Final Report

Heterogeneous Reactions on Aluminum Oxide Surfaces Modeling Rocket Exhaust Particles

AFOSR Grant No. F49620-96-1-0029

Prof. Steven M. George, PI
Prof. Margaret A. Tolbert, co-PI

Dept. of Chemistry and Biochemistry
Univ. of Colorado
Boulder, CO 80309
This research was performed by a graduate student, and post-doctoral research fellow. Our studies for the hydroxylation and dehydroxylation 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-Al1O3 (001) led to one publication in Surface Science. In addition, the study of HC1 and H2O adsorption on a_AL2O3 (001) and the displacement of Al-OH surface species by HC1 and displacement of Al-CI 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.
I. Program Objectives

During our support from the Air Force Office of Scientific Research, our research program has focused on heterogeneous reactions on Al$_2$O$_3$ surfaces that model the Al$_2$O$_3$ 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 Al$_2$O$_3$(0001) surfaces. The research concentrated on the initial definition of the Al$_2$O$_3$ surface coverage after rocket firing and the heterogeneous reactions on the Al$_2$O$_3$ surfaces that emerge from the wake. This research should help to determine the effect of Al$_2$O$_3$ rocket exhaust on atmospheric chemistry.

Our main tasks in this research were to:

- Measure reactive sticking coefficients on the dehydroxylated Al$_2$O$_3$ surfaces that exist shortly after rocket firing. These experiments concentrated on H$_2$O and HCl sticking on the dehydroxylated $\alpha$-Al$_2$O$_3$ single-crystal surface.

- Determine the efficiency and extent of displacement of Al-OH surface species by HCl and Al-Cl surface species by H$_2$O on $\alpha$-Al$_2$O$_3$ single-crystal surfaces.

- Measure the reaction kinetics of CF$_2$Cl$_2$, CF$_2$Br$_2$ and CCl$_4$ on the dehydroxylated $\alpha$-Al$_2$O$_3$ single-crystal surfaces for comparison with earlier results.

- Examine the reaction kinetics of CF$_2$Cl$_2$, CF$_2$Br$_2$, CCl$_4$ and CH$_3$CCl$_3$ on the hydroxylated, chlorinated and mixed (Al-OH & Al-Cl) $\alpha$-Al$_2$O$_3$ single-crystal surfaces.

- Measure the reaction kinetics of N$_2$O$_5$, ClONO$_2$ and HOCl with the chlorinated and mixed $\alpha$-Al$_2$O$_3$ single-crystal surfaces.

- Determine the effect of heterogeneous reactions on Al$_2$O$_3$ surfaces on atmospheric chemistry. Assess the likelihood that Al$_2$O$_3$ 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 $\alpha$-Al$_2$O$_3$(0001) surface for the proposed studies.
- Hydroxylation and dehydroxylation kinetics of the $\alpha$-Al$_2$O$_3$(0001) single-crystal surface.
- Adsorption and desorption kinetics of HCl on the dehydroxylated $\alpha$-Al$_2$O$_3$ (0001) single-crystal surface.
- Temperature dependence of H$_2$O and HCl adsorption on the $\alpha$-Al$_2$O$_3$(0001) single-crystal surface.
- Displacement of O-H surface species by HCl and displacement of Al-Cl surface species by H$_2$O.
- Growth of amorphous Al$_2$O$_3$ films by atomic layer deposition techniques
- Surface reactivity of amorphous Al$_2$O$_3$ 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 $\alpha$-Al$_2$O$_3$ (0001) led to two publications. The adsorption of H$_2$O on $\alpha$-Al$_2$O$_3$ (0001) was accepted and published in the Journal of Physical Chemistry. The desorption of H$_2$O from $\alpha$-Al$_2$O$_3$ (0001) was accepted and published in Surface Science.

Our study of HCl adsorption and desorption from $\alpha$-Al$_2$O$_3$ (0001) led to one publication in Surface Science. In addition, our study of HCl and H$_2$O adsorption on $\alpha$-Al$_2$O$_3$ (0001) and the displacement of Al-OH surface species by HCl and displacement of Al-Cl surface species by H$_2$O 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 Al$_2$O$_3$ 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 $\alpha$-Al$_2$O$_3$ (0001) surfaces revealed that the initial sticking coefficient for H$_2$O on this $\alpha$-Al$_2$O$_3$ surface is quite large with a magnitude of $S_0 \sim 0.1$ at 300 K. The H$_2$O sticking coefficient drops rapidly as a function of hydroxyl coverage and approaches $S \sim 10^{-10}$ at a hydroxyl coverage close to the saturation coverage of $0.5 \times 10^{15}$ cm$^{-2}$. Additional experiments with H$_2$O confirmed that the H$_2$O dissociated on the $\alpha$-Al$_2$O$_3$ (0001) surface at 300 K. Equal quantities of H$_2^{16}$O and H$_2^{18}$O were observed in TPD experiments after exposing the $\alpha$-Al$_2$O$_3$ (0001) surface to H$_2^{18}$O.

These adsorption results at 300 K predict that $\alpha$-Al$_2$O$_3$ particles in the atmosphere will be hydroxylated with hydroxyl coverages of $\sim 0.24 \times 10^{15}$ cm$^{-2}$ after emerging from the rocket plume. Additional exposure to H$_2$O in the stratospheric ambient will increase the hydroxyl coverage to $\sim 0.30 \times 10^{15}$ 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 $\alpha$-Al$_2$O$_3$(0001) surfaces. The removal of H$_2$O via recombinative desorption $\text{AlOH}^* + \text{AlOH}^* \rightarrow \text{Al-O-Al}^* + \text{H}_2\text{O}(g)$ 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 H$_2$O at $T < 500$ K will be stable on Al$_2$O$_3$ particles at stratospheric temperatures of 185-210 K. These adsorption and desorption results indicate that reactions between fluorochlorocarbons and Al$_2$O$_3$ particles from rocket exhaust will occur on hydroxylated $\alpha$-Al$_2$O$_3$ surfaces.

The broad range of desorption temperatures indicates that there are a variety of binding energy sites for O-H on $\alpha$-Al$_2$O$_3$ (0001). H$_2$O desorption results versus coverage prepared by progressively annealing a fully reacted $\alpha$-Al$_2$O$_3$(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 $\alpha$-Al$_2$O$_3$(0001). The TPD data showed that recombinatory H$_2$O desorption occurs from the original adsorption sites and that the initial H$_2$O 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 $\alpha$-Al$_2$O$_3$(0001), we studied the adsorption and desorption of HCl on $\alpha$-Al$_2$O$_3$(0001). HCl is an important gas in the wake of solid rocket motors. HCl dissociative adsorption on Al$_2$O$_3$ particles may alter their reactivity with chlorofluorocarbons and affect the stratospheric ozone layer. We measured the HCl sticking coefficient on $\alpha$-Al$_2$O$_3$(0001) and observed an initial sticking coefficient of $S_0 \sim 10^{-3}$ at 300K. The HCl sticking coefficient decreased nearly exponentially versus the chlorine coverage. The HCl coverage saturated at an HCl coverage of $0.10 \times 10^{15}$ cm$^{-2}$ after HCl exposures of $10^{10}$ Langmuir. These HCl adsorption results indicate that $\alpha$-Al$_2$O$_3$ 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 $\alpha$-Al$_2$O$_3$ (0001). HCl desorption results versus coverage prepared by progressively annealing a fully reacted $\alpha$-Al$_2$O$_3$(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 $\alpha$-Al$_2$O$_3$(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 H$_2$O 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 Al$_2$O$_3$ rocket exhaust particles at stratospheric temperature and pressures.

The adsorption measurements for H$_2$O and HCl were performed initially on $\alpha$-Al$_2$O$_3$(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 H$_2$O and HCl was measured on $\alpha$-Al$_2$O$_3$(0001) at 210K. These measurements revealed that the lower temperature affected both the initial sticking coefficient on the clean $\alpha$-Al$_2$O$_3$(0001) surface and the sticking coefficient at higher O-H and Al-Cl surface coverages.

For H$_2$O, the initial sticking coefficient on $\alpha$-Al$_2$O$_3$(0001) was $S_0 \sim 10^{-1}$ at both 298K and 210K. However, the H$_2$O sticking coefficient did not decrease nearly as dramatically with surface coverage at 210K. At a coverage of $1 \times 10^{14}$ H$_2$O/cm$^2$, the sticking coefficient was $S \sim 1 \times 10^{-7}$ at 298K. At this same coverage at 210K, the sticking coefficient was $S \sim 1 \times 10^{-3}$. The temperature effects were even more dramatic for HCl adsorption. The initial sticking coefficient for HCl was $S_0 \sim 1 \times 10^{-3}$ at 298K and increased to $S_0 \sim 1 \times 10^{-1}$ 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


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:


An invited talk on "Adsorption and Desorption Kinetics of H$_2$O on $\alpha$-Al$_2$O$_3$ (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 H$_2$O dissociative adsorption on $\alpha$-Al$_2$O$_3$ (0001).

We have corresponded with several theorists who are modeling H$_2$O adsorption and desorption from $\alpha$-Al$_2$O$_3$(0001). One theorist is Dr. Eugene Stefanovich and his theoretical group in the Dept. of Chemistry at the Univ. of Utah. They are modeling H$_2$O adsorption on $\alpha$-Al$_2$O$_3$ (0001). Another theorist who is modeling H$_2$O adsorption on $\alpha$-Al$_2$O$_3$(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. Macelwane Medal (1993) and the Camille Dreyfus Teacher-Scholar Award (1994). She is also a fellow of the American Geophysical Union (1993).