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Reductive transformation of CO₂: Fluoride-catalyzed reactions with waste silicon-based reducing agents

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ABSTRACT

CO₂ is one of the most important “renewable” carbon sources. To transform CO₂ to useful organic compounds, we examined the reactivity of two model silicon-based “waste” materials, disilanes and metallic Si powder, as reducing agents. In these reactions, fluoride salts were found to be active catalysts: CO₂ was converted to formic acid at atmospheric pressure in the presence of H₂O as a proton source and the silicon-based reducing reagents. Based on in-situ NMR and kinetics analyses, a hydrosilane and penta-coordinate Si species are proposed as the reaction intermediate and active species, respectively.

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1. Introduction

The reductive transformation of CO₂ to useful compounds represents a chemical process that would be ideal, and quite desirable from an environmental perspective [1–4]. However, because of its strong C–O bonds, this task is always energetically “uphill” and requires the input of energy to proceed [5]. Consequently, in the transformation of CO₂ to derivative chemicals and/or fuels, significantly more energy and/or fuel is consumed to promote the reductive reaction. To overcome this problem and balance the process economics, we considered lowering the cost of the reducing agents by using “waste” materials based on silicon, as shown on the right side of Fig. 1.

The “waste” reducing agents can be obtained as byproducts from the silicone process or from used solar cells (Fig. 1). In the silicone process, the most widely used silicon-based polymer,

polydimethylsiloxane (PDMS), is produced from metallic silicon, along with several byproducts containing Si–Si bonds, including disilanes and polysilanes [6]. These “waste” compounds contain Si–Si chemical bonds which can potentially act as reducing agents in chemical reactions. Similarly, versatile solar cells can usually contain as much as 2 wt% metallic silicon that can also act as a reductant [7], therefore, used solar panels constitute another possible source of a “waste” reducing agent. Further, because of the increasing demand of solar cells, the projected generation rate of waste solar panels in Japan in 2036 is 800000 tons/year [7].

We envisaged that a general solution for the “uphill task” of CO₂ transformation could be realized by the use of such waste silicon-based reducing agents. Our preliminary results indicated that the fluoride-catalyzed reaction of a model disilane with H₂O afforded a hydrosilane which reacted with CO₂ to give for-

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Fig. 1. CO₂ transformation process using “waste” silicon-based reducing agents.

mic acid [8–11]. In this case, the fluoride anion was effective for both Si–Si bond breaking and the activation of the Si–H bond for the reduction of CO₂, because fluoride anion has a high affinity for Si [12,13]. In this paper, we fully investigate the reactions between CO₂ and a disilane or metallic Si as model silicon waste compounds and potential CO₂ reducing agents.

2. Experimental

2.1. General methods

The ¹H, ¹³C, and ¹⁹F NMR spectra were recorded in CDCl₃ using a Bruker AVANCE 400 spectrometer operating at 400, 100.61, and 376.5 MHz, respectively. A Shimadzu QP2010 instrument equipped with a DB-1 column was used for the GC–MS analyses.

Tetrabutylammonium fluoride trihydrate (TBAF·3H₂O, >99%) was purchased from Arcos Organics. ¹³CO₂ (¹³C 99%, ¹⁸O <1%) was purchased from Cambridge Isotope Laboratories. CDCl₃ (>99.8%) was purchased from Kanto Kagaku Co. Dimethylacetamide (DMA, dehydrated, >99%) was purchased from Kanto Kagaku Co. and used without further purification. Si powder was purchased from Wako Chemicals (Si, 99.9%). Unless otherwise noted, all the other materials were purchased from Wako Pure Chemicals, Tokyo Kasei Co., Kanto Kagaku Co., and Aldrich Inc. Fluoride salts were used without any further pretreatment such as dehydration. Catalytic experiments were set up under an oxygen-free atmosphere using standard Schlenk techniques.

2.2. Typical procedure for formic acid synthesis from CO₂, H₂O, and disilane

To a glass reactor equipped with a CO₂ balloon was added TBAF·3H₂O (0.05 mmol), dimethyltetraphenyldisilane (0.50 mmol), water (2.4 mmol), and DMA (1 mL). The resulting reaction mixture was stirred vigorously at 80 °C for 24 h. The products were confirmed by the comparison of their GC–MS spectra and ¹H NMR spectra with those of authentic samples. The yields were determined by the internal standard technique using a CDCl₃ solution of the reaction mixture and mesitylene or triisopropylbenzene as the internal standard.

2.3. Typical procedure for formic acid synthesis from CO₂, H₂O, and Si powder

To a glass reactor equipped with a CO₂ balloon was added TBAF·3H₂O (0.05 mmol), Si powder (0.50 mmol), water (10 mmol), and DMA (2 mL). The resulting reaction mixture was stirred vigorously at 95 °C for 24 h. The reaction residue was filtered, and the residue was analyzed by X-ray photoelectron spectroscopy (XPS, vide infra) after vacuum drying at room temperature. The reaction products in the filtrate were confirmed by the comparison of their GC–MS spectra and ¹H NMR spectra with those of authentic samples. The yields were determined by the internal standard technique using a CDCl₃ solution of the reaction mixture and mesitylene or triisopropylbenzene as the internal standard.

2.4. Characterization

To a glass reactor equipped with an Ar balloon was added KF (0.50 mmol), dimethyltetraphenyldisilane (0.55 mmol), 2.2.2-cryptand (0.50 mmol), and DMSO-*d*₆ (1.5 mL). The resulting reaction mixture was stirred at room temperature for 10 min, and then transferred to an NMR tube under Ar. After the ¹H and ¹⁹F NMR measurements (Fig. 4(a) and (b)), ¹³CO₂ was introduced into the NMR tube. Then, further ¹H NMR measurements were acquired (Fig. 4(c)).

XPS analyses were performed on an ESCA1700R system equipped with a dual Mg/Al X-ray source and a hemispherical analyzer operating in the fixed analyzer transmission mode. Spectra were obtained using a pass energy of 58.7 eV, and the Al K_α X-ray source was operated at 350 W and 14 kV. Excess charges on the samples were neutralized by argon ion sputtering. The analysis area was 0.8 × 2 mm². The working pressure in the analysis chamber was less than 1 × 10^{−7} Pa. Spectra were acquired in the O 1s, C 1s, and Si 2p regions. The C 1s peak at a binding energy (BE) of 285 eV was taken as an internal reference.

3. Results and discussion

3.1. Optimization of reaction conditions

We began our investigation of this reductive transformation of CO₂ by using tetrabutylammonium fluoride trihydrate (TBAF·3H₂O), 1,2-dimethyl-1,1,2,2-tetraphenyldisilane (disilane), and DMSO as the catalyst, disilane, and solvent, respectively. Combining these reagents and H₂O under a balloon of CO₂ at 80 °C overnight afforded 0.13 mmol formate per 0.5 mmol disilane used, an 92% conversion of the disilane and 26% yield overall (Table 1, entry 1). Other fluoride salts, such as KHF₂ and KF, also showed catalytic activity for the reaction of disilane, however, the product yields were lower than TBAF as a catalyst (Table 1, entries 2 and 3) [8]. The product was not obtained without fluoride salt (Table 1, entry 5).

As shown in Table 1, entry 6, no formate product was obtained without disilane, indicating that disilane is necessary for the reductive transformation. To confirm the conversion of CO₂ and H₂O to the formic acid product, isotopic experiments were conducted [8]. The use of ¹³CO₂ instead of ¹²CO₂ afforded formic acid with >99% ¹³C incorporation (Scheme 1) [8]. This fact

Table 1

Formic acid synthesis from CO₂ and H₂O with (Ph₂MeSi)₂ with various fluorides.

$\text{CO}_2 \text{ (1 atm)} + \text{H}_2\text{O} + \begin{array}{c} \text{Ph} \quad \text{Ph} \\ \quad \\ \text{---Si---Si---} \\ \quad \\ \text{Ph} \quad \text{Ph} \end{array} \xrightarrow[\text{DMSO}]{\text{fluoride salt (0.05 mmol)}} \text{H}-\text{C}(=\text{O})-\text{OH} + \text{disiloxane}$				
Entry	Fluoride Salt	Conversion of disilane (%)	HCOOH produced ^a (mmol)	HCOOH yield based on disilane ^a (%)
1	TBAF·3H ₂ O	92	0.13	26
2	KHF ₂	94	0.11	22
3	KF	91	0.07	15
4	CsF	93	0.04	8
5	None	2	<0.00	<1
6 ^b	TBAF·3H ₂ O	<1	<0.00	<1

Reaction conditions: 1,2-dimethyl-1,1,2,2-tetraphenyldisilane (0.50 mmol), CO₂ (1 atm, balloon), H₂O (0.50 mmol), fluoride salt (0.05 mmol), DMSO (1.0 mL), 80 °C, 24 h.

^aThis value contains formic acid salt. ^bWithout disilane.

clearly indicates the transformation of CO₂ to formic acid and the formate salt. The use of D₂O instead of H₂O gave deuterated formic acid, as shown in Scheme 2 [8]. No deuterium incorporation into the co-produced disiloxane was observed. These results strongly support that the atoms in the formic acid product were originated from CO₂ and H₂O. The relatively lower content of deuterium (80%) compared with ¹³C may be due to hydrated water of TBAF and proton release from DMSO solvent under acidic conditions [14].

Since H₂O is the key substrate molecule for the formic acid production, the amount of H₂O was optimized. The amount of formate products were plotted against the amount of H₂O, as shown in Fig. 2. Addition of 2.4 mmol of H₂O to the reaction mixture containing 0.50 and 0.05 mmol of the disilane and TBAF afforded the highest amount of product. Further increasing of H₂O did not give good results, and this may be due to the decreasing solubility of the organic disilane compound.

Next, the effect of solvent on the yield of formic acid was investigated. The results are summarized in Table 2. In the case of the reaction using 2.4 mmol of H₂O and 1.0 mL of DMA, the highest product yield of 44% was achieved (Table 2, entry 1). Formate products are also obtained in other aprotic polar solvents such as 1,4-dioxane and acetonitrile (Table 2, entries 3 and 4), although the products are scarcely formed in nonpolar solvents or alcohols (Table 2, entries 7–10). It can be considered that due to the high solubility of CO₂, the aprotic nonpolar

Scheme 1. Transformation of ¹³CO₂ to formic acid. **Scheme 2.** Transformation of CO₂ to formic acid in the presence of D₂O. **Fig. 2.** Optimization of the amount of H₂O. Reaction conditions: dimethyltetraphenyldisilane (0.50 mmol), CO₂ (1 atm, balloon), H₂O (2.35 mmol), TBAF·3H₂O (0.05 mmol), DMA (1.0 mL), 80 °C, 24 h.

solvents, such as DMF and DMSO, show good results compared with nonpolar solvents. In the case of alcohol solvents, the strong interaction between hydroxyl group and fluoride anion may inhibit the catalytic reaction.

3.2. Reaction mechanism and active species

To elucidate the reaction pathway, the transformation of CO₂ was monitored over time, as shown in Fig. 3. After 5 min, similar amounts of hydrosilane and fluorosilane are obtained; thereafter, the amount of hydrosilane decreases with increasing formic acid formation. These results indicate the following two phenomena. First, the reaction of the disilane, H₂O, and the fluoride salt affords a hydrosilane, fluorosilane, and hydroxide anion (Eq. (1)). The detection of deuterated hydrosilane (PhMe₂Si-D) during the reaction using D₂O (Scheme 2) also indicate the reaction step (Eq. (1)). Second, the hydrosilane intermediate is converted into a silanol (or disiloxane) and

Table 2

Formic acid synthesis from CO₂ and H₂O with (Ph₂MeSi)₂ in various solvents.

$\text{CO}_2 \text{ (1 atm)} + \text{H}_2\text{O} + \begin{array}{c} \text{Ph} \quad \text{Ph} \\ \quad \\ \text{---Si---Si---} \\ \quad \\ \text{Ph} \quad \text{Ph} \end{array} \xrightarrow[\text{solvent}]{\text{TBAF} \cdot 3\text{H}_2\text{O (0.05 mmol)}} \text{H}-\text{C}(=\text{O})-\text{OH} + \text{disiloxane}$					
Entry	Solvent	Temperature (°C)	Conversion of disilane (%)	HCOOH produced ^a (mmol)	HCOOH yield based on disilane ^a (%)
1	DMA	80	80	0.22	44
2	DMSO	80	>99	0.17	33
3	1,4-dioxane	80	96	0.07	14
4	Acetonitrile	80	54	0.05	10
5	THF	60	88	0.03	6
6	Acetone	50	14	0.03	6
7	Hexane	50	18	<0.01	<1
8	Chloroform	60	10	<0.01	<1
9	Ethanol	70	<1	<0.01	<1
10	1-propanol	80	2	<0.01	<1

Reaction conditions: 1,2-dimethyl-1,1,2,2-tetraphenyldisilane (0.50 mmol), CO₂ (1 atm, balloon), H₂O (2.4 mmol), TBAF·3H₂O (0.05 mmol), solvent (1.0 mL), 24 h.

^aThis value contains formic acid salt.

Fig. 3. Time course of the transformation of CO₂ to formic acid with disilane. (Red) Formic acid; (green) disiloxane; (black) fluorosilane; (blue) hydrosilane. Reaction conditions: dimethyltetraphenyldisilane (0.50 mmol), CO₂ (1 atm, balloon), H₂O (2.50 mmol), TBAF·3H₂O (0.05 mmol), DMA (2.0 mL), 80 °C.

formic acid in the presence of CO₂ (Eq. (2)) [15]. It should be noted that the silyl formate, i.e., the hydrosilylation product of CO₂, was not detected during formic acid formation. This suggests that the formate salt directly reacts with H₂O to give the formic acid product.

To investigate the regeneration pathway of the fluoride catalyst, the reaction of the disilane, fluorosilane, and cesium hydroxide under CO₂ atmosphere was examined. In this case, the formate product was obtained, although no product was formed in the absence of cesium hydroxide (Scheme 3) [8]. The results indicate that the fluoride anion is regenerated by the reaction between the fluorosilane and hydroxide anion. A proposed overall catalytic reaction pathway is shown in Scheme 4.

We next conducted an in-situ NMR study to determine the catalytically active fluoride species. To increase the concentration of the active species, KF and 2.2.2-cryptand were reacted with dimethyltetraphenyldisilane (Scheme 5). In the absence of CO₂, the formation of a penta-coordinate silicate with two fluo-

Reagent (s)	Yield (%)
$\text{Ph}_2\text{Si}-\text{Si}-\text{Ph}_2 + \text{CsOH} \cdot \text{H}_2\text{O}$	18
$\text{Ph}_2\text{Si}-\text{Si}-\text{Ph}_2$	<1
$\text{CsOH} \cdot \text{H}_2\text{O}$	<1

Fluorosilane (0.06 mmol), CsOH·H₂O (0.06 mmol).

Scheme 3. Control experiments using fluorosilane and/or cesium hydroxide.

Scheme 4. Proposed reaction pathway for fluoride-catalyzed formic acid formation.

Scheme 5. Stepwise experiments for (i) penta-coordinate silicate formation and (ii) reduction of CO₂ to formic acid salt.

rides was detected by ¹⁹F and ¹H NMR, along with a similar amount of hydrosilane (Fig. 4(a) and (b), Scheme 5(i)) [16]. The hydrosilane might be formed from a small quantity of adventitious H₂O. The structure of the penta-coordinate silicate was also confirmed by ¹H-¹⁹F HOESY NMR (Fig. 5). Then, ¹³CO₂ and

Fig. 4. ¹⁹F (a) and ¹H NMR (b) spectra of penta-coordinate silicate species and ¹H NMR spectrum (c) after the treatment with ¹³CO₂ and H₂O. (a): Ph₂SiMeF₂⁻ (-82.9 ppm, *q*, *J*_{H-19F} = 9.5 Hz); (b) a: Ph₂SiMeF₂⁻ (0 ppm, *t*, *J*_{H-19F} = 9.5 Hz, 3H), b: Ph₂SiMeF₂⁻ (7.7 ppm, *m*, 2H), c, d: Ph₂SiMeF₂⁻ (7.0 ppm, *m*, 3H), Ph₂SiH (4.8 ppm, *q*, *J* = 3.9 Hz, 1H); (c) H¹³C(O)OK (8.4 ppm, *d*, *J*_{H-13C} = 181 Hz, 1H).

Fig. 5. ^1H - ^{19}F HOESY spectrum of the reaction mixture after the reaction of KF, [2.2.2] cryptand, and disilane. Reaction conditions: dimethyltetraphenyldisilane (0.55 mmol), KF (0.50 mmol), [2.2.2] cryptand (0.50 mmol), $\text{DMSO}-d_6$ (1.5 mL), room temperature, 10 min.

H_2O were added to the NMR sample tube. ^1H NMR analysis revealed that the hydrosilane signal disappeared, with the formation of a doublet at 8.4 ppm corresponding to the ^{13}C -labeled formic acid salt ($J = 181$ Hz) (Fig. 4(c), Scheme 5(ii)). These results strongly support not only a reaction pathway that includes the formation of the hydrosilane, as mentioned above (Scheme 4), but also the possible active species: the penta-coordinate silicate.

3.3. Application for reaction using hexamethyldisilane and metallic silicon

The reductive transformation of CO_2 with hexamethyldisilane, a possibly produced disilane as a waste compound from silicone industry [5], was examined using DMA solvent and fluoride salts. The results are summarized in Table 3. The reaction with TBAF catalyst, the 14% yield of formic acid was obtained (Table 3, entry 1). The reaction scarcely proceeded with KF, however, the addition of [2.2.2] cryptand enhanced product yield to 7% (Table 3, entry 3).

The good catalytic activity of the fluoride salt for the reductive transformation of CO_2 with the disilane encouraged us to examine the reduction of CO_2 with metallic Si powder as a reducing agent. The optimization of the reaction conditions is shown in Table 4. Interestingly, the reaction of 0.50 mmol Si powder with 10 mmol H_2O under the action of the TBAF catalyst afforded 0.10 mmol formic acid and its salt (Table 4, entry 1). Decreases in the amount of H_2O or reaction temperature resulted in decreased product yields (Table 4, entries 2–5). The combination of KF and [2.2.2] cryptand induced slightly better results (Table 4, entry 7) compared with KF alone (Table 4, entry 6), whereas the TBAF produced much better yields. The use of H_2O as solvent instead of DMA also afforded a small amount of formic acid product (Table 4, entry 9). Fig. 6 pre-

Table 3

Formic acid synthesis from CO_2 and H_2O with Me_6Si_2 .

$$\text{CO}_2 + \text{H}_2\text{O} + \text{Me}_6\text{Si}_2 \xrightarrow[\text{DMA (2 mL), 80 }^\circ\text{C, 24 h}]{\text{catalyst (0.05 mmol)}} \text{HCOOH} + \text{Me}_6\text{Si}_2\text{O}_2$$

Entry	Catalyst	Conversion of disilane (%)	HCOOH produced* (mmol)	HCOOH yield based on disilane* (%)
1	TBAF-3 H_2O	67	0.06	12
2	KF	35	0.01	2
3	KF + [2.2.2] cryptand	57	0.04	7

Reaction conditions: hexamethyldisilane (0.50 mmol), CO_2 (1 atm, balloon), H_2O (2.5 mmol), fluoride salt (0.05 mmol), DMSO (1.0 mL), 80 $^\circ\text{C}$, 24 h. * This value contains formic acid salt.

Table 4

Formic acid synthesis from CO_2 and H_2O using Si powder.

$$\text{CO}_2 + \text{H}_2\text{O} + \text{Si powder} \xrightarrow[\text{DMA}]{\text{catalyst (0.05 mmol)}} \text{HCOOH} + \text{SiO}_2$$

Entry	Catalyst	H_2O^a (mmol)	Temp. ($^\circ\text{C}$)	HCOOH produced ^a (mmol)
1	TBAF-3 H_2O	10	95	0.10
2	TBAF-3 H_2O	5.0	95	0.08
3	TBAF-3 H_2O	2.5	95	0.08
4	TBAF-3 H_2O	2.5	80	0.06
5	TBAF-3 H_2O	2.5	50	<0.01
6	KF	10	95	<0.01
7	KF + [2.2.2] cryptand	10	95	0.03
8	none	2.5	80	<0.01
9	TBAF-3 H_2O	110 ^b	95	0.008

Reaction conditions: silicon powder (0.5 mmol), CO_2 (1 atm, balloon), H_2O , catalyst (0.05 mmol), DMA (2 mL), 24 h. ^a This value contains hydrated water in TBAF-3 H_2O . ^b H_2O was used as solvent instead of DMA.

sents the Si 2p XPS spectra of fresh Si powder and the reaction residue after the reaction with CO_2 . After the reaction, the surface of the metallic Si was nearly completely oxidized to SiO_2 ,

Fig. 6. XPS spectra of Si powder (a) and reaction residue (b).

Graphical Abstract

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Reductive transformation of CO₂: Fluoride-catalyzed reactions with waste silicon-based reducing agentsKen Motokura, Masaki Naijo, Sho Yamaguchi, Akimitsu Miyaji, Toshihide Baba*
Tokyo Institute of Technology, JapanFluoride-catalyzed transformation of CO₂ to formic acid was examined using “waste” Si-based materials, disilane and metallic Si powder, as reducing agents.

suggesting that metallic Si also acts as an effective reducing agent toward CO₂ in the presence of a fluoride catalyst.

4. Conclusions

Model compounds of silicon waste, disilane and metallic Si, were found to be effective reducing agents for CO₂ in the presence of fluoride catalysts. In the case of disilane, the yield of formic acid was as high 44% based on the disilane used. Time-course and in-situ NMR experiments revealed the reaction pathway and possible active species. A catalytic CO₂ recycling process using waste silicon-based reducing agents has the potential to be one of the most effective solutions toward environmentally-friendly society.

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氟催化废弃硅基还原剂与CO₂还原转化反应

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摘要: CO₂是最重要的可再生碳源之一。为了将CO₂转化为有用的有机化合物, 我们研究了二种模型硅基“废”材料—乙硅烷和硅粉的反应活性。在这些反应中, 氟盐的催化活性最高, 在常压、在质子源水和硅基还原剂的存在下, CO₂可转化为甲酸。原位NMR和动力学分析表明, 含氢硅烷和五配位的硅物种分别是反应中间物和活性物种。

关键词: 二氧化碳; 氟; 均相催化; 甲酸; 乙硅烷

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