

Preparation and characterization of calcium fluorosilicate (CaSiF₆) as a fluorinating agent

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ABSTRACT

The calcium fluorosilicate (CaSiF₆) was prepared from calcium silicate (CaSiO₃) with fluorine gas at 25 ~ 200 °C and 1.013 × 10⁵ Pa for 1~24 h. Especially, the pure CaSiF₆ could be prepared at 25 °C for 24 h with F₂ gas from the results of X-ray diffraction. Increasing temperature to higher than 100 °C, the prepared CaSiF₆ was decomposed into calcium fluoride (CaF₂) and Silicon Tetrafluoride (SiF₄). The release of SiF₄ gas was confirmed by the results of gas-phase infrared spectroscopy. In this study, we tried to modify the surface of nickel hydroxide (Ni (OH)₂) using the SiF₄ gas released from CaSiF₆ particles. The results of X-ray photoelectron spectroscopy indicated the formation of fluorinated bonds on the sample after surface fluorination. Consequently, the CaSiF₆ particles can be useful for a new fluorinating agent.

1. INTRODUCTION

Surface fluorination using fluorinated gases has been attracting attention in various fields because it can precisely modify the surface of various functional materials. However, it is also true that handling highly reactive fluorinated gases requires safe reaction equipment and storage tanks, which limits the facility environment. On the other hand, compared to fluorinated gases, solid fluorinated agents are portable, Stable in air and easy to handle, and are expected to be applied as an alternative fluorinating agent to fluorinated gases. A typical fluorinating agent is KF (potassium fluoride), but it is mainly used in organic solvents. In this study, we focused on CaSiF₆(The calcium fluorosilicate), which has never been reported as a solid fluorinating agent, is inexpensive, and reacts only by heating. CaSiF₆ is produced as a byproduct together with CaF₂ (calcium fluoride) during the production of phosphoric acid and the treatment of hydrofluoric acid neutralization effluent. But until now there is no established method for its utilization, and

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it is discarded. If this can be used as a fluorinating agent, it will lead to improved environmental and facility issues.

In this study, we report on the possibility of fluorine modification of Ni (OH)₂ material surfaces using fluorine gas generated when CaSiF₆ is heated.

2. EXPERIMENTAL DETAILS

2.1 Preparation of CaSiF₆

CaSiF₆ used in this study was synthesized by treating 0.40 g of CaSiO₃ (039-14525, FUJIFILM Wako Pure Chemical Corporation) (A) with F₂ gas at a fluorine pressure of 1.013×10^5 Pa for 1 to 24 h, varying from room temperature (25 °C) to 200 °C [Table.1 (B)~(D)]. In the fluorination procedure, the samples were placed in a stainless-steel reaction tube under a vacuum of 1 Pa or less, and F₂ gas was introduced.

Table 1. Fluorine treatment conditions for CaSiO₃

| Sample name | Temperature (°C) | Time (h) | Pressure (Pa) |
|-------------|------------------|----------|---------------------|
| (A) | - | - | - |
| (B) | 100 | 1 | 1.013×10^5 |
| (C) | 200 | 1 | 1.013×10^5 |
| (D) | 25 | 24 | 1.013×10^5 |

2.1.1 Characterization of prepared samples

The crystal structures of untreated CaSiO₃ (A) and fluorine-treated CaSiO₃ (B)~(D) were investigated using XRD (X-ray diffraction; XRD-6100, SHIMAZU, Ltd.) It is also FE-SEM (Field Emission-scanning electron microscopy; ULTRA plus, ZEISS) observations were also made on (A) and (D).

2.2 Evaluation of CaSiF₆ as a fluorinating agent

The sample under condition (D), from which CaSiF₆ was prepared in 2.1, was evaluated as a fluorinating agent. The heating conditions for the use of 0.15 g of (D) as a fluorinating agent are shown in Table 2. Also, Ni (OH)₂ was used as the fluorinated target material. The prepared sample and target sample were isolated in a stainless-steel reaction tube, introduced into the reaction tube under a vacuum of 1 Pa or less, and then heating the following conditions shown in Table 3.

Table.2 Processing conditions (D)

| Sample name | Temperature (°C) | Time (h) |
|-------------|------------------|----------|
| (A) | - | - |
| (D) | - | - |
| (D)-1 | 100 | 1 |
| (D)-2 | 150 | 1 |
| (D)-3 | 200 | 1 |
| (D)-4 | 300 | 1 |
| (D)-5 | 150 | 24 |
| (D)-6 | 200 | 24 |

Table.3 Conditions heated in the same reaction tube as (D) for Ni (OH)₂

| Sample name (D) | Sample name (Ni (OH) ₂) | Temperature (°C) | Time (h) | (D) mass (g) | Ni (OH) ₂ mass (g) |
|-----------------|-------------------------------------|------------------|----------|--------------|-------------------------------|
| - | Ni (OH) ₂ -(A) | - | - | - | - |
| (D)-1 | Ni (OH) ₂ -(D)-1 | 100 | 1 | 0.15 | 0.10 |
| (D)-3 | Ni (OH) ₂ -(D)-3 | 200 | 1 | 0.15 | 0.10 |
| (D)-4 | Ni (OH) ₂ -(D)-4 | 300 | 1 | 0.15 | 0.10 |

2.2.1 Characterization of CaSiF₆ samples as fluorinating agents

The prepared (D) was used as a fluorinating agent. Sample (D) and (D)-1~(D)-6 after heat treatment were analyzed by XRD. The gases generated under the conditions of (D)-1 were collected and analyzed using FT-IR (Nicolet 6700, Thermo Electron Scientific Instruments).

2.2.2 Evaluation of the stability of the prepared CaSiF₆

After sample (D) was prepared, it was stored in air-filled and argon-filled conditions for a certain period of time (1(2) week and 6(7) months) and compared using XRD.

2.2.3 Characterization of target material Ni (OH)₂

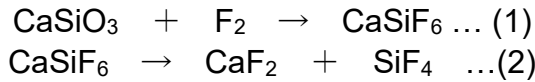
The particle surfaces of untreated Ni (OH)₂ and Ni (OH)₂-(D)-1, Ni (OH)₂-(D)- 3 and Ni (OH)₂-(D)- 4 were analyzed by XPS. (X-ray photoelectron spectroscopy; JPS-9010MC, JEOL, Ltd.).

3. RESULTS and DISCUSSION

3.1 Evaluation of fluorine treatment by X-ray diffraction

The results of XRD analysis of fluorinated CaSiO_3 are shown in Figure 1. Peaks corresponding to CaF_2 were obtained for samples (B) and (C).

On the other hand, a peak corresponding to CaSiF_6 was obtained around $\theta = 23^\circ \sim 25^\circ$ in sample (D). In the fluorination of CaSiO_3 , we considered that the reaction to form CaSiF_6 proceeds at room temperature (Eq. (1)) and that the reaction to decompose CaSiF_6 proceeds when CaSiO_3 is fluorinated while heated above 100°C (Eq. (2)).



The results of FE-SEM observations of CaSiO_3 untreated (A) and after fluorine treatment (D) are shown in Figure 2. (D) had an increased surface irregularity due to fluorine treatment compared to (A).

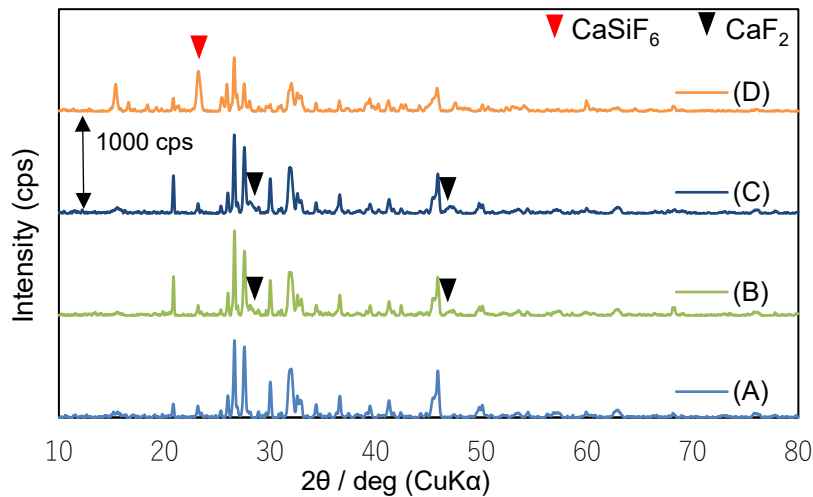


Fig.1 XRD patterns of CaSiO_3 samples fluorinated at different temperatures and times

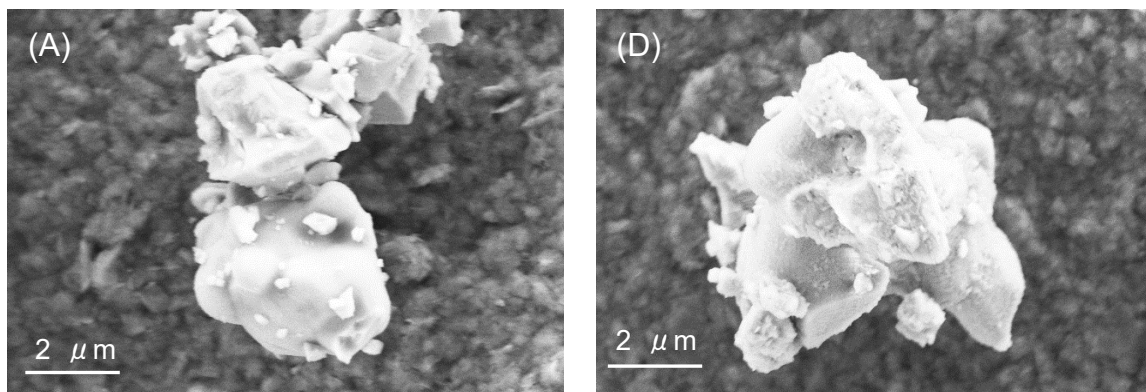


Fig.2 FE-SEM images before and after fluorine treatment

Therefore, we evaluated the sample (D) as a fluorinating agent using the conditions of sample (D), which was able to produce the most CaSiF_6 from the following.

3.2 Evaluation of CaSiF_6 sample as a fluorinating agent

3.2.1 Characterization of CaSiF_6 samples as fluorinating agents

The XRD analysis results for samples (D)-1~(D)-6, which were heat-treated using sample (D), are shown in Figure 3,4. XRD shows that CaSiF_6 does not decrease much in (D)-1 and (D)-2, but the peak intensity of $\text{CaSiF}_6/\text{CaSiO}_3$ decreases (Table 4). This indicates that the decomposition of CaSiF_6 (Eq. (2)) is beginning to progress. The peak of CaSiF_6 disappeared after heating at (D)-4, and a new peak of CaF_2 was observed. This indicates that the reaction in (Eq. (2)) has completely progressed. Also, the peak intensity decreased after heating for 24h, and the crystal peak of CaF_2 was also obtained in (D)-6. The peak intensity of (D)-5 is also reduced compared to (D)-(3). This consider that long-term heating is effective.

The results of FT-IR analysis of the gases generated under conditions (D)-1 are shown in Figure 5. At (D)-1, a new peak was observed around 1000 cm^{-1} . A new peak around 1000 cm^{-1} was obtained that could be attributed to SiF_4 gas. The peaks at 1400 cm^{-1} to 1900 cm^{-1} and 3500 cm^{-1} to 3900 cm^{-1} were due to water vapor (H_2O) contained in the air, and the peaks at 2300 cm^{-1} to 2600 cm^{-1} were the peak at 2300 cm^{-1} to 2600 cm^{-1} is due to carbon dioxide (CO_2) contained in the air and is considered to be due to noise. This also suggests that the decomposition reaction of CaSiF_6 in (Eq. (2)) has begun to progress upon heating above $100\text{ }^\circ\text{C}$.

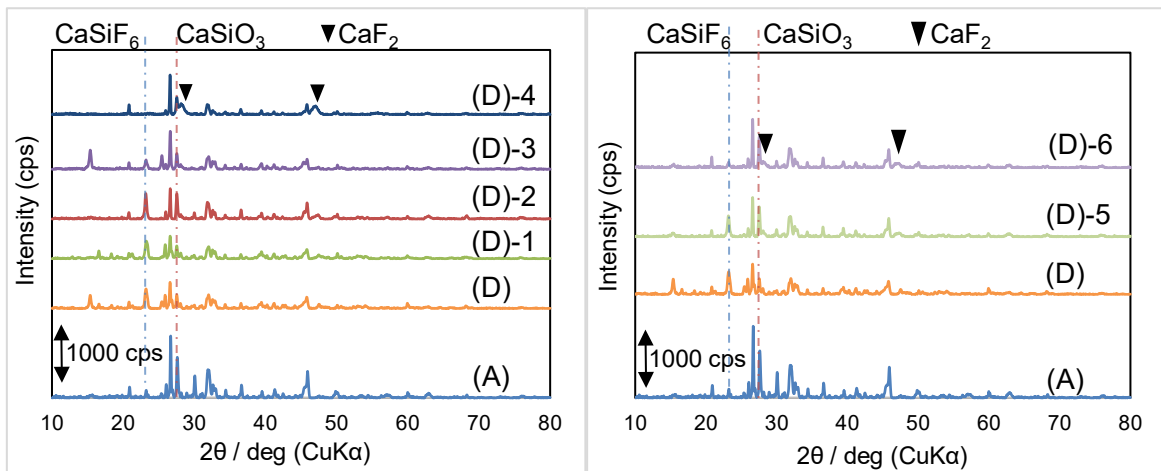


Fig.3,4 XRD patterns of CaSiO_3 samples after fluorination and heating

Table.4 Peak intensity ratio of CaSiF₆ and CaSiO₃ by XRD

| Sample name | CaSiF ₆ / CaSiO ₃ |
|-------------|---|
| (D) | 1.44 |
| (D)-1 | 1.38 |
| (D)-2 | 1.00 |
| (D)-3 | 0.60 |
| (D)-4 | 0.05 |
| (D)-5 | 0.70 |
| (D)-6 | 0.18 |

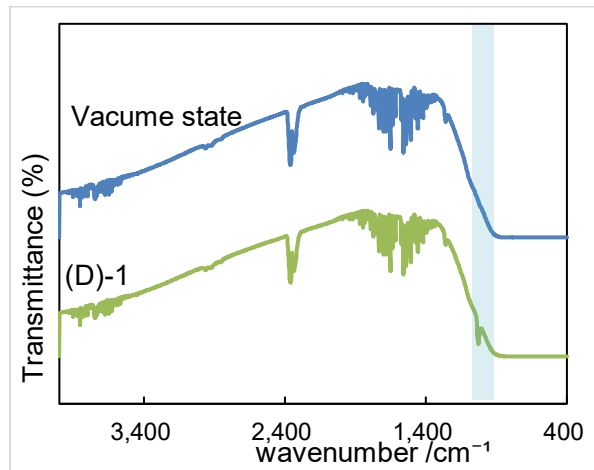


Fig.5 FT-IR of the gas released when the synthesized CaSiF₆ is heated

3.2.2 Evaluation of the stability of the prepared CaSiF₆ by X-ray diffraction

After sample (D) was prepared, it was stored under air-filled and Ar-filled conditions for a certain period of time (1(2) week and 6(7) months) and analyzed by XRD, the results of which are shown in Figure 6,7. A graph comparing the peak intensities of the two is also shown in Figure 8. Those stored under air decreased by 30% in one week. After six months, it decreased by 85%, and a new crystal peak of CaF₂ was obtained. On the other hand, samples stored under Ar atmosphere showed only 3% reduction even after seven months. This is considered that storage in an Ar atmosphere is suitable.

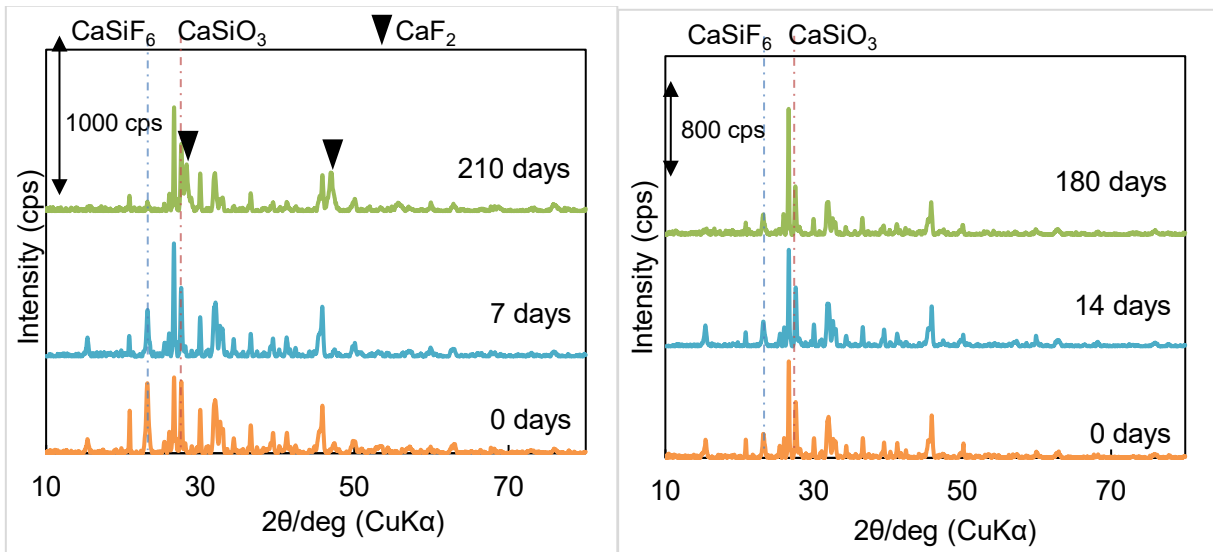


Fig.6 Changes in (D) under Air-filled

Fig.7 Changes in (D) under Ar-filled

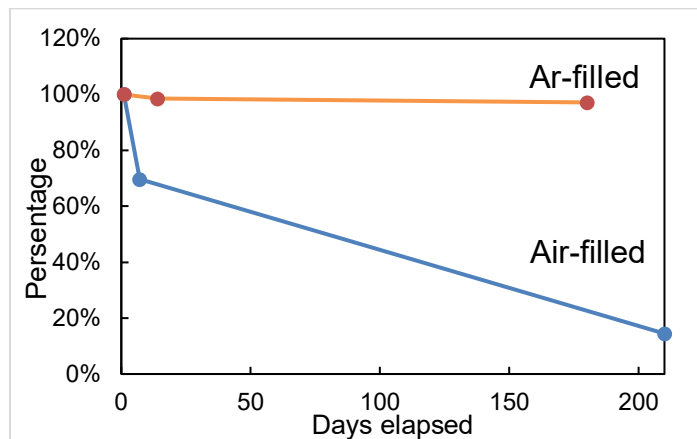


Fig.8 Decrease comparison between Air-filled and Ar-filled

3.2.3 Evaluation of CaSiF₆ on Ni (OH)₂ surface by heating

The XPS analysis results for each Ni (OH)₂ material are shown in Figure 9. The results of the F 1s show that The F peak on the Ni (OH)₂ surface by heating above 100 °C. A new Si peak was observed upon heating above 200 °C. The F peak shifted to the higher energy side at higher heating temperatures. This is considered to be due to more F binding. Atomic comparisons before and after the nickel hydroxide reaction are shown in Table 5. Compared to 100°C, F content increased at 200°C and 300°C but did not change much.

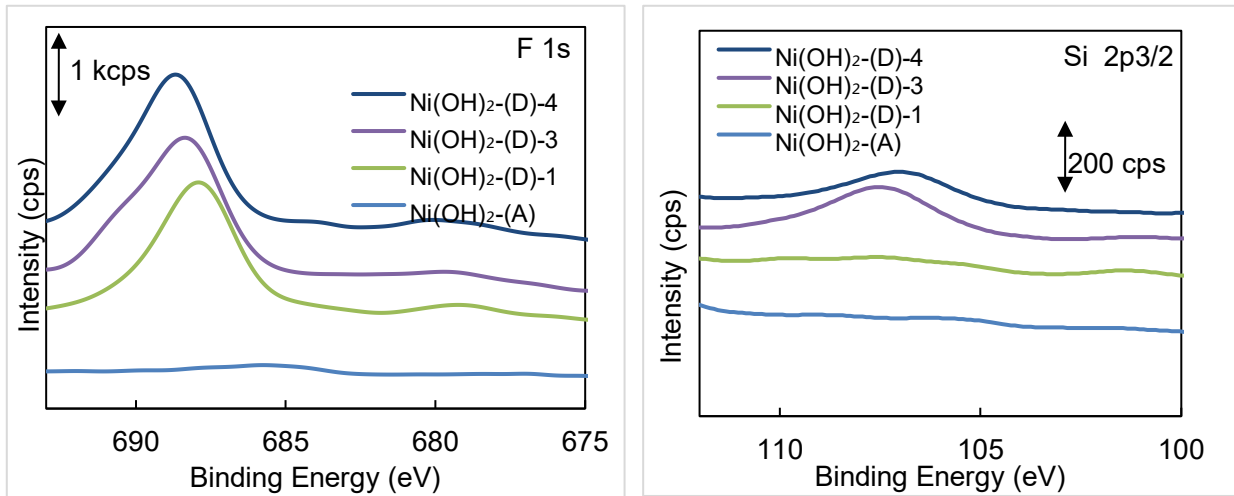


Fig.9 XPS graph of the Ni (OH)₂ when heated under various conditions.

Table 5. Atomic ratio before and after treatment by XPS

| Sample name | N (%) | O (%) | F (%) |
|-----------------------------|-------|-------|-------|
| Ni (OH) ₂ -(A) | 16.47 | 82.42 | 1.11 |
| Ni (OH) ₂ -(D)-1 | 20.65 | 60.55 | 18.80 |
| Ni (OH) ₂ -(D)-3 | 18.80 | 61.76 | 19.44 |
| Ni (OH) ₂ -(D)-4 | 19.04 | 61.70 | 19.26 |

4. CONCLISIONS

The fluorination of CaSiO₃ at 25 °C for 24 h at a fluorine pressure of 1.013×10^5 Pa resulted in the formation of CaSiF₆ on the surface of CaSiO₃. The decomposition reaction of CaSiF₆ proceeds when heated above 100 °C.

As for the evaluation of CaSiF₆ as a fluorinating agent, XRD and FT-IR results of the prepared CaSiF₆ showed that when CaSiF₆ is heated above 100 °C, a decomposition reaction begins to progress, releasing SiF₄ gas, and above 200 °C, CaF₂ is formed. As for the storage method, storage under argon atmosphere is considered effective. The prepared CaSiF₆ could be fluorinated to Ni (OH)₂. This gas is also considered to be extendable to all material surfaces.

REFERENCES

- [1] Vartika S. Singh, S.V. Moharil. An attempt to synthesize and study luminescence in CaSiF₆. *Materials Today: Proceedings* 28. 2020, p.112-114
- [2] Fang Ruan, Sakiko Kawanishi, Sohei Sukenaga, and Hiroyuki Shibata. Effect of the Silicate Skeleton Structure on the Dissolution Kinetics of Calcium Silicate Mineral Phases in Water. *Metallurgical and Materials Transactions B. Volume 52 B* .2021, p.1071-1084

*The 2023 World Congress on
Advances in Structural Engineering and Mechanics (ASEM23)
GECE, Seoul, Korea, August 16-18, 2023*

- [3] Ludmila Rodrigues Costa Tavares, Joaquim Francisco Tavares Junior, Leonardo Martins Costa, Augusto Cesar da Silva Bezerra, Paulo Roberto Cetlin & Maria Teresa Paulino Aguilar. Influence of quartz powder and silica fume on the performance of Portland cement:Scientific Reports volume 10, Article number: 21461.2020