J. Am. Chem. Soc. **1995**, *117*, 10969–10975

Environmental Catalysis: Adsorption and Decomposition of Nitrous Oxide on Zirconia

T. M. Miller and V. H. Grassian*

Contribution from the Department of Chemistry, University of Iowa, Iowa City, Iowa 52242

Received February 16, 1995[⊗]

Abstract: FT-IR spectroscopy has been used to study the adsorption and decomposition of nitrous oxide on zirconia nanoparticles. The room temperature IR spectrum of adsorbed nitrous oxide is characterized by two intense absorption bands corresponding to the symmetric stretch and asymmetric stretch that are shifted by approximately 45 and 18 cm^{-1}, respectively, from the gas phase values. Results from experiments as a function of sample pretreatment and site blocker adsorption indicate that nitrous oxide adsorbs on Lewis acid sites (Zr^{4+} and Zr^{3+}) at room temperature and the mode of attachment is through the oxygen atom. The nitrous oxide heat of adsorption is determined to be 9.6 ± 1.6 kcal/mol on zirconia. Dissociation of nitrous oxide (P = 75 Torr) over zirconia begins at temperatures above 350 °C. The data suggest that Lewis acid sites are the active site for nitrous oxide decomposition and the room temperature adsorbed species is a precursor to nitrous oxide decomposition.

Introduction

As stricter air quality standards are put in place, the development of better catalysts for air pollution abatement is essential. Environmental catalysis has been recently defined as the development of catalysts to either decompose environmentally unacceptable compounds or provide alternative catalytic syntheses of important compounds without the formation of environmentally unacceptable byproducts.[1,2] Nitrous oxide, a byproduct of several industrial processes, including the synthesis of Nylon and adipic acid,[3] has some environmentally damaging effects. It contributes to greenhouse warming, depletion of ozone in the stratosphere, and the formation of acid rain. Since it has an atmospheric lifetime of > 100 years, there is a great deal of interest in finding ways to limit the amount of nitrous oxide that is emitted into the atmosphere.

Metal oxides offer a possible way of disposing of nitrous oxide. It has been found that oxides, such as CaO, Fe_2O_3, and Cr_2O_3, catalyze the decomposition of nitrous oxide into dinitrogen and dioxygen, gases that obviously do not have the damaging environmental effects that nitrous oxide has.[4] Therefore, it is reasonable to explore the application of metal oxides as catalysts for decomposition of nitrous oxide on a large scale.

Recently, zirconia and zirconia-based catalysts have been shown to be effective in catalyzing the decomposition of nitrous oxide.[5] Zirconia is similar to other metal oxides, such as alumina and titania, in that it contains several types of sites that can play a role in the surface chemistry and, therefore, the catalytic activity of these materials.[6] The active sites include Brønsted acid (OH groups), Lewis acid (e.g. Zr^{4+}), and Lewis base (O^{2-}) sites.

In this study, we have used infrared spectroscopy to investigate the interaction between nitrous oxide and zirconia nanoparticles. FT-IR spectroscopy is a useful technique for studies of high surface area oxides.[7–9] From the IR data, it should be possible to determine the adsorption site and, perhaps, the active site for reaction. Nitrous oxide is a particularly suitable molecule for study with IR spectroscopy because it has only three normal modes of vibration; the symmetric stretch, the asymmetric stretch, and the doubly degenerate bend. Only the symmetric stretch and the asymmetric stretch are in a spectral region transparent to the zirconia catalyst and, therefore, are the only two fundamental modes in adsorbed nitrous oxide accessible for spectroscopic detection. As described below, this study focuses on the adsorption and decomposition of nitrous oxide on zirconia catalysts.

Experimental Section

An IR cell similar to the design of Yates and co-workers was used in this study.[10] The cell consists of a stainless steel cube fitted with two differentially pumped BaF_2 windows and a sample holder. A tungsten grid held in place by a set of Ni jaws was used to heat the sample. The temperature was monitored by spot welding thermocouple wires to the center of the sample grid. The IR cell is attached to a stainless steel vacuum chamber through a bellows hose. The vacuum chamber consists of an 80 L/s ion pump, an absolute pressure transducer for accurate pressure measurements in the 1 to 1000 Torr range, and a gas manifold.

The catalyst was prepared by pressing zirconia powder onto half of a tungsten grid. The other half of the grid was left blank so that gas phase measurements can be made. Approximately 13 mg of zirconia were pressed onto a 3 × 1 cm area of the grid. The zirconia samples were heated in air overnight at a temperature of 400 °C prior to being placed in the IR cell.

The IR cell was mounted on a linear translator inside of the FT-IR spectrometer so that both halves of the sample can be measured by simply moving the cell into the IR beam path. Infrared spectra were recorded with a Mattson RS-10000 equipped with a narrowband MCT detector. Typically, 500 scans were collected with an instrument resolution of 4 cm^{-1}. Background scans were collected by recording

---

[*] Author to whom correspondence should be addressed

[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1995.

(1) Armor, J. N. *Environmental Catalysis*; ACS Symp. Ser. No. 552; American Chemical Society: Washington, D.C., 1994.

(2) Armor, J. N. *Appl. Catal. B* **1992**, *1*, 221.

(3) Theimens, M. H.; Trogler, W. C. *Science (Washington)*, **1991**, *251*, 932.

(4) Winter, E. R. S. *J. Catal.* **1970**, *19*, 32.

(5) (a) Anseth, K.; Koch, T. A. U.S. Patent 5314673. (b) Zeng, H. C.; Lin, J.; Teo, W. K.; Wu, J. C.; Tan, K. L. *J. Mater. Res.* **1995**, *10*, 545.

(6) Yamaguchi, T. *Catal. Today* **1994**, *20*, 199.

(7) Little, L. H. *Infrared Spectra of Adsorbed Species*; Academic: London, 1966.

(8) Hair, M. L. *Infrared Spectroscopy in Surface Chemistry*; Marcel Dekker, Inc.; New York, 1967.

(9) Sheppard, N.; Nguyen, T. T. In *Advances in Infrared and Raman Spectroscopy*; Clark, R., Hester, R. E., Eds.; Heyden and Sons: London, 1978; Vol. 5.

(10) Basu, P.; Ballinger, T. H.; Yates, J. T., Jr. *Rev. Sci. Instrum.* **1988**, *59(8)*, 1321.

0002-7863/95/1517-10969$09.00/0

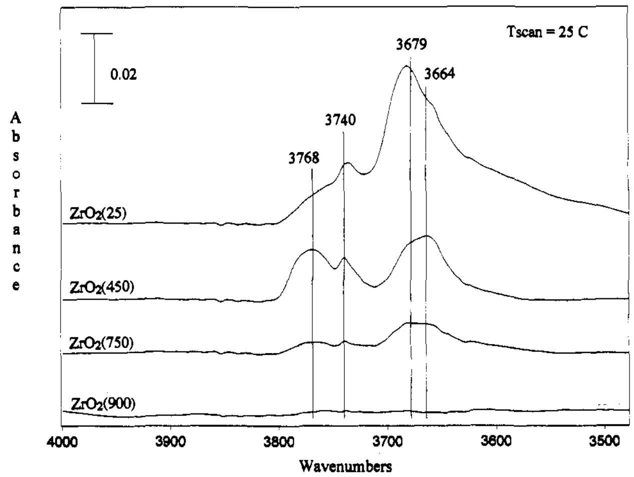


Figure 1. Changes in the hydroxyl group region in the IR spectra of ZrO_2 are shown above as a function of temperature: $ZrO_2(25)$, $ZrO_2(450)$, $ZrO_2(750)$, and $ZrO_2(900)$. The temperature given in parentheses refers to the temperature in degrees Celsius that the sample was heated to for 30 min under vacuum. All spectra were recorded at 25 °C.

a spectrum of both the zirconia and blank side of the tungsten grid before the introduction of nitrous oxide.

High surface area zirconia nanoparticles (78 m^2/g) were purchased from Nanotek. The Nanotek particles were used because they have approximately 2−4 times higher surface area than normally found for zirconia powders. The average particle size was 14 nm in diameter. The zirconia samples consist of two phases, the monoclinic and tetragonal.

Ultrahigh purity nitrous oxide (99.99%) was purchased from Matheson Gas Products. Pyridine (minimum purity of 99%) was purchased from Aldrich Chemical Co. and subjected to several freeze−pump−thaw cycles prior to use. CO_2 (99.995%) was purchased from Air Products and CO (99.5%) was purchased from Matheson. Both CO_2 and CO were used without any further purification.

Results

1. Thermal Activation of ZrO_2 under Vacuum.

The infrared spectrum recorded after a zirconia sample had been calcined at 400 °C overnight in air and evacuated in the IR cell at 25 °C is shown in Figure 1, $ZrO_2(25)$. Several bands are present in the spectrum in the surface hydroxyl groups region (3300−3800 cm^{-1}). Initially, some bands were present in the C−H stretching region, 2800−3200 cm^{-1}, and in the region between 1300 and 1650 cm^{-1} (both regions not shown); these bands are associated with adsorbed hydrocarbons and surface carbonates. However, after heating the surface to 450 °C under vacuum, $ZrO_2(450)$, these bands disappear from the spectrum. Also, there is a decrease in the intensity of the hydroxyl group region during heating (see Figure 1). After a pretreatment temperature of 450 °C, the bands in the hydroxyl group region have frequencies near 3768, 3740, 3679, and 3664 cm^{-1}. These bands are reasonably close in frequency to those reported in the literature[11,12] and are assigned to isolated, 3768 and 3740 cm^{-1}, and bridged, 3679 and 3664 cm^{-1}, hydroxyl groups for two phases of zirconia, monoclinic and tetragonal, respectively. As shown in Figure 1, as the sample is further heated to 750 °C the surface becomes more dehydroxylated, $ZrO_2(750)$, and at an activation temperature of 900 °C, $ZrO_2(900)$, the sample is completely dehydroxylated. Unless otherwise noted, the experiments were done on ZrO_2 samples that had been heated to 450 °C under vacuum for 30 min.

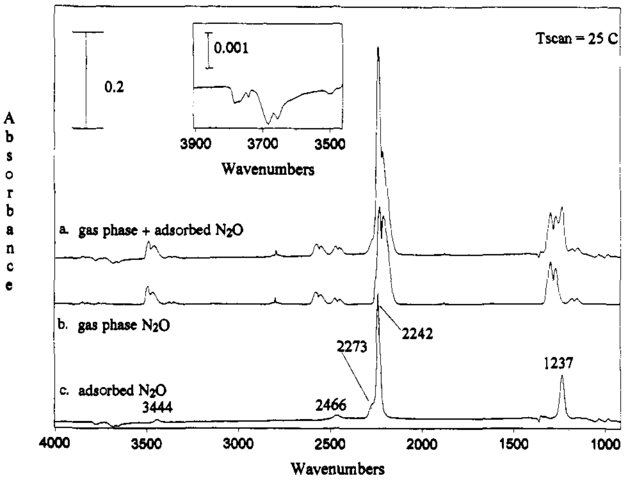


Figure 2. Infrared spectra recorded of gas phase and adsorbed N_2O. The top spectrum, a, shows the infrared spectrum of the zirconia catalyst in the presence of 20 Torr of gas phase N_2O. The middle spectrum, b, shows the spectrum of 20 Torr of gas phase N_2O. The difference spectrum of b from a gives spectrum c. The spectrum labeled c represents the spectrum of adsorbed N_2O on zirconia. An expanded view of the hydroxyl group region for spectrum c is shown in the inset.

2. Room Temperature Adsorption of N_2O on ZrO_2.

Figure 2 shows the room temperature IR spectra of gas phase and adsorbed N_2O. Figure 2a shows the spectrum recorded of the zirconia side of the sample in the presence of 20 Torr of N_2O. The spectrum shown in Figure 2b is the spectrum recorded of the blank side of the tungsten grid and represents the spectrum of 20 Torr of gas phase N_2O. Figure 2c is the subtracted spectrum of 2b from 2a and shows the spectrum of adsorbed N_2O. The spectrum of adsorbed N_2O at this pressure is characterized by two intense peaks at 2242 and 1237 cm^{-1}. Although the frequencies of the bands are shifted from the gas phase values of 2224 and 1285 cm^{-1},[13,14] these bands are identified as the asymmetric stretch and symmetric stretch, respectively, of adsorbed N_2O. The shoulder near 2273 cm^{-1} is identified as a combination band $\nu_1 + 2\nu_2$. Also visible in the spectrum of adsorbed N_2O is an absorption band at 2466 cm^{-1} assigned to $2\nu_1$ and another band at 3444 cm^{-1} assigned to $\nu_1 + \nu_3$.[13,14]

Infrared spectra of adsorbed N_2O as a function of pressure are shown in Figure 3. The spectra show that the bands decrease in intensity as the pressure is decreased from 70.0 to 1.0 Torr. The low-frequency absorption band shifts by 7 cm^{-1} to lower frequency, from 1240 to 1233 cm^{-1}, as the coverage decreases. The high-frequency absorption band exhibits a low-frequency shoulder near 2229 cm^{-1} sometimes at higher pressures which is probably due to a spectral artifact from the subtraction of the very intense gas phase absorption bands at the higher pressures. At room temperature, the integrated areas of the absorption bands for adsorbed nitrous oxide increase very little after a pressure of approximately 50 Torr is reached thus indicating saturation coverage.

If N_2O was hydrogen bonded to the surface hydroxyl groups, there would be a loss intensity in the band associated with the isolated OH groups and a growth of a broader band at lower frequency that would be indicative of hydrogen bonding.[7,8] A close look at the hydroxyl group region shown in the inset in Figure 2 reveals only a small decrease in the bands associated with surface hydroxyl groups upon N_2O adsorption and no new bands at lower frequency. This result indicates that hydroxyl

---

(11) Tsyganenko, A. A.; Filimonov, V. N. *Spectrosc. Lett.* **1972**, *5*, 477.

(12) Agron, P. A.; Fuller, E. L.; Holmes, H. F. *J. Colloid Interface Sci.* **1975**, *52*, 553.

(13) Herzberg, G. *Molecular Spectra and Molecular Structure*; D. Van Nostrand Company, Inc.: New York, 1945; Vol. 2.

(14) Pliva, J. *J. Mol. Spectrosc.* **1961**, *12*, 360.

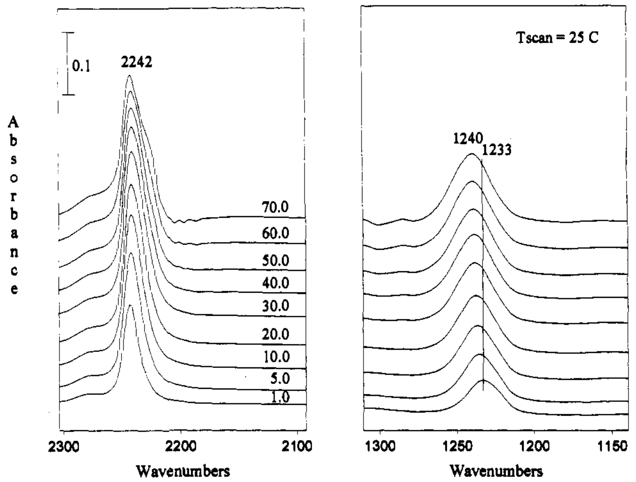


Figure 3. Infrared spectra of adsorbed N_2O recorded as a function of the equilibrium gas phase pressure of N_2O from 1.0 to 70.0 Torr. The left panel shows the band associated with the asymmetric stretch of adsorbed N_2O at 2242 cm^{-1} and the right panel shows the band associated with the symmetric stretch of adsorbed N_2O. The frequency of the asymmetric stretch at 2242 cm^{-1} is constant as a function of coverage whereas the frequency of the symmetric stretch increases with coverage. The shoulder near 2229 cm^{-1} is only sometimes seen in spectra recorded at higher pressures and is probably due to poor subtraction of the gas phase at the higher pressures. The integrated area of the bands levels off near a pressure of 50 Torr indicating saturation coverage is reached.

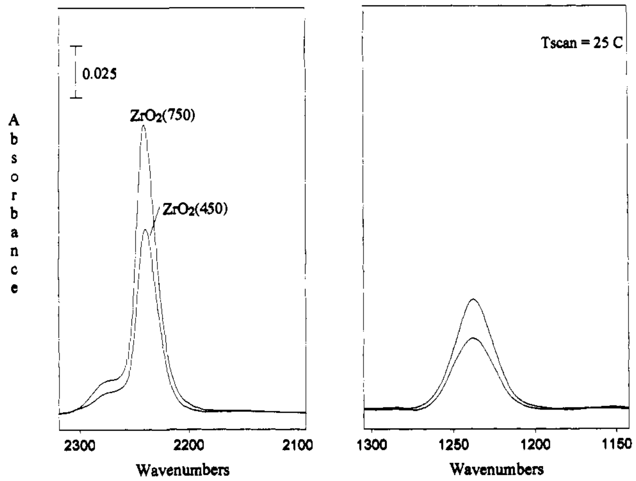


Figure 4. Infrared spectra of adsorbed N_2O on zirconia surfaces that have been pretreated at two different temperatures. At an equilibrium pressure of 20 Torr, there is an increase in the amount of N_2O adsorbed on the surface that has been further dehydroxylated by heating to 750 °C, $ZrO_2(750)$, as compared to a surface heated to 450 °C, $ZrO_2(450)$.

groups may not be the primary bonding site for N_2O adsorption. In order to determine the nature of the adsorption site, we have adsorbed N_2O on zirconia surfaces that have been further dehydroxylated by pretreatment at higher temperatures and preadsorbed with site blocker molecules.

Figure 4 shows the infrared spectra recorded of adsorbed N_2O at room temperature on a zirconia surface at a pressure of 20.0 Torr after heating to two different activation temperatures. First, the zirconia sample was heated in vacuum to 450 °C followed by adsorption of N_2O at 25 °C, then the sample was heated to 750 °C in vacuum followed again by N_2O adsorption at room temperature. As shown in Figure 4, there is an increase in the integrated area of the two absorption bands for adsorbed N_2O after adsorption at the same pressure (20 Torr) and temperature (25 °C) on the surface that had been pretreated at 750 °C compared to the one that had been pretreated at 450 °C. The surface hydroxyl group coverage decreases by roughly 80% after heating to 750 °C compared to 450 °C, as estimated by the integrated area of the IR absorption bands. The increase in the amount of N_2O adsorption inversely correlates with the amount of hydroxyl groups present on the surface. Therefore, we conclude that surface hydroxyl groups are not the primary bonding interaction for N_2O adsorbed on ZrO_2.

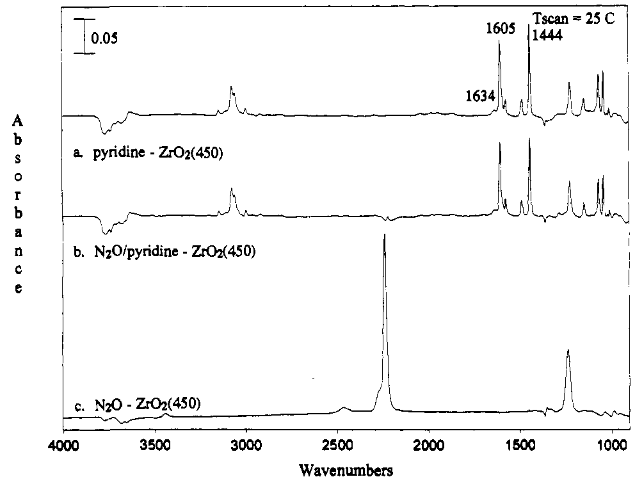


Figure 5. Preadsorbed pyridine on a zirconia surface blocks nitrous oxide adsorption. (a) Infrared spectrum recorded of pyridine adsorbed on zirconia. (b) Infrared spectrum recorded of nitrous oxide adsorbed on a pyridine-covered surface. (c) Infrared spectrum of nitrous oxide adsorbed on a surface that has not been exposed to pyridine.

In other experiments, pyridine was used as a probe molecule to aid in the determination of the adsorption site, as it is well-known that pyridine adsorbs to both Lewis and Brønsted acid sites.[15-18] Pyridine (10.0 Torr) was introduced into the IR sample cell. After several minutes, pyridine was evacuated and a scan was taken. Figure 5a shows the infrared spectrum after the adsorption of pyridine on a ZrO_2 sample. The spectrum presented in Figure 5a shows a loss in the intensity of the surface hydroxyl group bands, presumably to form the pyridinium ion, $C_5H_6N^+$, and the growth of several new bands associated with adsorbed pyridine. It should be noted that not all of the hydroxyl groups are consumed after adsorption with pyridine, indicating that some hydroxyl groups are not accessible for reaction with pyridine. These inaccessible hydroxyl groups may not be on the surface of the nanostructures but instead may be present in the internal pores.

The 1400–1700 cm^{-1} spectral region is commonly used to distinguish between $C_5H_6N^+$ and pyridine adsorbed on Lewis acid sites. The frequencies of the peaks in that region for adsorbed pyridine are given in Figure 5a. The frequencies of the bands for adsorbed pyridine recorded in this work are nearly identical to the values reported in the literature.[17,18] In particular, absorption bands at 1605 and 1444 cm^{-1} are associated with pyridine adsorbed on the Lewis acid sites and the band at 1634 cm^{-1} is associated with adsorption on Brønsted acid sites.[16,18]

N_2O was then introduced at a pressure of 20.0 Torr onto a sample that had been exposed to pyridine. After spectral subtraction of gas phase N_2O, the spectrum shows that there is essentially no N_2O adsorbed on the surface (see Figure 5b), indicating that N_2O adsorbs on Lewis acid sites. For comparison, the spectrum of adsorbed N_2O on a surface that had not been exposed to pyridine is shown as well (Figure 5c).

---

(15) Knozinger, H. *Adv. Catal.* **1976**, *25*, 184.

(16) Kung, M. C.; Kung, H. H. *Catal. Rev. Sci. Eng.* **1985**, *27*, 425.

(17) Fierro, J. L. G.; Garcia De La Banda, J. F. *Catal. Rev. Sci. Eng.* **1986**, *28*, 265.

(18) Hertl, W. *Langmuir* **1989**, *5*, 96.

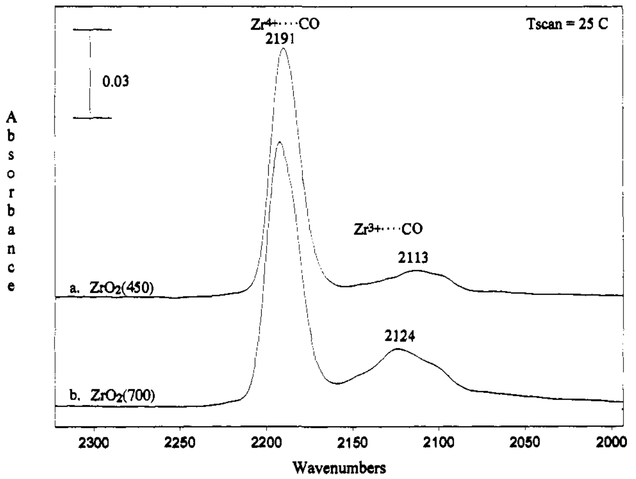


Figure 6. CO adsorption on a zirconia surface that has been activated by heating under vacuum at 450 and 700 °C: (a) $ZrO_2(450)$ and (b) $ZrO_2(700)$. The equilibrium pressure of CO was 40 Torr. Gas phase contributions to the above spectra have been subtracted out.

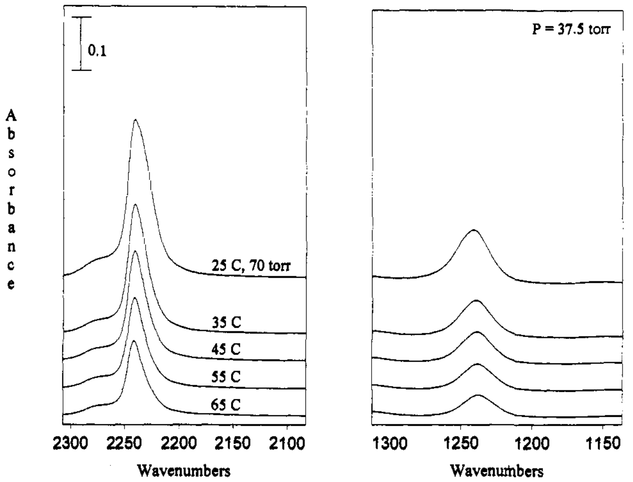


Figure 7. The infrared spectrum recorded of a saturated surface of nitrous oxide at a pressure of 70 Torr at 25 °C is shown in the top trace. The other spectra shown were recorded at an equilibrium pressure of 37.5 Torr of N_2O at various temperatures: 35, 45, 55, and 65 °C.

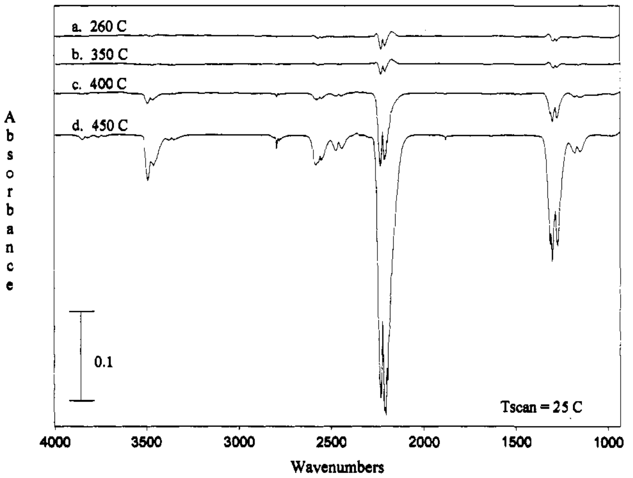


Figure 8. Difference spectra recorded of gas phase N_2O after reaction of approximately 75 Torr for 20 min at a temperature of (a) 260, (b) 350, (c) 400, and (d) 450 °C. Under these conditions, the decomposition on N_2O is estimated to be <1% at temperatures below 350 °C.

To further probe the nature of the Lewis acid site, CO was adsorbed on ZrO_2. Previous studies have shown that CO adsorption can be used as an indirect probe of the charge on the surface zirconium atoms.[19,20] Figure 6 shows the IR spectra recorded at room temperature for adsorbed CO on ZrO_2 activated at two temperatures, 450 and 700 °C. The equilibrium pressure of CO was 40 Torr in these experiments; gas phase absorptions have been subtracted out from the spectra shown in Figure 6. The high-frequency band at 2191 cm^{-1} is assigned to CO adsorbed on Zr^{4+} sites. The low-frequency band near 2113 cm^{-1} in the $ZrO_2(450)$ spectrum is assigned to CO adsorbed on Zr sites that are reduced to the 3^+ oxidation state. Heating the ZrO_2 catalyst under vacuum to 700 °C under vacuum causes an increase in the integrated area of the two CO bands. There is only a slight increase, a factor of 1.1 times greater, in the integrated area for CO adsorbed on Zr^{4+} sites when the sample is heated from 450 to 700 °C. For CO adsorbed on Zr^{3+} sites, the band blue shifts to 2124 cm^{-1} (see Figure 6b) and the integrated area increases by a factor of 1.8 when the sample is heated to 700 °C compared to 450 °C.

3. Adsorption of N_2O as a Function of Temperature. The spectrum of adsorbed N_2O as a function of temperature from 35 to 65 °C is shown in Figure 7. The top IR spectrum shown in Figure 7 is for a saturated surface of adsorbed N_2O when 70 Torr of gas phase N_2O is present at 298 K. The other IR spectra shown in Figure 7 are for adsorbed N_2O in the presence of an equilibrium pressure of 37.5 Torr of gaseous N_2O at various temperatures. As can be seen from the data, the amount of adsorbed N_2O decreases at higher temperatures at a constant pressure.

4. Dissociation of N_2O on ZrO_2. The dissociation of N_2O on the ZrO_2 catalyst was studied with IR spectroscopy as well. Because the gas phase products, N_2 and O_2, are IR inactive, the loss of gas phase N_2O was used to monitor the decomposition reaction. To determine at what temperature the decomposition reaction begins, approximately 75 Torr of N_2O was heated from 260 to 450 °C. Figure 8 shows the difference spectrum of the gas phase after reaction of N_2O for 20 min at 260, 350, 400, and 450 °C in the presence of the ZrO_2 catalyst. The negative absorbance features correspondence to a decrease in the amount of gas phase N_2O present in the cell after reaction to form N_2 and O_2. Up to a temperature of 350 °C, there is <1% loss of gas phase N_2O. However, at 400 °C, there is a significant loss of gas phase N_2O and an even greater amount after reaction at 450 °C, 9% and 43%, respectively.

The decomposition reaction of 100.0 Torr of gas phase N_2O was monitored at 400 °C for 6 h. The integrated area of the 2224-cm^{-1} band plotted as a function of reaction time is shown in Figure 9. In order to ensure that the observed decomposition of N_2O was due to the zirconia catalyst, a blank tungsten grid was put into the sample holder. Approximately 100 Torr of N_2O was introduced and the grid was heated to 400 °C for 6 h. As can be seen in Figure 9, there is no loss of N_2O in the absence of the zirconia catalyst. This indicates that the decomposition reaction is occurring on the surface of the catalyst.

After the decomposition of N_2O proceeded for several hours, the only changes seen in the gas phase IR spectrum are associated with a loss of N_2O and the formation of a small amount of gas phase CO_2; no other nitrogen oxides, e.g. NO_2 and NO, were detected. After 6 h of reaction, some carbonate was present on the zirconia surface, from reaction of gas phase CO_2 with zirconia. Carbonate formation is marked by absorption bands near 1625, 1573, 1429, 1362, 1336, and 1229 cm^{-1}, in agreement with literature values for bidentate carbonate

---

(19) Morterra, C.; Giamello, E.; Luciana, O.; Volante, M. *J. Phys. Chem.* **1990**, *94*, 3111.

(20) Jacob, K.-H.; Knozinger, E.; Benfer, S. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2969.

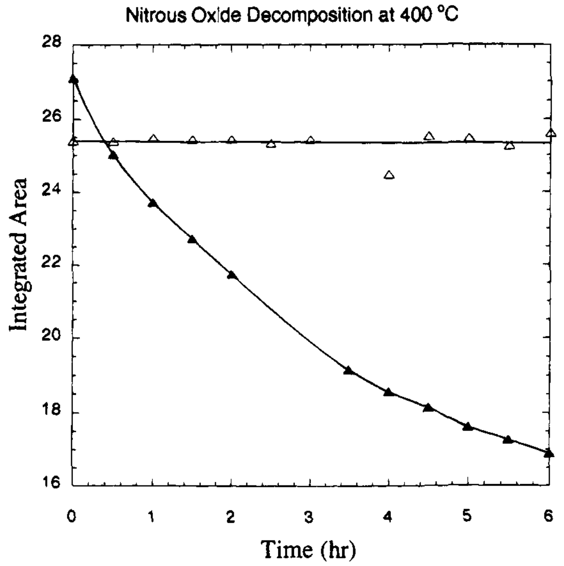


Figure 9. A plot of the integrated area of gas phase N_2O as a function time during the dissociation reaction in the presence (closed triangles) and the absence of the zirconia catalyst (open triangles) is shown.

species and some hydrogenocarbonate (HCO_3^-).[18,21-23] CO_2 formation may come about from oxidation of small quantities of hydrocarbon impurities in the nitrous oxide gas. Additional CO_2 formation may result from small quantities of carbon residue on the catalyst itself. As discussed below, CO_2 adsorption has a deleterious effect on the adsorption and dissociation of N_2O.

The nature of the active site for the decomposition reaction is of fundamental importance. Molecules that block the active site could in principle be used for these experiments. One possibility is that adsorbed N_2O observed in room temperature experiments is the precursor to decomposition; if so Lewis acid sites (e.g. Zr^{4+} sites) should be the active site. Unfortunately, pyridine could not be used as a site blocker for reaction because it desorbs/reacts near 250 °C, a temperature below the decomposition temperature of N_2O. Similar to other studies, we found that CO_2 reacts with the surface to form carbonate on the surface (see Figure 10a).[18,21-23] The adsorbed carbonate inhibits the room temperature adsorption of N_2O (see Figure 10b) and is stable up to temperatures near 425 °C. Therefore, we have used the CO_2 reaction to form carbonate to inhibit the adsorption of N_2O and possibly the decomposition reaction.

Gas phase N_2O (74.1 Torr) was reacted with a carbonate covered zirconia surface at a temperature of 400 °C. Scans were taken at 30-min intervals for 2 h. The chamber was evacuated and the sample heated to 450 °C under vacuum to remove carbonate from the surface. The experiment was then repeated with the clean ZrO_2 sample. Integration of the 2224-cm^{-1} band allows for us to determine the amount of loss of gas phase N_2O. Figure 10c shows that the amount of N_2O that has decomposed over a period of 2 h is less over the carbonate covered ZrO_2 surface. There was a 50% greater loss of gas phase N_2O on the clean surface as compared to a surface with adsorbed carbonate. Although the reactivity of the ZrO_2 surface with respect to N_2O decomposition is not totally quenched with preadsorbed CO_2, it is substantially reduced.

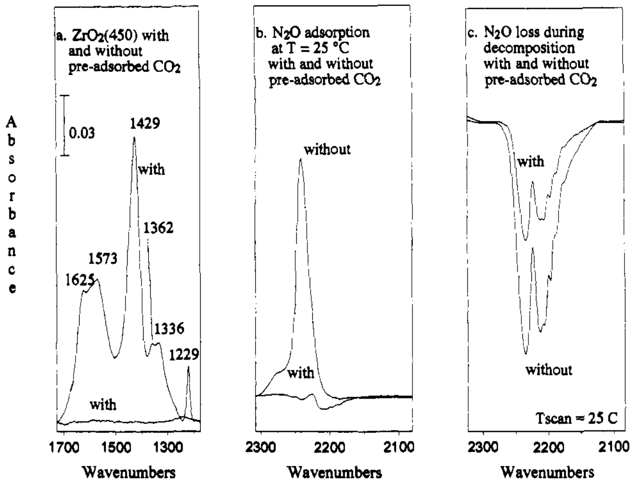


Figure 10. (a) Infrared spectra recorded of ZrO_2 with and without adsorbed CO_2. (b) Infrared spectra recorded of N_2O adsorbed at room temperature on ZrO_2 with and without preadsorbed CO_2. (c) The difference spectra of gas phase N_2O is shown after reaction at 400 °C on ZrO_2 with and without preadsorbed CO_2. As shown above, CO_2 reacts with the zirconia surface to form adsorbed carbonates with characteristic bands at 1625, 1573, 1429, 1362, 1336, and 1229 cm^{-1}. The IR data show that surface carbonates inhibit the adsorption and decomposition of N_2O on ZrO_2.

Discussion

1. N_2O Adsorption Sites. To determine the adsorption site of N_2O on ZrO_2, we looked at the effect of surface hydroxyl group coverage and site-blockers on the adsorption of N_2O. It was shown that the amount of adsorbed N_2O was inversely correlated with the OH coverage. These results show that N_2O does not bond to Brønsted acid sites. Site-blocking experiments with pyridine yielded even more information about the adsorption site. It is known that pyridine adsorbs onto Lewis acid sites.[15-18] The infrared bands at 1605 and 1444 cm^{-1} in the spectrum shown in Figure 5a indicated that pyridine is adsorbed on Lewis acid sites. The adsorption of pyridine on the ZrO_2 surface totally quenched the adsorption of N_2O. Therefore, we conclude from the pyridine site blocking experiment that N_2O adsorbs onto the surface at Lewis acid site. This is consistent with the site of adsorption of N_2O with other transition metal oxides, such as α-Cr_2O_3,[24,25] ZnO,[26] η-Al_2O_3,[27] and TiO_2.[28]

If the surface stoichiometry was similar to the bulk, the Lewis acid sites would correspond to Zr^{4+} sites. However, it is well-known that upon heating in vacuum, metal oxides can be reduced. The results of the CO IR measurements provide information about the oxidation state of the zirconium cation. For ZrO_2 samples that are activated at a temperature of 450 °C under vacuum, the CO IR absorption spectrum shows a strong band associated with CO coordinated to Zr^{4+} and a much weaker band associated with CO coordinated to Zr^{3+}. Room temperature CO adsorption on a surface that has been heated in vacuum to 700 °C shows a slight increase in the amount of Zr^{4+} and an even larger increase in the amount of Zr^{3+} sites. The CO adsorption data provide evidence for two types of Lewis acid sites on the surface, Zr^{4+} and Zr^{3+}. As the activation temperature of the zirconia catalyst increases, Zr^{3+} sites become more abundant, in accord with other studies.[19,20] Therefore, the role

---

(21) Bensitel, M.; Moravek, V.; LaMotte, J.; Saur, O.; LaValley, J. *Spectrochim. Acta* **1987**, *43A*, 1487.

(22) Morterra, C.; Orio, L.; Emanuel, C. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 3003.

(23) Kondo, J.; Abe, H.; Sakata, Y.; Maruya, K.; Domen, K.; Onishi, T. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 511.

(24) Borello, E.; Cerruti, L.; Ghiotti, G.; Guglielminotti, E. *Inorg. Chim. Acta* **1972**, *6*, 45.

(25) Zecchina, A.; Cerruti, L.; Borello, E. *J. Catal.* **1972**, *25*, 55.

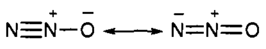
(26) Hussain, G.; Rahman, M. M.; Sheppard, N. *Spectrochim. Acta* **1991**, *47A*, 1525.

(27) Morterra, C.; Boccuzzi, F.; Coluccia, S.; Ghiotti, G. *J. Catal.* **1980**, *65*, 231.

(28) Ramis, G.; Busca, G.; Bregani, F. *Gazz. Chim. Ital.* **1992**, *122*, 79.

of Zr^{3+} sites become increasingly important at higher activation temperatures and should contribute to the adsorption and chemistry of N_2O on ZrO_2.

2. Mode of Attachment: Is N_2O N or O Bonded to ZrO_2? N_2O can bond through either the nitrogen or oxygen end of the molecule to the zirconia surface. This is due to a considerable amount of electron density at both terminal atoms in the molecule. Two resonance structures can be drawn for N_2O,



$$\mathrm{N{\equiv}\overset{+}{N}{-}\overset{-}{O} \longleftrightarrow \overset{-}{N}{=}\overset{+}{N}{=}O}$$

1 **2**

the interaction with the surface could stabilize one of these two forms of nitrous oxide. Ab initio calculations have shown that nitrogen and oxygen bound adducts of N_2O with the silanol molecule H_3SiOH have very close interaction energies.[29]

Nitrous oxide adsorption has been studied on many different types of surfaces including alkali halides,[30] metal oxides,[24-28] and metals.[31-33] For nitrous oxide adsorption on these surfaces, there is evidence for both N- and O-bonded complexes. The evidence for these two adsorbate structures, which differ in their bonding configuration, has been primarily through analysis of vibrational data. An early study by Zecchina et al. of nitrous oxide adsorption on α-chromia surfaces showed the presence of both N- and O-bonded N_2O surface species both of which were bonded to Cr^{3+} sites.[25] They assigned one species with absorptions at 2238 and 1237 cm^{-1} to an O-bonded complex and the other species with absorptions at 2305 and 1339 cm^{-1} to an N-bonded complex. They argued that bonding through the oxygen atom should stabilize resonance structure **1** shown above. Stabilization of resonance structure **1** would result in an increase in the N−N force constant and a decrease in the N−O force constant resulting in a blue and red shift for the asymmetric stretch and symmetric stretch, respectively, of the adsorbed molecule. Normal mode calculations for O-bonded species do show an increase and decrease in the force constants, k_{NN} and k_{NO}, respectively, for N_2O coordinated through the oxygen atom.[34,35]

In contrast, Zecchina et al. proposed bonding through the nitrogen atom should result in a stabilization of resonance structure **2** whose bonding characteristics could be compared to the isostructural and isoelectronic CO_2 molecule. The frequencies of the asymmetric and symmetric stretch for gas phase CO_2 are at 2349 (IR active) and 1388 cm^{-1} (Raman active). Therefore, stabilization of resonance structure **2** should result in blue shifts for both the asymmetric stretch and symmetric stretch of the adsorbed molecule. Recent calculations of vibrational frequencies for nitrous oxide both O- and N-bonded to silanol are in agreement with the frequency shifts (although not the frequencies) discussed above.[29]

Table 1 shows the frequencies observed for N_2O adsorbed on ZrO_2 as well as on several other oxide surfaces including ZnO,[26] Al_2O_3,[27] Cr_2O_3,[24,25] and TiO_2.[28] By comparison of the shifts of the adsorption bands of adsorbed N_2 on ZrO_2 to these other oxides, and based on the above discussion, it can be seen that the data presented here for N_2O on ZrO_2 correlate well with an O-bonded adsorbed molecule. For N_2O adsorbed on ZrO_2, the frequency of ν_3, the asymmetric stretch, blue shifts by 18 cm^{-1} from the gas phase value whereas the frequency of ν_1, the symmetric stretch, red shifts by 45−52 cm^{-1}, depending on surface coverage, from the gas phase value. The asymmetric stretch can be described primarily as a nitrogen−nitrogen stretching motion, and the symmetric stretch can be described as a nitrogen−oxygen stretching motion. For the adsorbed molecule, the force constant increases for the asymmetric stretch indicating a stronger bond between the nitrogen atoms whereas the force constant decreases for the symmetric stretch indicating a weaker bond between the central nitrogen and oxygen atoms. Therefore, the vibrational data suggest that resonance structure **1** is stabilized on the surface of zirconia. As can be seen from Table 1, of all the oxides studied thus far that form O-bonded complexes of nitrous oxide, zirconia causes the largest decrease in ν_1, the N−O stretching mode.

Table 1. Comparison of the Vibrational Frequencies for Adsorbed Nitrous Oxide on Zirconia to Other Oxides

	vib freq		
oxide	ν_3	ν_1	mode of attachment
gas phase[a]	2224	1285	
ZnO[b] (Zn^{2+})[c]	2237	1255	O-bonded
Al_2O_3[d] (Al^{3+})	2236	1240	O-bonded
Cr_2O_3[e] (Cr^{3+})	2238	1237	O-bonded
	2305	1339	N-bonded
TiO_2[f] (Ti^{4+})	2250	1235	O-bonded
	2238	1252	O-bonded
	2290	1322	N-bonded
	2267	1310	N-bonded
ZrO_2[g] (Zr^{4+})	2242	1233[h]	O-bonded

[a] Reference 13. [b] Reference 26. [c] Bonding sites are noted in parentheses. [d] Reference 27. [e] References 24 and 25. [f] Reference 28. [g] This work. [h] Low coverage value.

3. Determination of ΔH_{ads}. The infrared spectra of adsorbed N_2O as a function of temperature can be used to determine the heat of adsorption, ΔH_{ads}. Assuming Langmuir-type adsorption behavior, the equilibrium constant, K_{eq}, for the reaction $N_2O(g) + \text{site} \rightarrow N_2O(a)$ can be expressed as $K_{eq} = \theta/P(1 - \theta)$, where θ = surface coverage. The coverage at a given pressure and temperature can be determined from the ratio of the integrated area of the infrared absorption band at that pressure and temperature relative to the integrated area at saturation coverage. Saturation coverage in these experiments was determined at pressures above 50 Torr and a temperature of 25 °C. The ln K_{eq} is then plotted as a function of inverse temperature to obtain ΔH_{ads}. The analysis assumes that the integrated area increases linearly with coverage, saturation coverage has been accurately determined, and the heat of adsorption is independent of coverage.

The two fundamental bands near 2242 and 1235 cm^{-1} can be used to determine K_{eq}. $K_{eq} = \theta/P(1 - \theta)$ is then equal to $(A/A_{sat})/P(1 - (A/A_{sat}))$, where A = integrated area of the peak and A_{sat} = the integrated area of the peak at saturation coverage. Using the data presented in Figure 7, a plot of ln K_{eq} against $1/T$ was obtained. The plot is shown in Figure 11. The van't Hoff equation was used to determine the heat of adsorption from the slope of the two lines in Figure 11. The heat of adsorption is calculated to be 8.0 and 8.9 kcal/mol for the 1235- and 2242-cm^{-1} bands, respectively. We have repeated this measurement in ten separate experiments with temperatures ranging from 25 to 95 °C and pressures ranging from 10 to 40 Torr. Each plot contained at least four data points and the slope was determined using both absorption bands at 2242 and 1235 cm^{-1}. From this analysis, an average value of 9.6 kcal/mol was determined with a standard deviation of 1.6 kcal/mol.

---

(29) Garrone, E.; Ugliengo, P.; Ghiotti, G.; Borello, E.; Saunders, V. R. *Spectrochim. Acta* **1993**, *49A*, 1221.

(30) Kozirovski, Y.; Folman, M. *Trans. Faraday Soc.* **1969**, *65*, 244.

(31) Avery, N. *Surf. Sci.* **1983**, *131*, 501.

(32) Umbach, E.; Menzel, D. *Chem. Phys. Lett.* **1981**, *84*, 491.

(33) Kim, Y.; Schreifels, J. A.; White, J. M. *Surf. Sci.* **1982**, *114*, 349.

(34) Diamantis, A. A.; Sparrow, G. J. *J. Colloid Interface Sci.* **1974**, *47*, 455.

(35) It should be noted that the validity of the calculations by Diamantis and Sparrow has been questioned. See: Bottomley, F.; Brooks, W. V. F. *Inorg. Chem.* **1977**, *16*, 501.

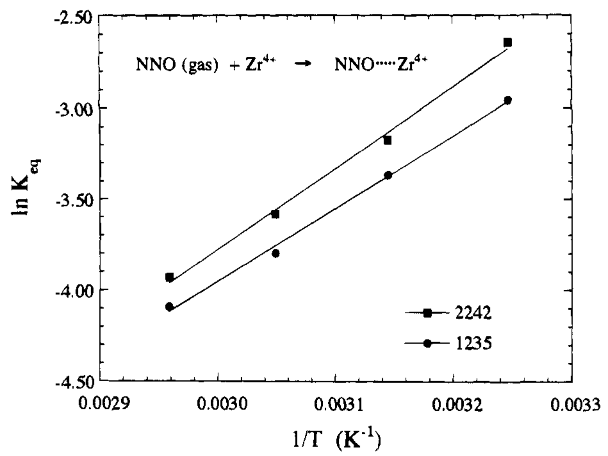
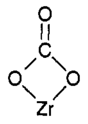


Figure 11. A plot of the ln K_{eq} as a function of $1/T$ is shown. Using the van't Hoff equation, the heat of adsorption is calculated to be 8.0 and 8.9 kcal/mol from the slope of the lines for the 1235- and 2242-cm^{-1} bands, respectively. This analysis was done for ten experiments. From these measurements, an average value of 9.6 kcal/mol with a standard deviation of 1.6 kcal/mol was determined.

4. Thermal Decomposition of N_2O. The experiments with preadsorbed CO_2 show that N_2O adsorption and decomposition are suppressed. When CO_2 reacts with zirconia carbonate species form at the surface. The structure of bidentate carbonate is shown below. Although reaction of CO_2 with ZrO_2 occurs primarily with the lattice oxygen atoms, it can be seen that zirconium cation sites are blocked after formation of surface carbonate.



3

The data suggest that for zirconia catalysts activated at 450 °C, the Zr^{4+} site is not only the predominant site for adsorption of N_2O at room temperature but may be the site for N_2O dissociation as well at higher temperatures. A possible mechanism for this reaction is as follows:

$$N_2O(a) \rightarrow O(a) + N_2(g) \tag{1}$$

$$2O(a) \rightarrow O_2(g) \tag{2}$$

Initially in Step 1, nitrous oxide adsorbs onto Zr^{4+} sites in an oxygen-bonded configuration. The oxygen atom is then extruded from the molecule to form a more tightly bonded oxygen atom. Dinitrogen desorbs into the gas phase under reaction conditions. The adsorbed oxygen atom then combines with another oxygen atom to give dioxygen in the gas phase. Currently, we are investigating the mechanism of nitrous oxide decomposition in more detail. The role of Zr^{3+} sites will be investigated as well as the role of lattice oxygen atoms in the decomposition of N_2O on zirconia. The results of that study will be reported later.[36]

Conclusions

The main conclusions derived from this study of nitrous oxide adsorption and decomposition are summarized below.

1. The adsorption site for nitrous oxide on zirconia has been determined to be primarily Zr^{4+} sites for samples that have been activated at 450 °C under vacuum.

2. A vibrational assignment of adsorbed N_2O has been made. The frequencies of the two absorption bands associated with the asymmetric and symmetric stretching motions are blue and red shifted from the gas phase values by approximately 45 and 18 cm^{-1}, respectively.

3. The mode of attachment for nitrous oxide to zirconia is suggested to be through the oxygen atom.

4. The heat of adsorption is determined to be 9.6 ± 1.6 kcal/mol.

5. For 75 Torr of N_2O, decomposition does not begin until temperatures above 350 °C on zirconia.

6. The data suggest that Lewis acid sites, predominantly Zr^{4+} sites for samples activated at 450 °C, are the active sites for decomposition of nitrous oxide and the room temperature adsorbed structure may be a precursor to decomposition.

7. Preadsorbed CO_2 as well as small quantities of CO_2 produced in the reaction chamber during N_2O decomposition form surface carbonates that can lead to catalyst deactivation.

Acknowledgment. The authors gratefully acknowledge support from the National Science Foundation and du Pont de Nemours and Co. The authors also thank Drs. Sau Lan Tang and Theodore A. Koch (at duPont) for many helpful discussions during the course of this work.

JA950543M

---

[36] Miller, T. M.; Grassian, V. H. To be published.