

# Stainless-Steel-Mediated Quantitative Hydrogen Generation from Water under Ball Milling Conditions

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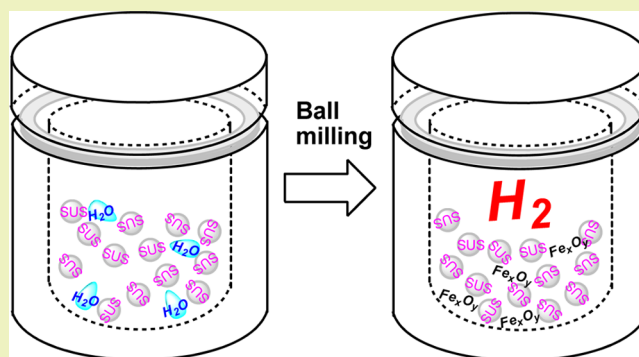
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## Supporting Information

**ABSTRACT:** A robust and quantitative gaseous hydrogen generation method has been developed in an effort to achieve efficient H<sub>2</sub> generation derived from H<sub>2</sub>O. The present reaction could be achieved by a simple ball friction (milling) reaction of H<sub>2</sub>O using a planetary ball mill machine with a stainless-steel vessel and balls. It was mediated by metals with an element of stainless steel of the ball mill and also promoted by mechanochemical processing.

**KEYWORDS:** Hydrogen generation, oxygen free, mechanochemistry, stainless steel, chromium



## INTRODUCTION

Gaseous H<sub>2</sub> is an environmentally friendly and clean next-generation energy source, because it is efficiently converted into only water together by 237.13 kJ/mol of standard combustion heat with complete combustion without the emission of carbon dioxide. Therefore, the development of a revolutionary, cost-conscious, and quantitative H<sub>2</sub> production method from nonfossil sources is strongly desired. Although hydrogen generation by water electrolysis is a traditionally established method, it requires the use of the platinum group metals as electrocatalysts.<sup>1</sup> The light<sup>2–14</sup> and pulsed-laser<sup>15</sup> driven water oxidation methods using one or more metal complexes, such as Ti, W, V, Mn, Pt, Ru, Ir, Fe, Ta, and so on, as photocatalysts have been widely investigated for over 3 decades and further enhancement of their energy efficiencies will encourage their prospective and potential as sources of renewable energy. On the other hand, mechanochemical energy-promoted hydrogen generation methods by water splitting in the presence of metal oxides are also reported in the literature. Domen et al. reported a pioneering mechanochemical and catalytic water splitting method using metal oxides under magnetically stirring conditions at the end of the last century,<sup>14,16–18</sup> although

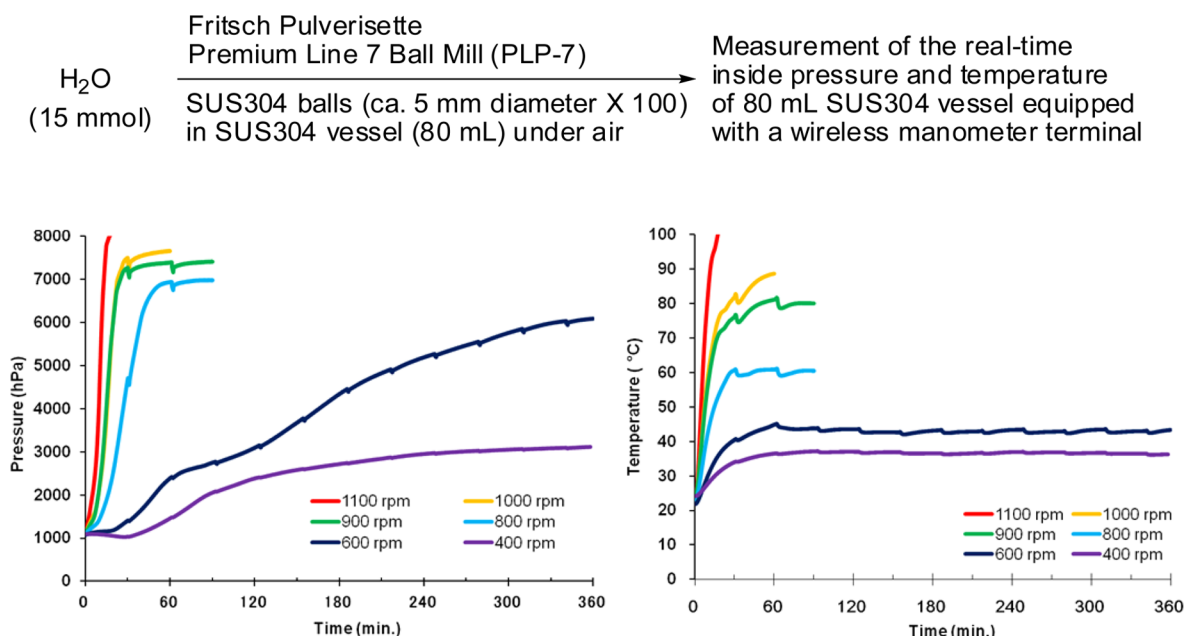
both H<sub>2</sub> and O<sub>2</sub> gases were generated at a time during the water splitting reaction despite the possibility of the thermodynamically favorable reverse reaction to form water,<sup>19</sup> and no subsequent development has been reported. Recently, an overall water splitting method by mechanochemical energy using quartz powder has been reported in the literature, even though there are still some problems to solve such as hydrogen generation efficiency.<sup>20</sup> Although several hydrogen generation methods that take advantage of the mechanochemical reaction have also been reported,<sup>21,22</sup> these reactions occurred based on the oxidation (dissolving) of Al metal in water and the mechanochemical reaction only acts as a remover of the oxidized Al surface to accelerate the Al corrosion by water.

We now report a mechanochemically (using a planetary ball mill) promoted nearly quantitative and selective H<sub>2</sub> generation method from water. Oxygen, a component of water, was scavenged by the structural component of stainless-steel (SUS) balls. Although the present method is still far from a solution

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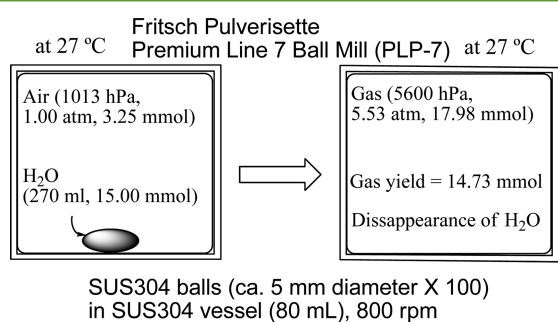


**Figure 1.** Time dependence of the internal pressure (top) and temperature (bottom) in the SUS304 vessel at each rotation number using 270  $\mu\text{L}$  of H<sub>2</sub>O (15.00 mmol) in the presence of 100 SUS304 balls. The rotation was turned off for 1 min every 30 min (to prevent the breakage failure of the planetary ball mill), then continuously restarted (inverse rotation) to complete the gas generation. During the reaction process, the inside pressure and gas were monitored approximately every 1 s.

for the sustainable hydrogen generation and needs to be improved in the energy efficiency and practical aspects, the concept is innovative as a fundamental study with hidden growth potential.

## RESULTS AND DISCUSSION

Although ball mills were developed for the miniaturization of solids or powders, a wide variety of organic reactions utilizing



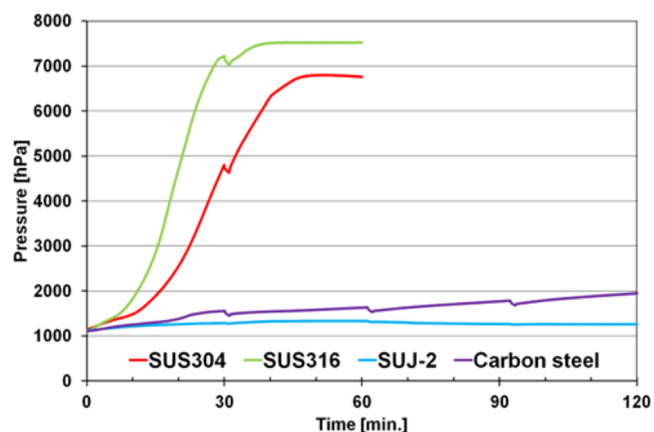
**Figure 2.** Calculation of H<sub>2</sub> generation amount in the 80 mL SUS304 vessel after the ball milling reaction at 800 rpm for 60 min and subsequent cooling to 27 °C.

ball mill-mediated mechanochemical energy, which can influence the covalent bonding, have recently been reported in the literature.<sup>23–33</sup> We have observed the generation of a significant amount of a flammable gas different from water vapor in the closed stainless-steel vessel of a planetary ball mill using a moistened solid reagent. Because gas chromatography thermal conductivity detection (GC-TCD) analysis indicated that the principal element of the gas was H<sub>2</sub>, we expected an efficient H<sub>2</sub> generation reaction.

To confirm the relationship of the gas yield and usage of H<sub>2</sub>O, the ball friction (milling) of distilled H<sub>2</sub>O (270  $\mu\text{L}$ , 15.00 mmol) in the presence of 100 stainless-steel (SUS304) balls

Fritsch Pulverisette  
Premium Line 7 Ball Mill (PLP-7)

H<sub>2</sub>O (270 mL, 15 mmol) → ca. 5 mm diameter balls (100) Air, 800 rpm, 30 min in 80 mL SUS304 vessel



**Figure 3.** Discrepancy of the hydrogen generation efficiencies due to the structural components in each of the stainless alloy balls [composition pattern of commercial SUS 304: Fe (ca. 69%), Cr (18–20%), Ni (8–10%); SUS316, Fe (ca. 65%), Cr (16–18%), Ni (10–14%); SUJ-2, Fe (ca. 96%), Cr (1.3–1.6%); carbon steel, Fe (ca. 99%)]. The rotation was turned off for 1 min every 30 min (to prevent the breakage failure of the planetary ball mill), then continuously restarted (inverse rotation) to complete the gas generation. During the reaction process, the inside pressure and gas were monitored approximately every 1 s.

(ca. 5 mm diameter) was simply performed using a planetary ball mill [Fritsch Pulverisette Premium Line 7 (PLP-7)] in an 80 mL SUS304 vessel equipped with a wireless manometer terminal to observe the real-time internal pressure and temperature. The internal pressures in the 80 mL SUS304

Table 1. Hydrogen Generation under Ball Milling Conditions in the Presence of Water

entry	reaction vessel	H <sub>2</sub> O ( $\mu$ L)	number of balls	additive	collected gas volume (mL)	gas proportions (%) <sup>a</sup>		
						N <sub>2</sub>	H <sub>2</sub>	O <sub>2</sub>
1	SUS304 (80 mL)	270, 15 mmol	100 <sup>b</sup>		120	44	51	1.5
2	SUS304 (80 mL)	270, 15 mmol	100		100	35	50	1.3
3	ZrO <sub>2</sub> (20 mL)	68, 3.8 mmol	25		23	78	0.3	20
4	ZrO <sub>2</sub> (20 mL)	68, 3.8 mmol	25 <sup>b</sup>		40	62	33	3.8
5	ZrO <sub>2</sub> (20 mL)	68, 3.8 mmol	25	Ni (1.88 mmol, 0.5 equiv)	20	89	2.2	8.0
6	ZrO <sub>2</sub> (20 mL)	68, 3.8 mmol	25	Fe (1.88 mmol, 0.5 equiv)	20	86	>0.1	13
7	ZrO <sub>2</sub> (20 mL)	68, 3.8 mmol	25	Cr (0.38 mmol, 0.1 equiv)	35	62	20	13
8	ZrO <sub>2</sub> (20 mL)	68, 3.8 mmol	25	Cr (0.76 mmol, 0.2 equiv)	45	50	39	8.9
9	ZrO <sub>2</sub> (20 mL)	68, 3.8 mmol	25	Cr (1.88 mmol, 0.5 equiv)	56	42	47	4.7
10	ZrO <sub>2</sub> (20 mL)	68, 3.8 mmol	25	Cr (3.75 mmol, 1.0 equiv)	65	40	47	4.3
11	ZrO <sub>2</sub> (20 mL)	68, 3.8 mmol	25	SUS304 58.5 mg (0.21 mmol as Cr) <sup>c</sup>	35	63	29	3.6

<sup>a</sup>Determined by a Shimadzu gas chromatograph. <sup>b</sup>SUS304 balls were used. <sup>c</sup>18.89% of Cr was contained in SUS304 purchased from Fritsch Japan Co. Ltd.

vessel (gas generation efficiencies) dramatically increased, totally depending upon the rotation number (Figure 1, left). The complete conversion (disappearance) of H<sub>2</sub>O was achieved at 600–1100 rpm for 30–360 min, and the internal pressures after cooling at 27 °C were all around 5600 hPa (ca. 5.53 atm), although the inside pressure of the end point at each rotation number was significantly different depending on the obvious difference in each internal temperature (Figure 1, right). In the case of the 400 rpm reaction, the hydrogen generation was incomplete and water in the vessel still partially remained even after 360 min. The internal temperature and pressure milling-time dependently increased by the energy transfer due to collisions of the balls and both achieved a plateau at around 50 min at 800 rpm (Figure 1, light-blue graphs). Because the internal pressure indicated around 5600 hPa (ca. 5.53 atm) after cooling at 27 °C, the total amount of gas in the vessel was 17.98 mmol, namely, the gas yield was 14.73 mmol except for the original internal air (1.00 atm, 3.25 mmol, see Figure 2). The H<sub>2</sub>O completely disappeared from the vessel after the reaction, and the newly generated gas quantity was nearly equal to the initial use of water (15.00 mmol).

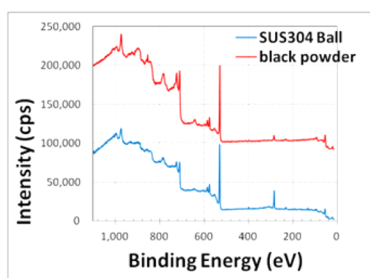
Furthermore, the relative proportions of the internal gases after the ball milling reaction of H<sub>2</sub>O (15 mmol) in the 80 mL SUS304 vessel were collected by the downward displacement of water and the relative proportions of the collected gases (250 mL) were determined by GC (Shimadzu GC-TCD). The relative proportion of H<sub>2</sub> reached 75% together with 15% N<sub>2</sub> and 1% O<sub>2</sub> after 60 min at 800 rpm. It should be noted that the gas proportions in the vessel filled with only gaseous H<sub>2</sub> without H<sub>2</sub>O and milling indicated unavoidable contamination by small amounts but significant N<sub>2</sub> (7.0%) and O<sub>2</sub> (2.1%) during the downward displacement of water resulting from the dissolved air in a large quantity of water, although 84% H<sub>2</sub> was detected in ca. 80 mL of collected gases. Thus, it is justified that the internal gases after the ball milling reaction were made up of mostly H<sub>2</sub> gas. N<sub>2</sub> and O<sub>2</sub> were contaminated from the dissolved air. Because the relative proportions of oxygen obviously decreased in connection with the reaction progress, the oxygen sources derived from both the quantitative hydrogen generation from H<sub>2</sub>O and original air should be

scavenged by the SUS304 components (see the Supporting Information).

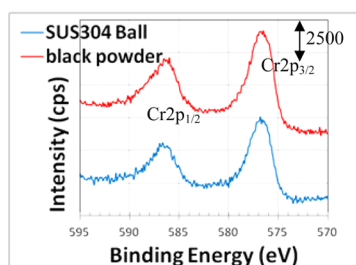
The H<sub>2</sub> generation efficiency was strongly influenced by compositional pattern of balls (see the Supporting Information). Although the milling with SUS304 and SUS316 made up of appreciable amounts of Cr and Ni other than Fe smoothly produce H<sub>2</sub> in a quantitative manner, SUJ-2 and carbon steel balls composed mostly of Fe never promoted the H<sub>2</sub> generation reaction (Figure 3; the slight pressure increase in the vessel for the SUJ-2 and carbon steel balls should be affected by the increase in temperature and/or the use of a SUS304 vessel). Therefore, zerovalent Cr and/or Ni are essential for the reaction progress.

We have subsequently investigated the metal efficiencies of Ni, Fe, and Cr to clarify the hydrogen generation reaction using a 20 mL zirconia (ZrO<sub>2</sub>) vessel and balls of ca. 5 mm diameter (the use of H<sub>2</sub>O and number of balls were proportionally adjusted on the basis of the vessel volume) because the chemical inactivity of ZrO<sub>2</sub> has been clarified by our research (see Table 1, entry 3). Significant amounts of H<sub>2</sub> gas were generated (the collected gas volumes were in excess of the vessel size, 80 and 20 mL, respectively, see, the column of “collected gas volume” and “gas proportions”) in the 80 mL SUS304 vessel using both SUS304 and ZrO<sub>2</sub> balls and in the 20 mL ZrO<sub>2</sub> vessel using SUS304 balls after 30 min milling reactions at 800 rpm (entries 1, 2, and 4), although the reaction using the 20 mL ZrO<sub>2</sub> vessel and ZrO<sub>2</sub> balls never proceeded (entry 3). Although no significant effect was observed by the addition of 1.88 mmol (0.5 equiv of H<sub>2</sub>O) of Ni and Fe powder as the constituent elements of SUS304 together with Cr (entries 5 and 6), the addition of Cr powder obviously and dependently promoted H<sub>2</sub> gas generation (entries 7–10). Furthermore, the use of SUS304 powder as an additive (58.5 mg containing 0.21 mmol of Cr) also produced similar results (entry 11). Although our results indicated that the presence of zerovalent Cr is definitely essential for such reaction progress under the stated ball milling reaction conditions (Table 1, entries 1, 2, 4, and 7–11), the direct formation reactions of Fe powder to Fe<sub>2</sub>O<sub>3</sub> (or Fe<sub>3</sub>O<sub>4</sub>) associated with the generation of H<sub>2</sub> in the stainless-steel ball mill apparatus have been reported

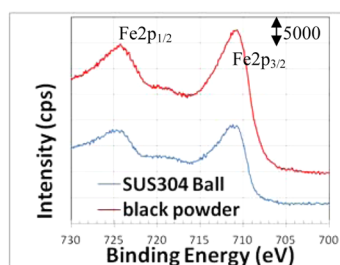
H<sub>2</sub>O  
(270 mL,  
15 mmol) →  
Fritsch Pulverisette  
Premium Line 7 Ball Mill (PLP-7)  
ca. 5 mm diameter balls (100)  
Air, 800 rpm, 30 min  
in 80 mL SUS304 vessel



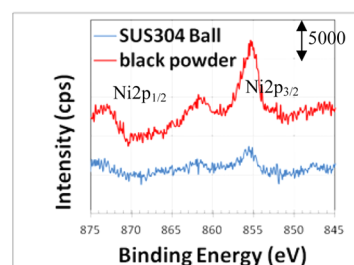
**a: The surface of the black powder (red) and fresh SUS304 ball (blue)**



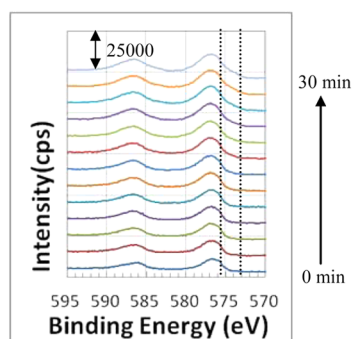
**b: 570-595 eV range**



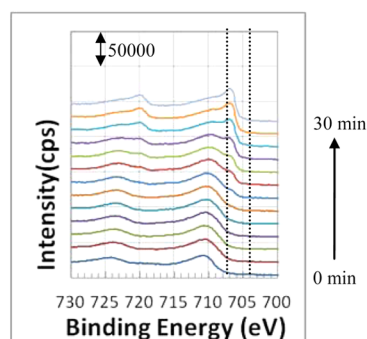
**c: 700-730 eV range**



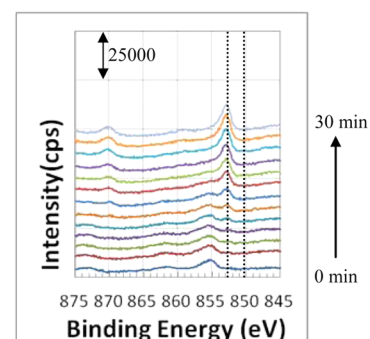
**d: 845-875 eV range**



**e: 570-595 eV range**

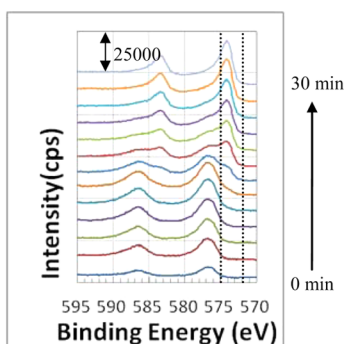


**f: 700-730 eV range**

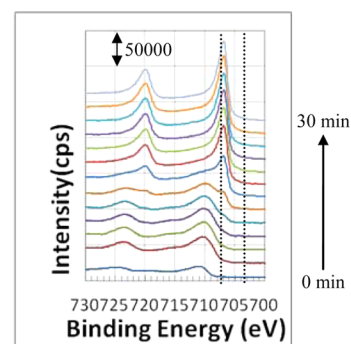


**g: 845-875 eV range**

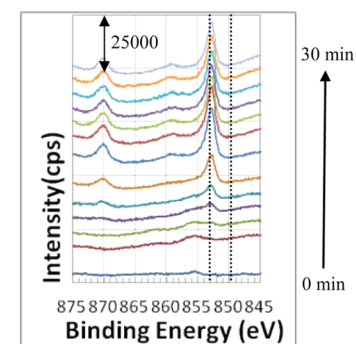
**The consecutive depth profiling experiment of the black powder**



**h: 570-595 eV range**



**i: 700-730 eV range**



**j: 845-875 eV range**

**The consecutive depth profiling experiment of the fresh SUS304 ball**

**Figure 4.** XPS results of the black fine powder.

in the literature.<sup>34,35</sup> Although the authors have never mentioned the metal effect and only focused on the mediation

of the milling energy, these reactions are sure to occur by the Cr as a constituent of the stainless steel.



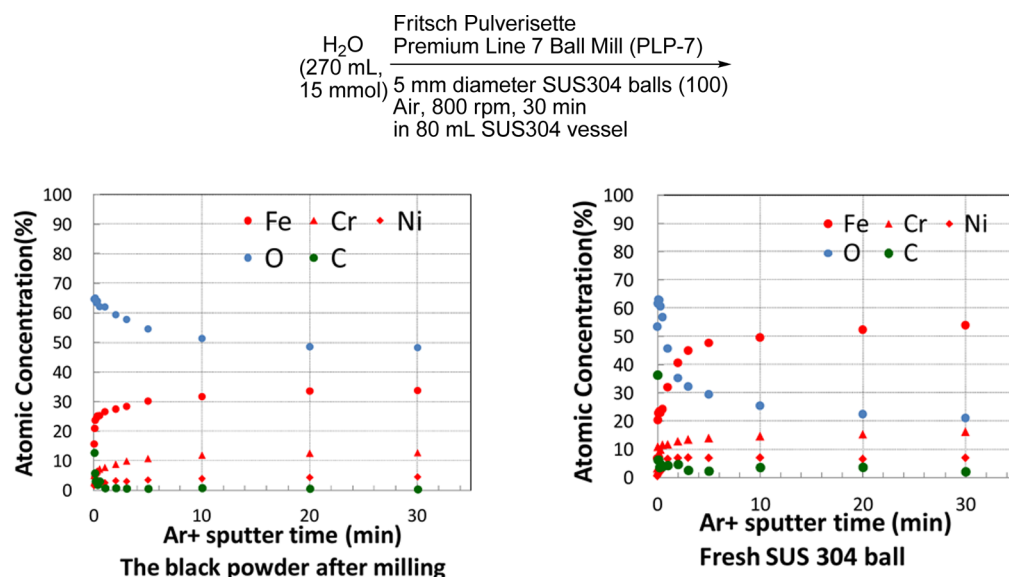


Figure 5. XPS depth profile of Fe, Cr, Ni, O, and C of the black powder and fresh SUS304 ball.

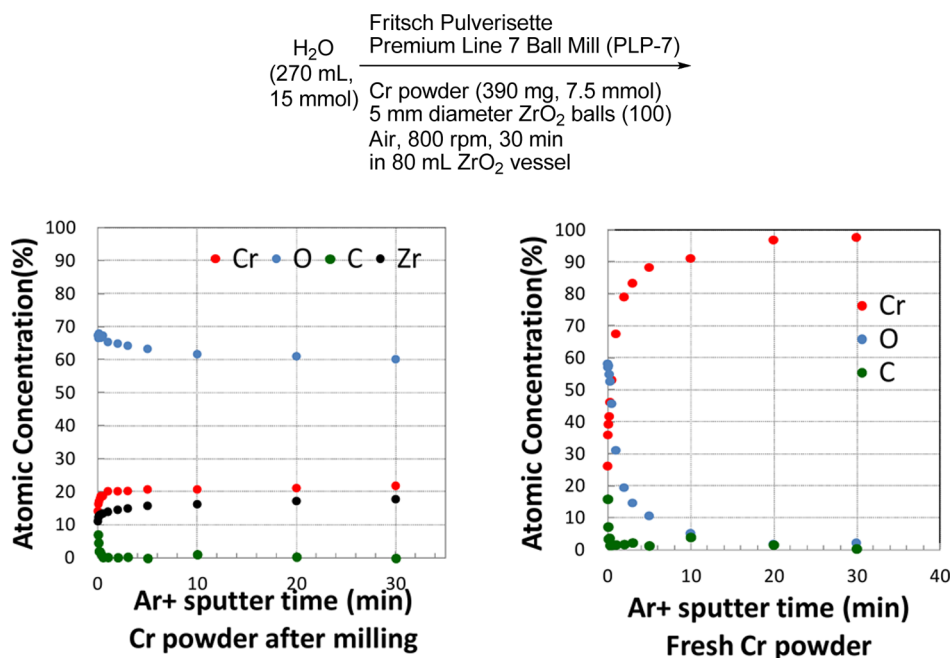


Figure 6. XPS results of Cr powder after milling in ZrO<sub>2</sub> vessel.

In the present hydrogen generation reaction using a SUS304 vessel and balls, the production of a significant amount of black fine powder was observed in association with the generation of H<sub>2</sub>. The formation of oxidized Cr, Fe, and Ni ion peaks detected by X-ray photoelectron spectroscopy (XPS) of the black powder is obviously shown in the charts (red lines in comparison with blue lines indicating the reference spectra of fresh SUS304 ball in Figure 4a–d). The XPS charts of the consecutive depth profiling experiment under sputter etching conditions (sputter rate: 20.0 nm/min@SiO<sub>2</sub>) also visibly indicated that the oxidized Cr, Fe and Ni ions are each eccentrically located in a superficial area of the black powder. The proportions of oxidized metals continuously decreased with the sputter etching time and the peaks gradually shifted to the zerovalent metal peaks (e–g relative to fresh SUS304 ball peaks h–j, lines on the graphs indicates after sputter etching 0,

0.05, 0.1, 0.2, 0.3, 0.5, 1, 2, 3, 5, 10, 20, and 30 min, respectively, from the bottom). The atomic concentration of oxygen in the black powder around the deeper area after sputter etching for more than 10 min constantly indicated a very high elemental ratio (little below 50%), whereas that of fresh SUS304 is equal to the metal composition of commercial SUS304 (Figure 5, see also the caption of Figure 3).

The atomic concentration of oxygen by XPS analysis of the resulting powder after the ball milling of H<sub>2</sub>O at 800 rpm for 30 min in the Cr powder-doped (0.5 equiv) ZrO<sub>2</sub> vessel using ZrO<sub>2</sub> balls indicated an approximately constant ratio among the oxygen and chromium together with a significant amount of zirconium (ca. 15%) derived from the slightly crushed balls although fresh Cr powder included almost no oxygen (Figure 6). Because the resulting powder is green in color, Cr<sub>2</sub>O<sub>3</sub> is significantly formed by the oxidation of the zerovalent Cr.

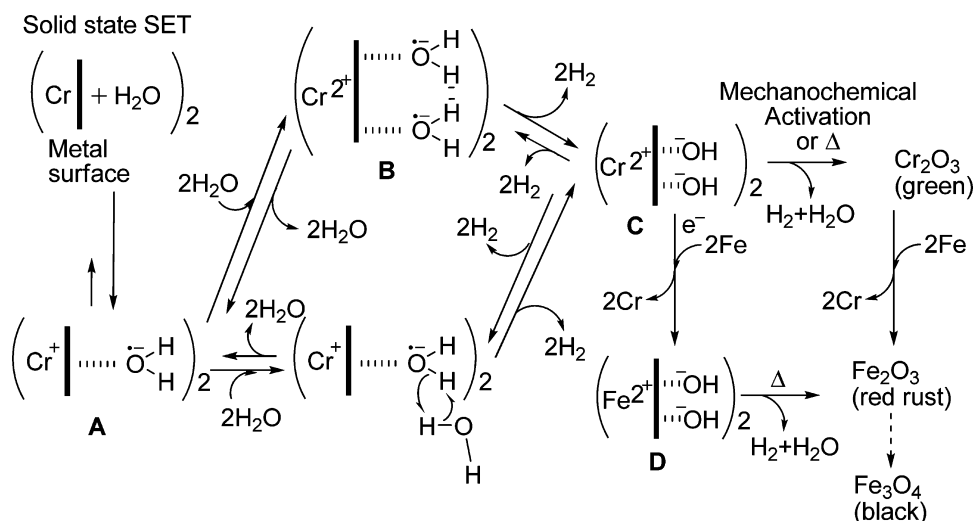


Figure 7. Plausible mechanisms.

Therefore, metals in the SUS304 alloy should scavenge oxygen simultaneously produced during the quantitative hydrogen generation reaction. It is a rational and precise explanation that the Cr single-electron reductively acquires the oxygen from H<sub>2</sub>O and subsequently transfers it mainly to the Fe and Ni.

The plausible reaction mechanisms are depicted in Figure 7. First of all, it is assumed that the solid state single electron transfer (SET) from zerovalent Cr to H<sub>2</sub>O might proceed on the surface of the SUS304 due to its lower first ionization energy (652.9 kJ/mol in comparison with 737.1 and 762.5 kJ/mol for Ni and Fe) envisaged as intermediate (A).<sup>36</sup> The subsequent alternative pathway can also be determined. The first of these is the second SET from the monovalent Cr<sup>+</sup> to another H<sub>2</sub>O to form C via the intermediate (B) with the emission of H<sub>2</sub>. Meanwhile, the second SET after the emission of gaseous H<sub>2</sub> via the radical reaction between the intermediate (A) and another H<sub>2</sub>O can also form C. The migration of hydroxide anions to the Fe surface (D) and subsequent H<sub>2</sub> and H<sub>2</sub>O elimination or the formation of Cr<sub>2</sub>O<sub>3</sub> accompanied by H<sub>2</sub> and H<sub>2</sub>O elimination, then oxygen migration to form Fe<sub>2</sub>O<sub>3</sub> by the intensive grinding and increasing temperature effects.

## CONCLUSIONS

In conclusion, metals as elements in SUS304 mediated the quantitative hydrogen generation from H<sub>2</sub>O, which is promoted by a mechanochemical reaction. Full conversion of H<sub>2</sub>O in the reaction vessel was achieved by the rotation frequency-dependent ball milling reaction, enabled by especially Cr metal as a structural component of stainless steel. The feature of the present reaction should be the highlighting of its distinct possibility as an innovative basic method of the specific hydrogen generation while it requires further detailed research in-depth consideration to energy balance. Further research has been ongoing in our group.

## ASSOCIATED CONTENT

### Supporting Information

Details of general procedures, procedures for XPS analysis, XRD analysis of the fresh SUS304 powder and black fine powder, and hydrogen generation procedures under air or atmospheric nitrogen. This materials available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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