

H₂ Formation from the Radiolysis of Liquid Water with Zirconia

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The formation of H₂ in the radiolysis of liquid water containing nanometer sized ZrO₂ particles was found to be dependent on the crystalline structure of the particle. Zirconia particles of a few tens of nanometer diameter may be formed with the tetragonal crystalline structure at room-temperature rather than the more stable monoclinic form for bulk zirconia. Radiolysis of liquid water containing tetragonal ZrO₂ particles exhibits a significant increase in the decomposition of water to H₂ compared to the monoclinic form. Annealing the tetragonal particles to the monoclinic structure results in the loss of excess H₂ production above that found with water alone. The results show that surface morphology is extremely important in the decomposition of liquids at solid interfaces, which may have many consequences ranging from nuclear waste storage to the H₂ economy.

Introduction

Understanding the decomposition of liquids at the surface of solid particles presents a significant scientific challenge with considerable practical importance. Recent articles have concluded that more efficient methods of H₂ production will be required if economic viability is to be achieved.^{1,2} A promising potential source of H₂ is the decomposition of water at solid interfaces. Considerable effort has been placed on the photochemical production of H₂ from water at TiO₂ interfaces, especially interfaces modified by dyes or dopants.³ Studies from several diverse fields suggest that nanoparticles sometimes exhibit surface properties that may be exploited to produce H₂. For instance, nanometer sized gold clusters on titanium dioxide water were shown to catalyze the water–gas shift reaction to produce H₂ and carbon dioxide from water and carbon monoxide.⁴ Low-temperature experiments simulating the formation of H₂ from interstellar dust particles suggest that surface morphology of small particles is important.⁵ Wide-angle X-ray scattering patterns of 3.4 nm ZnS particles show considerable more disorder and strain relative to bulk material.⁶ These studies suggest that chemistry at nanoparticle interfaces may be different than predicted from normal bulk material. This work will show how the crystal structure of ZrO₂ nanoparticles can have a dramatic effect on the production of H₂ in the radiolysis of liquid water. H₂ formation in the radiolysis of water at oxide interfaces is also important in the safe management of radioactive waste materials stored in sealed containers containing significant humidity.⁷ Deviations in the chemistry from that associated with bulk oxides can have a deleterious effect on long-term stability.

Experimental Section

Two different sources of ZrO₂ nanoparticles were used. Particles of 107 nm average diameter were supplied by Alfa

Aesar and particles of 60 nm average diameter were supplied by TAL Materials, Ann Arbor, MI. Both sources have stated impurity levels of about 0.05%. BET surface area measurements were determined on a Quantachrome Autosorb 1 analyzer. This instrument operates by measuring nitrogen adsorption and desorption from the surface at an equilibrium vapor pressure using the BET (Brunauer-Emmet-Teller) method of surface area calculation. Specific areas of the powders were determined to be 10 and 18 m²/g for the Aesar and TAL particles, respectively. Average diameters were determined from the surface areas assuming spherical particles. Both sets of particles were initially baked at 100 °C in a vacuum to remove traces of organic materials that may interfere with H₂ production. Water/oxide mixtures or slurries were made by the addition of specific weights of the oxides to 2 mL of a 1 mM KBr aqueous solution. OH radicals are produced by the radiolytic decomposition of water and the addition of bromide is required to suppress its reaction with H₂ on the long time scale.

Radiolysis with γ rays was performed using a Shepherd 109 ⁶⁰Co source at the Radiation Laboratory of the University of Notre Dame. The dose rate was about 120 Gy/min as determined using the Fricke dosimeter.⁸ Dosimetry in the mixtures was performed relative to the 2 mL aqueous solution present in all samples; that is, radiation chemical yields were determined with respect to the energy absorbed by the water only.⁹ The water/oxide mixtures were degassed with argon and flame sealed in 1 cm diameter Pyrex tubes 10 cm long. Samples were rotated at 10 rpm throughout the irradiation to ensure complete mixing of the particles and water. Hydrogen was determined by breaking the sample cell in the gas flow to a SRI 8610C gas chromatograph with a thermal conductivity detector. Ultrahigh purity argon was the carrier gas with a flow rate of about 50 mL/min through a 3-meter 5 \times molecular sieve column. Calibration of the gas chromatograph was performed by injecting pure gases with a gastight microliter syringe. Error in gas measurement is estimated to be about 10%.

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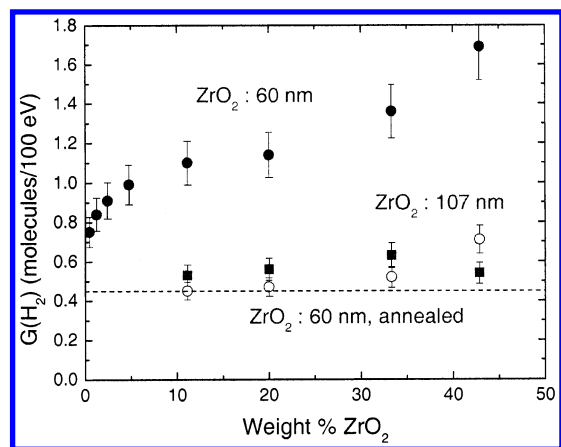


Figure 1. Molecular hydrogen yields as function of ZrO₂ weight percent in the γ -radiolysis of aqueous mixtures: (●) 60 nm diameter, (■) 107 nm diameter, (○) annealed 60 nm diameter. The dashed line shows the H₂ yields for the γ -ray radiolysis of water with no added ZrO₂.

Results and Discussion

The production of H₂ from the γ -radiolysis of water has been examined for many years and the microsecond yield is about 0.45 molecules/100 eV.^{9,10} Recent studies have shown that the mechanism is mainly due to the fast reactions of the precursor to the hydrated electron.^{11,12} Figure 1 shows the yield of H₂ as a function the weight percent of added ZrO₂ oxide. Virtually no effect is observed for the H₂ yields with 107 nm sized particles even with the addition of more than 40 wt % of oxide. On the other hand, even a small addition of 60 nm diameter ZrO₂ particles results in a large increase in H₂ yields. Two different responses for H₂ production were observed in the radiolysis of water mixtures with SiO₂ particles.¹³ In that study, the increased yield with smaller sized particles was attributed to an increase in the probability of an energy loss event in the SiO₂ particle resulting in escape of that energy into the bulk water. Pulse radiolysis studies have shown that an excess of hydrated electrons can be observed in aqueous suspensions of small sized SiO₂ particles.¹⁴ Additional hydrated electron production in the bulk water can account for the observed increase in H₂. However, the SiO₂ particles were widely different in size, 8 and 343 nm, whereas the ZrO₂ particles used in this study are much too close in size to account for the large difference in H₂ yields.

The functional dependence of the H₂ yield for 60 nm particles seems to be bimodal with respect to oxide weight percent. At greater than about 20% oxide weight, the increase in H₂ yields has the expected functional dependence due to an increase in the absorption of energy by the ZrO₂ followed by the production of excess electrons in the bulk water. The very sharp increase in H₂ yields with only a few added weight percent of ZrO₂ appears to be more catalytic in nature. Besides the effects due to the difference in particle sizes, another source for the variation in H₂ yields is some intrinsic property of the ZrO₂ particles. Two different vendors of the ZrO₂ particles were used and variations in a critical property due to particle synthesis could have occurred.

Zirconia normally has a monoclinic crystalline structure at room temperature and is converted to the tetragonal form at about 1100 °C. A very early study by Garvie shows that tetragonal ZrO₂ can be prepared in the form of a fine powder.¹⁵ Garvie also found that annealing the tetragonal powder at a few hundred °C converts it to the monoclinic form. A more recent study shows that the tetragonal volume fraction is equal to one

with increasing particle size up to about 20 nm diameter followed by a sigmoidal decrease to zero at particle diameters of greater than 200 nm.¹⁶ In other words, small ZrO₂ particles tend to have a tetragonal structure even though that is not the stable form of the bulk oxide. Excess surface energy due to the small particle size is given as the reason for this observation.

A powdered X-ray diffraction of the powders used in this study revealed that the Aesar 107 nm particles are mainly monoclinic, whereas the TAL 60 nm particles are mainly tetragonal. Annealing the 60 nm particles at 500 °C for 48 h converted them to the monoclinic form as confirmed by powdered X-ray diffraction. Addition of these annealed ZrO₂ particles to water followed by radiolysis gave the result shown by the open circles in Figure 1. Virtually no difference is seen in the yield of H₂ formation with particles of 60 or 107 nm diameters if they are both monoclinic. The excess production of H₂ observed with the tetragonal particles appears to be due to the surface morphology.

A few other possible sources for the high yield of H₂ with tetragonal ZrO₂ particles must be eliminated before the effect can be attributed to surface morphology alone. Two sources of ZrO₂ were used in these studies, each using different manufacturing techniques. The stated impurity level for both vendors is about 0.05%, so the particles are comparable in content. Trace amounts of impurities can lead to catalytic effects, but there is no reason heating the 60 nm particles to 500 °C would lead to a change in their composition. It is very unlikely that impurities are responsible for the observed increase in H₂ yields with tetragonal 60 nm particles.

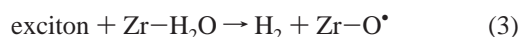
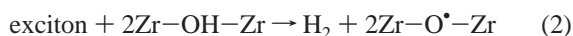
Rearrangement of the crystalline structure of small particles can be accompanied by a change in surface area. Previous studies have shown a strong dependence of H₂ production on specific surface area in the radiolysis of water adsorbed on ZrO₂ of a certain size range.¹⁷ This size dependence arises from the finite diffusive range of energy carriers within the particle. Very small particles will not exhibit size dependent yields because essentially all precursors to H₂ are capable of reaching the surface. The particles used in this study are in the appropriate range that variation in size should lead to observable changes in H₂ production at the surface. BET analysis of the annealed 60 nm ZrO₂ particles gave a specific surface area the same as that before annealing indicating no major rearrangement of the particles. Therefore, variation in particle surface area is not responsible for the observed decrease in H₂ yield upon annealing the ZrO₂ particles.

Heating the samples can have a profound effect on the molecules bound to the surface. Temperature programmed desorption studies of water on ZrO₂ show the loss of physisorbed water up to 300 and the loss of chemisorbed water at higher temperatures.¹⁷ The loss of surface water is not important in these studies because the samples will obviously be rehydrated when placed in solution. The high temperatures used in this study are not expected to be sufficient to cause permanent change in surface charge. Solution pHs are about the same so the points of zero charge, PZC, are probably not changing on annealing. Future studies will specifically examine the effects of PZC and pH on H₂ formation. These further studies will also examine the effects of pH on added solutes. Bromide was added to the water to stop the reaction of OH radicals with H₂. Most of the radiation energy is being deposited in the water phase, and substantial production of OH radicals is expected. Under certain pH conditions, the bromide may be forced onto the particle surface and thereby modify the mechanism for H₂ production. However, other studies under conditions similar to

those in this work suggest that bromide remains predominately in solution.¹⁸ Adsorption of bromide is not expected to be a factor in the variation in H₂ yields in the solutions examined here.

Water is not the only compound that may be adsorbed on the particle surfaces. Carbon dioxide and other gaseous contaminants may be found, which are very difficult to completely remove. However, these compounds never manifested themselves in other studies on H₂ production from the radiolysis of adsorbed water.¹⁹ Any physisorbed contaminants are expected to simply migrate to the liquid phase with no subsequent effects. Strongly bound hydrocarbons may not be completely removed by baking at 100 °C in a vacuum and may contribute to excess H₂ production. However, there is no reason to expect such contamination. Samples of monoclinic ZrO₂ baked at 100 °C in a vacuum, 500 °C in air, or not baked gave similar H₂ yields. Likewise, tetragonal ZrO₂ baked at 100 °C in a vacuum or not baked gave similar H₂ yields. The lack of any dependence of H₂ yields on surface preparation strongly suggests that adsorbed species are not playing a role in the observed H₂ production.

The reason for the increased in H₂ yield with tetragonal ZrO₂ is not known. If the crystal structure of the ZrO₂ affects the formation of H₂ then the mechanism is probably not due to the excess formation of electrons in the bulk water as observed in the radiolysis of small SiO₂ particles in water.¹³ Electrons energetic enough to pass through the oxide–water interface are not likely to be influenced by the crystalline structure. Excitons are thought to be the source of excess H₂ production in the radiolysis of water adsorbed on ZrO₂.¹⁷ The migration of excitons or their surface reaction could be influenced by the crystalline structure, for instance the number of exciton trapping sites may be structure dependent. Possible mechanisms for the production of H₂ at the surface might include the following reactions:



where the exciton is reacting with free OH groups (1), bridged OH groups (2), or with bound/near-surface water (3). Each of these processes may have a different efficiency for the production of H₂. In addition to affecting the number of excitons reaching the surface, the crystalline structure may influence the relative importance of reactions 1–3. Neutron scattering studies of chemisorbed OH surface groups and physisorbed water on tetragonal ZrO₂ show a shift to lower energy in the vibration bands when the oxide is stabilized by the addition of a lanthanide dopant.²⁰ An investigation of the adsorption of CO and CO₂ on monoclinic and tetragonal ZrO₂ particles of about the same size shows the monoclinic particles to have considerably more OH groups on the surface and they are more basic than the tetragonal particles.²¹ The fewer, but higher energy and more acidic, OH groups on tetragonal ZrO₂ particles may contribute to the increased capacity to produce H₂ when an additional source of energy is available, as in radiolysis. Further experiments will try to identify the radiation dependence of the species adsorbed on the surface of ZrO₂ particles.

Conclusions

Energy loss in the solid phase of water mixtures is usually assumed to be “wasted” and not available for decomposition of the water. Photolysis studies have long showed the enhanced production of H₂ from water due to the presence of an oxide surface.³ Recent results on adsorbed water have shown that radiation energy deposited in the bulk solid can lead to H₂ production at the surface.^{17,19} This work shows that radiation induced chemistry can also lead to a significant production of H₂ from liquid water–oxide interfaces. In particular, the formation of H₂ in the radiolysis of liquid water containing nanometer sized ZrO₂ particles may be dependent on the crystalline structure of the particle. More investigations must be performed on a variety of materials to identify the precursors and the mechanism for H₂ formation. Besides the fundamental importance, there are many types of applications for which the production of H₂ in the radiolysis of water at heterogeneous interfaces is important including the storage of wet radioactive waste, nuclear reactor maintenance, and the H₂ economy.

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Supporting Information Available: Figures S1 and S2 showing the powdered X-ray diffraction pattern of the 60 nm zirconia particles before and after annealing are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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