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Fixation of Carbon Dioxide and Production of Hydrogen Gas by Iron Powder at Room Temperature

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In order to reduce the atmospheric concentration of carbon dioxide (CO_2), a greenhouse effect gas, the collection and fixation of the emitted gas must be carried out. In the experiment iron carbonation reaction was examined. Iron powder absorbed CO_2 and converted into carbonate in water at room temperature. One gram of iron powder can absorb 450 ml of CO_2. The important element for successfully and efficiently absorbing CO_2 is maintaining the anaerobic conditions. The rate depended on the partial pressure of CO_2 when a sufficient amount of iron was provided. In this reaction, besides carbonate, hydrogen gas (H_2) with a volume equal to that of absorbed CO_2 was produced by the decomposition of water. The process can reduce CO_2 and supply H_2 simultaneously at low cost especially when waste iron is effectively used.

Key words: carbon dioxide absorption, hydrogen production, iron carbonate, fine particle, ball mill

1. INTRODUCTION

The reduction of CO_2, a greenhouse effect gas is an urgent problem in the world. The emissions-reduction efforts of the gas from industrial plants are promoted, however further reduction will be needed and collection and fixation of the emitted gas must be carried out. [1] Here, we report the CO_2 absorption by metal powder and fixation as carbonate in water medium. Along with the reaction, hydrogen gas, H_2, with a volume equal to that of absorbed CO_2 was produced.

2. EXPERIMENTAL

Pure iron powder (particle size: ~45 μm), water, and CO_2 were mixed together by the following two procedures:

A) Simple mixing of the reactants: Iron powder (10 g) and water (10 ml) were inserted in a 300-ml polypropylene bottle. The bottle was filled with 101.3-kPa CO_2 and sealed. In order to mix the reactants well, the bottle was shaken on a rotation table with a rotation speed of 200 rpm at room temperature.

B) Milling and mixing of the reactants: Iron powder (0.44 g) and water (2 ml) were inserted in a stainless-steel (SUS304) pot with stainless-steel balls with a diameter of half an inch. The inner volume of the pot, subtracting the volume of the 15 balls, is approximately 65 ml. The pot was filled with 101.3-kPa CO_2 and sealed. Milling was performed using a planetary ball mill with a rotation speed of 200 rpm. During milling, the pot was cooled by an air conditioner from the outside at temperatures slightly lower than room temperature. The CO_2-absorbing reaction was repeated three times by substituting the gas in the pot. After the third run, the remaining water was completely evaporated under vacuum; the pot was then opened and dry powder was collected.

While mixing, changes in the gas concentration with time in both the experiments were observed using a gas chromatograph.

3. RESULTS and DISCUSSION

The changes in the gas concentration with time in both the experiments are shown in Fig. 1(a). As the amount of CO_2 decreased, an equal volume of H_2 was generated. In experiment A (without milling), half the CO_2 in the bottle was used within 5 h. By maintaining the shaking, CO_2 reached an undetectable level within 20 h, and the bottle was filled with nearly pure H_2. In experiment B (with milling), though the initial amount of iron per unit CO_2 volume was about one fifth that of experiment A, the reaction rate was considerably higher. CO_2 was repeatedly absorbed three times by refilling the pot. In the second run, half the CO_2 in the bottle was used within only about 15 min. After the complete absorption of CO_2 in the third run, a dark-green-colored powder was collected from the pot. The X-ray diffraction (XRD) pattern of the powder is shown in Figure 2. The pattern was identified as hexagonal $FeCO_3$ (PDF #: 29-696, Siderite). Though a small *contamination* of α-Fe was detected, nearly the entire amount of iron reacted with CO_2 and altered to $FeCO_3$ by the 3-cycle batch processing. The reaction is expressed by the following equation:

$$Fe + H_2O + CO_2 \rightarrow FeCO_3 + H_2 \qquad (1)$$

This equation shows that iron reacts with equimolar H_2O and CO_2 and produces equimolar $FeCO_3$ and H_2. The iron powder used in experiment B (0.44 g) absorbed (65 × 3) ml of CO_2 in equal proportion.

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Reaction (1) can be divided into the following three processes: (i) CO_2 dissolution into water to produce carbonic acid, which ionizes to form protons and a carbonate ion ($CO_2(g) \rightarrow CO_2(aq)$, $CO_2(aq) + H_2O \rightarrow H_2CO_3 \rightarrow 2H^+ + CO_3^{2-}$). (ii) Redox reaction between iron and protons ($Fe + 2H^+ \rightarrow Fe^{2+} + H_2$). (iii) Precipitation of $FeCO_3$ by the reaction of ferrous and carbonate ions ($Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3$). Metals such as iron powder are easily oxidizable. Although the dissolution of CO_2 (step (i)) does not proceed easily, the generated protons are readily removed by iron (step (ii)). This removal promotes further ionization of H_2CO_3 and the dissolution of CO_2 in water. Basically, reaction (1) proceeds spontaneously as an exothermic reaction ($\Delta H = -68$ kJ mol^{-1}). It has been reported that by heating at a higher temperature than room temperature, iron nano-particles react with H_2O to produce H_2 and oxidize to Fe_3O_4 [2]. With regard to H_2 production at room temperature in the present experiment, CO_2 acts as a promoter by producing carbonic acid in water. Although CO_2 is highly undesirable with regard to global warming, it can be used effectively for H_2 production.

The reaction in experiment B could be accelerated by milling, which mainly contributes to the efficient supply of iron. Fresh non-oxidized surfaces are supplied continuously by breaking the solid material, and at the same time the specific surface of the particles are increased by pulverization. The mechanical process also facilitates the total mass transfer by intensive agitation. Simultaneously, iron might become self-energized due to its stored mechanical energy and further promote the reaction; this mechano-chemical effect is observed sometimes and is used for the synthesis of a variety of solid phases [3].

The reaction rates were varied during the three runs of experiment B. The micronized iron in the order of several micrometres by milling accelerates the reaction in the second run. In the third run, the rather slow reaction is attributed to the limited amount of iron available after the first and the second run. Figure 1(b) shows an enlarged graph of the partial pressure of CO_2 in the second run. This pressure decreases exponentially with time, and the t-log(p_{CO2}) plot (inset in Figure. 1(b)) shows a roughly linear relation. The rate constant k is determined from the slope of the line to be 0.048 by the weighted (1/t) least-square method, i.e.

$$\ln(p_{CO2}/p_{CO2,init}) = -kt, \quad k = 0.048 \qquad (2)$$

where p is the partial pressure and t is the time in minutes. In the reaction the rate equation is $v = kp_{CO2}$; therefore, the reaction is first order in p_{CO2} It is known that the rate-determining step is the dissolution of CO_2 ($CO_2(g) \rightarrow CO_2(aq)$, step (i)) during carbonation [4], this is also the case in this reaction. This condition is kept only in the second run in which a sufficient amount of iron is present. Thus, it was proved that both sufficient supply of fresh iron and promotion of the dissolution of CO_2 into water speed the reaction.

An important element for efficiently and successfully absorbing CO_2 is maintaining the airtight conditions. Although the large surface area of the fine iron particles accelerates the reaction, such particles are naturally active and are easily oxidized by O_2. Therefore, the simultaneous pulverization and reaction with CO_2 and H_2O in the milling pot under anaerobic conditions is an effective method. It is known that iron carbonate is stable in dry air but decomposes slowly in wet air. Therefore, in order to avoid the decomposition of $FeCO_3$

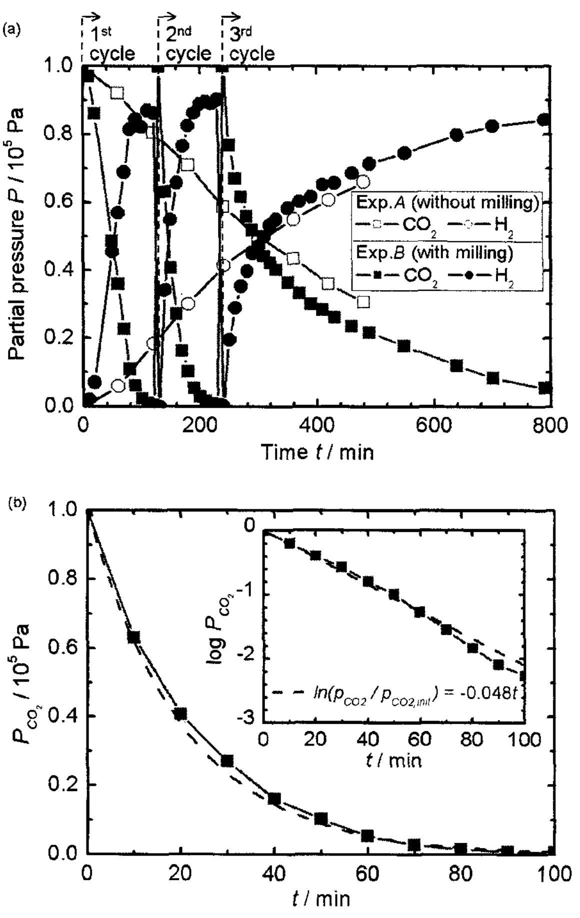

Fig. 1 (a) Decrease in CO_2 and increase in H_2 with time during iron carbonation reaction. (b) Focus on the CO_2 decrease in the second run of experiment B. The inset is the t-log(p_{CO2}) plot.

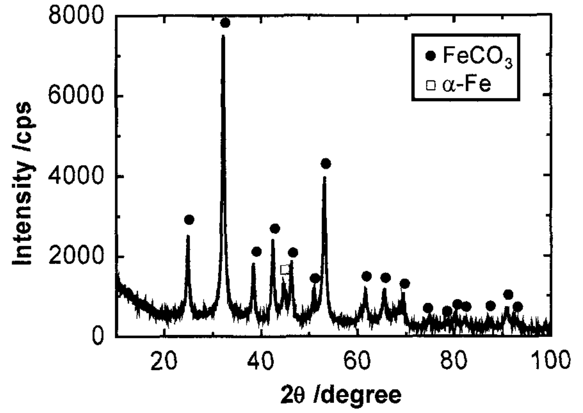

Fig. 2 XRD pattern of the collected iron carbonate ($FeCO_3$) observed using X-ray CuKα radiation.

to iron oxide in moist air, $FeCO_3$ should be carefully dried before airing.

There are some reports [5, 6] describing the chemical conversion of CO_2 using the iron oxidation reaction. Their processes differ from the present one in that no water is used and CO_2 is decomposed to carbon at temperature higher than room temperature (around 300 °C). Guan et al. observed the generation of H_2 and CH_4 at room temperature from the mixture of iron powder, water and CO_2.[7] However, the yields of both compounds were very small, and the reduction of CO_2 as a result of the conversion to CH_4 was small in their experiment. In our experiment, trace amounts of CH_4 were detected; however, most of the CO_2 converted to iron carbonate. The fixing amount per unit mass of iron is higher than many other CO_2 absorbing materials. It is more than double that of lithium silicate [8], a ceramic absorbent, which has recently been developed.

In the present experiment, steel obtained from beverage cans or stainless steel as the iron material was also used, and CO_2 absorption and H_2 production were observed. Among metals, iron is the cheapest and common, and a large amount of steel has been used as various materials; thus, they are easily available at a low cost. A large amount of scrap iron is emitted, and the amount is increasing now. The scrap can be recycled as steel, but it will be in a state of excess-supply in near future [8]. Thus such scrap will be used effectively for CO_2 reduction. The reaction could be also carried out using another metal. Fine manganese powder simply mixed with H_2O absorbed CO_2 to produce manganese carbonate—$MnCO_3$.

Because the reaction is simple and progresses at room temperature, the CO_2-treating system can be easily realized. It has many advantages such as low cost, easy scale-up, high efficiency, and additional profit due to H_2 production. Currently, the steam reforming of fossil fuels is mainly used for H_2 production. If the mixed gas of H_2 and CO_2 obtained by the reforming is treated by the present process, both CO_2 removal and H_2 production in addition to those produced by the reforming process can be realized on site. This process will contribute to both preventing the global warming and providing clean energy by efficiently using scrap, the production of which is another environmental problem; thus, it can greatly contribute to solving environmental issues.

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