33] Although the presence of excess O_2 can also continuously produce a large number of active sites in the N_2O−carbon system, the newly formed active sites are occupied again by the excess O_2 because N_2O is weaker in competing for the active sites, resulting in a reduced N_2O−carbon reaction rate. However, in the present experimental study, when the O_2/N_2O ratio is low, the influence of O_2 on N_2O−carbon reaction becomes negligible. A simple explanation for the observed (seemingly contrasting) results can be obtained through the kinetics of chemisorption.[41] At the steady state, the reaction rate can be assumed to be proportional to the rate of chemisorption.[42] For the N_2O−carbon reaction, in the absence of oxygen, the chemisorption rate of N_2O is

$$r_1 = \delta(\theta)\, p(2\pi m k T)^{-1/2} f(\theta)\, e^{-E(\theta)/RT} \qquad (2)$$

where, r_1 is the rate of chemisorption, at pressure p and temperature T. The collision frequency from the gas-phase molecules per unit surface area is given by $p(2\pi m k T)^{-1/2}$, m being the mass of a molecule and k the Boltzmann constant. $\delta(\theta)$ is the condensation coefficient; $f(\theta)$ is the probability that a collision will take place at an unoccupied site; $E(\theta)$ is the activation energy for chemisorption, all three being functions of the surface coverage θ. The forms of these functions can be approximated by

(1) Molecule occupying single surface sites,

$$f(\theta) = 1 - \theta \qquad (3)$$

(2) E varies linearly with θ, i.e., via the Elovich equation:[41,42]

$$E = E_0 + \alpha\theta \qquad (4)$$

(3) δ does not vary significantly with θ, hence a constant,

$$\delta(\theta) = \delta \qquad (5)$$

Then (2) can be rewritten as

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$$r_1 = \delta p (2\pi mkT)^{-1/2} (1-\theta) e^{-(E_0+\alpha\theta)/RT} \quad (6)$$

After the addition of O_2, the surface coverage θ is increased to $\theta + \Delta\theta$, and the new chemisorption rate of N_2O becomes

$$r_2 = \delta p (2\pi mkT)^{-1/2} (1-\theta-\Delta\theta) e^{-(E_0+\alpha\theta+\alpha\Delta\theta)/RT} \quad (7)$$

The ratio of the chemisorption rates after and before the addition of oxygen is

$$\frac{r_2}{r_1} = \frac{\delta p (2\pi mkT)^{-1/2} (1-\theta-\Delta\theta) e^{-(E_0+\alpha\theta+\alpha\Delta\theta)/RT}}{\delta p (2\pi mkT)^{-1/2} (1-\theta) e^{-(E_0+\alpha\theta)/RT}} =$$

$$\left(1 - \frac{\Delta\theta}{1-\theta}\right) e^{-\alpha\Delta\theta/RT} \quad (8)$$

Equation 8 is a direct consequence of the Elovich equation, which fits well the kinetics of chemisorption. Furthermore, under the steady-state assumption, and assuming the rate of reaction is proportional to the rate of chemisorption, eq 8 expresses the ratio of the rates with and without O_2 addition. A numerical example is given below for the two cases in discussion.

When the initial N_2O concentration is very low (as in previously reported experiments), the surface coverage θ is also very low, assuming $\theta = 0.01$. Addition of large excess O_2 (as in previous cases) will greatly increase the surface coverage, assuming $\Delta\theta = 0.2$. Let $\alpha = 10^4$ m kg^{-1} s^{-1} (for strong chemisorption), $T = 1000$ K, the ratio of the chemisorption rates of N_2O with and without O_2 addition is

$$r_2/r_1 = [1 - 0.2/(1 - 0.01)] e^{-10000*0.2/(8.31*1000)} = 0.62 \quad (9)$$

When the initial N_2O concentration is much higher (as in our experiments), the surface coverage is also much higher, assuming $\theta = 0.2$. The addition of low ratios of O_2 ($O_2/N_2O < 1$) (as in our experiments) will also lead to a lower $\Delta\theta$, assuming $\Delta\theta = 0.01$. Then the ratio of the chemisorption rates for N_2O with and without O_2 addition is

$$r_2/r_1 = [1 - 0.01/(1 - 0.2)] e^{-10000*0.01/(8.31*1000)} = 0.98 \quad (10)$$

Apparently, the presence of O_2 will always inhibit the N_2O-carbon reaction. In the case of a high initial N_2O concentration, the addition of O_2 with a ratio O_2/N_2O less than 1.0 can only lead to small decreases in the N_2O chemisorption rate. The example above shows a 2% decrease in the rates (eq 10), which is well within the experimental error. This is the reason for the lack of inhibition by O_2 on the N_2O-carbon reaction in the present study. While an addition of excess of O_2 to very low concentration of N_2O will lead to a significant reduction of N_2O chemisorption rate, which in turn results in a much lower rate of N_2O-carbon reaction as shown in the previous experiments.[3,6] The example above yielded a 38% reduction (eq 9), in the range of the reported data. For other cases such as molecule occupying two sites and nonuniform surface (E varies nonlinearly with coverage), similar results can be obtained.

As for the $O_2/NO-$carbon reaction, the situation is much more complicated as NO can even adsorb on the carbon surface site already covered by oxygen in the form of NO_2,[33] therefore it is not discussed further here.

In addressing the difference between the previously reported experiments and our experiments, a further discussion may be added regarding the possible role of homogeneous reactions. As mentioned, in previous experiments only gaseous products were measured. There were two possible reasons that introduc-
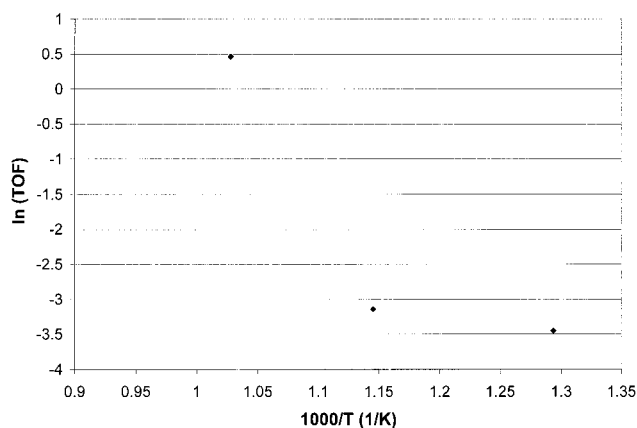

Figure 6. Arrhenius plot of N_2O/SP-1 graphite ($P_{N_2O} = 0.05$ atm) rates.

tion of CO would inhibit the N_2O decomposition, and CO could be introduced when O_2 was introduced, since CO was a product of the $C-O_2$ reaction, particularly at higher temperatures. The two possible reasons are as follows. First, CO is a common product of both reactions of carbon with N_2O and O_2. Hence adding O_2 would inhibit the reaction with N_2O. The second one is a more subtle one. At high temperatures, homogeneous decomposition of N_2O as well as the reaction of N_2O with O atoms could occur.[43] The latter increases the conversion of N_2O to N_2. When CO is added, CO competes for O atoms and consequently lowers the observed N_2O conversion (to N_2). Therefore, adding O_2 could lead to inhibition of the observed N_2O decomposition rate. However, Pels[6] did examine the effects of added CO on the $C-N_2O$ reaction, and reported no effects. He also studied the effects of added CO on the $C-NO$ reaction and confirmed the well-known increased rates due to CO.[44−48]

From the above discussion, it may be concluded that at high temperatures, addition of O_2 could lead to decreased N_2O decomposition. In the temperature range of our study, it is unlikely that such effects would occur. This is obviously a subject for future work.

Temperature Break Phenomenon. There has been some disagreement over the existence of a "temperature break" in the Arrhenius plots for the N_2O/carbon reaction.[1,6,29−32] The data shown in Figure 6 supports the existence of a temperature break on SP-1 graphite. Unfortunately only three data points were taken so that the exact temperature cannot be identified. However, these three data points show unmistakably the existence of a temperature break. The Arrhenius plot, given in Figure 6, suggests that the break is between 600 and 700 °C, which is consistent with earlier findings.

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