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See page 1 and 2 of report

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SUBMITTED FOR PUBLICATION TO (applicable only if report is manuscript):

Sincerely,

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Enclosure 3

Do Electrons or Holes Activate Molecular O_2 on TiO_2 Surfaces?

Final Report

John T. Yates, Jr.

30 November 2000

U.S. ARMY RESEARCH OFFICE

DAAG55-97-1-0169

36939-CH-AAS

University of Pittsburgh

FINAL REPORT

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1. **ARO PROPOSAL NUMBER:** 36939-CH-AAS

2. **PERIOD COVERED BY REPORT:** June 1997 – May 2000

3. **TITLE OF PROPOSAL:** Do Electrons or Holes Activate Molecular O_2 on TiO_2 Surfaces?

4. **CONTRACT OR GRANT NUMBER:** DAAG55-97-1-0169

5. **NAME OF INSTITUTION:** University of Pittsburgh

6. **AUTHOR OF REPORT:** John T. Yates, Jr.

7. **LIST OF MANUSCRIPTS SUBMITTED OR PUBLISHED UNDER ARO SPONSORSHIP:**

1. "Comparison of Thermal and Photochemical Behavior of O_2 Chemisorbed on Pt(335)." D. V. Heyd, R. J. Scharff and J. T. Yates, Jr. *J. Chem. Phys.* **110**, 6939 (1999).

The thermal and photochemical behavior of O_2 chemisorbed on a stepped Pt(335) surface have been compared using temperature programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS). Molecular O_2 adsorbs preferentially at 85 K on step sites, followed by adsorption on terrace sites. On heating below 250 K, depopulation of terrace sites occurs first followed by depopulation of step sites. Both desorption and dissociation of $O_2(a)$ occur below 250 K. Photolysis of O_2 occurs preferentially on step sites, with a cross section $\approx 3\times10^{-21}$ cm^2. The chemisorbed O(a) produced by either thermal dissociation or photodissociation of $O_2(a)$ is identical, exhibiting a Pt-O stretching mode at 480 cm^{-1} and a frustrated translation mode at 330-350 cm^{-1}. Two regimes of photodepletion are observed, dominated by photolysis of step bound-O_2 (regime I) and of terrace bound-O_2 (regime II). Regime II is characterized by the presence of interactions of photoproduced electronegative O(a) with remaining $O_2(a)$, causing an increase of the O-O mode frequency due to electron withdrawal from the $O_2(a)$ π^* orbital.

2. "Infrared Spectral Evidence for the Etching of Carbon Nanotubes: Ozone Oxidation at 298 K." Douglas B. Mawhinney, Viktor Naumenko, Anya Kuznetsova, John T. Yates, Jr., J. Liu and R. E. Smalley, *J. Am. Chem. Soc.* **122**, 2383 (2000).

   We have employed infrared spectroscopy to monitor the reaction of O_3 with single walled carbon nanotubes. Ester and quinone groups are produced, as well as gas phase CO and CO_2. The rate of formation of these species decreases at higher O_3 exposures as active sites are consumed. The O_3-derived functional groups may be removed as CO_2 gas by heating in vacuum to 873 K, leaving the carbon nanotube walls intact.

3. "Enhancement of Adsorption Inside of Single-Walled Nanotubes: Opening the Entry Ports." Anya Kuznetsova, Douglas B. Mawhinney, Viktor Naumenko, John T. Yates, Jr., J. Liu and R. E. Smalley, *Chem. Phys. Lett.* **321**, 292 (2000).

   Opening the ends of the single-walled carbon nanotube by thermal activation increases both the kinetic rate and the saturation capacity of the nanotubes for Xe adsorption at 95 K. Infrared studies show the existence of carboxylic acid and quinone groups on the nanotube surface prior to heating above 623 K. These groups decompose during heat treatment of the nanotube sample from 623 to 1073 K producing CO, CO_2, CH_4 and H_2. The removal of a large number of these groups opens the entry ports for adsorption on the inner surface of the nanotube and leads to dramatically enhanced Xe adsorption.

4. "Surface Defect Site Density on Single Walled Carbon Nanotubes by Titration." Douglas B. Mawhinney, Viktor Naumenko, Anya Kuznetsova, John T. Yates, Jr., J. Liu and R.E. Smalley, *Chem. Phys. Lett.* **324**, 213 (2000).

   Closed end single walled carbon nanotubes (c-SWNT) purified by acidic oxidation have been studied in order to determine the fraction of oxidized carbon sites present. This has been done by measuring the evolution of $CO_2(g)$ and CO(g) on heating to 1273 K. Following a 1273 K treatment, the defect sites were titrated repeatedly with O_3. The results indicate that ~ 5% of the carbon atoms in the c-SWNT samples pretreated to 1273 K are located at defective sites, capable of facile oxidation by O_3. This high defect site density indicates that a significant number of these sites exist on the graphene walls of the nanotubes.

8. SCIENTIFIC PERSONNEL:

Mr. R. Jason Scharff, M.S.
Dr. Douglas B. Mawhinney, Ph.D.

9. REPORT OF INVENTIONS:

The discovery of a method to enhance adsorption inside of single walled nanotubes by thermal activation, removing blocking functional groups at the entry ports to the interior, is the subject of a patent application which is being processed at the U. S. Patent Office.

10. Brief Review of Research Findings

A. OXYGEN PHOTOCHEMISTRY ON SURFACES

This project began with the study of the photochemistry of O_2 chemisorbed on a stepped Pt single crystal surface. The study found that photolysis of O_2 occurred primarily on step sites and that both photodissociation and photodesorption occur together. The experiments compared thermal dissociation of O_2 and photodissociation. In both cases the O_2 molecules were more rapidly depleted on the step sites than on the terrace sites.

ASSERT Student: Mr. R. Jason Scharff

B. NANOTUBE CHEMISTRY

Because of the great interest in nanotubes, our attention then turned to this topic. We were the first to employ infrared spectroscopy to observe the chemistry of the nanotubes under oxidizing conditions, observing the production of specific organic moieties by oxidation. The thermal stability of these groups was studied by infrared spectroscopy, and their conversion into CO and CO_2 was monitored. We pioneered the use of ozone as an oxidizing agent to probe the defect sites on the nanotube surface, finding that nanotubes which have been treated in HNO_3 to remove impurities are defective to about the 5% level. Removal of these defect sites opens the entry ports into the nanotube interior, causing the kinetics of adsorption of a test molecule, Xe, to be markedly enhanced.

ASSERT Student: Dr. Douglas B. Mawhinney