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Author(s)	Hiraki, Takehito; Hiroi, Shun; Akashi, Takuya et al.
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Chemical equilibrium analysis for hydrolysis of magnesium hydride to generate hydrogen

Takehito Hiraki^a, Shun Hiroi^b, Takuya Akashi^b, Noriyuki Okinaka^b and Tomohiro Akiyama^{b,*}

^aGraduate School of Environmental Studies, Tohoku University, 6-6-11-1004, Aza-Aoba Aramaki, Aoba-ku, Sendai 980-8579, Japan

^bCenter for Advanced Research of Energy and Materials, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan

*Corresponding author: Phone: +81-11-706-6842, Fax: +81-11-726-0731,

Email: takiyama@eng.hokudai.ac.jp

Abstract

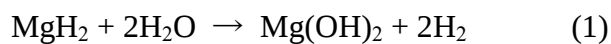
Magnesium hydride is a promising hydrogen source because of its high mass density of hydrogen, 15.2%, when it is hydrolyzed; $\text{MgH}_2 + 2\text{H}_2\text{O} = \text{Mg(OH)}_2 + 2\text{H}_2 + 277 \text{ kJ}$. However, a magnesium hydroxide, Mg(OH)_2 , layer forms rapidly on the surface of the unreacted MgH_2 as the pH increases, hindering further reaction. The purpose of this study is to find acids that could effectively accelerate the reaction by using a chemical equilibrium analysis where the relationships of pH to concentration of ionized Mg were calculated. For the best performing acid, the calculated and measured relationships were compared, and the effects of acid concentration on hydrogen release were measured. The analysis revealed that citric acid and ethylenediamine-tetraacetic acid were good buffering agents. The calculated and measured relationships between pH and concentration of ionized Mg were in good accord. Hydrogen release improved considerably in a relatively dilute citric acid solution instead of pure distilled water. The maximum amount of hydrogen generated was $1.7 \times 10^3 \text{ cm}^3 \cdot \text{g}^{-1}$ at STP after 30 min. We estimated the exact concentration of citric acid solution for complete MgH_2 hydrolysis by a chemical equilibrium analysis method.

Keywords; Hydrolysis, Equilibrium analysis, Magnesium hydride, Hydrogen, Buffer

capacity

1. Introduction

Metal hydrides are a hot topic of discussion among the modern scientific community worldwide because they are used for storage and transport of hydrogen as well as for use in heat pumps as a cold energy supply [1–4] and hydrogen generator [5, 6]. Hydrogen is considered clean energy with a large combustion value that can be used in internal combustion engines or fuel cells. The need for compact, safe, and inexpensive hydrogen sources is a key issue for the development of fuel cells. One of the most attractive metal hydrides for hydrogen generation is magnesium hydride, (MgH_2) [7–17]. It is an especially promising material owing to its quite high hydrogen capacity of 7.6 mass% and relatively low production cost. Saita *et al.*, demonstrated that MgH_2 can be produced by hydriding chemical vapor deposition (HCVD) in which the MgH_2 absorbs and desorbs as much as 7.6 mass% hydrogen without any activation treatments [18–20], and clarified that the total exergy loss of metal hydride production process without activation treatment is smaller than conventional process [21]. Hydrogen is generated by MgH_2 hydrolysis according to the following reaction:



$$\Delta H_{298}^0 = -277 \text{ kJ}$$

$$\Delta G_{298}^0 = -323 \text{ kJ}$$

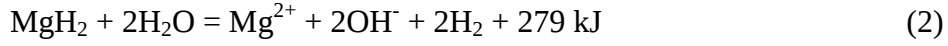
In fuel cell applications, if the water produced by the fuel cell is redirected to MgH_2 hydrolysis, the density of hydrogen increases to 15.2 mass%. Moreover, this reaction has the advantage that the residual magnesium hydroxide is environmentally friendly. However, the hydrolysis of MgH_2 is rapidly hindered by the formation of a passive $\text{Mg}(\text{OH})_2$ layer on top of the reactive material as the pH increases. This is the major problem with generating hydrogen by MgH_2 hydrolysis. Acids, with or without the use of catalysts, can suppress the formation of $\text{Mg}(\text{OH})_2$ by decreasing the pH [7, 8, 15]. For example, the kinetics of MgH_2 and Mg hydrolysis were determined by using weak acids or sodium chloride solutions with platinum catalysts [8]. Several studies have used metallic powders with high chemical activity via a ball-milling method [7, 9–16]. However, acids in general are detrimental to equipment and are potential hazards for users, and the price of using catalysts may make their widespread use impractical. In addition, the preparation of ball-milled powders typically requires a large energy input.

The purpose of this study was to use chemical equilibrium analysis to find an effective acid to accelerate the hydrolysis reaction. The main calculation was the effect of the weak-acid on the concentration of ionized Mg after hydrolysis of MgH_2 at room temperature. Thus, we found an effective weak acid for MgH_2 hydrolysis at room temperature without catalysts or ball-milling. Additionally, two experiments were

implemented based on the analysis. In the first experiment, the relationship between the pH and the concentration of ionized Mg was investigated. In the second experiment, the effects of weak-acid concentration on hydrogen generation were investigated.

2. Equilibrium Analysis

Equation (1) can be divided into the following equations:



When MgH_2 is hydrolyzed, the pH increases with the release of OH^- . As a result, $\text{Mg}(\text{OH})_2$ is generated on the surface of MgH_2 , because of the high local concentration of magnesium. In equation (2), the pH change is calculated as follows. Ion balance before the hydrolysis of MgH_2 is expressed by the following equation:

$$[\text{H}^+]_b = [\text{OH}^-]_b + [\text{HCO}_3^-]_b + 2[\text{CO}_3^{2-}]_b \quad (4)$$

The subscript b indicates concentrations before hydrolysis of MgH_2 , and the carbonate ions are derived from CO_2 in the air. Table 1 gives the reaction equations and their equilibrium constants at a temperature of 298 K.

By equation (4) and the equilibrium constants, the pH before hydrolysis, $\text{pH}_b = -\log[\text{H}^+]_b$, is determined solely by $p\text{CO}_2$ (0.037%). The ion balance after hydrolysis is written as equation (5-1).

$$[\text{H}^+]_a + 2[\text{Mg}^{2+}]_a = [\text{OH}^-]_a + [\text{HCO}_3^-]_a + 2[\text{CO}_3^{2-}]_a \quad (5-1)$$

The subscript a denotes concentrations after hydrolysis of MgH_2 . Manipulating equation (5-1), we show that the concentration of magnesium ions after hydrolysis of MgH_2 is

given by the following equation:

$$[\text{Mg}^{2+}]_a = (-[\text{H}^+]_a + [\text{OH}]_a + [\text{HCO}_3^-]_a + 2[\text{CO}_3^{2-}]_a) / 2 \quad (5-2)$$

Substituting the constants into equation 5-2 allows the concentration of magnesium to be calculated by determining the pH after the hydrolysis. In this analysis, $[\text{Mg}^{2+}]_a$ was calculated in pH intervals of 0.1. Figure 1 shows the relationship between $[\text{Mg}^{2+}]_a$ and pH after the hydrolysis of MgH_2 and the solubility curve of $\text{Mg}(\text{OH})_2$ at 25°C. When $[\text{Mg}^{2+}]_a$ is high, the pH after the hydrolysis is likewise high. When the $[\text{Mg}^{2+}]_a$ reaches 7 $\text{mmol} \cdot \text{dm}^{-3}$, the $[\text{Mg}^{2+}]_a$ curve crosses the solubility curve of $\text{Mg}(\text{OH})_2$. This calculation suggested that beyond 7 $\text{mmol} \cdot \text{dm}^{-3}$, further dissolution of MgH_2 was hindered by the deposition of $\text{Mg}(\text{OH})_2$ on its surface.

Figure 2 presents several methods to promote MgH_2 hydrolysis. The $\text{Mg}(\text{OH})_2$ layer can be cracked, or fine MgH_2 particles with greater surface area can be used. Heating the solution would be expected to increase the rate constant of the MgH_2 hydrolysis. In addition, acetic acid as a buffer, citric acid as a chelator, or zeolite as an ion-exchanger are considered promising additives to accelerate MgH_2 hydrolysis by preventing $\text{Mg}(\text{OH})_2$ formation. In this analysis, several acids in a range of concentrations were evaluated to buffer the solution during the hydrolysis.

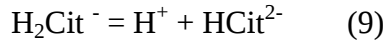
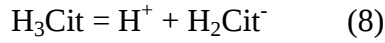
The buffer capacities of the acids were evaluated according to the example

below for citric acid. Ion balance equations for before and after the hydrolysis are shown as equations (6) and (7-1) respectively.

$$\begin{aligned}
 [\text{H}^+]_{\text{b}} &= [\text{OH}^-]_{\text{b}} + [\text{HCO}_3^-]_{\text{b}} + 2[\text{CO}_3^{2-}]_{\text{b}} \\
 &+ [\text{H}_2\text{Cit}^-]_{\text{b}} + 2[\text{HCit}^{2-}]_{\text{b}} + 3[\text{Cit}^{3-}]_{\text{b}}
 \end{aligned} \quad (6)$$

$$\begin{aligned}
 [\text{H}^+]_{\text{a}} + 2[\text{Mg}^{2+}]_{\text{a}} &= [\text{OH}^-]_{\text{a}} + [\text{HCO}_3^-]_{\text{a}} + 2[\text{CO}_3^{2-}]_{\text{a}} \\
 &+ [\text{H}_2\text{Cit}^-]_{\text{a}} + 2[\text{HCit}^{2-}]_{\text{a}} + 3[\text{Cit}^{3-}]_{\text{a}}
 \end{aligned} \quad (7-1)$$

Here, Cit refers to $\text{C}_6\text{H}_5\text{O}_7$. Equations for the dissociation of citric acid are given below.



Finally, the material balance of citric acid is represented by the following equation.

$$\text{Total Cit (mol}\cdot\text{dm}^{-3}) = [\text{H}_3\text{Cit}] + [\text{H}_2\text{Cit}^-] + [\text{HCit}^{2-}] + [\text{Cit}^{3-}] \quad (11-1)$$

The buffer capacities of many different acids were calculated according to the two equations of ion and material balance (6 and 7-1). Figure 3 shows the effect of acid on the pH buffer capacity at $1 \text{ mol}\cdot\text{dm}^{-3}$ on the rate of MgH_2 hydrolysis. The magnesium concentration at the intersection of the buffer capacity and solubility curves indicated the dissolution ratio of MgH_2 before $\text{Mg}(\text{OH})_2$ forms. Citric acid and ethylenediamine-tetraacetic acid (EDTA) have $[\text{Mg}^{2+}]_{\text{a}}$ curves that intersected the

solubility curve of $\text{Mg}(\text{OH})_2$ at much higher concentrations than the other acids. This result indicates that citric acid and EDTA have good buffer capacities and thus accelerate MgH_2 hydrolysis. Additionally, citric acid and EDTA could chelate metal ions. From these results, citric acid was selected as a buffering agent to accelerate MgH_2 hydrolysis in this work.

When MgH_2 is hydrolyzed in a citric acid solution, magnesium citrate ions are generated. As a result, the magnesium citrate ions needed to be taken into consideration in the equations of ion and material balance. The two modified equations are given as (7-2) and (11-2) respectively.

$$[\text{H}^+]_a + 2[\text{Mg}^{2+}]_a = [\text{OH}^-]_a + [\text{HCO}_3^-]_a + 2[\text{CO}_3^{2-}]_a + [\text{H}_2\text{Cit}^-]_a + 2[\text{HCit}^{2-}]_a + 3[\text{Cit}^{3-}]_a + [\text{MgCit}^-] \quad (7-2)$$

$$\begin{aligned} \text{Total Cit (mol} \cdot \text{dm}^{-3}) \\ = [\text{H}_3\text{Cit}] + [\text{H}_2\text{Cit}^-] + [\text{HCit}^{2-}] + [\text{Cit}^{3-}] + [\text{MgCit}^-] \end{aligned} \quad (11-2)$$

According to these equations, the concentrations of magnesium ions and magnesium citrate ions were calculated by determining the pH after hydrolysis and applying them to the above equations. Figure 4 shows the calculated relationships among $[\text{Mg}^{2+}]_a$, $[\text{MgCit}^-]_a$, and pH_a when MgH_2 is hydrolyzed in citric acid solutions of 0, 0.01, 0.02, 0.05, and 0.1 $\text{mol} \cdot \text{dm}^{-3}$. The sum of $[\text{Mg}^{2+}]_a$ and $[\text{MgCit}^-]_a$ gives the total amount of

MgH_2 that has dissolved and depends on a value of $[\text{Mg}^{2+}]$. Then, the maximum amount of MgH_2 dissolution depends on the maximum value of $[\text{Mg}^{2+}]_a$, which is the intersection of the $[\text{Mg}^{2+}]_a$ curve and the solubility curve of $\text{Mg}(\text{OH})_2$. In other words, a higher intersection means a larger amount of MgH_2 will dissolve. In Fig. 4, the intersection of the $[\text{Mg}^{2+}]_a$ curve and the solubility curve rises with increasing citric acid concentration. The amount of MgH_2 that could dissolve in a citric acid solution of $0.1 \text{ mol}\cdot\text{dm}^{-3}$, calculated from the sum of the maximum values of $[\text{Mg}^{2+}]_a$ and $[\text{MgCit}^-]_a$, was more than 25 times that which could dissolve in only water ($0 \text{ mol}\cdot\text{dm}^{-3}$). Therefore, instead of plain water, citric acid as a buffering agent should greatly accelerate the hydrolysis of MgH_2 .

3. Experimental

In the first experiment, the pH and concentration of ionized Mg after the hydrolysis reaction was investigated. MgH_2 was formed into particles by gas-solid reaction (GSR), 99.9 % pure by mass (Biocoke Lab. Co., Pty.), with an average particle size of 60 μm . Ten MgH_2 samples were prepared with different masses; from 0.020 g to 0.20 g in intervals of 0.020 g. The samples were soaked in 100 cm^3 of 0.05 $\text{mol}\cdot\text{dm}^{-3}$ citric acid and stirred for 24 h. Then, the pH and the concentration of ionized Mg were measured with a pH meter (MP125, Mettler Toledo Co., Ltd.) and inductively-coupled plasma atomic emission spectrometry (ICP-AES, iCAP 6300 DUO, Thermo Electron Co., Ltd.) respectively.

In the second experiment, hydrogen release was investigated. Figure 5 shows the experimental setup for investigating the MgH_2 hydrolysis in various concentrations of citric acid. The apparatus consisted of two sections, one for hydrolysis and the other for hydrogen collection. The hydrolysis section consisted of a 500 cm^3 reaction flask charged with 0.1 g of MgH_2 powder set in a constant-temperature water bath adjusted to 25°C and thermistor thermometers set in the reactor and water bath. In the hydrogen collection section, a 250 cm^3 measuring cylinder filled with water was set in a water bath, and the reactor and the measuring cylinder were connected by a teflon tube having

an inner diameter of 2 mm and length of 1100 mm. Citric acid solutions of 0.005, 0.01, 0.02, 0.05, and 0.1 mol·dm⁻³ were prepared by dissolving the powdered reagent (>99.5 % by mass, Kishida Chemical Co., Pty.) in distilled water. The citric acid solution and distilled water were preheated to 25°C in a constant-temperature bath. At the beginning of the experiment, 100 cm³ of the citric acid solution was added to the reactor. The hydrogen generated during the experiment passed through the teflon tube and was collected by the water substitution method. The amount of hydrogen generated was evaluated from the volume and temperature data. The volume changes were monitored by the naked-eye at intervals of 30 s from 0 to 5 min, 60 s from 5 to 10 min, and 120 s from 10 to 30 min. The reaction degree, f , was calculated by the following equation:

$$\text{Reaction degree, } f (\%) = \frac{V_{H_2} P M_{MgH_2}}{2 \Theta_{MgH_2} W_{MgH_2} R T} \times 100 \quad (12)$$

Here, V_{H_2} , P , M_{MgH_2} , Θ_{MgH_2} , W_{MgH_2} , R , and T indicate the measured gas volume (m³), standard pressure (1.00×10^5 Pa), molar weight of MgH₂ (g), purity of the MgH₂ sample (-), weight of the MgH₂ sample (g), gas constant (8.314 J·mol⁻¹·K⁻¹), and gas temperature (K), respectively.

4. Results and Discussion

Figure 6 shows the calculated and measured relationships between the pH and the concentration of ionized Mg in the $0.05 \text{ mol}\cdot\text{dm}^{-3}$ citric acid solution. The measured and calculated curves for the sum of $[\text{Mg}^{2+}]$ and $[\text{MgCit}^-]$ were very close. The chemical equilibrium analysis was confirmed to be precise.

Figure 7 shows the hydrogen release of the MgH_2 hydrolysis in different concentrations of citric acid: 0 (distilled water), 0.01, 0.02, 0.05, and $0.1 \text{ mol}\cdot\text{dm}^{-3}$. After 30 min in distilled water, the reaction progress was limited to only 13% because the passive $\text{Mg}(\text{OH})_2$ layer formed on the surface of the unreacted MgH_2 , as expected. In contrast, with citric acid, the hydrogen release improved considerably. Both the rate and degree of hydrogen evolution increased with higher concentrations of citric acid. With the low concentration ($0.01 \text{ mol}\cdot\text{dm}^{-3}$), the reaction proceeded to 40% after 30 min. The reaction in $0.1 \text{ mol}\cdot\text{dm}^{-3}$ citric acid went to 99% of completion after 30 min, 7.7 times as far as in distilled water. During the experiment, the solution temperature remains constant at 298 K regardless of the citric acid concentration.

Comparing the hydrogen release (Fig. 7) with the calculated pH and concentration of ionized Mg (Fig. 4) showed that the hydrogen release reflected the results of the calculated pH and concentration of ionized Mg. The second vertical axis

of Fig. 4 refers to the amount of MgH_2 that should dissolve per 100 cm^3 of solution. This makes the intersection of $0.1 \text{ mol}\cdot\text{dm}^{-3}$ and the curve of the calculated sum of Mg^{2+} and MgCit^- very important because the ratio between MgH_2 and citric acid concentration was the same as that seen in the above experimental conditions. With citric acid concentrations of 0.05 and $0.1 \text{ mol}\cdot\text{dm}^{-3}$, the curves intersected in the area where Mg^{2+} is stable; thus, a $\text{Mg}(\text{OH})_2$ layer should not have formed and the hydrolysis reaction should have proceeded unhindered. In the other cases, there are no intersections; therefore, the $\text{Mg}(\text{OH})_2$ layer should form to suppress the hydrolysis. The experimental results were consistent with the calculations as 0.05 and $0.1 \text{ mol}\cdot\text{dm}^{-3}$ citric acid solutions achieved nearly 100% reaction degree, whereas in the 0 , 0.01 , and $0.02 \text{ mol}\cdot\text{dm}^{-3}$ citric acid solutions, the reactions stalled out before completion.

These results showed that calculations corresponded closely with the measured results. By this chemical equilibrium analysis method, we can estimate that the exact concentration of citric acid solution necessary for MgH_2 hydrolysis. This method will make MgH_2 much more attractive as a hydrogen source.

5. Conclusions

A chemical equilibrium analysis was carried out on the formation of $\text{Mg}(\text{OH})_2$ during MgH_2 hydrolysis with various weak acids, and the effects of the selected acid at various concentrations on hydrogen generation were evaluated experimentally. The three main results are shown below:

- 1) Citric acid and ethylenediamine-tetraacetic acid have good capacity as pH buffering agents for accelerating the hydrolysis reaction of MgH_2 at room temperature than tartaric, phosphoric, formic, phthalic, acetic, oxalic, and benzoic acids.
- 2) The hydrogen release was considerably improved by using a low concentration of citric acid solution instead of only distilled water.
- 3) The calculated relationships between pH and the concentration of ionized Mg by the chemical equilibrium analysis corresponded well with the measured results. The exact concentration of citric acid necessary for complete MgH_2 hydrolysis can be easily estimated.

MgH_2 is a promising hydrogen generator for fuel cells and other energy storage systems. A citric acid solution effectively promotes MgH_2 hydrolysis at room temperature without catalysts or ball-milling.

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Table 1 Equations and equilibrium constants

Equations	Equilibrium constant, K
$[\text{H}_2\text{CO}_3] / p\text{CO}_2$	3.50×10^{-2}
$[\text{H}^+][\text{HCO}_3^-] / [\text{H}_2\text{CO}_3]$	4.31×10^{-7}
$[\text{H}^+][\text{CO}_3^{2-}] / [\text{HCO}_3^-]$	4.68×10^{-11}
$[\text{H}^+][\text{H}_2\text{PO}_4^-] / [\text{H}_3\text{PO}_4]$	5.90×10^{-3}
$[\text{H}^+][\text{HPO}_4^{2-}] / [\text{H}_2\text{PO}_4^-]$	6.22×10^{-8}
$[\text{H}^+][\text{PO}_4^{3-}] / [\text{HPO}_4^{2-}]$	3.87×10^{-13}
$[\text{H}^+][\text{CH}_3\text{COO}^-] / [\text{CH}_3\text{COOH}]$	1.55×10^{-5}
$[\text{H}^+][\text{H}_3\text{Y}^-] / [\text{H}_4\text{Y}^*]$	1.00×10^{-2}
$[\text{H}^+][\text{H}_2\text{Y}^{2-}] / [\text{H}_3\text{Y}^-]$	2.10×10^{-3}
$[\text{H}^+][\text{HY}^{3-}] / [\text{H}_2\text{Y}^{2-}]$	6.90×10^{-7}
$[\text{H}^+][\text{Y}^{4-}] / [\text{HY}^{3-}]$	6.00×10^{-11}
$[\text{H}^+][\text{COOHCOO}^-] / [(\text{COOH})_2]$	5.60×10^{-2}
$[\text{H}^+][(\text{COO})_2^{2-}] / [\text{COOHCOO}^-]$	5.20×10^{-5}
$[\text{H}^+][\text{C}_6\text{H}_5\text{COO}^-] / [\text{C}_6\text{H}_5\text{COOH}]$	6.30×10^{-5}
$[\text{H}^+][\text{H}_2\text{Cit}^-] / [\text{H}_3\text{Cit}^{**}]$	7.40×10^{-4}
$[\text{H}^+][\text{HCit}^{2-}] / [\text{H}_2\text{Cit}^-]$	1.80×10^{-5}
$[\text{H}^+][\text{Cit}^{3-}] / [\text{HCit}^{2-}]$	4.00×10^{-7}

$[\text{H}^+][\text{HCOO}^-] / [\text{HCOOH}]$	1.70×10^{-4}
$[\text{H}^+][\text{C}_6\text{H}_5\text{O}^-] / [\text{C}_6\text{H}_5\text{OH}]$	1.10×10^{-10}
$[\text{H}^+][\text{C}_6\text{H}_4\text{COOH}(\text{COO})^-] / [\text{C}_6\text{H}_4(\text{COOH})_2]$	1.10×10^{-3}
$[\text{H}^+][\text{C}_6\text{H}_4(\text{COO})_2^{2-}] / [\text{C}_6\text{H}_4\text{COOH}(\text{COO})^-]$	3.90×10^{-6}
$[\text{H}^+][\text{HC}_4\text{H}_4\text{O}_6^-] / [\text{H}_2\text{C}_4\text{H}_4\text{O}_6]$	9.10×10^{-4}
$[\text{H}^+][\text{C}_4\text{H}_4\text{O}_6^{2-}] / [\text{HC}_4\text{H}_4\text{O}_6^-]$	4.30×10^{-5}
$[\text{Mg}^{2+}][\text{OH}^-]$	4.03×10^{-12}
$[\text{Mg}^{2+}][\text{Cit}^{3-}] / [\text{MgCit}^-]$	2.80×10^{-4}
$[\text{H}^+][\text{OH}^-]$	1.01×10^{-14}

*H₄Y: C₂H₄[N(CH₂COOH)₂]₂ ** H₃Cit: H₃C₆H₅O₇

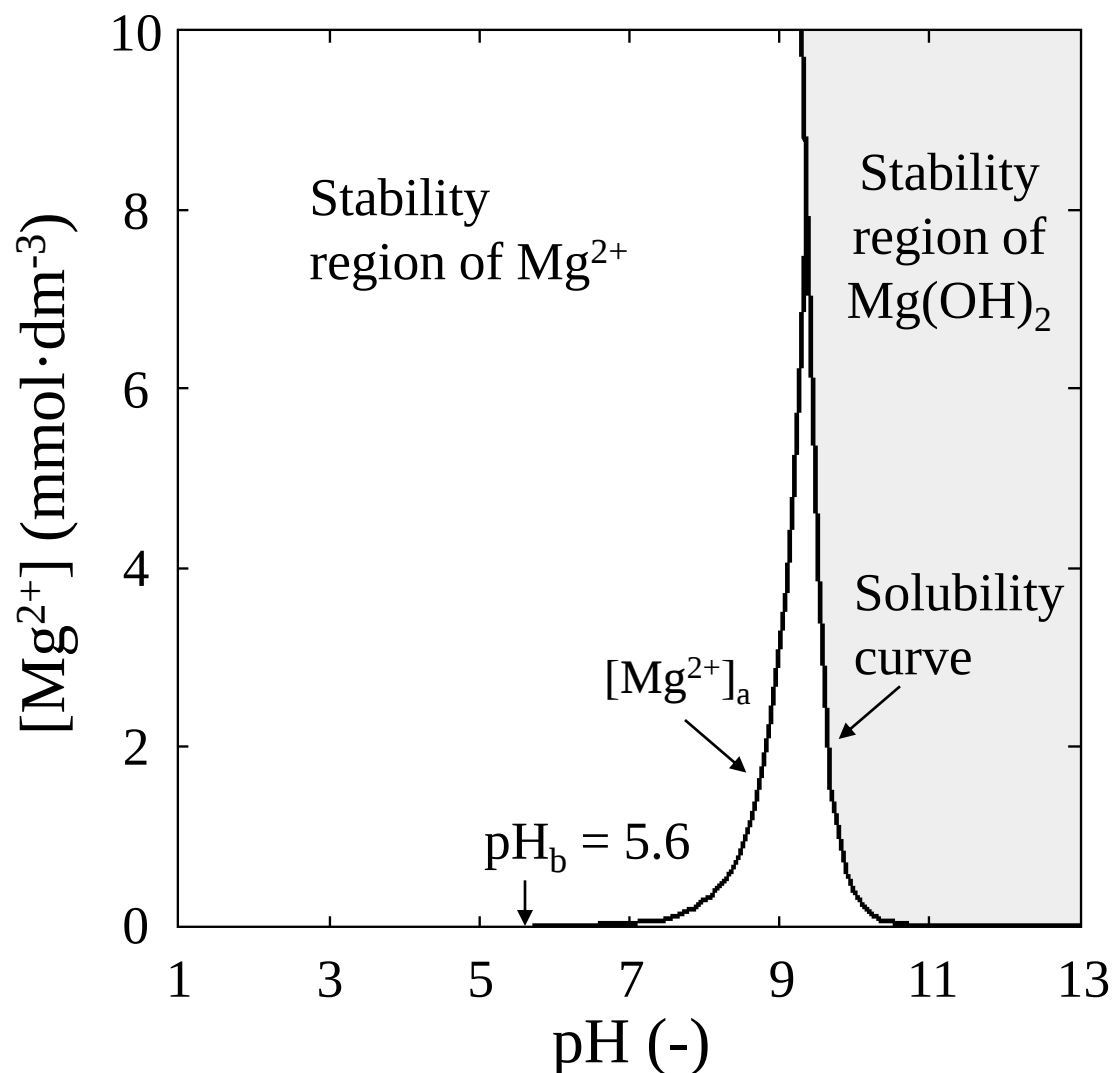


Fig.1 Relationship of magnesium ion and pH in the solution after hydrolysis of MgH_2 with water and the solubility curve of $\text{Mg}(\text{OH})_2$ at temperature of 25°C . Note that the subscripts a and b indicate the after and before hydrolysis reaction.

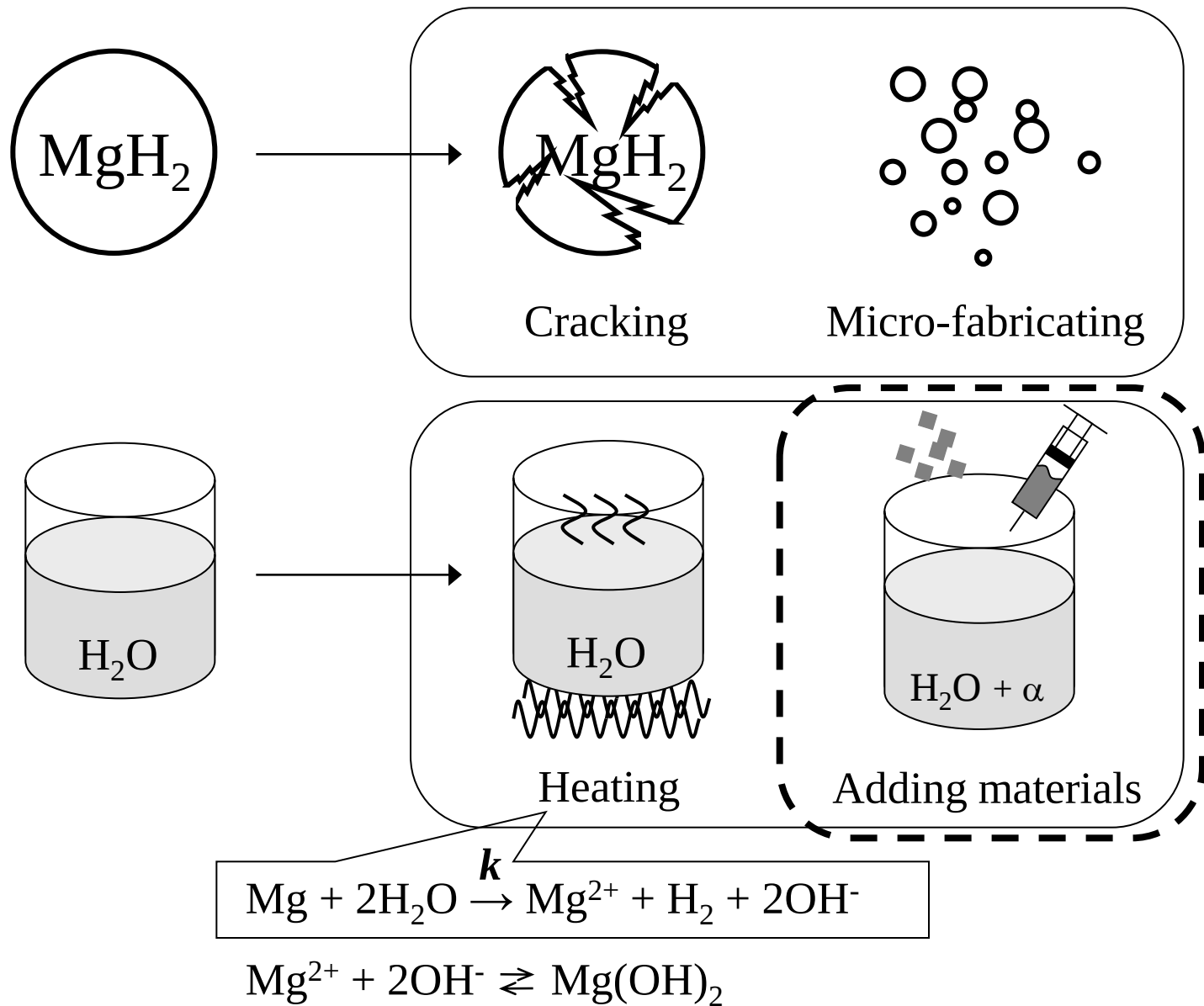


Fig. 2 Several processing for accelerating of MgH_2 hydrolysis.

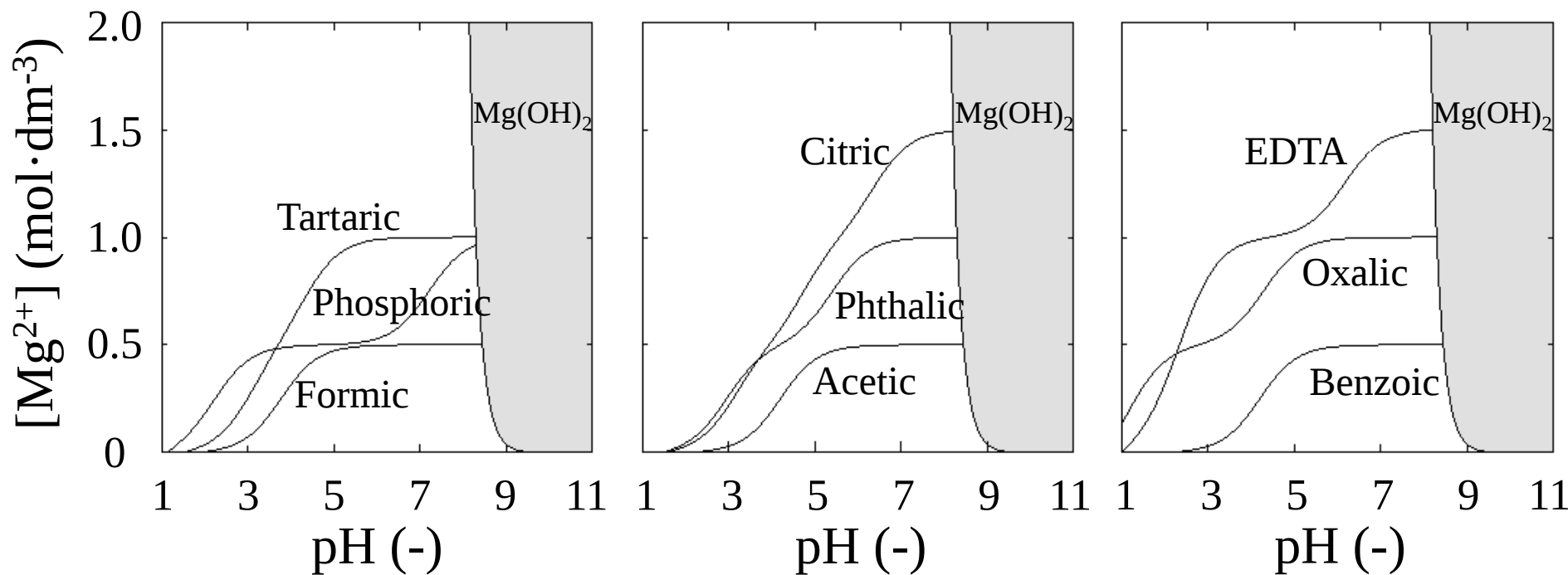


Fig.3 Effect of acid type on buffer capacity of pH under MgH_2 hydrolysis. The concentration of acid is $1.0 \text{ mol}\cdot\text{dm}^{-3}$ and the temperature of the solution is 25°C .

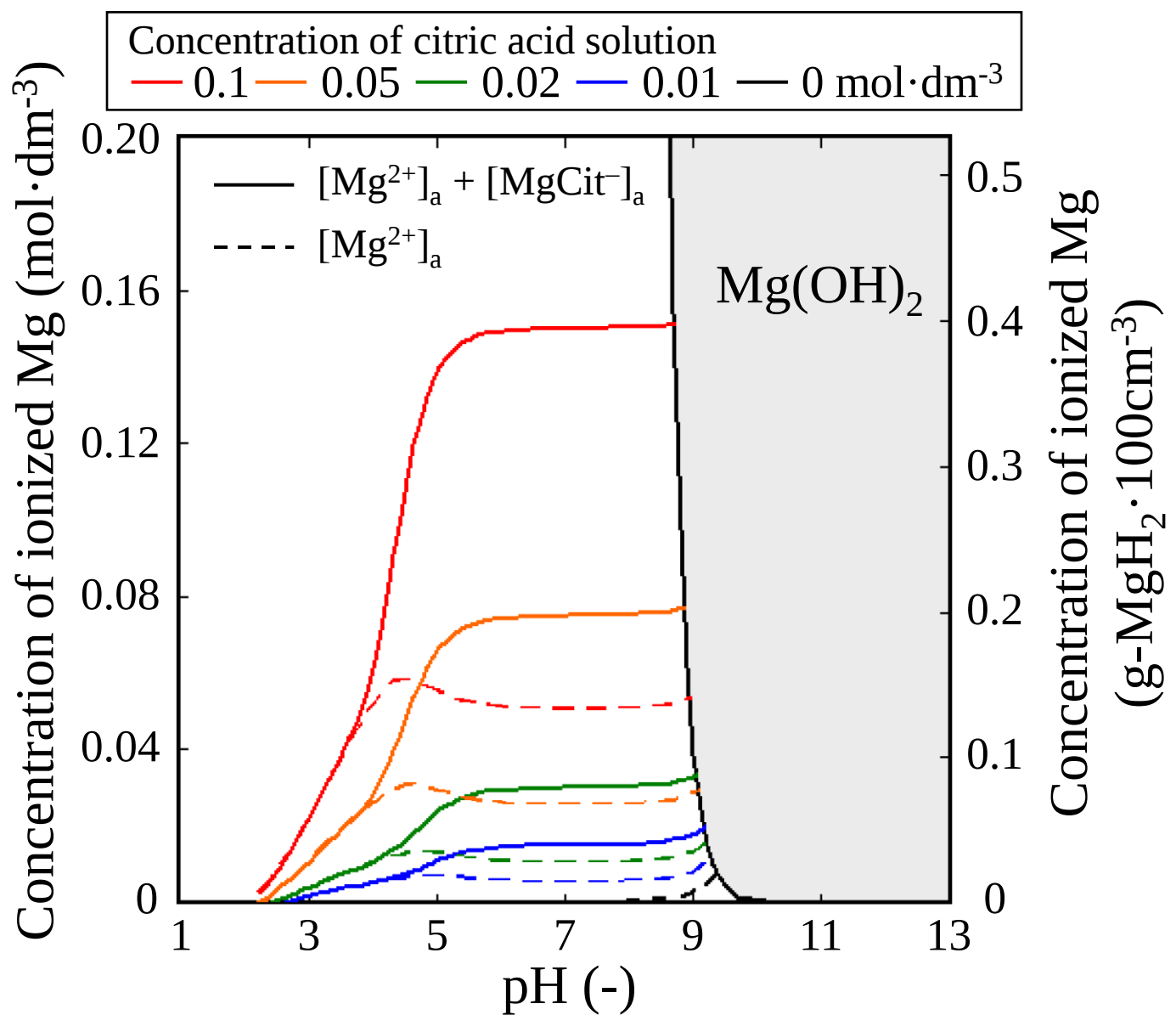


Fig.4 Effect of concentration of citric acid on buffer capacity of pH under MgH₂ hydrolysis in temperature of 25 °C.

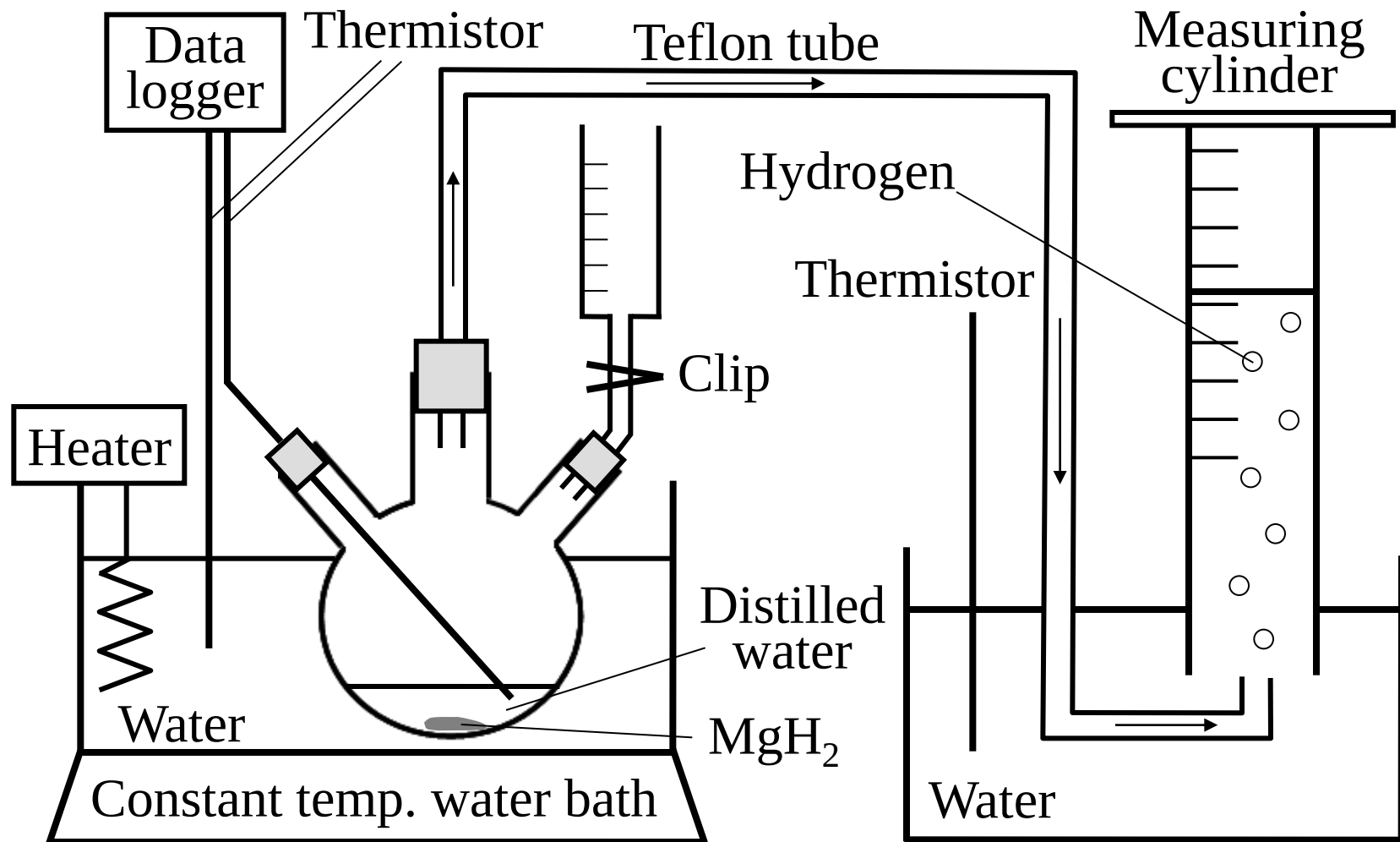


Fig.5 Schematic diagram of the experimental setup for measuring the amount of hydrogen generated from the hydrolysis of MgH_2 .
 100 cm³ of distilled water or citric acid solution was added to the reactor containing 0.1g of MgH_2 at 25 °C and the generated H_2 was collected by a water substitution method.

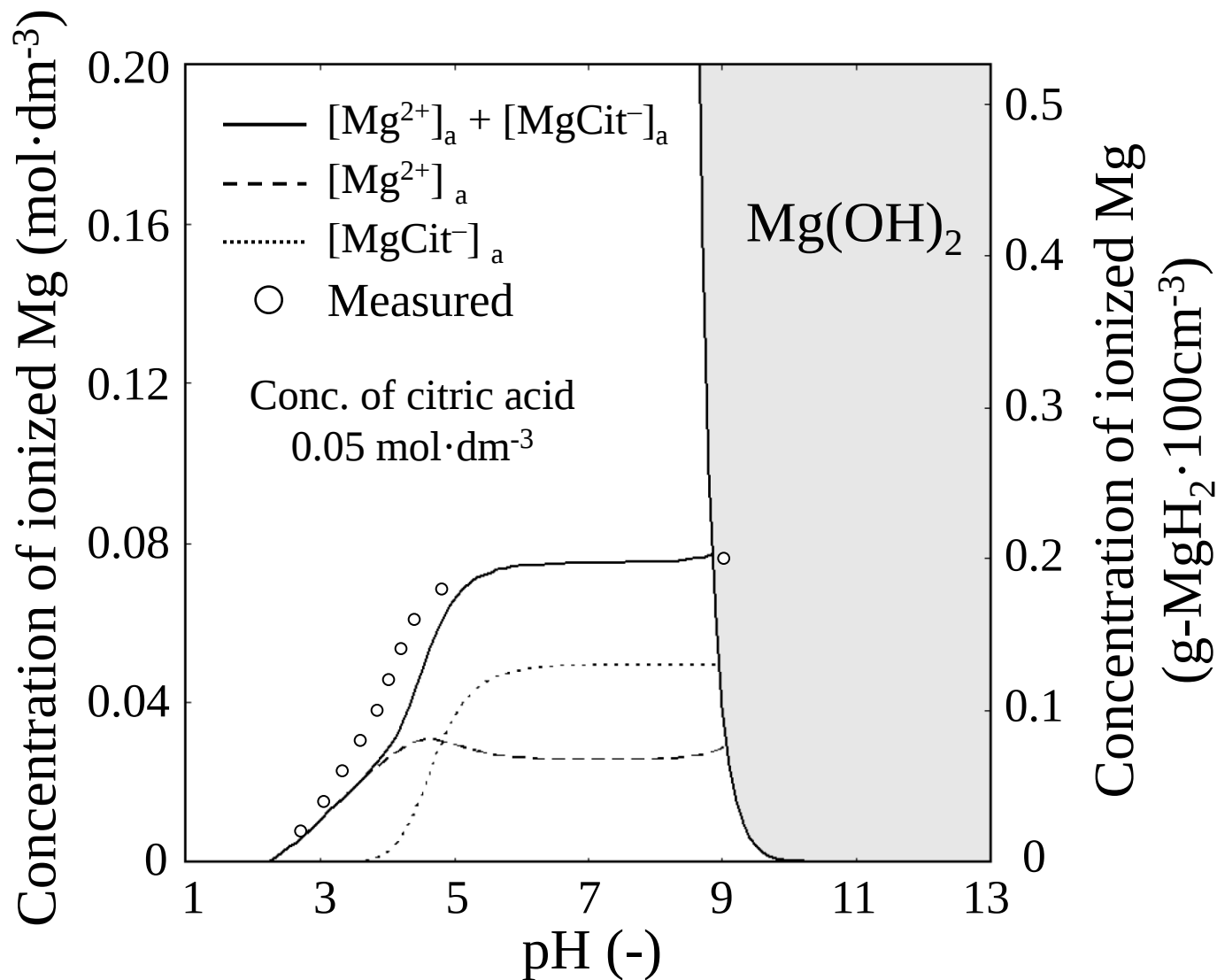


Fig.6 Calculated and measured relationships between pH and concentration of ionized Mg under the condition using citric acid solution of $0.05 \text{ mol} \cdot \text{dm}^{-3}$

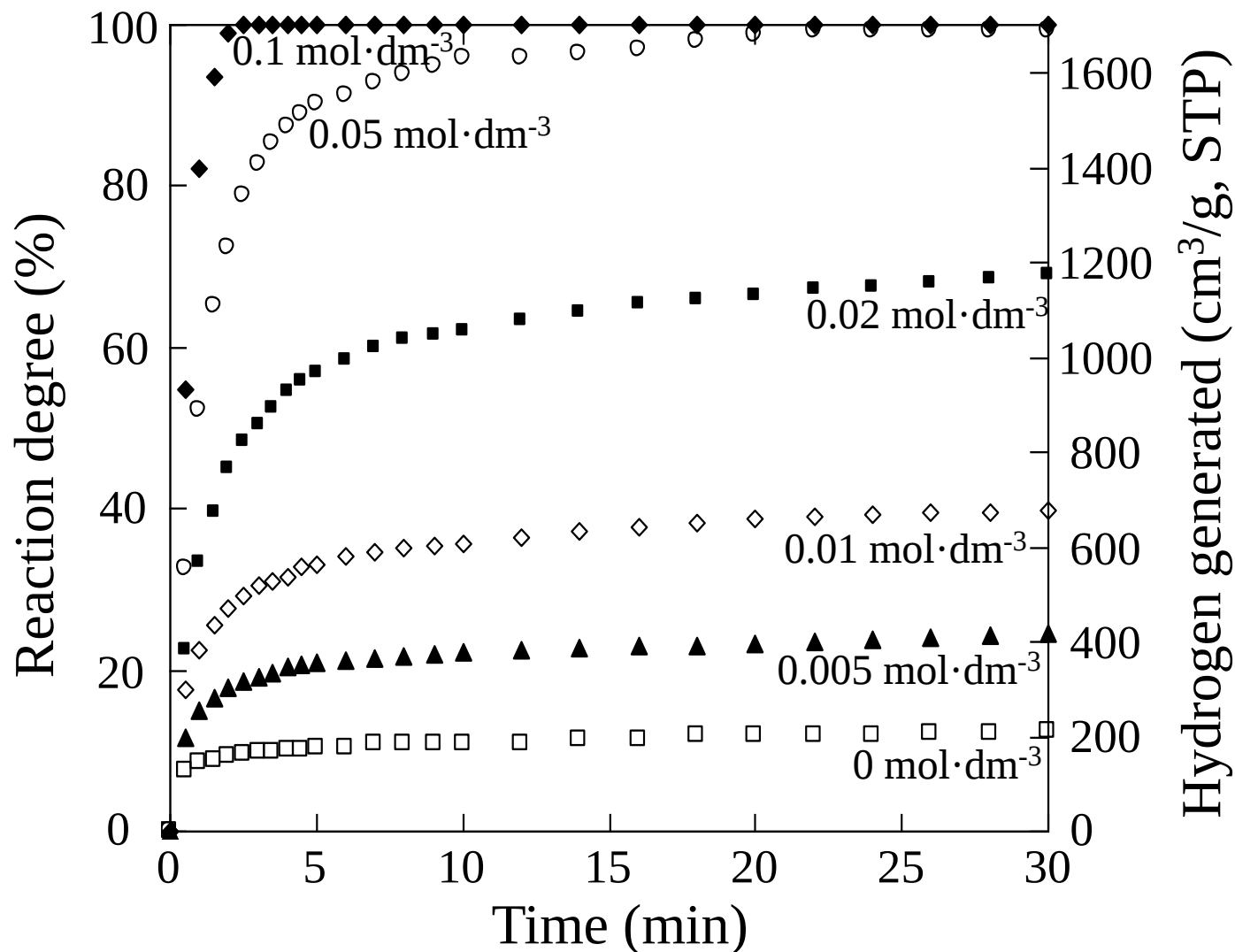


Fig.7 Effect of concentration of citric acid on the hydrogen generation from hydrolysis of 0.1g of MgH_2 was hydrolyzed with 100 cm^3 of distilled water or citric acid solution.