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In situ Generation of Fluoride Catalysts for CO_2-to-Formic Acid Conversion With Silicon Reducing Agent

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ABSTRACT

The activation and catalytic reduction of carbon dioxide (CO_2) using silicon-based reducing agents is an important strategy for sustainable C1 chemistry and silicon waste upcycling. Tetraalkylammonium fluoride salts are highly effective promoters of silicon hydride formation; however, their direct use introduces challenges in terms of expense and handling. Here, we report the first example of in situ generation of fluoride catalysts for the reduction of CO_2 to formic acid from a simple inorganic fluoride salt, such as NaF. A neutral precursor releases fluoride under mild conditions, enabling selective CO_2 reduction using powdered silicon. Mechanistic studies reveal that the catalytically active fluoride species are generated in situ from three components: inorganic fluoride, amine, and acid. The method eliminates the need for expensive and unstable organic fluoride. This work establishes a new fluoride-mediated catalytic platform for coupling CO_2 valorization with silicon waste utilization.

1 | Introduction

Carbon dioxide (CO_2) is an abundant C_1 feedstock already utilized in nonreductive processes such as urea and carbonate synthesis, and the development of efficient reductive pathways is essential for producing a variety of organic molecules [1–4]. The catalytic transformation of carbon dioxide (CO_2) into formic acid and formate derivatives is an increasingly important strategy for sustainable chemical synthesis, hydrogen storage, and the development of circular carbon technologies [5–17]. In parallel, large volumes of silicon-containing wastes—including silicon waste, silicon sludge from wafer slicing, and end-of-life photovoltaic (PV) materials—are generated globally, creating a significant need for technologies capable of simultaneously valorizing CO_2 and upcycling silicon resources [9–12, 14, 16–18]. Silicon-based reducing agents, including hydrosilanes [19–25], disilanes [7, 26], and powdered silicon, are highly effective reductants for CO_2 owing to the strong thermodynamic driving force associated with Si—O and Si—F bond formation [13, 15].

Fluoride anions (F^-) serve as powerful activators of hydrosilanes and silicon materials by generating hypervalent siliconate intermediates that facilitate hydride transfer. The foundational work of Fujita et al. established fluoride-catalyzed hydrosilane reduction of carbonyl compounds, revealing the critical role of fluoride in Si—H activation pathways [27]. Subsequent studies by our group extended fluoride catalysis to the reductive transformation of CO_2, demonstrating that simple fluoride (e.g., CsF) catalyzes hydrosilylation of CO_2 to yield formylated products under mild conditions [8]. They further showed that silicon wastes and disilanes can reduce CO_2 in the presence of fluoride catalysts, enabling formic acid synthesis through in situ generation of Si—H species [11].

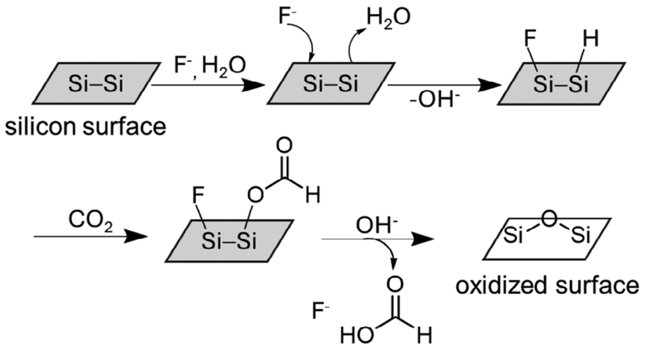


FIGURE 1 | Pathway for the fluoride-catalyzed reduction of CO_2 to formic acid with silicon.

Fluoride-mediated CO_2 reduction has since been applied to a range of silicon-based reductants, including crushed silicon wafers, waste silicon powders, and metallic silicon recovered from PV panel production [12, 14–18]. Tetraalkylammonium fluoride (e.g., TBAF) is particularly effective in activating silicon substrates to form reactive Si—H intermediates capable of reducing CO_2 to formic acid, methanol, or formamide, depending on the additive and reaction environment [14–18]. The reaction pathway of the fluoride-catalyzed reduction of CO_2 to formic acid using metallic silicon is shown in Figure 1. Notably, fluoride-catalyzed systems have been shown to operate even with silicon sludge and exhaust-gas CO_2, highlighting the practicality and industrial relevance of these transformations [16, 17].

Despite the advances in fluoride-catalyzed CO_2 reduction with waste silicon, virtually all reported systems rely on direct addition of expensive organic fluoride salts (Scheme 1a). Also, the handling of hygroscopic and strongly basic fluoride anions presents challenges in safety. Generating catalytically active fluoride in situ, from neutral or less-reactive precursors, remains largely unexplored in the context of silicon-mediated CO_2 reduction.

In other domains of organic chemistry, however, in situ fluoride generation is established [28–31]. For example, Manabe and coworkers demonstrated that glycosylations using glycosyl fluorides and $BF_3 \cdot Et_2O$ proceed via HF formation and subsequent generation of catalytically active fluoride species on glass surfaces [28]. Jung et al. reported enantioselective protonation of fluorinated silyl enol ethers under cooperative cation-binding catalysis, wherein fluoride—released and organized in situ—participates directly in the stereocontrolling environment [29]. Additional evidence for dynamically generated fluoride catalysis appears in early work by Goldberg and Lukevics, who showed that alkali metal fluorides in the presence of crown ethers efficiently mediate hydrosilylation of carbonyl compounds, despite being introduced in substoichiometric amounts—indicating in situ liberation of catalytically competent fluoride under phase-transfer conditions [30]. Collectively, all these examples highlight that catalytically active fluoride species can arise dynamically within the reaction environment, eliminating the need for discrete addition of free F^- salts. However, a method to generate fluoride catalysts in situ through the reaction between inorganic fluoride salts, tertiary amine, and protonic acid has not been achieved. In addition, in situ generated fluoride catalysis for CO_2-to-formic acid conversion using silicon-based reductants has not yet been reported. Such an approach could improve economy and safety by circumventing the direct use of aggressive organic fluoride salts.

Herein, we report the first example of in situ generation of catalytically active fluoride species from simple inorganic fluoride, amine, and acid that promote the reduction of CO_2 to formic acid using powdered silicon as a reducing agent (Scheme 1b). We show that fluoride released from a neutral precursor under mild conditions is sufficient to activate silicon reductants and drive the selective reduction of CO_2. This strategy provides a new platform for coupling CO_2 valorization with silicon-waste upcycling through controlled fluoride catalysis.

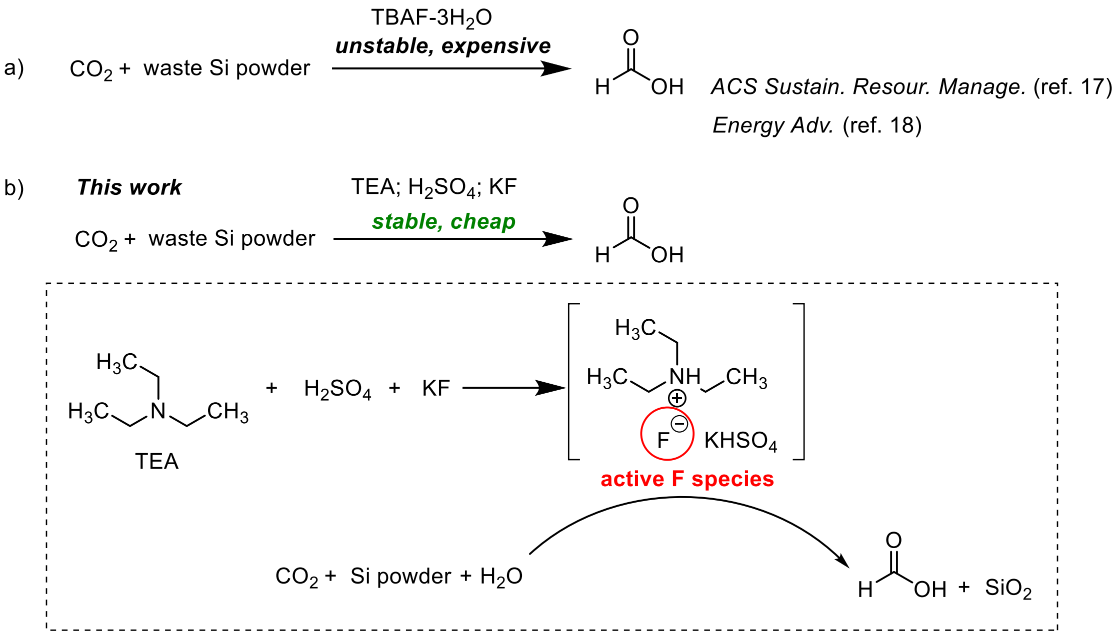
2 | Results and Discussion

2.1 | Promotion of CO_2 Reduction by Ternary Combination

To evaluate the feasibility of generating catalytically active fluoride in situ, we investigated a three-component system composed of KF, triethylamine, and H_2SO_4 in the reduction of CO_2 with waste silicon powder (Table 1). Under the reaction conditions (NMP solvent, 100 °C), only a negligible amount of formic acid was detected in the presence of KF alone (entry 1). No reaction occurred when triethylamine was used as the sole additive (entry 2). Binary mixtures of KF and triethylamine (entry 3), or triethylamine and H_2SO_4 (entry 4), also failed to promote the reaction. Due to the formation of free HF, the experiment with only KF and H_2SO_4 was omitted. Interestingly, the ternary combination of KF, triethylamine, and H_2SO_4 significantly enhanced CO_2 reduction, yielding 0.07 mmol of formate (entry 5). Further optimization of the water content increased the formate yield to 0.32 mmol (entry 6). Replacing waste silicon powder with fresh silicon further improved the yield (entry 7). The turnover number (TON) with respect to fluoride (for entry 7) was estimated to be approximately 2.2, based on the ratio of formic acid produced (0.44 mmol) to the amount of fluoride introduced (0.20 mmol). These results clearly indicate the role of fluoride as a catalyst. The holistic trends in Table 1 indicate that the ternary combination creates a reactive fluoride environment capable of initiating silicon activation pathways for reductive transformation of CO_2 to formic acid, as shown in Figure 1.

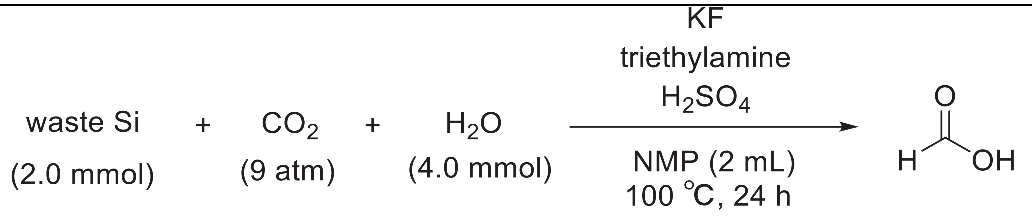
2.2 | Optimization of Fluoride, Amine, and Acid Components

We next investigated the effects of different fluoride salts, tertiary amines, and acids in the three-component reaction system, as summarized in Figure 2. Both KF and NaF exhibited good catalytic activity for the reduction of CO_2 to formic acid. Other potassium-containing fluoride salts, such as KHF_2 and K_3AlF_6, showed moderate activity, whereas the remaining salts were largely inactive. We also examined the role of various tertiary amines. In the presence of either KF or NaF, triethylamine and DBU served as effective components for CO_2 reduction. Formate formation was also observed with other tertiary amines, including trihexylamine and pyridine. Primary and secondary amines were excluded due to the potential formation of corresponding amide byproducts [13]. Among the acid additives tested, H_2SO_4



SCHEME 1 | (a) TBAF-catalyzed reductive transformation of CO_2 and (b) in situ generation of active fluoride species followed by the reductive transformation of CO_2 to formic acid.

TABLE 1 | Reduction of CO_2 with waste silicon powder promoted by KF/triethylamine/H_2SO_4.[a]



Entry	KF (mmol)	Triethylamine (mmol)	H_2SO_4 (mmol)	Formic Acid (mmol)	TON of fluoride
1	0.20	—	—	< 0.01	< 0.01
2	—	0.20	—	< 0.01	—
3	0.20	0.20	—	< 0.01	< 0.01
4	—	0.22	0.20	< 0.01	—
5	0.20	0.22	0.20	0.07	0.35
6	0.20	0.22	0.20	0.32[b]	1.6
7	0.20	0.22	0.20	0.44[b,c]	2.2

[a] Reaction conditions: KF, triethylamine, H_2SO_4, waste Si powder (2.0 mmol), CO_2 (9 atm), H_2O (4.0 mmol), NMP (2 mL), 100°C, 24 h.
[b] H_2O (10 mmol).
[c] Fresh silicon powder prepared from silicon wafer.

demonstrated the highest performance. While $NaHSO_4$ yielded formic acid, its fully neutralized counterpart, Na_2SO_4, failed to promote the reaction. These results indicate that sufficient proton-donating ability is essential for generating the catalytically active species.

The effects of the amounts of NaF, triethylamine, and H_2SO_4 on the reduction of CO_2 were next examined, as shown in Figure 3. As the amount of NaF increased, the formate yield rose proportionally, indicating the pivotal catalytic role of the fluoride species. While no reaction was observed in the absence of acid additives (Table 1), the amount of H_2SO_4 had no significant impact on the formate yield. In contrast, the amount of triethylamine strongly influenced the yield: optimal formate production was observed when the amine amount was in the range of 0.08–0.16 mmol. Acids with sufficiently low pK_a are required to protonate the amine and promote the release of reactive fluoride species from inorganic fluoride salts, while remaining compatible with the silicon-mediated reduction environment. Weaker acids are insufficient to drive this equilibrium effectively,

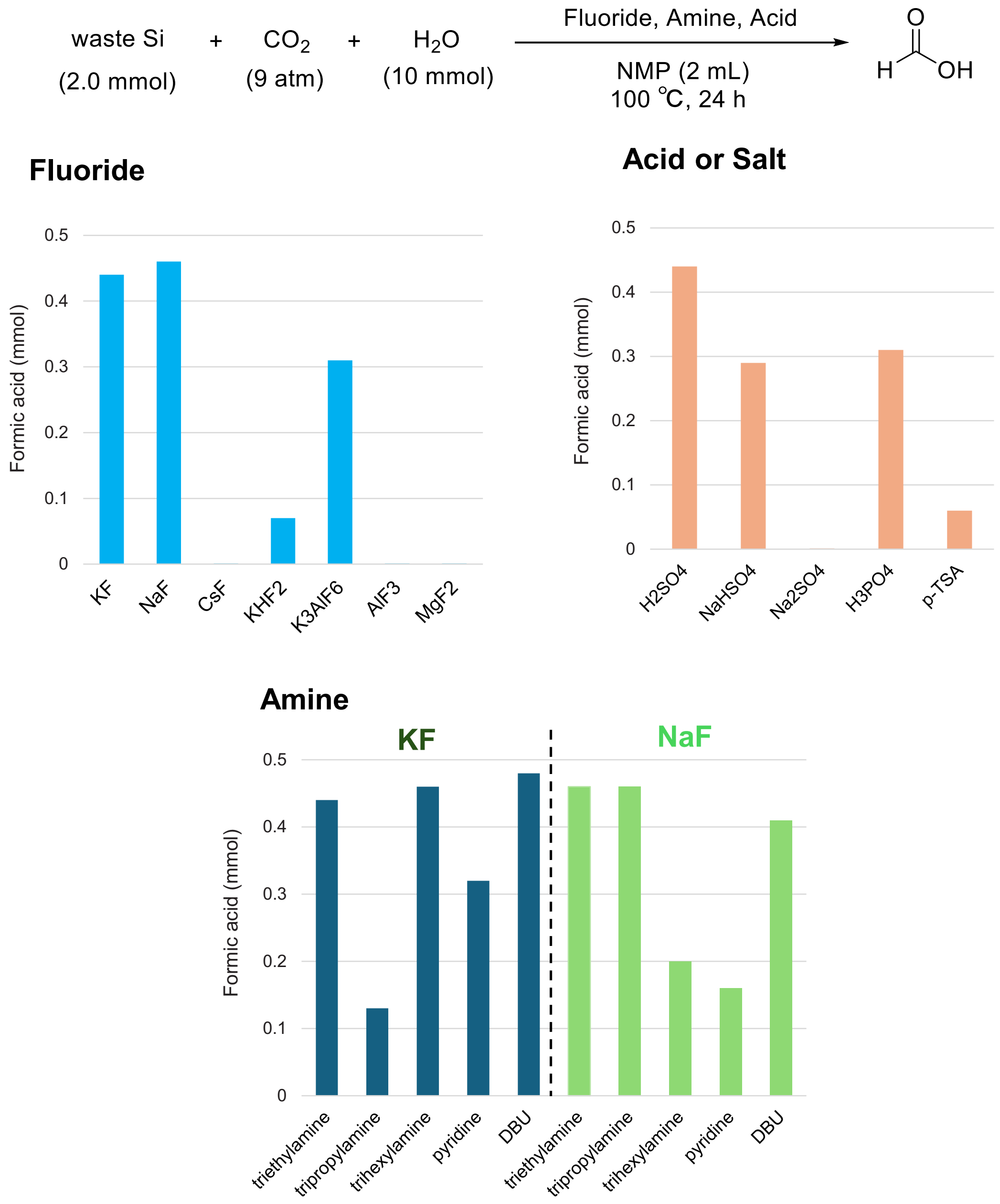


FIGURE 2 | Effect of fluoride catalyst, amine, and acid or salt on the reduction of CO_2 with silicon waste. Basic reaction conditions: waste silicon (2.0 mmol), CO_2 (9 atm), H_2O (10 mmol), KF (0.20 mmol), triethylamine (0.22 mmol), H_2SO_4 (0.20 mmol), NMP (2 mL), 100°C, 24 h. DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene. *p*-TSA: *p*-toluenesulfonic acid.

whereas excessively harsh conditions could suppress silicon hydride formation. Due to the formation of the corresponding formamide, secondary and primary amines were not examined [15].

2.3 | Application to Industrial Exhaust Gas

A key advantage of fluoride-mediated silicon activation is its robustness toward contaminants. To demonstrate practical applicability, the optimized system was applied to exhaust gas obtained from a thermal power facility containing 14% CO_2, 5% O_2, and N_2 balance (Figure 4). Despite the dilute CO_2 concentration and presence of oxygen, the system successfully reduced CO_2 to formic acid, highlighting the operational stability of the in situ-generated fluoride catalyst under realistic flue-gas conditions. This result is particularly significant for large-scale CO_2 mitigation, as it bypasses the need for high-purity CO_2 sources and enables direct coupling of silicon waste upcycling with industrial exhaust treatment.

2.4 | Reaction Mechanism Including Generation of Active Fluoride Species

To probe the mechanism of fluoride liberation, we analyzed mixtures of triethylamine, H_2SO_4, and KF by ^1H NMR spectroscopy (Figure 5). Triethylamine alone exhibited a characteristic signal

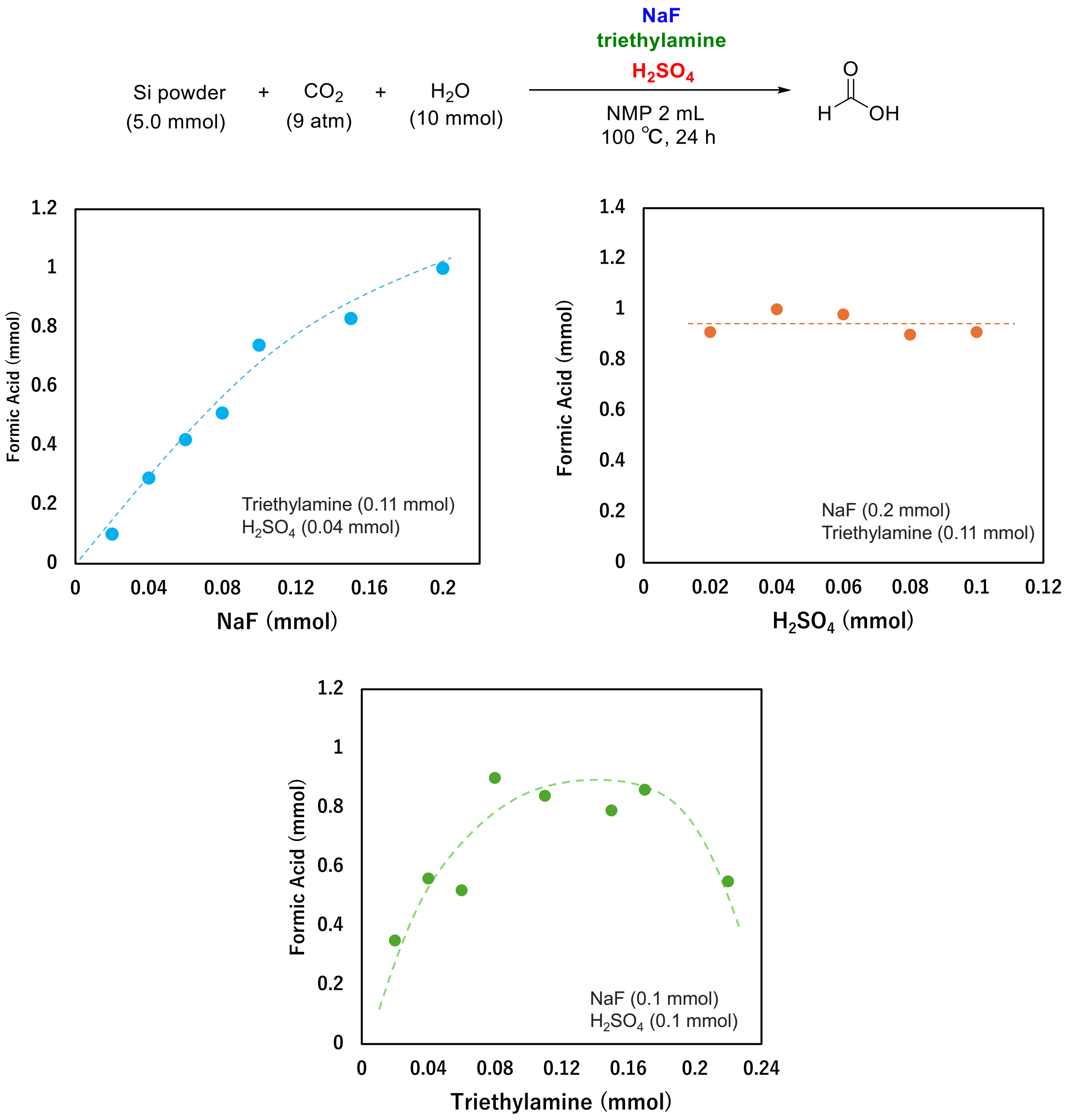


FIGURE 3 | Effect of NaF/H_2SO_4/triethylamine amount on the reduction of CO_2 with silicon powder. Reaction conditions: powdered silicon wafer (2.0 mmol), CO_2 (9 atm), H_2O (10 mmol), NaF, triethylamine, H_2SO_4, NMP (2 mL), 100°C, 24 h. The lines are provided solely as eye-guides.

pattern, but addition of H_2SO_4 resulted in downfield shifts of both methyl and methylene proton signals, indicative of the formation of triethylammonium hydrogen sulfate. Incremental addition of KF gradually perturbed the NMR signals, consistent with interactions between the ammonium salts and KF leading to partial formation of fluoride-containing species. The systematic spectral evolution with increasing KF strongly suggests the formation of fluoride–amine ion pairs (Et_3NH^+–F^-). The formation of the ion pair was also supported by ^{19}F NMR (Figure 6). The peak position of the three-component mixture differed from that of KF and TBAF, in which the free fluoride ion appears around −125 ppm. The upfield shift observed for the mixture suggests a strong F—H interaction, consistent with the formation of the proposed ternary complex. These intermediates are well known to be potent activators of silicon to generate Si—H bonds from bulk silicon (Figure 1).

Based on the combined results, a mechanistic model is proposed (Figure 7). The sequence begins with protonation of triethylamine by H_2SO_4, forming triethylammonium hydrogen sulfate. Reaction with KF yields a mixture of organic fluoride-like species [30], which are known to be much more reactive toward Si—O and Si—F bond formation. These species nucleophilically attack silicon powder surfaces, generating hypervalent fluorosilicate intermediates. Subsequent protonation of these intermediates generates Si—H species, which serve as the actual reductants for CO_2 (Figure 1). This pathway is consistent with the following experimental findings: (i) absence of any product when one component is omitted (Table 1): all three are required to achieve catalytic activity. (ii) Higher activity with stronger acids and suitable amines (Figure 2): fluoride speciation depends sensitively on acid–base equilibria. (iii) NMR evidence for evolving Et_3NH–fluoride species (Figure 5). To probe the role of amine–HF species, we performed control experiments using triethylamine-3HF salt (TEA-3HF) under otherwise identical reaction conditions (TEA-3HF 0.2 mmol; H_2O 10.0 mmol; CO_2 0.9 MPa). As a result, the formation of 0.49 mmol of formic acid was detected. This result supports the proposed reaction mechanism, including the in situ

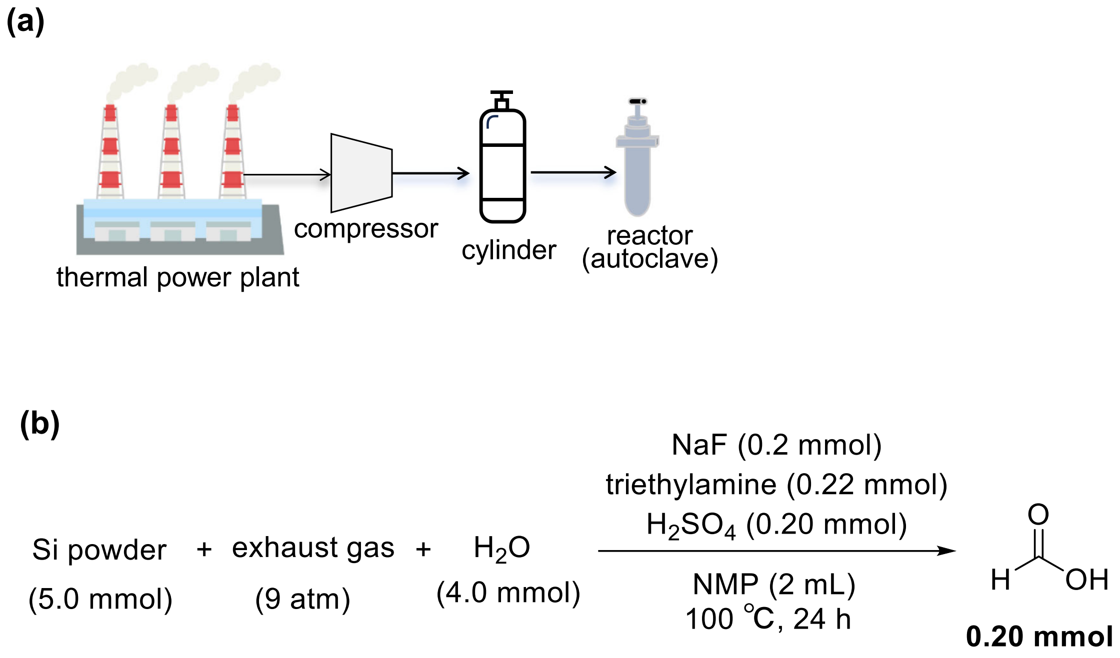


FIGURE 4 | (a) Exhaust-gas sample (14.0%CO_2-5.0%O_2-N_2 bar.) extraction from a thermal power plant. (b) Reduction of CO_2 in exhaust gas to formic acid.

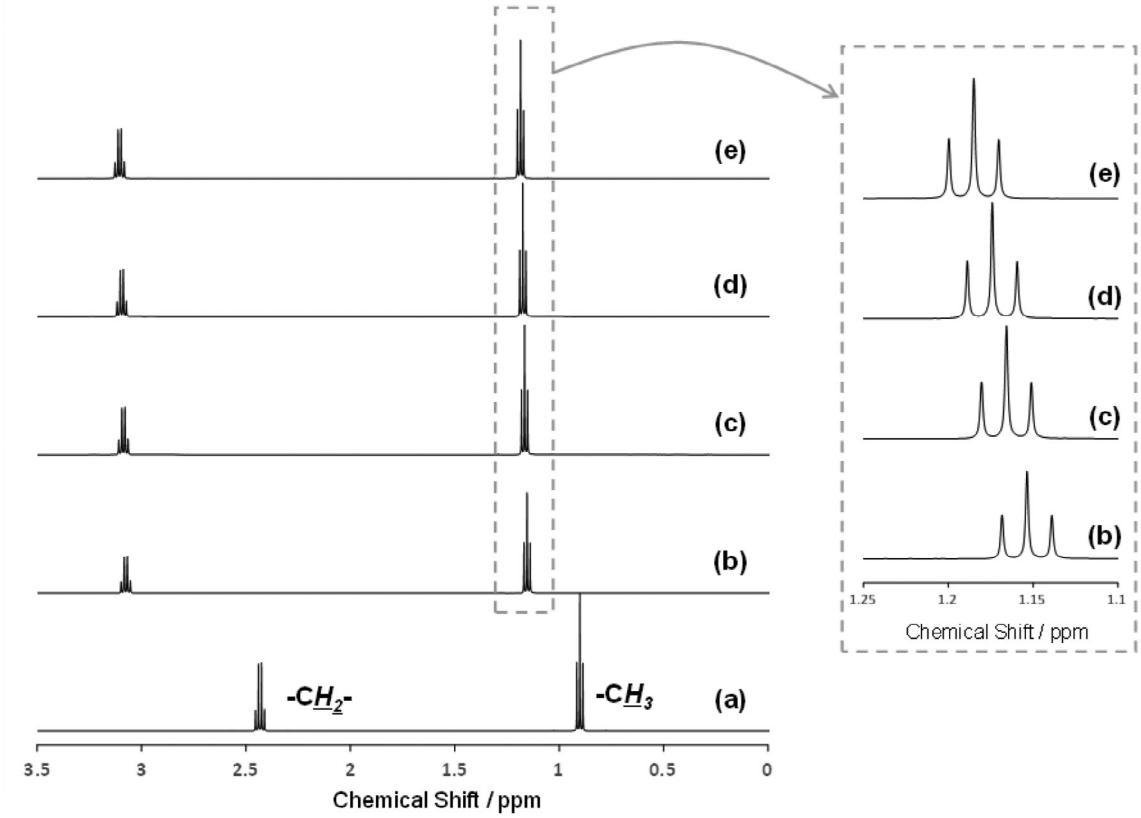


FIGURE 5 | ^{1}H NMR spectra of (a) triethylamine, (b) triethylamine + H_2SO_4, (c) triethylamine + H_2SO_4 + KF (0.05), (d) triethylamine + H_2SO_4 + KF (0.10), (e) triethylamine + H_2SO_4 + KF (0.15). Conditions: D_2O (2 mL), triethylamine (0.22 mmol), H_2SO_4 (0.20 mmol), KF (0~0.20 mmol).

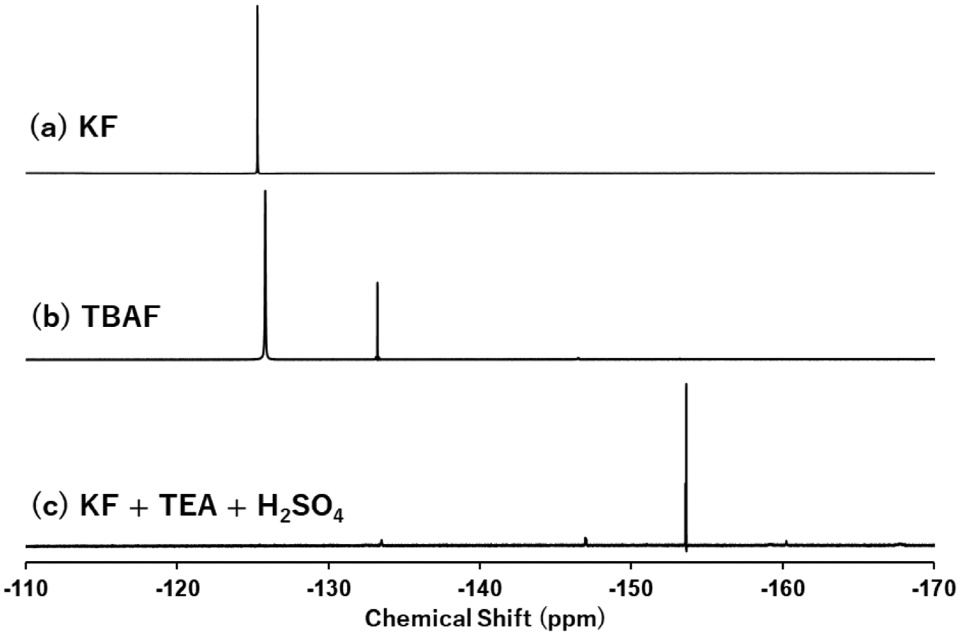


FIGURE 6 | $^{19}F\{^1H\}$ NMR spectra of (a) KF, (b) TBAF, and (c) triethylamine + H_2SO_4 + KF. D_2O solvent was used.

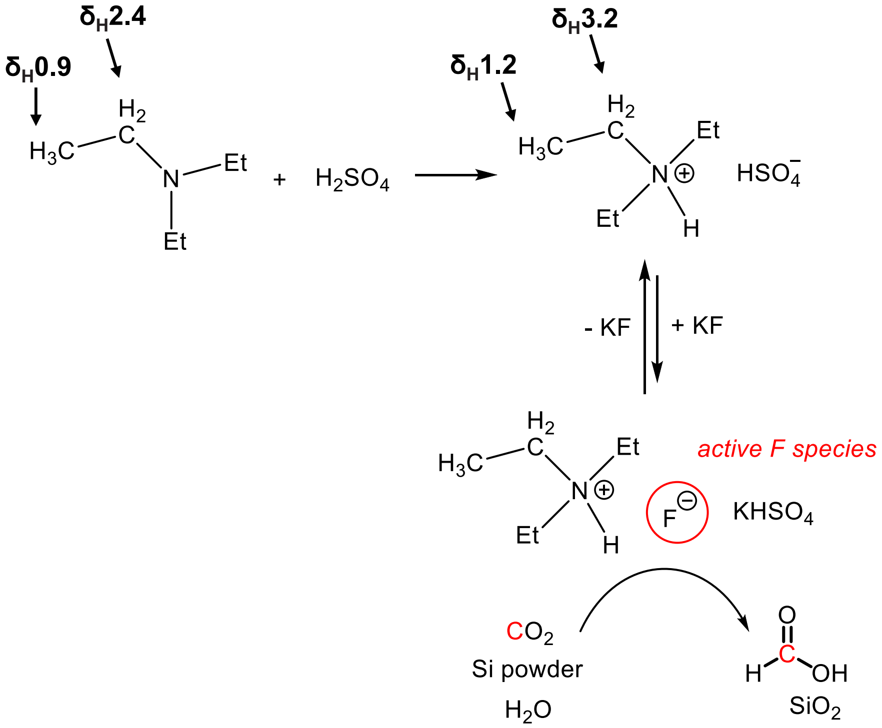


FIGURE 7 | Proposed formation pathway to active fluoride species from triethylamine, H_2SO_4, and KF.

formation of fluoride species with protonated triethylamine. In addition, the XRD and XPS analysis of the recovered solid after the reaction indicates that most of the silicon powder was oxidized to SiO_2 (Figure S1). The ability to control fluoride generation from benign precursors provides a safer, more selective route for silicon activation than using hygroscopic or strongly basic fluoride salts directly.

To further probe the proton-transfer pathway and identify the hydrogen source in formic acid, we performed an isotope-labeling experiment. We conducted the reaction using D_2O as the deuterium source. When D_2O was employed under otherwise identical conditions, the formation of deuterated formic acid ($\underline{D}COOH$, > 90% D) was detected. This result supports the reaction mechanism shown in Figure 1: CO_2 is reduced by

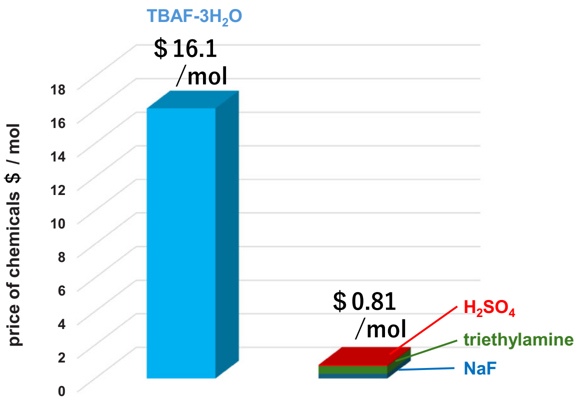


FIGURE 8 | Price of chemicals: dollar ($) per mol. This price is based on the market price of industrial bulk products. For the three-component system, the total of each chemical's price per mol was calculated. Prices were last checked in December 2025.

Si—H species generated through the reaction between silicon and proton sources such as H_2O.

2.5 | Economic Perspective: Cost Comparison of Fluoride Sources

The relative cost of KF, Et_3N, and H_2SO_4 underscores the practical benefit of this approach (Figure 8). All components, KF/triethylamine/H_2SO_4, are inexpensive, and the calculated cost of the three-component system per gram compares favorably with conventional organic fluoride sources such as TBAF. The method therefore offers both technical and economic advantages for industrial CO_2 valorization processes, especially when coupled with abundant silicon waste streams.

3 | Conclusion

The in situ generation of fluoride catalysts from KF or NaF, triethylamine, and H_2SO_4 enables efficient reduction of CO_2 to formic acid using silicon powder, including silicon waste and freshly milled silicon. Mechanistic studies support the formation of active organic fluoride-like species that activate silicon to form Si—H intermediates. The method is applicable to industrial exhaust gas and uses locally available, inexpensive reagents, offering a practical platform for integrated CO_2 valorization and silicon-waste upcycling.

4 | Experimental Section

4.1 | Materials

Recovered silicon wafers originating from end-of-life PV modules were kindly provided by a solar panel recycling company. Potassium fluoride (special grade) and dehydrated *N*-methyl-2-pyrrolidone (NMP, > 99%) were obtained from Kanto Chemical Co., Inc. and used without further purification. Sodium hydrogen sulfate and tripropylamine were purchased from Sigma–Aldrich and used as received. Cesium fluoride, trihexylamine, DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), and 1,3,5-triisopropylbenzene were supplied by Tokyo Chemical Industry Co., Ltd. Carbon dioxide (gas cylinder) was purchased from Jonan-Fuji-Bussan Co., Ltd. A CO_2-containing exhaust gas stream was obtained from the Isogo coal-fired thermal power plant (Electric Power Development Co., Ltd.). Unless otherwise noted, all additional reagents were purchased from Fujifilm Wako Pure Chemical Corporation and used as received.

4.2 | NMR Measurement

The solution NMR spectra were recorded on a JEOL RESONANCE ECA 500 NMR spectrometer at 500 MHz for ^{1}H, and 125 MHz for ^{13}C NMR. The chemical shift values for ^{1}H and ^{13}C were referenced to chloroform. The chemical shifts are reported in δ ppm.

4.3 | XPS Measurement

XPS analyses were performed on a ULVAC-PHI Quantera-SXM system equipped with an Al x-ray source. Spectra were obtained using a pass energy of 69.0 eV, and the Al Kα x-ray source was operated at 50 W and 15 kV with a beam size of 200 µm. Excess charges on the samples were neutralized by argon ion sputtering. The working pressure in the analysis chamber was less than 1×10^{-7} Pa. Spectra were acquired in the C 1s and Si 2p regions. XPS element peaks were shifted to the C 1s position of 284.8 eV.

4.4 | XRD Measurement

Powder x-ray diffraction (XRD) patterns were recorded using a Rigaku Ultima IV diffractometer with Cu Kα radiation.

4.5 | Preparation of Silicon Powders for Use as Reducing Agents

Fresh silicon samples were prepared from silicon wafers (Czochralski monocrystalline silicon wafers, solar grade, Si: > 99.9999%). Wafers were manually crushed in an alumina mortar to obtain fine powders, which were subsequently sieved through a 40 µm mesh using an automated sifter. The BET surface area of the obtained fresh silicon powder was 4.9 m^2g^{-1} [14]. The detailed SEM and XPS results are reported elsewhere [15]. The resulting powders were stored in sealed containers under an argon atmosphere and kept inside a desiccator to minimize moisture uptake.

Waste silicon samples were obtained from a solar panel recycling company. The waste silicon wafer was crushed and treated with aqueous HCl solution as follows: into a 35wt% solution of HCl, 5.0 g of powdered silicon was added. The mixture was stored for 12 h at room temperature, then the solid was filtered, washed with deionized water and acetone. The obtained solid was dried under vacuum and stored under an Ar atmosphere. The BET surface area of the obtained waste silicon powder was 15.0 m^2g^{-1} [17]. The detailed SEM and XPS results are reported elsewhere as the Si-2 sample [17].

4.6 | Typical Procedure for Fluoride-Catalyzed CO_2 Reduction Using Waste Silicon Powder and H_2O

A SUS (stainless steel) autoclave was employed as the reaction vessel. In a separate vial, KF (0.20 mmol), triethylamine (0.22 mmol), H_2SO_4 (0.20 mmol), the solvent (typically NMP, 2 mL), and deionized water (typically 10.0 mmol) were combined and subsequently transferred to the autoclave. Waste silicon powder (2.0 mmol, 0.056 g) was then added to the reactor. After sealing the autoclave, CO_2 gas was introduced to a pressure of 9 atm (typical reaction pressure). The reaction mixture was stirred vigorously at 100°C for 24 h. Upon completion, the products were analyzed by ^1H NMR spectroscopy. The yield of formic acid was quantified by liquid-phase ^1H NMR using $CDCl_3$ as the solvent and 1,3,5-triisopropylbenzene as an internal standard. The quantitative relationship between the ^1H NMR peak area of formic acid and the internal standard was validated using calibrated standard samples.

Acknowledgments

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Conflicts of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File: Chem71108-sup-0001-SuppMat.Pdf