RADIOLYTIC HYDROGEN PRODUCTION FROM WATER-OXIDE NANOPARTICLES INTERFACES.

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INTRODUCTION

The safe storage of PuO2 following reprocessing is a continuing challenge for the NDA and the Sellafield Site License holder. Among the problems associated with PuO2 storage is the requirement of understanding the consequences of surface adsorbed water on the canned oxide powder. One component of this problem is the role of the radiation induced decomposition of water: there is a concern that the production of potentially explosive gases like H2 and O2 will result in the prolonged storage of PuO2.

EXPERIMENTAL SECTION

Hydrogen production from gamma irradiated water in contact with a solid surfaces has been investigated for a number of oxides nanoparticles, specifically Al2O3 (99.95%), SiO2 (99.9%), BeO (99.95%), TiO2 (99.995%) and ZrO2 (99.998%). Experiments were performed for systems with water content varying from a single monolayer up to 95(wt)%.

Preparation of the material before the use of oxides involved backing at 500°C for 24h to remove residual hydrocarbons and adsorbed water, and then cooling in vacuum, weighting and conditioning in constant relative humidity chambers. The constant level of humidity was maintained with water soluble salt slurry [1] at room temperature 25°C. Samples with higher water loadings than 1wt% were prepared by adding appropriate amount of water to the oxide.

All samples were gamma irradiated using Shepherd 109 60Co source at the Radiation Laboratory of the University of Notre Dame with dose rate 55.3 Gy/min measured with Fricke dosimeter.

RESULTS

Experiments at a gamma dose rate of 27.2 krad/min show increasing hydrogen production with increasing water content for all of the oxides except Al2O3 and ZrO2. At water loadings above 1(wt)%, the water-Al2O3 system also demonstrates this trend, however, at near-zero water loading (and for dose rates of 5.22 krad/min and 27.2 krad/min), the yield of molecular hydrogen increases as the H2O weight percentage in the sample decreases to 0(wt)%. G(H2) has a minimum value of 0.02 molecules/100eV at 0.24(wt)% of water and then increases with an increase or a decrease of water loading. Similar behaviour to that demonstrated by Al2O3 was found for ZrO2 with the minimum observed at a much higher 10(wt)% of water.

The yields of H2 observed for all the systems at intermediate and high water loading are higher than expected from simply water radiolysis. Several potential mechanisms for the transfer of energy from oxide nanoparticles to surface water have been proposed in literature, including the formation of an exciton in the bulk oxide and its migration to the surface. When reaching the surface exciton needs to find an appropriate active site in order to split successfully an adsorbed water molecule.

CONCLUSION

Our preliminary conclusion concerning the minimum in the value of G(H2) observed in the water-Al2O3 and the water-ZrO2 systems is that the observation can be attributed to the increasing energy of the water bonding to the surface at a certain water coverage.

REFERENCES