Hydrogen Generation by Wet Grinding of Quartz Powders and Its Dependence on the pH and Ionic Strength of Liquid Media

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Hydrogen generation was investigated by grinding quartz powder in pH- and ionic strength-controlled liquid media. The effect of ionic strength on hydrogen generation was negligible, while the decrease of generated hydrogen in the acidic pH region (>5.0) was observed. The mechanism of these mechanochemical reactions was discussed.

It is well known that hydrogen is generated during wet grinding of inorganic powders in water or organic compounds.[1,2] When the powders are ground with steel balls, hydrogen may be generated by the reaction between liquid media and iron,[3] while, when ground with ceramic balls, hydrogen may be generated by the mechanochemical reaction between mechanoradicals on a fractured surface of powders and liquid media.[2] On the other hand, it has been well known that anomalously high concentration of hydrogen is observed in soil gas along an active fault[4] or in bubble gas from a deep well.[5] Such an anomaly is proposed as an indicator of the activity of earthquakes. These types of hydrogen are considered to be generated by the mechanochemical reaction between crushed rocks and groundwater. Kita et al. have experimentally investigated hydrogen generation by crushing quartz or granite with pure water.[6] Since the water within a fault zone has complex chemical composition, it is necessary to consider the effect of solution chemistry on the hydrogen generation for more precise understanding of relationship between the earthquake activity and observed hydrogen concentration. In this paper, the effects of pH and ionic strength of a solution on the mechanochemical formation of hydrogen by grinding quartz are investigated.

Experimental

Grinding was conducted using a centrifugal ball mill (Fritsch, P-6) running at 600 rpm. This mill pot was made of zirconia (80 cm^3) and was sealed by a viton O-ring. Feed materials were quartz powders SIL-CO-SIL 250 (U.S. SILICA). Quartz powder was ultrasonically washed with distilled water and dried at 130 °C for 1 h before experiments. No contaminant mineral was detected in quartz powder by X-ray diffraction. The surface area of sample was measured with a BET (Brunauer–Emmet–Teller) argon adsorption apparatus (Beckman, Coulter SA-3100). Initial specific surface area of quartz powder is 0.072 m^2/g. pH of the liquid media was buffered by adding an appropriate volume of HCl–NaCl (pH 1.9) or CH_3COOH–CH_3COONa (pH 3.2, pH 3.5, pH 4.0 and pH 5.0) or KH_2PO_4–Na_2HPO_4 (pH 6.1 and pH 7.2) or H_3BO_4–NaOH (pH 9.1 and pH 9.9), respectively. Ionic strength of a solution was controlled by adding an adequate amount of NaCl. Although the effect of these species on grindability and hydrogen generation was evaluated by grinding quartz samples in 1 M sodium salts of these anions, no crucial effect was observed. Buffer solutions mentioned above were bubbled by pure argon (99.995%) in a glove box (Unico UN-650F, O_2 concentration $<$ 100 ppm) to purge dissolved gases. 5 g of quartz powder, 10 mL of liquid media and 70 g of zirconia beads (5 ϕ) were put in a mill pot. Thereafter the pot was sealed in the glove box to exchange the inner gas phase by argon. Duration time of grinding was 60 min for all experiments. After grinding, suspensions were poured into a polypropylene vessel to measure the pH value (Orion, ROSS pH electrode). In all experiments, the pH change before and after grinding was within 0.3. The gas phase after grinding was sampled by using a gas-tight syringe and was analyzed by gas chromatography (Yanako, G-2700 with MS-5A column, TCD, carrier gas argon). Ground powder was separated by centrifuging and BET surface area was determined.

Figure 1 shows the results of hydrogen analyses as a function of pH of liquid media at the constant values of ionic strength. The concentration of hydrogen gas increases rapidly from pH 2 to 5. At around pH 5, the concentration of hydrogen shows the highest value (57 ppm). Above pH 5, the concentration of hydrogen gradually decreases toward the basic region. Throughout the entire pH range, no ionic strength dependence on the concentration of hydrogen is observed.

Figure 2 shows the results of BET surface area analyses of ground samples. The specific surface area is within the range from about 3.5 to 4 m^2/g and the conspicuous effect of pH on the grindability of quartz powder is not observed. The slightly low values at $I = 1.0$ may be due to adhesion of powders by deposition of NaCl while drying the samples.

Figure 3 shows the relationship between pH values and the amount of generated hydrogen per increase of specific surface

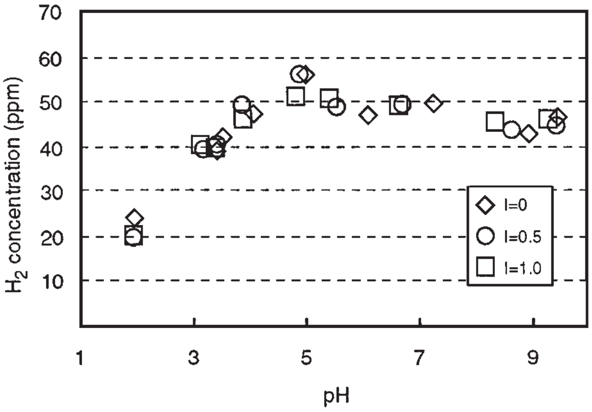

Fig. 1. Hydrogen concentration within mill pot after grinding. Ionic strengths: 1.0 M (□), 0.5 M (○) and 0 M (◇).

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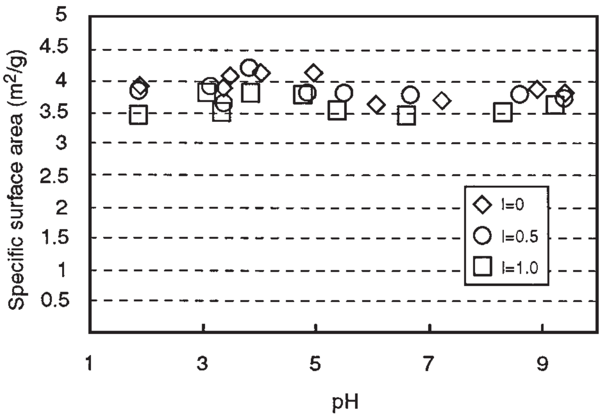

Fig. 2. Specific surface area of powder after grinding. Ionic strengths: 1.0 M (□), 0.5 M (○) and 0 M (◇).

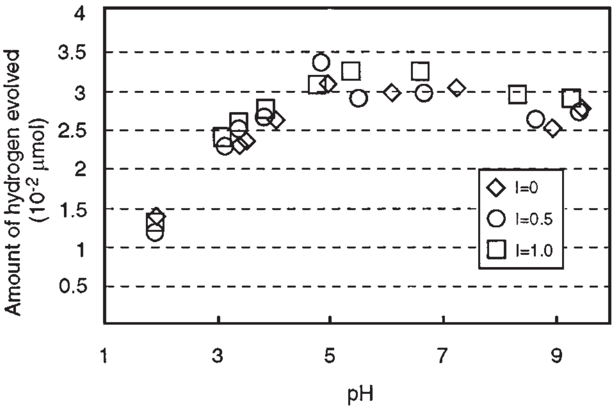

Fig. 3. Amount of hydrogen evolved on 1 m^2/g of fresh quartz surface. Ionic strengths: 1.0 M (□), 0.5 M (○) and 0 M (◇).

area of crushed samples. These results clearly show a dependence of ability of hydrogen formation of fractured quartz surface on the pH of a liquid media. Because there was only a little variation in specific surface area among experiments, Fig. 3 is quite similar to Fig. 1.

The most striking feature of the present result is that hydrogen generation by grinding quartz depends on the pH of the liquid media, particularly in the acidic region. The origin of such an effect is explained by the behavior of OH^- ions as below.

Suzuki et al.[2] discussed the reaction mechanism of hydrogen generation by grinding SiC in water as follows: (1) Scission of silicon–carbon bond and surface mechanoradicals creation, (2) formation of surface hydroxyl groups and (3) hydrogen atom combination to form hydrogen gas.

In the case of quartz, hydrogen is also considered to be formed by similar mechanoradicals on a freshly created surface as follows:[6,7]

$$2{\equiv}\mathrm{Si}\bullet + 2\mathrm{H_2O} \rightarrow 2({\equiv}\mathrm{SiOH}) + \mathrm{H_2} \qquad (1)$$

The radicals on a freshly created surface may react with OH^- ions. The abrupt decrease of the amount of hydrogen in acidic region may be attributed to the decrease of OH^- in the solution. The slight decrease of hydrogen generation at high pH region may be due to the electrical repulsion between the negatively charged silica surface and OH^- ions. This consumption of OH^- ions is also able to explain the pH decrease of the solution by crushing quartz powders in pure water.[8]

According to the experimental results of Suzuki et al.,[2] about 20 μmol of hydrogen was detected by 1 m^2/g of SiC fresh surface. In our experiments, the saturated amount of hydrogen evolved in the pH range from 5 to 9 is about 0.03 μmol by 1 m^2/g of SiO_2 fresh surface (Fig. 3). This is about three orders lower than the amount in the case of SiC powder. It is considered that the minor part of hydrogen atoms combine to form hydrogen, while the major part of hydrogen atoms react with ≡SiO• to form surface silanol as follows:

$$ {\equiv}\mathrm{Si{-}O{-}Si}{\equiv} + \mathrm{H_2O} \rightarrow 2({\equiv}\mathrm{SiOH}) \qquad (2)$$

This mechanochemically induced hydrolysis may result in the amount of hydrogen generation in quartz being much smaller than is the case in SiC.

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