Radiolysis of Water with Aluminum Oxide Surfaces

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Abstract

Aluminum oxide, Al_2O_3 , nanoparticles with water were irradiated with γ -rays and 5 MeV He ions followed by the determination of the production of molecular hydrogen, H_2 , and characterization of changes in the particle surface. Surface analysis techniques included: diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), nitrogen absorption with the Brunauer – Emmett – Teller (BET) methodology for surface area determination, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). Production of H_2 by γ -ray radiolysis was determined for samples with adsorbed water and for Al_2O_3 – water slurries. For Al_2O_3 samples with adsorbed water, the radiation chemical yield of H_2 was measured as 80 ± 20 molecules/100 eV ($1 \text{ molecule}/100 \text{ eV} = 1.04 \times 10^{-7} \text{ mol/J}$). The yield of H_2 was observed to decrease as the amount of water present in the Al_2O_3 – water slurries increased. Surface studies indicated that the α -phase Al_2O_3 samples changed phase following irradiation by He ions, and that the oxyhydroxide layer, present on the pristine sample, is removed by γ -ray and He ion irradiation.

1. Introduction

Aluminum oxide, Al_2O_3 , has a number of useful properties including a high band gap energy, high electrical resistivity, good thermal insulation, and chemical inertness. (Kumar et al., 1994) There are also a large number of OH groups on the surface that influence the binding of additional materials (Konstadinidis et al., 1992) leading to applications in catalysis (Al-Abadleh and Grassian, 2002) and photochemistry. (Thomas, 2005) Studies have focused on methods of producing nanometer sized Al_2O_3 particles (Kim et al., 1994; Kumar et al., 1994) and uniform anodic aluminum oxidation membranes. (Xiong et al., 2005) The interaction between Al_2O_3 with other materials such as poly(methyl methacrylate), PMMA, has been previously examined for industrial applications, such as protective coatings. (Konstadinidis et al., 1992) Studies have shown that Al_2O_3 is useful in transistor applications because of the resistance to radiation induced changes. (Kaya and Yilmaz, 2014; Zaininger and Waxman, 1969) Radiolysis experiments have focused on examination of amorphous Al_2O_3 , $\gamma\text{-Al}_2\text{O}_3$, with electrons (Milosavljevic and Thomas, 2003; Nakamura et al., 2013) and γ -rays (Acres et al., 1965; Seino et al., 2001), and $\alpha\text{-Al}_2\text{O}_3$ with γ -rays. (Yamamoto et al., 1999) However, a systematic study and characterization of the Al_2O_3 powders before and after irradiation with γ -rays and He ions is desired to fully understand the radiation induced modifications occurring at the surfaces.

This work probed the radiolysis of water in association with the surface of Al_2O_3 nanoparticles to determine how each component affected radiolytic changes in the other. Adsorbed water and water – oxide slurries were examined in order to obtain the relative dependence of radiolytic yields on the amount of each compound. Molecular hydrogen, H_2 , was used as a probe of the relative sensitivity of the water with a nearby surface. The Al_2O_3 surfaces were characterized before and after radiolysis using diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), nitrogen adsorption using the Brunauer – Emmett – Teller

(BET) methodology for surface area determination, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). Irradiations were performed with γ -rays and accelerated He ions to mimic the radiation typically associated with nuclear waste materials.

2. Experimental Procedure

2.1 Characterization of Oxide Surface

Alpha phase Al_2O_3 powder samples were obtained from Alfa Aesar in the highest purity possible, 99.9%, and were used as received except for baking at 250°C. Surface area and porosity of the powder was determined using a Quantachrome Autosorb 1 and the Brunauer – Emmett – Teller (BET) methodology. Prior to the surface area measurements, the powders were baked at 250°C to remove any contaminants from the surfaces. The specific surface area was measured as $7.4 \pm 0.1 \text{ m}^2/\text{g}$. By assuming that the particles were perfect spheres this value corresponds to a particle diameter of around 200 nm. Nitrogen adsorption and desorption measurements indicated a smooth surface with no major porosity.

The arrangement of adsorbed water on the Al_2O_3 samples was measured using two complimentary techniques: temperature programmed desorption (TPD) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFT). The samples were prepared by first baking samples of Al_2O_3 at 500°C and then depositing them in a 53% relative humidity chamber for water adsorption, which took about a week as determined by observing weight change. TPD measurements were made using a custom cell heated from room temperature to 500°C at a rate of 2°C/minute. During this heating the desorbing gases were monitored using a Pfeiffer Prisma quadrupole mass spectrometer. DRIFT measurements were taken in a Bruker Vortex 70 instrument with Harrick Praying Mantis high temperature cell. *In situ* temperature studies were performed at room temperature, 100°C, 200°C, 300°C, and 400°C.

A Jasco Micro-Raman Spectrometer MRS-5100 was used for Raman spectroscopy measurements of the Al_2O_3 surface. Spectra were normalized by the height of the most intense peak. Another surface sensitive technique, X-ray photoelectron spectroscopy (XPS) was employed to determine the oxidation state of the surface. These measurements were performed in a PHI VersaProbe II, equipped with a monochromatic Al-K α X-ray source. Bulk crystal structure X-ray diffraction measurements (XRD) were done using a Bruker D8 Advance Davinci Powder X-ray diffractometer using Cu- K α X-rays. The samples for the Raman, XPS, and XRD measurements were deposited on a SEM stub using a carbon tab from Ted Pella. Additional information, including measurement parameters are discussed in Reiff and LaVerne. (Reiff and LaVerne, 2015)

2.2 Gamma Ray Irradiation and H_2 Production

Irradiations with γ -rays were done in a self-contained Shepard ^{60}Co source at the University of Notre Dame Radiation Laboratory. The dose rate was nominally about 179 Gy/min as determined using the Fricke dosimeter. Two types of samples were used for measurements of the amount of H_2 produced. Samples with adsorbed water layers were prepared in a 53% relative humidity chamber, using the same process described previously for the TPD analysis. These samples were connected to a SRI 6810 gas chromatograph, GC, in an inline mode. The sample was contained in a modified cuvette that had an entrance and exit port and connected to the GC with a four-way valve. The second type of samples analyzed for the production of H_2 were slurries of Al_2O_3 with varying amounts, 5, 10, 20, 40, 60, 80, and 90%, of water. The slurries were prepared in Pyrex tubes measuring 10 cm long by 10 mm in diameter. They were flame sealed under vacuum following freezing, pumping with vacuum, and thawing three times to evacuate the cells. (Reiff and LaVerne, 2015) The cells were rotated during the irradiation at a

speed of 10 RPM in order to maintain homogeneously mixed samples. Following irradiation, the sample cells were inserted into Tygon tubing, connected to the GC, flushed with the carrier gas, and cracked open to allow for the measurement of the gases produced during irradiation. The SRI 8610 GC has a thermal conductivity detector (TCD) and was used with a carrier gas of ultra-high-purity (99.9999%) argon. In this configuration, the system had a sensitivity limit of 1 μL of H_2 and the error in gas measurement is estimated to be within 10%. Radiation chemical yields, G values, are given in the traditional units of molecules/100 eV ($1 \text{ molecule}/100 \text{ eV} = 1.04 \text{ mol/J}$).

2.3 He ion irradiations

Ion irradiations were performed using accelerated 5 MeV ^4He ions obtained using the facilities of the Nuclear Science Laboratory at the University of Notre Dame. The beam diameter was approximately 6.4 mm, with a beam current of 1.5 nA charge. Energy loss to the machine exit window was determined using standard range tables and fully stripped ions were used for irradiations. (Ziegler et al., 1985) Samples for He ion irradiation were prepared by pressing Al_2O_3 powders into a carbon tab attached to an SEM stub and were irradiated to 1×10^{15} ions/ cm^2 . The SEM stub and exit window were tied together electrically and current from them was integrated to give the fluence. The gap between the exit window and sample stub was purged with N_2 to minimize ozone production.

3. Results and discussion

3.1 Characterization of Al_2O_3 Surfaces and Adsorbed Water Layers

Analysis of the water present on the oxide surface was done using the TPD and DRIFT methods. Gas desorption during the TPD measurement for other species was orders of magnitude lower than the response for the desorption of water. The curve for water, shown in Figure 1, shows three peaks for water desorption, occurring at temperatures of 110 $^\circ\text{C}$, 164 $^\circ\text{C}$, and 265

°C. These peaks correspond to desorption energies of 1.2, 1.4, and 1.7 eV, calculated using Redhead's method. (Redhead, 1962) Energies this high suggest that chemisorbed water is desorbing from the surface, since the energies are higher than the desorption energy for physisorbed water, 0.35 eV. (Dyar et al., 2010) The DRIFT measurements, shown in Figure 2, give a better indication of the physisorbed water present on the samples. In the room temperature measurements, a broad peak at 3400 cm^{-1} was visible corresponding to the OH stretch peak of hydrogen bonded water on the surface. (Al-Abadleh and Grassian, 2002; Hudgins et al., 1993; Lavalley et al., 1988) A smaller, sharper peak was also visible at 3700 cm^{-1} which is attributed to a free surface OH group bonding at a specific site. (Lavalley et al., 1988) A peak at 1640 cm^{-1} attributed to the OH bending vibration is also visible. (Al-Abadleh and Grassian, 2002) The region below 1500 cm^{-1} contains information on the bonds present in the bulk oxide. The peak around 1100 cm^{-1} corresponds to the Al-O-Al arrangement. (Lavalley et al., 1988) As the sample is heated to 400°C the broad water peak at 3400 cm^{-1} and the bending peak at 1640 cm^{-1} are observed to decrease, suggesting that the hydrogen bonded water is desorbing from the sample. This observation is consistent with a previous study on alumina by LaValley et al. (Lavalley et al., 1988) The peak for chemisorbed water around 3700 cm^{-1} becomes more pronounced suggesting that while the physisorbed water desorbs from the sample by 400°C some chemisorbed water remains.

3.2 Hydrogen Production with γ -ray Radiolysis

Following water loading in the 53% relative humidity chamber, samples of Al_2O_3 were irradiated with γ -rays and the production of H_2 was measured. The amount of water amounted to 0.1 % of the total mass and about 0.7 mL of water on the surface. The radiation chemical yield for H_2 was measured at 80 ± 20 molecules/ 100 eV. This value was calculated with respect to the

energy deposited in the water layer only and it is much greater than the known yield for bulk water, 0.45 molecules / 100 eV. Other oxides including Fe₂O₃ (Reiff and LaVerne, 2015), CeO₂ (LaVerne and Tandon, 2002), ZrO₂ (LaVerne, 2005; LaVerne and Tandon, 2002), and UO₂ (LaVerne and Tandon, 2003) had yields of 150, 20, 150 , and 40 molecules / 100 eV, respectively, which are comparable to the value observed here for Al₂O₃. Energy deposited by γ -rays is proportional to the electron density of each component so the vast majority of the energy is being deposited in the Al₂O₃ component. As with the other oxides examined, the excess H₂ observed is due to energy migration from the oxide to the water. Previous studies on a different phase of Al₂O₃, γ - Al₂O₃, measured the production of H₂ by pulse radiolysis with 0.4 MeV electrons. (Milosavljevic and Thomas, 2003; Thomas, 2005) They suggested that the production of H₂ occurs due to the ionic nature of the Al₂O₃ surface through the interaction of a hole, h^+ , created in the ionization event, with a surface OH group:

A similar mechanism can be predicted to occur in this work, but no other evidence has been obtained to verify this mechanism.

In order to determine how the structure of water around the Al₂O₃ effects the H₂ production, slurries with varying amounts of water were prepared ranging from 5% to 90% water by mass. The yield of H₂ was measured for each slurry and as shown in Figure 3 the yield of H₂ was observed to decrease as the percentage of water increased from 10% to 60%. There is a considerable drop in the H₂ yield of 80 molecules/ 100 eV for absorbed water to that found for a 10% water slurry. This result agrees with earlier work showing that most of the H₂ is produced at

or near the surface. (Roth et al., 2012) From about 40% to 90% of water the yield of H_2 leveled off at around 0.8 molecules / 100 eV, which is higher than the yield for pure water, 0.45 molecules / 100 eV. The near constant and relatively high yield of H_2 over such a large range of water fraction is unexpected from a simple energy transfer mechanism, but it has been observed with copper oxides (Reiff and La Verne, 2015). There may be other water radiolysis chemistry by the transient radicals or H_2O_2 occurring at the oxide interface. The increased yield of H_2 in the presence of the Al_2O_3 is not consistent with previous work by Yamamoto et al. who found that the amount of H_2 produced with α - Al_2O_3 was almost eight times as much as produced from a sample of pure water. (Yamamoto et al., 1999) In the Yamamoto study, samples of 0.25 g of Al_2O_3 were mixed with 75 mL of water, producing samples that were greater than 99% water. No explanation can be given for the discrepancy. All other studies suggest that any observed increase in the yield of H_2 occurs with a small amount of water because of the surface effect. The production of H_2 production in very dilute slurries should be similar to that for pure water.

3.3 Chemical Changes to the Al_2O_3 Surface

Samples of Al_2O_3 were analyzed prior to γ -ray and He ion irradiation using Raman, XRD and XPS techniques. Changes in the bulk crystalline structure of the powders would be detected by XRD. Comparison of the XRD patterns (not shown) for the pristine and irradiated Al_2O_3 powders to samples in the international center for diffraction data (ICDD) particle diffraction file (PDF) confirmed that the samples were α -phase Al_2O_3 . (2010) Diffraction patterns taken of samples following irradiation exhibited no changes to the patterns, which indicates that the bulk of the Al_2O_3 powder is largely unaffected by γ -ray and He ion irradiation up to the fluences used in this work.

Raman spectroscopy measurements were made on irradiated Al_2O_3 samples to analyze the chemical changes at the surface and the spectra are shown in Figure 4. The pristine sample had peaks at 381, 419, 578, 646, and 749 cm^{-1} , which agree with previously reported peaks for α - Al_2O_3 . (Misra et al., 2001; Porto and Krishnan, 1967) A few peaks assigned in the literature were not observed, but additional peaks were found at 182, 220, 846, 1064, 1122, 1349, 1450, 1595, and 1727 cm^{-1} . The 1349 and 1595 cm^{-1} peaks can be attributed to the carbon tab sample holder. (Huong, 1991; Kraft et al., 1998) Following irradiation with γ -rays, only peaks at 172, 211, 381, 419, 580, and 642 were observed, suggesting that there is still α -phase Al_2O_3 present on the surface. However, after irradiation with He ions, no peaks were visible in the spectrum. This observation is consistent with previously reported spectra of amorphous Al_2O_3 that showed a flat Raman spectra using a 244 nm laser, (Xiong et al., 2005) or of γ and δ -phase Al_2O_3 , which also have a flat Raman spectra. (Roy and Sood, 1995) Irradiation with He ions causes the samples to become more disordered as the α - Al_2O_3 changes phase or becomes amorphous. This phase conversion is not observed with XRD because He ions only penetrate about $20\text{ }\mu\text{m}$ into the surface leaving the bulk properties unchanged.

XPS measurements were used to analyze any changes to the electronic state of surface atoms following irradiation. A survey scan from $1400 - 0\text{ eV}$ revealed no contamination other than inevitable carbon, which was used to charge correct the scans by setting the C-C peak to 285.0 eV . Spectra of the Al 2p core electron are shown in Figure 5. The pristine Al_2O_3 sample has a wide peak centered around 75 eV , which is consistent with previous experiments by Kim et al (Kim et al., 1994) on single crystal α - Al_2O_3 . Upon further analysis, this main peak can be formed by two contributions, one at 74.4 eV , corresponding to Al^{3+} bound to O in the Al_2O_3 oxide (Kumar et al., 1994) and one at 75.5 eV which is suggested to be from an O-Al-OH

oxyhydroxide layer, which could be present on the surface due to thermal oxidation. (Konstadinidis et al., 1992) Both γ -ray and He ion radiolysis show that the contribution from the oxyhydroxide layer decreased compared to the oxide contribution. This decrease suggests that the OH groups on the surface are disrupted, perhaps contributing to the formation of H_2 . Following He ion irradiation, the oxyhydroxide contribution disappeared; however, a lower binding energy shoulder developed at 72.8 eV. This peak corresponds to previously reported values of Al metal at 72.7 eV (Konstadinidis et al., 1992; Kumar et al., 1994), which suggests that the He ions completely removed the oxyhydroxide layer and even started reducing the exposed Al_2O_3 to Al metal. The large energy deposition by the He ions is disrupting the Al-O bonds and completely destroying the stoichiometry. Further studies using electron paramagnetic resonance techniques may identify the resulting oxygen species.

XPS O 1s spectra are shown in Figure 6 for Al_2O_3 samples and were analyzed for any changes in the peak structure. The pristine sample has two contributions to the O 1s signal, a peak at 531.7 eV and one at 533.4 eV. These peaks can be assigned to oxygen present in the Al_2O_3 oxide and to oxygen in the attached OH groups, respectively (Konstadinidis et al., 1992; Kumar et al., 1994). In the samples exposed to γ -rays and He ions, the higher binding energy peak, corresponding to the OH groups, is observed to decrease relative to the main oxide peak. This decrease is consistent with the results observed in the Al 2p spectra and is due to the decrease in the surface oxyhydroxide layer. The O 1s spectrum for the He ion irradiated sample appears to have shifted towards lower binding energy due to the formation of a new peak at 530.6 eV. Further work is needed to identify this peak. The atomic concentrations were also calculated for each of the Al_2O_3 samples and are found to be about 68% O and 32% Al. Errors in XPS atomic concentration are estimated to be $\pm 5\%$ so the results suggest that there is no

significant change to the atomic concentration following irradiation with either γ -rays or with He ions. This result suggests that the loss of OH groups is accompanied by a relocalization of the O atom within the solid matrix.

4. Conclusions

Water decomposition to give H_2 and changes in Al_2O_3 oxide nanoparticle surfaces were observed following radiolysis with γ -rays and with 5 MeV He ions. Adsorbed water was characterized using TPD and DRIFT to show that physisorbed and chemisorbed water is present at room temperature; however, as the samples were heated the physisorbed water desorbed from the sample revealing the chemisorbed water. The physisorbed water is predicted to be crucial for the production of H_2 in radiolysis (Reiff and LaVerne, 2015) and its radiation chemical yield in γ -ray radiolysis was measured at 80 ± 20 molecules/100 eV for Al_2O_3 samples with adsorbed water. Slurries of Al_2O_3 with varying amounts of water were also examined and the yield of H_2 was found to be higher than that expected for bulk water, but these yields were considerably lower than that observed for adsorbed water suggesting a strong surface effect for H_2 production. This result indicates that there is transfer of energy between the oxide and water in radiolysis where the water is in very close contact to the surface. Bulk crystal structure of Al_2O_3 was not observed to change following irradiation with γ -rays or He ions. However, analysis of the oxide surface using XPS suggested that the pristine sample has an oxyhydroxide surface layer that decreased with radiolysis. He ions seem to even reduce the Al_2O_3 to the Al metal.

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Figure Legends

Figure 1. Temperature programmed desorption spectrum for water on an Al_2O_3 surface. Desorption energies are calculated using Redhead's method. (Redhead, 1962)

Figure 2. DRIFT spectra for Al_2O_3 nanoparticles at room temperature, and heated to 100°C , 200°C , 300°C , and 400°C . The top curve is for H_2O ice at 10 K shown for comparison for the positions of the OH peaks. (Hudgins et al., 1993)

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Figure 4. Normalized Raman spectra for pristine (top), γ -ray irradiated (middle), and He ion irradiated (lower) Al_2O_3 samples. Spectra are offset for clarity.

Figure 5. XPS spectra with fitted peaks of Al 2p core electrons for pristine (top), γ -ray irradiated (middle), and He ion irradiated (lower) Al_2O_3 samples. Spectra are offset for comparison.

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