Final Report

Heterogeneous Reactions on Aluminum Oxide Surfaces Modeling Rocket Exhaust Particles

AFOSR Grant No. F49620-96-1-0029

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This research was performed by	y a gra	duate student, and post-do	ctoral res	earch fellow.	Our stuc	hes for the hydroxyla	ation and	
denydroxylation of a-Al2O3 (001) led to two publications. The adsorption of H2O on a-Al2O3 (001) was accepted and								
published in the Journal of Physical Chemistry. The desorption of H2O from a-Al2O3 (001) was accepted and published in								
Surface Science. The study of HC1 adsorption and desorption from a-A1103 (001) led to one publication in Surface Science.								
in audition, the study of RC1 and R2O ausorption on a A12O3 (001) and the displacement of A1-OH surface species by HC1 and displacement of A1-C1 surface species by HC0 lad to one additional manuscript that is still up der review. Since the								
conclusion of this research grant, we have continued to examine the surface chemistry of amornhous A12O3 surfaces. Oxide								
surface chemistry is still a largely unexplored area. Our surface reactivity studies have helped to define this new territory in								
surface science. These studies have also improved our understanding of heterogeneous reactions on aluminum oxide rocket								
exhaust particles in the atmosphere.								
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I. Program Objectives

During our support from the Air Force Office of Scientific Research, our research program has focused on heterogeneous reactions on Al₂O₃ surfaces that model the Al₂O₃ exhaust particles from solid-fueled rockets. Surface reaction kinetics and product formation were examined using laser induced thermal desorption (LITD) and temperature programmed desorption (TPD) studies on single-crystal Al₂O₃(0001) surfaces. The research concentrated on the initial definition of the Al₂O₃ surface coverage after rocket firing and the heterogeneous reactions on the Al₂O₃ surfaces that emerge from the wake. This research should help to determine the effect of Al₂O₃ rocket exhaust on atmospheric chemistry.

Our main tasks in this research were to:

- Measure reactive sticking coefficients on the dehydroxylated Al₂O₃ surfaces that exist shortly after rocket firing. These experiments concentrated on H₂O and HCl sticking on the dehydroxylated α -Al₂O₃ single-crystal surface.
- Determine the efficiency and extent of displacement of Al-OH surface species by HCl and Al-Cl surface species by H₂O on α -Al₂O₃ single-crystal surfaces.
- Measure the reaction kinetics of CF₂Cl₂, CF₂Br₂ and CCl₄ on the dehydroxylated α -Al₂O₃ single-crystal surfaces for comparison with earlier results.
- Examine the reaction kinetics of CF₂Cl₂, CF₂Br₂, CCl₄ and CH₃CCl₃ on the hydroxylated, chlorinated and mixed (Al-OH & Al-Cl) α-Al₂O₃ single-crystal surfaces.
- Measure the reaction kinetics of N₂O₅, ClONO₂ and HOCl with the chlorinated and mixed α -Al₂O₃ single-crystal surfaces.
- Determine the effect of heterogeneous reactions on Al₂O₃ surfaces on atmospheric chemistry. Assess the likelihood that Al₂O₃ exhaust particles could lead to stratospheric ozone depletion by activating chlorine in CFCs.

II. Program Achievements

During our funding for this program, we concentrated on the following topics:

- Preparation of a model single-crystal α -Al₂O₃(0001) surface for the proposed studies.
- Hydroxylation and dehydroxylation kinetics of the α -Al₂O₃(0001) singlecrystal surface.
- Adsorption and desorption kinetics of HCl on the dehydroxylated α -Al₂O₃ (0001) single-crystal surface.
- Temperature dependence of H₂O and HCl adsorption on the α -Al₂O₃(0001) single-crystal surface.
- Displacement of O-H surface species by HCl and displacement of Al-Cl surface species by H₂O.
- Growth of amorphous Al₂O₃ films by atomic layer deposition techniques
- Surface reactivity of amorphous Al₂O₃ films

This research was performed by a graduate student, Christine Nelson, and a post-doctoral research fellow, Jeff Elam. Christine Nelson graduated in December 1999 and recently started a new job at Intel Corporation in Hillsboro, Oregon. Jeff Elam is currently working on another research project in Steven George's Research Group.

Our studies for the hydroxylation and dehydroxylation of α -Al₂O₃ (0001) led to two publications. The adsorption of H₂O on α -Al₂O₃ (0001) was accepted and published in the *Journal of Physical Chemistry*. The desorption of H₂O from α -Al₂O₃ (0001) was accepted and published in *Surface Science*.

Our study of HCl adsorption and desorption from α -Al₂O₃ (0001) led to one publication in *Surface Science*. In addition, our study of HCl and H₂O adsorption on α -Al₂O₃ (0001) and the displacement of Al-OH surface species by HCl and displacement of Al-Cl surface species by H₂O led to one additional manuscript that is still under review.

Since the conclusion of this research grant, we have continued to examine the surface chemistry of amorphous Al₂O₃ surfaces. Oxide surface chemistry is still a largely unexplored area. Our surface reactivity studies have helped to define this new territory in surface science. These studies have also improved our understanding of heterogeneous reactions on aluminum oxide rocket exhaust particles in the atmosphere.

III. New Results from AFOSR Support

Our study of the hydroxylation of α -Al₂O₃ (0001) surfaces revealed that the initial sticking coefficient for H₂O on this α -Al₂O₃ surface is quite large with a magnitude of S₀~0.1 at 300 K. The H₂O sticking coefficient drops rapidly as a function of hydroxyl coverage and approaches S~10⁻¹⁰ at a hydroxyl coverage close to the saturation coverage of 0.5 x 10¹⁵ cm⁻². Additional experiments with H₂¹⁸O confirmed that the H₂O dissociated on the α -Al₂O₃ (0001) surface at 300 K. Equal quantities of H₂¹⁶O and H₂¹⁸O were observed in TPD experiments after exposing the α -Al₂¹⁶O₃ (0001) surface to H₂¹⁸O.

These adsorption results at 300 K predict that α -Al₂O₃ particles in the atmosphere will be hydroxylated with hydroxyl coverages of ~0.24 x10¹⁵ cm⁻² after emerging from the rocket plume. Additional exposure to H₂O in the stratospheric ambient will increase the hydroxyl coverage to ~0.30 x 10¹⁵ cm⁻² before the particle falls out from the stratosphere. Consequently, the hydroxyl coverage is expected to be close to one monolayer.

We also determined the thermal stability of hydroxyl groups on α -Al₂O₃(0001) surfaces. The removal of H₂O via recombinative desorption AlOH* + AlOH* --> Al-O-Al* + H₂O(g) occurs at temperatures between 300-500 K. Consequently, the hydroxyl coverage is negligible above 500 K. These results indicate that hydroxyl groups formed by the dissociative adsorption of H₂O at T<500K will be stable on Al₂O₃ particles at stratospheric temperatures of 185-210 K. These adsorption and desorption results indicate that reactions between fluorochlorocarbons and Al₂O₃ particles from rocket exhaust will occur on hydroxylated α -Al₂O₃ surfaces.

The broad range of desorption temperatures indicates that there are a variety of binding energy sites for O-H on α -Al₂O₃ (0001). H₂O desorption results versus coverage prepared by progressively annealing a fully reacted α -Al₂O₃(0001) surface confirmed a wide range of binding energies. The TPD experiments also indicated that there is very low mobility for the O-H species on α -Al₂O₃(0001). The TPD data showed that recombinatory H₂O desorption occurs from the original adsorption sites and that the initial H₂O adsorption randomly populates the various binding energy sites. Surprisingly, the O-H species do not appear to diffuse on the surface to find the lowest energy binding sites prior to thermal desorption.

Following the studies of the hydroxylation and dehydroxylation of α -Al₂O₃(0001), we studied the adsorption and desorption of HCl on α -Al₂O₃(0001). HCl is an important gas in the wake of solid rocket motors. HCl dissociative adsorption on Al₂O₃ particles may alter their reactivity with chlorofluorocarbons and affect the stratospheric ozone layer. We measured the HCl sticking coefficient on α -Al₂O₃(0001) and observed an initial sticking coefficient of S₀ ~10⁻³ at 300K. The HCl sticking coefficient decreased nearly exponentially versus the chlorine coverage. The HCl coverage saturated at an HCl coverage of 0.10 x 10¹⁵ cm⁻² after HCl exposures of 10¹⁰ Langmuir. These HCl adsorption results indicate that α -Al₂O₃ rocket exhaust particles will be partially covered with O-H and Al-Cl surface species in the stratosphere.

HCl recombinative desorption also occurred over a wide temperature range from 300K to 650K. This broad temperature range indicates that there are a variety of binding energy sites for O-H and Al-Cl on α -Al₂O₃ (0001). HCl desorption results versus coverage prepared by progressively annealing a fully reacted α -Al₂O₃(0001) surface confirmed a wide range of binding energies. The TPD experiments also indicated that there is very low mobility for the O-H and Al-Cl species on α -Al₂O₃(0001). The TPD data showed that recombinatory HCl desorption occurs from the original adsorption sites and that the initial HCl adsorption randomly populates the various binding energy sites. Like the previous results following H₂O adsorption, the O-H and Al-Cl species do not appear to diffuse on the surface to find the lowest energy binding sites prior to thermal desorption. The HCl desorption results predict that O-H and Al-Cl surface species will be stable on Al₂O₃ rocket exhaust particles at stratospheric temperature and pressures.

The adsorption measurements for H₂O and HCl were performed initially on α -Al₂O₃(0001) at 298K. The stratosphere has much colder temperatures of 180-220K. To determine the effect of temperature on the sticking coefficients, the uptake of H₂O and HCl was measured on α -Al₂O₃(0001) at 210K. These measurements revealed that the lower temperature affected both the initial sticking coefficient on the clean α -Al₂O₃(0001) surface and the sticking coefficient at higher O-H and Al-Cl surface coverages.

For H₂O, the initial sticking coefficient on α -Al₂O₃(0001) was S₀~10⁻¹ at both 298K and 210K. However, the H₂O sticking coefficient did not decrease nearly as dramatically with surface coverage at 210K. At a coverage of 1 x10¹⁴ H₂O/cm², the sticking coefficient was S~1x10⁻⁷ at 298K. At this same coverage at 210K, the sticking coefficient was S~1x10⁻³. The temperature effects were even more dramatic for HCl adsorption. The initial sticking coefficient for HCl was S₀~1x10⁻³ at 298K and increased to S₀~1x10⁻¹ at 210K. The effect of O-H and Al-Cl surface coverage on the HCl sticking coefficient also was much less at

210K. These temperature effects reveal that the Al₂O₃ rocket exhaust particles will be easily hydroxylated and chlorinated at stratospheric temperatures.

H₂O and HCl will be present simultaneously in the rocket exhaust wake and in the stratosphere. Consequently, O-H species on the Al₂O₃ surface could be displaced by HCl and Al-Cl species on the Al₂O₃ surface could be displaced by H₂O. These displacement reactions were confirmed by exposing a Al-Cl coverage on the α -Al₂O₃(0001) surface to H₂O. A H₂O exposure of 10⁸L could replace ~1/2 of the Al-Cl surface species with O-H. Likewise, a O-H coverage on the α -Al₂O₃(0001) surface was exposed to a 10⁹ L HCl exposure. This HCl exposure replaced ~1/3 of the O-H surface species with Al-Cl. These experiments reveal that the surface coverage on Al₂O₃ particles may change and evolve with time depending on gas exposure.

Additional experiments explored new methods of depositing amorphous Al₂O₃ films. These amorphous Al₂O₃ films are representative of another class of Al₂O₃ rocket exhaust particles. The deposition of amorphous Al₂O₃ films was examined on tungsten and molybdenum surfaces using atomic layer deposition techniques. This method utilizes sequential exposures of Al(CH₃)₃ and H₂O to achieve the atomic layer control of Al₂O₃ film growth. Auger electron spectroscopy experiments revealed the layer-by-layer growth of continuous Al₂O₃ films. These amorphous Al₂O₃ films should be useful in future studies of Al₂O₃ surface chemistry.

IV. Personnel Supported

Faculty

1. Prof. Steven M. George

2. Prof. Margaret A. Tolbert

Postdoctoral Research Associates

1. Dr. Jeff Elam

Graduate Students

1. Christine Nelson

V. Publications

J.W. Elam, C.E. Nelson, M.A. Cameron, M.A. Tolbert and S.M. George, "Adsorption of H₂O on Single-Crystal α-Al₂O₃(0001) Surfaces", *J. Phys. Chem.* **B102**, 7008-7015 (1998).

C.E. Nelson, J.W. Elam, M.A. Cameron, M.A. Tolbert and S.M. George, "Desorption of H₂O from a Hydroxylated Single-Crystal α -Al₂O₃(0001) Surface", *Surf. Sci.* **416**, 341-353 (1998).

J.W. Elam, C.E. Nelson, M.A. Tolbert and S.M. George, "Adsorption and Desorption of HCl on a Single-Crystal α -Al₂O₃(0001) Surface", *Surface Science* (in press).

C.E. Nelson, J.W. Elam, M.A. Tolbert and S.M. George, "Effect of Temperature on H₂O and HCl Adsorption on Single-Crystal α -Al₂O₃(0001)", submitted to *Appl. Surf. Sci.*

VI. Interactions/ Transitions

The results from this research have been presented at various meetings and workshops around the country. A listing of these presentations is given below:

- "Dehydroxylation and Rehydroxylation of α-Al₂O₃ Surfaces", <u>S.M. George</u>, M.A. Cameron, C.E. Nelson, M.A. Tolbert and S.M. George, National Symposium of the American Vacuum Society, Philadelphia, Pennsylvania, October 17, 1996.
- "Adsorption and Desorption of H₂O on α-Al₂O₃(0001) Surfaces Modeling Rocket Exhaust Particles", <u>C.E. Nelson</u>, J.W. Elam, M.A. Tolbert and S.M. George, Rocky Mountain American Vacuum Society Meeting, Denver, Colorado, August 21, 1997.
- 3. "Adsorption and Desorption of HCl on α-Al₂O₃(0001) Surfaces Modeling Rocket Exhaust Particles", <u>J.W. Elam</u>, C.E. Nelson, M.A. Tolbert and S.M. George, Rocky Mountain American Vacuum Society Meeting, Denver, Colorado, August 21, 1997.
- 4. "Adsorption and Desorption of H₂O from α-Al₂O₃(0001)", <u>S.M. George</u> (INVITED), Symposium on Heterogeneous and Homogeneous Processes in Atmospheric Chemistry, National American Chemical Society Meeting, Las Vegas, Nevada, September 8, 1997.
- "Adsorption and Desorption of H₂O on α-Al₂O₃(0001) Surfaces Modeling Rocket Exhaust Particles", <u>J.W. Elam</u>, C.E. Nelson, M.A. Tolbert and S.M. George, 44th Annual National Symposium of the American Vacuum Society, San Jose, California, October 20, 1997.
- "Adsorption and Desorption of H₂O from α-Al₂O₃(0001)", <u>S.M. George</u>, Air Force Workshop on Atmospheric Effects of Rocket Exhaust, Beckman Center, Univ. of California, Irvine, California, January 9, 1998.

- "Adsorption and Desorption of HCl from α-Al₂O₃(0001)", <u>J.W. Elam</u>, Air Force Workshop on Atmospheric Effects of Rocket Exhaust, Beckman Center, Univ. of California, Irvine, California, January 9, 1998.
- H₂O Adsorption and Desorption Kinetics on α-Al₂O₃(0001)", <u>S.M. George</u>, Air Force Office of Scientific Research, Molecular Dynamics Review, Naval Postgraduate School, Monterey, California, May 18, 1998.
- "HCl Adsorption and Desorption on a Single-Crystal α-Al₂O₃(0001) Surface, <u>C.E. Nelson</u>, J.W. Elam, M.A. Tolbert and S.M. George, Session on Oxide Surface Chemistry, 45th International Symposium of the American Vacuum Society, Baltimore, Maryland, November 5, 1998.

An invited talk on "Adsorption and Desorption Kinetics of H₂O on α -Al₂O₃ (0001)" was presented at the symposium on *Heterogeneous and Homogeneous Processes in Atmospheric Chemistry* at the National American Chemical Society Meeting in Las Vegas, Nevada on September 8, 1997. This presentation stimulated discussion and attracted the interests of several theoretical groups that are now modeling H₂O dissociative adsorption on α -Al₂O₃ (0001).

We have corresponded with several theorists who are modeling H₂O adsorption and desorption from α -Al₂O₃(0001). One theorist is Dr. Eugene Stefanovich and his theoretical group in the Dept. of Chemistry at the Univ. of Utah. They are modeling H₂O adsorption on α -Al₂O₃(0001). Another theorist who is modeling H₂O adsorption on α -Al₂O₃(0001) is Prof. William Hase in the Dept. of Chemistry at Wayne State University.

VII. Inventions or Patent Disclosures

NONE

VIII. Honors/Awards

Prof. Steven M. George was elected a fellow in the American Physical Society (Fall 1997). He also has received the Presidential Young Investigator Award (1988-1993), the Alfred P. Sloan Foundation Award (1988), an IBM Faculty Development Award (1988), a Dreyfus Award for Newly Appointed Faculty in Chemistry (1985) and an AT&T New Faculty Award (1985).

Prof. Margaret A. Tolbert received the National Science Foundation Young Investigator Award (1992-1996), the AAAS Newcomb Cleveland Award (1987), the James B. Maccelwane Medal (1993) and the Camille Dreyfus Teacher-Scholar Award (1994). She is also a fellow of the American Geophysical Union (1993).