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Radiolysis of water with aluminum oxide surfaces

Sarah C. Reiff, Jay A. LaVerne*

Radiation Laboratory and Department of Physics, University of Notre Dame, Notre Dame, IN 46556, United States

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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 molecule/100 eV=1.04×10^{-7} 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, γ-Al_2O_3, with electrons (Milosavljevic and Thomas, 2003; Nakamura et al., 2013) and γ-rays (Acres et al., 1965; Seino et al., 2001), and α-Al_2O_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 power 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 ± 0.1 m^2/g. By assuming that the particles were perfect spheres this value corresponds to a particle diameter of around

* Corresponding author.

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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/min. 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-Kα 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- Kα 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 molecule/100 eV=1.04 × 10^{-7} 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 widow 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.

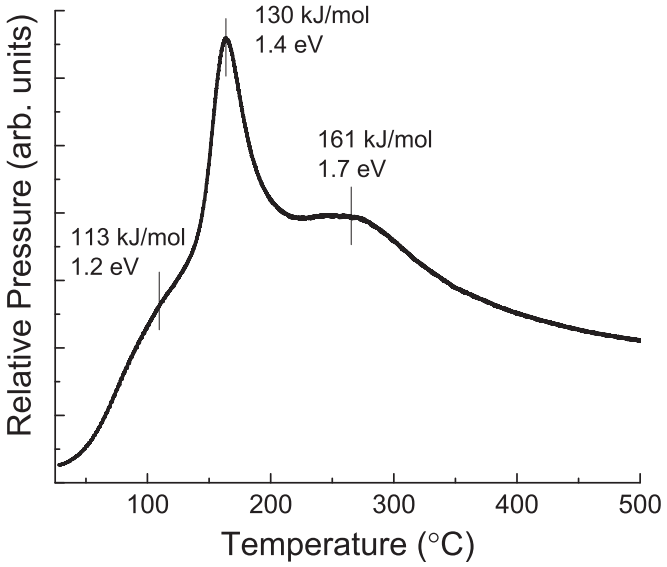

Fig. 1. Temperature programmed desorption spectrum for water on an Al_2O_3 surface. Desorption energies are calculated using Redhead's method (Redhead, 1962).

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 Fig. 1, shows three peaks for water desorption, occurring at temperatures of 110 °C, 164 °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 Fig. 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. (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.