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# Quantitative Mechanochemical Methanation of CO<sub>2</sub> with H<sub>2</sub>O in a Stainless Steel Ball Mill

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Hironao Sajiki received his Ph.D. from Gifu Pharmaceutical University in 1989 under the direction of Prof. Yoshifumi Maki. After serving as a Postdoctoral Fellow at the State University of New York at Albany and Massachusetts Institute of Technology, he joined Metasyn, Inc. (subsequent Epix Pharmaceuticals), MA, the USA as a group leader. In 1995, he moved to Gifu Pharmaceutical University as an Assistant Professor (Professor Kosaku Hirota). He became an Associate Professor in 1999 and Professor in 2006. He has also been the president of the Japanese Society of Process Chemistry since 2017.

#### Abstract

Herein, we achieved nearly quantitative and selective mechanochemical conversion of  $CO_2$  to  $CH_4$  in the presence of  $H_2O$  mediated by collision and friction of stainless steel balls without external heating, revealing that this conversion involves the formation of metal carbonates and hydrogenation by  $H_2$  gas *in situ* generated from  $H_2O$ .

Keywords:	carbon	dioxide;	methanation;
mechanochemica	al		

# Introduction

Human activity such as fuel combustion rapidly increases the atmospheric levels of CO2 and thus contributes to global warming and related climate change<sup>1</sup>. Consequently, much interest has been directed at the transformation of CO2 to CH4 as a reusable energy source to protect the global environment and reduce fossil fuel consumption.<sup>2-6</sup> To date, several highly selective CO2 methanation methods based on transition metalcatalysed thermal hydrogenation with H<sub>2</sub> have been developed. However, these techniques generally require the use of high temperature (>250 °C) and pressure and exhibit the drawback of low conversion, which makes them poorly suited for practical use.<sup>2-26</sup> Moreover, the industrial production of H<sub>2</sub> by steam reforming of CH4 results in the emission of significant amounts of CO<sub>2</sub>,<sup>27,28</sup> and the handling of flammable H<sub>2</sub> gas is strictly regulated by law. Therefore, industrial-scale CO2 methanation utilises H<sub>2</sub> produced by water electrolysis using surplus electricity.<sup>2-6</sup> Alternatively, CO<sub>2</sub> can be electro-/photochemically reduced to CH4 with H2O as a hydrogen source, although these processes suffer from low conversion efficiency and CH4 formation selectivity, generating significant amounts of byproducts, e.g., C<sub>2</sub>H<sub>6</sub>, CO, and CH<sub>3</sub>OH.<sup>2,29</sup> Metal hydrides (LiH, MgH<sub>2</sub>, etc.) can also facilitate the reduction of CO<sub>2</sub> to CH<sub>4</sub>;<sup>30-32</sup> however, appreciable amounts of toxic CO are produced during ball milling-induced mechanochemical reduction of CO2 in the presence of metal hydrides.<sup>32</sup> In view of the above limitations, the geological storage of CO<sub>2</sub> in carbon capture and storage systems<sup>33,34</sup> has emerged as a workable technology to substantially reduce CO<sub>2</sub> emissions. In this case, nearly pure CO<sub>2</sub> is stored in deep water-bearing geological formations under high pressure, and carbonic acid (H<sub>2</sub>CO<sub>3</sub>) produced by CO<sub>2</sub> hydration is gradually mineralised to form metal carbonates (M<sub>x</sub>CO<sub>3</sub>) as storage materials. Although the catalytic hydrogenation of metal carbonates at high temperature and high H<sub>2</sub> pressure can also be used to reduce CO<sub>2</sub> emission,<sup>35</sup> this process has not yet been optimised in terms of product (CH<sub>4</sub> or CO) selectivity and reaction efficiency. Recently, Ru-catalysed hydrogenation [H<sub>2</sub> (70 bar), 170 °C] of acyclic organic carbonates to CH<sub>4</sub> was reported as a relatively mild and practically valuable method of CO<sub>2</sub> methanation.<sup>36</sup>

We have recently developed an innovative method of H<sub>2</sub> generation from water, liquid hydrocarbons, and ether without CO2 emission based on the utilisation of mechanochemical collision and friction energy of stainless steel balls (alloy of Fe, Cr, and Ni) in a planetary ball mill.<sup>37,39</sup> The H<sub>2</sub> gas in situ generated under these conditions can be directly used for the hydrogenation of reducible species such as ketones, nitro compounds, and aromatic halides.<sup>38,39</sup> Mechanochemistry is recently spotlighted as novel technology to facilitate various reactions using solid or gaseous reactants.40-42 Herein, we describe the direct hydrogenation of CO2 with H2O as a hydrogen source, realising quantitative CO2 methanation in a stainless steel (SUS304) ball mill without external heating. The reaction is believed to involve H2 generation from H2O and the subsequent hydrogenation of metal carbonates (formed by the reaction of SUS304 components with CO2 gas dissolved in H2O) to afford CH4 in nearly quantitative yield and excellent selectivity (Fig. 1).



**Figure 1.** Quantitative and selective conversion of CO<sub>2</sub> to CH<sub>4</sub> in the presence of water in a stainless steel (SUS304) ball mill.

# **Results and Discussion**

CO2 reforming (reduction) was performed under different conditions for 90 min in the presence of distilled H<sub>2</sub>O (270  $\mu$ L, 15 mmol) and 100 SUS304 balls (each ~5 mm in diameter) in an 80-mL stainless steel (SUS304) planetary ball mill (Fritsch Pulverisette Premium Line 7 (PLP-7) Table 1). The internal volume of the vessel excluding the volume of  $\mathrm{H_{2}O}$  and SUS304 balls was equivalent to 3.1 mmol of gas at standard temperature and pressure and was filled with CO2 for reduction (see Supporting Information). At 200 or 400 rpm, only a small amount of CO2 was consumed (captured), and hardly any CH4 and H2 were generated, as determined by gas chromatographythermal conductivity detection (GC-TCD; Table 1, entries 1 and 2). Notably, the efficiency of H2 generation from H2O increased with increasing rpm (see ref. 10a and Fig. S1 and S2, Supporting Information). At 400 rpm, CO2 consumption equalled 20%, i.e., 2.48 [3.1 mmol (initially filled  $CO_2$ ) – 3.1 × 0.20] mmol of  $CO_2$ was detected by GC-TCD. Although 78% of CO2 was consumed, and 6.1 mmol of H<sub>2</sub> was generated at 600 rpm, CH<sub>4</sub> was not detected (entry 3). In contrast, CO2 was completely consumed, and CH4 was obtained in 21% yield at 800 rpm (entry 4). Finally, at 1,100 rpm, CH4 was nearly quantitatively generated together with a trace of  $C_2H_6$  (0.8%) and 9.3 mmol of  $H_2$  (entry 5). In all cases, no CO was detected. Since the quantitative conversion of 3.1 mmol CO2 to CH4 consumes 6.2 mmol of H2 derived from  $H_2O$ , 8.8 (15 – 6.2) mmol of  $H_2$  should theoretically remain in the vessel. The actual amount of residual hydrogen was slightly higher (9.2 mmol, entry 5), which was ascribed to the presence of a slight excess of H2O as moisture or metal hydroxides on the balls and vessel. At 200-800 rpm, CO2 consumption was not correlated with CH4 yield, which indicated that CO2 was not directly reduced to CH<sub>4</sub> by in situ generated H<sub>2</sub>. Both CO<sub>2</sub> consumption and CH<sub>4</sub> generation increased rotation speeddependently, which clearly indicated that the mechanochemical energy was essential to promote the present CO2 reforming reaction.

Table 1. Reduction of CO2 with H2O under various conditions.<sup>a</sup>

CO <sub>2</sub> + H <sub>2</sub> O (3.1 mmol) (15 mmol; - 270 بل <i>ا</i> )		5 mm diamete SUS304 balls	er (100) Interna	Internal gases were analyzed by GC-TCD	
		) 90 min	analyz		
entry	rotation	$\mathrm{CO}_2$	$CH_4$	$H_2$	
	speed	consumption	generation	generation	
	(rpm)	(%)	(%)	(mmol)	
1	200	9	0	< 0.1	
2	400	20	0	0.3	
3	600	78	<1	6.1	
4	800	>99	21	13.3	
$5^b$	1,100	>99	>99	9.2	

<sup>*a*</sup>The 80-mL SUS304 vessel was charged with 3.1 mmol of CO<sub>2</sub>, and the reaction was carried out using a planetary ball mill (PLP-7). <sup>*b*</sup>0.8% of C<sub>2</sub>H<sub>6</sub> was detected, while no CO was observed.

Next, we investigated the time profiles of  $CO_2$  consumption and CH<sub>4</sub> generation at 1,100 rpm (Fig. 2a),

revealing that ~70% of CO2 was consumed within the first 15 min and that the remainder was completely eliminated in 60 min. On the other hand, a small amount of CH4 was detected in 15 min, and the CH<sub>4</sub> production rate significantly increased between 30 and 60 min. As a result, CH<sub>4</sub> gas was nearly quantitatively produced within 90 min. These results clearly indicated the formation of reactive intermediate(s) during the transformation of CO<sub>2</sub> to CH<sub>4</sub>. Subsequently, we monitored the correlation between the amounts of produced H<sub>2</sub> and CH<sub>4</sub> (Fig. 2b). H<sub>2</sub> generation from H<sub>2</sub>O<sup>37</sup> smoothly proceeded during the initial 15 min (~9 mmol), and up to 12 mmol of H<sub>2</sub> accumulated in the vessel after 30 min, at which point the amount of H2 started to decrease because of CH4 production. Thus, under adequate internal pressure (~413 kPa43 after cooling to room temperature after the 30-min reaction; device structure precluded reaction temperature measurement in the vessel), H<sub>2</sub> could directly act as a reductant to facilitate CH4 production. Although traces of C2H6 were detected at the early stage of the reaction, higher alkanes such as C3H8 and C4H10 were not observed.



**Figure 2.** Time profiles of (a)  $CO_2$  consumption and  $CH_4$  generation and (b)  $H_2$ ,  $CH_4$ , and  $C_2H_6$  generation at 1,100 rpm.

To identify intermediate(s) produced during the transformation of CO2 to CH4, the solid products formed after 15, 30, 60, and 90 min were analysed by X-ray photoelectron spectroscopy (XPS; Fig. 3). During the SUS304-mediated H<sub>2</sub> generation from H<sub>2</sub>O, water-derived oxygen was consumed by the oxidation of SUS304 components (Fe, Cr, Ni) to form metal oxides, as shown in Figs. 3a-c. Moreover, a peak at ~289 eV (carbonate) was detected, especially at the early stage of the reaction, along with a carbon peak at ~285 eV (minor component (<0.08%) of SUS304) (Fig. 3d).<sup>44</sup> O 1s peaks at ~531 and 530 eV were assigned to metal carbonates and metal oxides, respectively (Fig. 3e).43 The intensity of C 1s (Fig. 3d) and O 1s (Fig. 3e) carbonate peaks was high at the early stage of the reaction (especially after 15 min) but decreased with time. Consecutive depth profiling  $(Ar^+ \text{ sputter rate} = 15.3)$ nm/min@SiO<sub>2</sub>, total time  $\approx 26$  min) of solid products obtained after 1,100-rpm ball milling for 15 min revealed that metal carbonates were present only on the surface of these products (Figs. 3f and g), since only the metal oxide peak (530 eV) was observed in the inside portion (Fig. 3g). During the present milling using SUS304 balls, fine powders including metal oxides, metal carbonates, mother SUS304 etc. were obtained by the collision of balls and vessel.45 H2 generation and metal carbonate formation can be carried out on the surface of balls as well as the generated fine SUS304 powder. Mechanochemical energy may activate liquid and solid components such as metal-surfaces and reagents (H2O and metal carbonates) in a sealed stainless-steel vessel. H<sub>2</sub> is comparatively absorbed into metal surfaces.

Gaseous CH<sub>4</sub> was not activated by mechanochemical agitation, and H<sub>2</sub> was not generated, while liquid pentane (n-C<sub>5</sub>H<sub>12</sub>) was converted to H<sub>2</sub> under ball milling conditions. as shown in our previous report.39



**Figure 3.** (a–e) XPS spectra of solid products obtained at different reaction times and (f, g) results of consecutive depth profiling of these products.<sup>*a*</sup>  ${}^{a}Ar^{+}$  sputtering was carried out for 26 min at a sputter rate of 15.3 nm/min@SiO<sub>2</sub>.

Although 78% of CO2 was consumed, and a sufficient amount (6.1 mmol) of H<sub>2</sub> was generated in the SUS304 vessel after 90-min milling at 600 rpm, no CH<sub>4</sub> production was observed (Table 1, entry 3). An increase of milling time to 3 h led to a nearly complete consumption of CO2 gas, while CH4 was generated in only 5% yield (Fig. 4). The solid (A) obtained after 3-h milling at 600 rpm also contained metal carbonates on the surface (other XPS spectra focused on Fe, Cr, Ni and O are provided in the Supporting Information) and could be transformed to CH<sub>4</sub> by ball-milling at 1,100 rpm in the presence of 100 SUS304 balls (5 mm) and H<sub>2</sub>O (Scheme 1, eq. 1). Furthermore, CH4 could also be generated from A (eq. 2) by ballmilling in a ZrO2 vessel with 100 balls in an atmosphere of H2 at 1,100-rpm, i.e., under conditions precluding H<sub>2</sub> generation from H<sub>2</sub>O and the hydrogenation of reducible functionalities.<sup>37,38</sup> In our previous study,<sup>38</sup> Ni was revealed to catalyse the mechanochemical hydrogenation of reducible functionalities mediated by the collision and friction of ZrO<sub>2</sub> balls. Since Ni is a major component of SUS304, it could be incorporated into A during ball-milling and thus catalyse the hydrogenation of A even in a ZrO<sub>2</sub> vessel. These results clearly indicated that metal carbonates are formed as intermediates during CO<sub>2</sub> methanation and that in situ generated H<sub>2</sub> plays an important role as a reductant.



**Figure 4.** XPS spectra (275–300 eV range) of the solid product (A) obtained after 3-h milling at 600 rpm.



**Scheme 1.** CH<sub>4</sub> production from the solid product (**A**) formed in the SUS304 vessel after 3-h ball-milling at 600 rpm (Fig. 4).

H<sub>2</sub> generation from H<sub>2</sub>O and subsequent CH<sub>4</sub> generation could smoothly proceed at below 100 °C under ball-milling conditions at speeds above 600 rpm, as shown in SI, Figure S2. However, H<sub>2</sub>O (15 mmol, 270  $\mu$ L) in the presence of 100 SUS304 balls in a sealed stainless-steel tube was never converted to H<sub>2</sub> under simple heating conditions at 100 °C without mechanochemical agitation (Scheme2, eq. 3). Similarly, the solid **A** was also never transformed to  $CH_4$  under  $H_2$  atmosphere (1 atm or 4 atm) at 100 °C without mechanochemical agitation (eqs. 4 and 5). These results indicated that the mechanical agitation of balls was essential for both  $H_2$  generation and  $CO_2$  reduction.



Scheme 2. Inefficient reactions without mechanochemical agitation.

According to the proposed mechanism of CO2 methanation (Scheme 3), H<sub>2</sub>O is mechanochemically degraded to H<sub>2</sub> via double solid-state single-electron transfer (SET) from SUS metals, which is accompanied by the formation of metal hydroxides (C).<sup>37</sup> C is easily converted to the corresponding metal oxides (M<sub>2</sub>O<sub>3</sub>, etc.) upon the release of H<sub>2</sub> gas and H<sub>2</sub>O. On the other hand, CO<sub>2</sub> dissolves in H<sub>2</sub>O to form H<sub>2</sub>CO<sub>3</sub>, which is rapidly captured by C and/or metal oxides to produce metal carbonates (component of A) as water-soluble solids. These solids or their aqueous solution are more susceptible to mechanochemical reduction than gaseous CO2. The subsequent Ni-catalysed hydrogenation<sup>38</sup> of metal carbonates in A with in situ generated H<sub>2</sub> smoothly affords CH<sub>4</sub> in nearly quantitative yield with excellent selectivity. CH4 was never generated under the ball milling conditions without H<sub>2</sub>O, which indicates that H<sub>2</sub>O is required for the formation of H<sub>2</sub>CO<sub>3</sub> and H<sub>2</sub> source. Because CO<sub>2</sub> consumption via the generation of H<sub>2</sub>CO<sub>3</sub> and H<sub>2</sub> generation are competing, the generation of H<sub>2</sub>CO<sub>3</sub> and metal carbonates should be completed before the full conversion of H<sub>2</sub>O to H<sub>2</sub>. Probably, the reaction between CO<sub>2</sub> and H<sub>2</sub>O more smoothly proceeded in comparison with H2 generation from H2O under the present CO2 methanation, since the metal carbonate formation can be generally performed under non-ball milling condtions. However, pure metal carbonates (FeCO3 and NiCO3), which are commercially available, instead of A, were hardly converted to CH4 in an atmosphere of H2 at 1,100-rpm ballmilling conditions similar to eq. 2 (See Supporting Information, eqs. S3, and S4). The details are unclear.



Scheme 3. Proposed mechanism of mechanochemical  $CO_2$  reduction.

The number of balls strongly influenced the efficiency of CO<sub>2</sub> methanation (eq. 6). When a SUS304 vessel containing 5mm-diameter SUS304 balls (250) and H<sub>2</sub>O (12.5 mmol) was charged with 3.0 mmol of CO<sub>2</sub>, CH<sub>4</sub> was efficiently produced in 95% yield together with a small amount (1%) of C<sub>2</sub>H<sub>6</sub> after 90min ball-milling at 800 rpm (eq. 6; see also Table 1, entry 4).

CO- + H-O -	5 mm diameter SUS304 balls (250)	CH₄: 95 %	(eq. 6)
(3.0 mmol) (12.5 mmol)	SUS304 vessel 800 rpm, 90 min	<sup>►</sup> C <sub>2</sub> H <sub>6</sub> : 1 %	

### Conclusion

Quantitative and highly selective methanation of CO<sub>2</sub> under planetary ball milling conditions in the presence of H2O and stainless steel balls was accomplished without the external addition of H<sub>2</sub> or external heating. The results of XPS analysis revealed that the reaction mechanism involves the formation of metal carbonates and their subsequent hydrogenation by H2 in situ generated from H2O. The present CO2 methanation proceeded, following H<sub>2</sub> generation from water and stainless steel to metal oxides without the emission of CO<sub>2</sub>. However, the steel is generally manufactured from heating iron ore with coal together with CO2 releasing. Although further improvements of reaction efficiency and reaction design are required to make this method practically applicable to global CO<sub>2</sub> sequestering, the developed technique is utilzed as a beneficial use of the discarded stainless steel to contribute environmental conservation.

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- 44. For example, 0.3 g, 1.5 g, and 3.0 g of fine powders were obtained under ball milling conditions at 400, 600, and 1,100 rpm for 90 min, respectively (Table 1, entries 2, 3, and 5). Excess amounts of metals might be consumed by grinding balls and vessels. And energy, generated under mechanochemical ball milling conditions, could not be measured due to the characteristics of the planetary ball mill machine. Therefore, the energy balance of input and output is quite difficult to be calculated.
- 45. 342 kPa, 354 kPa and 382 kPa were observed as the internal pressure after cooling to room temperature after the 15, 60 and 90-min reaction, respectively.