RESEARCH COMMUNICATIONS


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**Hydrogen generation by gamma radiolysis of aqueous suspension of nano zirconia**

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Aqueous suspension of nano zirconia with methanol was irradiated with gamma (γ) rays. Hydrogen (H2) generated in this process was studied as a function of pH and γ-dose. In the presence of 1 M methanol and at pH 3.0, low gamma dose irradiation showed optimum H2 generation. This is explained on the basis zeta potential and surface charge on zirconia particles. Positive surface charge at low pH could be the reason for enhanced H2 generation. Maximum H2 yield G(H2) of 3.7 was observed. This is 400 times more compared to nano pure water. The method can be utilized for building a medium-scale H2 generation plant.

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HYDROGEN (H$_2$) is a clean fuel and energy storage medium of the 21st century as it is a non-polluting and environment-friendly energy source. Water is an easily available and cheap source of H$_2$. But to get significant amount of H$_2$, water thermolysis (water splitting at high temperature) is required. This involves handling of highly corrosive chemicals at high temperatures (1000–2000°C). Water splitting using gamma (γ)-energy (γ-radiolysis) is one of the safe and easy methods for medium-scale H$_2$ generation. In this method γ-ray energy from nuclear power reactor or nuclear waste is used. It is similar to the use of nuclear waste stem for sea-water desalination to get potable water. Thus, γ-energy, otherwise hazardous to health can be used here beneficially for H$_2$ production. H$_2$ yield of pure water by γ-radiolysis is ~0.01 (ref. 1). There are various methods of increasing this yield$^2$–$^5$. The history of water radiolysis with focus on H$_2$ production is given by Sophia$^6$. Gamma-irradiation of zirconia (ZrO$_2$) loaded with water vapour was found to give increased H$_2$ yield. This was due to effective energy transfer to H$_2$O molecule absorbed on the oxide surface. It was attributed to the matching of 5.1 eV energy required for H–OH bond splitting of water with resonant maximum zirconia band gap of 5.0 eV. Upon interaction of zirconia with γ-ray, this energy is released in the form of excited photon (exciton), and is used for splitting of water molecules absorbed on the zirconia surface to produce H$_2$. Doping with Nb$^{5+}$ decreased H$_2$ yield, whereas doping with Li$^+$ doubled the H$_2$ yield. The sensitivity of energy transfer due to the presence of Nb$^{5+}$ or Li$^+$ was found to affect the radiation-enhanced oxidation of ZrO$_2$ in high-temperature water. This is particularly relevant to nuclear power plants where zirconium is used for fuel cladding and pressure tubes.

The proposed mechanism of H$_2$ generation was based on coupling of migrated excitants with H$_2$O absorption complex on zirconia surface and H–OH bond splitting. Nano-sized tetragonal ZrO$_2$ was found to increase radiolytic water splitting compared to monoclinic ZrO$_2$ (ref. 8). Presence of high energy and acidic OH groups on tetragonal ZrO$_2$ particles may be the reason for its increased H$_2$ generation capacity. Thus, studies of γ-radiolysis of water in the presence ZrO$_2$ are of significance from the point of view of H$_2$ economy and safety of both wet radioactive waste and nuclear reactors. This communication explains results of our H$_2$ generation studies by γ-irradiation of aqueous suspension of nano ZrO$_2$ in the presence methanol at various pH values.

Tetragonal dominant nanocrystalline (10–15 nm) zirconia was obtained via direct precipitation route$^9$. The zirconia was suspended in nanopure water and sonicated for 1 h, and then allowed to stand still overnight. The white-coloured, stable supernatant suspension thus obtained was filled in a glass vial.

A 17 ml sampling vial was prepared by fixing a 1/4 inch tube fitting at the top of a 84 mm long and 20 mm diameter glass tube (Figure 1). A 9.0 mm diameter and 3.5 mm thick silicon septum was tightened with a screw cap of the tube fitting on top of the vial to make it leak-proof. The samples for gas analysis were withdrawn through this septum using Hamilton gas tight syringe. For larger volume samples 100 ml volumetric flask was fixed with an airtight cone socket adaptor having gas sampling arrangement as described above (Figure 1). Liquid phase to gas phase volume ratio of 1.0 was maintained in all irradiations.

The vial was purged with high-purity N$_2$ gas to remove dissolved O$_2$. Then it was exposed to various γ-doses using Co$^{60}$ source with 2.0 kGy/h dose rate. The pH of solution was adjusted to the desired value using perchloric acid (HClO$_4$). H$_2$ generated in the vials after γ-irradiation was measured using a gas chromatograph (CIC make; GC 2011 model) with 2 m long, 1/8th inch diameter molecular sieve column. High-purity argon gas was used as carrier and thermal conductivity detector (TCD) was used as detector. The zeta potential of the zirconia particles in an aqueous suspension as a function of pH was measured using Malvern Zeta meter.

Gamma radiolysis of suspension obtained just by stirring nano zirconia powder and nano pure water on magnetic stirrer for 1 h did not show any significant increase in H$_2$ generation. The white-coloured stable supernatant zirconia suspension was generated by 1 h sonication of aqueous mixture of nano zirconia and allowing it to stand still overnight. Gamma-irradiation of this suspension gave significant amount of H$_2$. Methanol (CH$_3$OH) acts as OH radical scavenger and its reactions with H$^*$ and $c_{aq}$ further helps in H$_2$ generation$^{10}$.

The reactions and their rate constants are as follows

\[ \text{CH}_3\text{OH} + \text{OH}^* \rightarrow \text{CH}_2\text{OH} + \text{H}_2\text{O} \]  
(10$^9$ dm$^3$ mol$^{-1}$ s$^{-1}$),

\[ \text{CH}_3\text{OH} + \text{H}^* \rightarrow \text{CH}_2\text{OH} + \text{H}_2 \]  
(10$^7$ dm$^3$ mol$^{-1}$ s$^{-1}$),

\[ c_{aq} + c_{aq} \rightarrow \text{H}_2 + 2\text{OH}^- \]  
(5 $\times$ 10$^9$ dm$^3$ mol$^{-1}$ s$^{-1}$).

The gamma radiolytic H$_2$ yield G(H$_2$) of the aqueous methanol solution is 2.5 as given below

\[ G(\text{H}_2) = G(\text{H}_2) + G(\text{H}) + 1/2G(c_{aq}) \]

2.5 = 0.45 + 0.55 + 1.4.

At high alcohol (methanol) concentration (~ 1.0 M), the alcohol scavenges OH radicals formed in the spars as well$^{11}$. Thus, in the presence of methanol (1.0 M) total scavenging of OH radical takes place. Further, as OH radical is a precursor of H$_2$O$_2$, in the absence of OH...
radical there is no chance of formation of H_2O_2 and O_2 (degradation product of H_2O_2). In all our experimental studies no oxygen was observed in gas phase.

H_2 was generated by exposing this suspension containing methanol (1 M) to Co^{60} \gamma-dose. pH values of the mixture were varied using HClO_4. Liquid to gas volume ratio of 1.0 was maintained throughout the experiments to get optimum H_2 yield\textsuperscript{12}. Figure 2 shows the variation of H_2 yield G(H_2) and total quantity of H_2 (ml) generated in the gas phase as a function of methanol concentration at 182.6 kGy \gamma-dose. Although methanol concentration of 0.6 M was found to give optimum yield, in all experiments 1.0 M methanol concentration was kept constant throughout.

Figure 3 shows the percentage of H_2 generated in the gas phase of irradiated vial as a function of pH values at various \gamma-doses. Except for the maximum dose of 370 kGy, with increasing \gamma-dose increase in percentage of H_2 formed was observed. At 370 kGy dose it was less than that of 288 kGy dose. This can be due to increased combination reactions of OH radical with H_2 at high dose due to high concentrations of H_2 and OH\idot formed in spur as well as due to lowered probability of H_2 escape into the gas phase. The maximum H_2 yield of 2.8 was observed for 288 kGy dose at pH 3.0.

Figure 4 shows the H_2 yield, G(H_2) as a function of pH at various \gamma-doses. Increase in G(H_2) with decreasing \gamma-dose was observed. At pH 3.0, it was maximum for all \gamma-exposures. This indicates more efficient utilization of \gamma-energy at low dose irradiation for H_2 production.

As shown in Figure 5, at high-dose irradiations it can be observed that with increasing \gamma-dose there is a proportionate increase in hydrogen content and decrease in nitrogen content in the gas phase of the irradiated sample. This is one of the main reasons for not increasing pressure in the gas phase of the irradiated sample.
Following mechanism for nitrogen to nitrate conversion was suggested in our earlier studies:\footnote{13}

\begin{align}
N_2 & \rightarrow 2N, \quad (5) \\
N_2^+ + [H_2O]_n & \rightarrow NO_2 + H^+, \cdot OH, \quad (6) \\
NO_2 + \cdot OH & \rightarrow HNO_3 \\
& \text{(rate constant: } 1.0 \times 10^7 \text{ l mol}^{-1} \text{s}^{-1}). \quad (7)
\end{align}

Increased conversion of nitrogen from gas phase to nitrate with increasing $\gamma$-dose resulted in the increased nitrate concentration in liquid phase as observed in our earlier studies (Figure 6). As a conservative assumption, even if there is 70% hydrogen and 50% nitrogen in the gas phase there will be only 0.2 atm. pressure excess, i.e. overall pressure in the sample vial will be 1.2 atm. This will be taken care by very little inflation of silicon rubber septum and wall strength of the vial.

In the case of $N_2$ as cover gas, the atomic nitrogen formed by radiolysis of dissolved nitrogen (eq. (5)) scavenges even dissolved oxygen (DO) by a reaction leading to NO formation.

\begin{align}
N + O_2 & \rightarrow NO + O. \quad (8) \\
\text{NO}_3 & \text{ is the oxidation product of NO and oxygen reaction.}
\end{align}

Atomic nitrogen also reacts with activated water molecules to form $NH_3$ and NO as reaction products.

\begin{align}
2N + H_2O^* & \rightarrow NH_2 + NO. \quad (9)
\end{align}

These products further remove $\cdot OH$ and DO through the following reactions.

\begin{align}
\text{Rate constant (dm}^3\text{ mol}^{-1}\text{s}^{-1}). \\
\text{NO} + O & \rightarrow NO_2 \quad 1.66 \times 10^9, \quad (10) \\
\text{NO}_2 + \cdot OH & \rightarrow HNO_3 \quad 1.00 \times 10^7, \quad (11) \\
N + H & \rightarrow NH \quad 2.00 \times 10^7, \quad (12) \\
\text{NH} + O_2 & \rightarrow NO + \cdot OH \quad 1.00 \times 10^7. \quad (13)
\end{align}

Thus, the oxygen and hydroxyl radicle formed by water radiolysis and if any DO present in water containing methanol under nitrogen atmosphere get scavenged. Hence there is no formation of $H_2O_2$ and $O_2$.

Figure 7 shows the plot of pH versus zeta potential of nano zirconia particles suspended in aqueous medium. It is observed that in the pH range 3.0–4.0 charge on zirconia particle is maximum. Similarly, the observed $H_2$ generation by $\gamma$-radiolysis is also maximum at pH 3. The point of zero charge (PZC) of zirconia particles in aqueous medium is found to be 7.0. Hence, zirconia will have positive charge at pH 3.0, which will attract partially negatively polarized oxygen atoms of the absorbed water molecule to rest on the zirconia particle surface and making partially positively polarized hydrogen atoms bit farther,

Figure 4. Variation of $G(H_2)$ as a function of pH at various $\gamma$-doses with MeOH (1 M).

Figure 5. Variation of $H_2$ and $N_2$ contents in gas phase of irradiated vial as a function of $\gamma$-dose.

Figure 6. NO$\text{}_3$ production by $\gamma$ irradiation of nano pure water containing 5.7 ppm dissolved oxygen and upper space covered with $N_2$. 

\begin{align}
\text{}\quad \text{Thus, the oxygen and hydroxyl radicle formed by water radiolysis and if any DO present in water containing methanol under nitrogen atmosphere get scavenged. Hence there is no formation of $H_2O_2$ and $O_2$.}
\end{align}
as shown in Figure 9. This can facilitate the easy and quick escape of $\text{H}_2$ generated in gas phase before it reacts with the hydroxyl radical to produce water by back reaction as shown below.

\[
\begin{align*}
{^\cdot \text{OH}} + \text{H}_2 & \rightarrow \text{H}_2\text{O} + \text{H}, \\
\text{H} + \text{H}_2\text{O}_2 & \rightarrow \text{H}_2\text{O} + {^\cdot \text{OH}}, \\
\text{H}_2 + \text{H}_2\text{O}_2 & \rightarrow 2\text{H}_2\text{O}.
\end{align*}
\]

(14) (15) (16)

A particle suspended in liquid medium carries an electrical charge on its surface\textsuperscript{14}. This electric potential due to the charge on the particle surface is known as zeta ($\zeta$) potential. PZC of a particle suspended in a medium is the pH of the medium at which the particle surface charge (zeta potential) is zero. It gives an idea about the surface charge of a particle in a particular medium and hence its interaction with other charged surfaces.

\[
\zeta = k \cdot (\text{PZC} - \text{pH}),
\]

(17)

where $\zeta$ is the potential of the suspended particle, PZC is point of zero charge and ‘pH’ is the solution acidity in pH units.

PZC is measured from the ‘S’-shaped curve obtained by plotting pH versus potential of a medium in which the particle is suspended. In the range of few millivolts from PZC, i.e. one or two units pH value on both the positive and negative sides of PZC, there is a sharp change in the properties of the particle. Subsequently, there is very less change in particle properties on both the sides of PZC. To get this curve on both positive and negative sides of PZC, sufficient measurements are required. Hence measurements were carried out in the 2.0–10.0 pH unit range. PZC of nano zirconia was found to be 7.0.

The following reactions contribute to hydrogen generation by water radiolysis.

- Rate constants (dm$^3$ mol$^{-1}$ s$^{-1}$).
  
  \[
  \begin{align*}
  e_{\text{aq}}^- + \text{H}_3\text{O}^+ & \rightarrow \text{H}_2\text{O} + \text{H} \quad 2.4 \times 10^{10}, \\
  e_{\text{aq}}^- + e_{\text{aq}}^- & \rightarrow \text{H}_2 + 2\text{OH}^- \quad 5.0 \times 10^9, \\
  {^\cdot \text{H}} + {^\cdot \text{H}} & \rightarrow \text{H}_2 \quad 1.0 \times 10^{10}.
  \end{align*}
  \]

(18) (19) (20)

Effects of pH on the $\gamma$-radiolytic yield of water indicate rapid decrease in $\text{H}$ yield in the pH range 2.0–4.0 with...
increasing pH and then subsequent stabilization up to pH 10.0. Contrarily, $c_{aq}$ yield increases with increasing pH in the pH range 1.0–5.0 and subsequently stabilizes up to pH 10.0 (ref. 1). Both curves intercept in the pH range 3.0–3.5. Hence this is the optimum range for hydrogen production studies. As described above and as seen in Figure 7, the maximum positive charge on the nano zirconia surface favourable for hydrogen production was also observed in the pH range 2.0–4.0. Hence $G(H_2)$ was measured in the pH range 2.0–4.0, as shown in Figure 4. Nevertheless, the study was performed in the pH range 2.0–7.0 (Figure 8).

With increasing pH, OH\(^{-}\) concentration in the medium increases and reactions given below compete with hydrogen production as counteracting reactions and decrease the hydrogen production as shown in Figure 8.

Rate constants (dm\(^3\) mol\(^{-1}\) s\(^{-1}\)).

\[
\begin{align*}
H^+ + OH^- &\rightarrow H_2O \quad 1.44 \times 10^{11}. \\
OH^- + H^+ &\rightarrow e_{aq} + H_2O \quad 2.0 \times 10^7.
\end{align*}
\]

Further, in the pH range 2.0–4.0, positive charge on nano zirconia leads to absorption of more number of water molecules on ZrO\(_2\) particle surface for interaction with $\gamma$-excitons, as shown in Figure 9. This results in the cleavage of more H–O bonds and formation of more H\(^+\) as observed in this study. Excitons are generated by interaction of $\gamma$-radiation with zirconia particles suspended in water.

When pH of the medium is more than PZC of ZrO\(_2\) (7.0), its surface acquires a negative charge. In this case oxygen atoms move away and partially positively charged hydrogen atoms comes closer to the ZrO\(_2\) surface due to electrostatic attraction. This provides firm and stable grip and more proximity to H atom of water molecule absorbed on zirconia surface, as shown in Figure 9. In turn, this reduces the possible escape of H\(_2\) generated in gas phase and converting back into H\(_2\)O as shown by eqs (1)–(3). This arrangement also decreases the number of water molecules absorbed on the zirconia surface as each water molecule occupies more surface area than the earlier arrangement where the zirconia surface was positively charged (Figure 9).

Figure 10 shows the percentage of H\(_2\) present in gas phase and $G(H_2)$ as a function of $\gamma$-dose in the presence of 1.0 M methanol. It can be seen that in a closed space, although the amount of H\(_2\) increases with $\gamma$-dose, $G(H_2)$ decreases. This means that the low-dose irradiation and continuous extraction of H\(_2\) formed in the gas phase is more beneficial than the high-dose irradiation.

In conclusion, gamma radiolysis of aqueous suspension of nano zirconia in the presence of methanol was found to enhance water splitting and gave increased H\(_2\) production. At medium pH of 3.0 and lower $\gamma$-dose, the yield was found to be optimum. This is due to pH-dependent zirconia surface charge variation. PZC of zirconia was found to be 7.0. At pH 3.0 positively charged ZrO\(_2\) surface facilitates absorption of partially negatively charges O\(_2\) of H\(_2\)O molecule to rest on it. This arrangement occupies less surface area resulting in absorption of more number of water molecules and keeping H\(_2\) away for easy escape resulting in more H\(_2\) generation. But, after pH 7.0 the ZrO\(_2\) surface becomes negatively charged. This facilitates two partially positively charged H atoms resting on the ZrO\(_2\) surface occupying more area resulting in less number H\(_2\)O molecules absorption on the surface and less H\(_2\) generation. This can be envisaged from Figure 9.