Catalysts for hydrogen generation from water vapor

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Received 15 September 2005; received in revised form 18 October 2005; accepted 9 November 2005
Available online 2 February 2006

Abstract

Phosphate glasses dissociating hydrogen from water vapor were prepared and their performance was evaluated. Glasses with compositions of 30Na2O–10BaO–30P2O5–(30−x)Nb2O5−xWO3 (5<x<25) dissociated water vapor into hydrogen and oxygen around 500 °C. The best dissociation performance was observed on a specimen with the tungsten composition of x = 15. The result suggests that the coexistence of Nb2O5 and WO3 is important in obtaining a high performance of hydrogen dissociation. When Nb2O5 was replaced by other transition metal oxides such as MoO3, the amount of hydrogen dissociation decreased by one-third.

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Keywords: Phosphate glass; Catalyst; Hydrogen generation; Dissociation adsorption; Proton

1. Introduction

It is an urgent mission to search for new energy sources that can substitute for petroleum. Hydrogen has come to be noticed as a substitute fuel for petroleum, and there is an urgent need to develop techniques of making practical use of hydrogen. Although various devices, such as fuel cell and hydrogen engine, have been developed to make better use of hydrogen, it seems definitely important to look for new materials that can produce hydrogen efficiently.

Phosphate glasses are interesting materials from the viewpoint of hydrogen generation because some of the glasses containing tungsten oxides can decompose water and absorb hydrogen as a proton [1]. Previous studies on such phenomenon by spectrometric analysis showed that the IR absorption at 600–650 nm was assigned to the vibration modes of W5+ and O–H. This IR absorption increases when the water vapor pressure or exposure time increases. This phenomenon is mainly attributed to the conversion of tungsten ions from W6+ to W5+. The reduction is thought to occur when an electron of hydrogen, which is produced by the dissociation of a water molecule on the surface of glass, is trapped by a W6+ ion. Furthermore, gradient in the color observed from the surface to the inside of the glass suggests the diffusion of W5+ ions inside the glass. In other words, this indicates that hydrogen migrates into the glass as a proton by exchanging an electron with W6+ ions. Therefore, these glasses must be a good catalyst for water dissociation and hydrogen generation.

In this study, phosphate glasses with various proportions of WO3 to Nb2O3 were prepared and their performance in decomposing water vapor was evaluated.

2. Experiment

Phosphate glass specimens of 30Na2O–10BaO–30P2O5–(30−x)Nb2O5−xWO3 were prepared using reagent grade powder of Na2CO3, NaPO3, Ba(PO3)2, Nb2O5, and WO3 as raw materials. Glass specimens were obtained by melting the mixture of powder with the appropriate composition ratio in a platinum crucible at 1050 °C for 45 min with intermittent mixing, casting the mixture into a graphite mold (10×5×50 mm3), which had been heated to 400 °C, and subsequent slow cooling of the solidified mixture in an electric furnace. After being cut into 10×5×1 mm3 rectangular plates, the glass samples were annealed at 560 °C for 40 h in an oxygen atmosphere to remove surface strain and to fully oxidize W ions.
The performance of glasses as a catalyst for water vapor decomposition was evaluated by using an apparatus shown in Fig. 1. The apparatus consists of a reaction chamber, a furnace, a quadrupole mass spectrometer (Q-mass), and vacuum pumps. The reaction chamber has two rooms divided by a partition wall made of a palladium plate (thickness of 0.5 mm). One of the rooms (room-1) was kept at ambient pressure, while another room (room-2) was evacuated to $10^{-6}$ Torr by a turbo molecular pump (TMP). A glass catalyst was placed in room-1 just in front of the palladium partition. Prior to the experiment, one side of the sample was coated with palladium film using vacuum evaporation. The reaction chamber was heated by the electric furnace with argon gas flowing to room-1 and evacuating room-2. After the chamber was heated to 500 $^\circ$C, water vapor was carried to room-1 by argon gas via a water babbler. Partial pressures of H$_2$, O$_2$, CO$_2$, and N$_2$ were monitored by the quadrupole mass-spectrometer and the spectroscopic data were collected on an interfaced personal computer.

3. Results and discussion

Photographs of as-cast glass ingots are shown in Fig. 2. The glass ingots are transparent and their color changes from dark brown to bluish gray as the composition ratio of WO$_3$ to Nb$_2$O$_5$ increases. It is commonly accepted that Pd metal decomposes hydrogen molecules to hydrogen atoms, and the hydrogen atoms penetrate into the Pd[2]. Therefore, there is a possibility that Pd decomposes water vapor. Fig. 3 shows the time dependence of H$_2$ partial pressure, $P_{H_2}$, in room-2 measured at 500 $^\circ$C without installing a glass specimen in room-1. When water vapor with the flow rate of $6.5 \times 10^{-3}$ ml/min was introduced into room-1 by Ar gas (1 atm), no change was observed in the $P_{H_2}$ over the course of time. The results of the above experiments clearly show that Pd has no influence in the decomposition of water molecules at 500 $^\circ$C. When the glass specimen was installed in room-1 and heated to 500 $^\circ$C followed by the introduction of water vapor into room-1, $P_{H_2}$ in the room-2 immediately showed a remarkable change. Fig. 4 shows time dependence of $P_{H_2}$ in room-2, measured for a specimen with a composition of 30NaO$_{12}$–10BaO–30PO$_{32}$–15NbO$_{52}$–15WO$_3$. $P_{H_2}$ increased rapidly and tended to be saturated after 5 min. When the introduction of water vapor was stopped, $P_{H_2}$ in the room-2 returned to the previous pressure level. These results obviously suggest that the phosphate glass decomposes H$_2$O into hydrogen and oxygen molecules. As shown in the inset of the figure, the change of $P_{H_2}$ was reproducible when the same procedure was repeated, and the best performance was obtained at 500 $^\circ$C. The amount of hydrogen produced by the glass catalyst can be estimated by the above result. When a glass specimen with a size of $10 \times 5 \times 1$ mm$^3$ exposed to water vapor with flow rate of $6.5 \times 10^{-3}$ ml/min, $4 \times 10^{-9}$ ml/min of H$_2$ was produced. The efficiency of hydrogen generation presently is very low, never the less it is expected to be increased by making porous structure with large effective surface.

It is well known that W and Nb have a superior ability to adsorb and dissociate H$_2$O into H$_2$ and O$_2$ molecules [3–5]. When the adsorbing power of W$^{6+}$ and Nb$^{5+}$ is stronger than the bonding power of H$_2$O, the dissociation adsorption of H$_2$O molecule takes place on the surface of a glass specimen. H$_2$O molecules in a vapor state adsorbed on the surface of glass dissociate into H$_2$ and O$_2$ molecules. A portion of the H$_2$ molecules is further dissociated into hydrogen atoms, and the hydrogen atom is oxidized by the W$^{6+}$ ions producing W$^{5+}$ and a proton H$^+$. Since the density of H$^+$ inside the specimen was low, $P_{H_2}$ in the room-2 returned to the previous pressure level. These results obviously suggest that the phosphate glass decomposes H$_2$O into hydrogen and oxygen molecules. As shown in the inset of the figure, the change of $P_{H_2}$ was reproducible when the same procedure was repeated, and the best performance was obtained at 500 $^\circ$C. The amount of hydrogen produced by the glass catalyst can be estimated by the above result. When a glass specimen with a size of $10 \times 5 \times 1$ mm$^3$ exposed to water vapor with flow rate of $6.5 \times 10^{-3}$ ml/min, $4 \times 10^{-9}$ ml/min of H$_2$ was produced. The efficiency of hydrogen generation presently is very low, never the less it is expected to be increased by making porous structure with large effective surface.

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is smaller than that near the surface area, H\(^+\) will diffuse into the specimen. H\(^+\) would move along the distribution of W\(^{5+}\) to keep the electrical neutrality. This is why a change in the depth of color was observed when the specimen was removed from the reaction chamber after finishing the experiment. Since W\(^{5+}\) ion has an absorption in the wavelength range of 600–650 nm, the color is mainly attributed to the W\(^{5+}\) ion that exists in the specimen with H\(^+\). On the other hand, another part of H\(_2\) will leave the glass surface and diffuse through the Pd partition which separates room-1 and room-2 as shown in Fig. 1. The hydrogen molecule is decomposed into hydrogen atoms on the surface of the Pd partition. Due to the gradient in the hydrogen partial pressure, the hydrogen atoms pass through Pd and reach room-2. Some of the hydrogen atoms in room-2 are recombined to hydrogen molecules which are detected by the quadrupole mass spectrometer. The performance of the glass for hydrogen dissociation was investigated for specimens of 30NaO\(_{1/2}\)–10BaO–30P\(_2\)O\(_5\)–(30–x)Nb\(_2\)O\(_5\)–xWO\(_3\) (0 \(\leq x \leq 30\)). Fig. 5 shows the change in the partial pressure, \(\Delta P_{H_2}\), in room-2 as a function of WO\(_3\) content \(x\). \(\Delta P_{H_2}\) is the largest at a WO\(_3\) content of 15%. This is the composition where the proportion of WO\(_3\) is equal to that of Nb\(_2\)O\(_5\). Although the reason of this result is presently unclear, W\(^{6+}\)–Nb\(^{5+}\) pairs may form the most suitable network to incorporate H\(_2\)O into the glass and promote dissociation adsorption of H\(_2\)O molecules. When the other metal oxides were used instead of Nb\(_2\)O\(_5\), the dissociation performance decreased considerably. Fig. 6 shows the time dependence of hydrogen partial pressure, measured respectively for specimens containing Nb\(_2\)O\(_5\) and MoO\(_3\). The performance of a specimen with MoO\(_3\) decreased by one-third of that of a specimen with Nb\(_2\)O\(_5\). This result suggests that the coexistence of Nb\(_2\)O\(_5\) and WO\(_3\) is important in obtaining a high performance of hydrogen dissociation.

The penetration of H\(^+\) into the glass was confirmed by investigating hydrogen evolution from the specimen. Fig. 7 shows time dependence of the H\(_2\) partial pressure, \(P_{H_2}\), measured for a specimen used in the hydrogen dissociation experiment. The specimen was inserted into the furnace kept at 500°C. The specimen was inserted into the furnace kept at 500°C.
of hydrogen decreases immediately. However, the decrease rate is slow because the hydrogen contained in the specimen as the form of H⁺ is released by the diffusion process. Therefore, the result of hydrogen evolution measurement along with the color change observed on the glass specimen suggests that a portion of hydrogen penetrates into the specimen as H⁺.

4. Conclusion

Glass–catalysts composed of 30Na₂O–10BaO–30P₂O₅–(30−x)Nb₂O₅–xWO₃ (0 ≤ x ≤ 30) were prepared, and their performance to dissociate water vapor into hydrogen and oxygen was evaluated. The best dissociation performance was observed for the specimen with the composition of x = 15 at 500 °C. When Nb₂O₅ was replaced by MoO₃, the amount of hydrogen dissociation decreased by one-third. Therefore, the coexistence of Nb₂O₅ and WO₃ is considered to be important to obtain a high catalytic performance. W⁶⁺–Nb⁵⁺ pairs may form the most suitable network to incorporate H₂O into the glass and promote dissociation adsorption of H₂O molecule. Gradient of color was observed in the glass after heat treatment in water vapor. A portion of H₂ produced on the surface of glass via decomposition of H₂O seems to penetrate into the glass as H⁺. The efficiency of hydrogen generation is likely to be improved by making porous specimen with large effective surface.

Acknowledgements

The work done at Aoyama Gakuin University was supported by a Grant-in-Aid for 21st COE Program from the Ministry of Education, Culture, Sports, Science and Technology, Japan and a Grant-in-Aid for The Private School High-tech Research Center Program of the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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