Upgrading Low-Grade Iron Ore through Gangue Removal by a Combined Alkali Roasting and Hydrothermal Treatment

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ABSTRACT: In this study, a combination of alkali roasting and hydrothermal treatment is used as a method of gangue (Si, Al, and P) removal from iron ores as a means to upgrade low-grade iron ore (limonite) into a high-grade iron ore with low gangue content, low porosity, and high Fe and Fe$_2$O$_3$ content to enhance the sustainable development of iron and steel industries. The effects of the combined treatments (NaOH hydrothermal treatment and H$_2$O/NaOH hydrothermal treatment of the alkali roasted sample), the iron ore type, their physical properties, and their calcination/roasting temperatures on the removal extent of gangue are investigated. The extent of Si, Al, and P removal by subjecting iron ores to a 5 M NaOH hydrothermal treatment at 300 °C reached 10–91%, 39–70%, and 38–76%, respectively. When the iron ores are roasted with NaOH at 350 °C, $\alpha$-FeOOH in limonite transfers to NaFeO$_2$. On the other hand, for alkali roasted iron ores that inherently contain Fe$_2$O$_3$, Fe$_3$O$_4$, and Na$_2$CO$_3$ are also observed after the roasting treatment. Higher Al and P removal extents are observed for H$_2$O leaching at room temperature in the prepared roasted samples (Roasting/H$_2$O$_{RT}$) as compared to NaOH hydrothermal treatment, whereas that of Si is low for all samples, except the iron ore with the highest Fe content. After the H$_2$O leaching process, the Fe form is found to be in the amorphous form for all samples, except for the iron ore sample of the highest Fe content. The reason for this is thought to be due to the large amount of unreacted Fe$_3$O$_4$ with NaOH during the roasting process. The specific surface area significantly increases after the Roasting/H$_2$O$_{RT}$ treatment in all samples due to the dehydration of goethite ($\alpha$-FeOOH $\rightarrow$ Fe$_2$O$_3$ + H$_2$O) during the roasting treatment and gangue removal during H$_2$O leaching. When the roasted samples are supplied for hydrothermal treatment by H$_2$O at 300 °C (Roasting/H$_2$O$_{SC}$), the removal rate of Si and P increases as compared with the Roasting/H$_2$O$_{RT}$ treatment. The influence of temperatures of calcination and the roasting treatment on the extent of gangue removal in 5 M NaOH hydrothermal, Roasting/H$_2$O$_{RT}$, and Roasting/H$_2$O$_{SC}$ treatments is small. When NaOH hydrothermal treatment is carried out on the samples that have undergone the Roasting/H$_2$O$_{RT}$ treatment, a gangue removal extent of above 70–97% was achieved, except for the iron ore with the lowest P content, which had the largest loss of ignition and the lowest Fe content. In addition, it is revealed that low-grade iron ore with a high pore properties, $\alpha$-FeOOH content, and gangue content can be upgraded to a high-grade iron ore with a low pore property (low specific surface area and pore volume), high Fe$_2$O$_3$ content, and low gangue content using the above method. Therefore, this method is promising as a method for upgrading low-grade iron ore.

INTRODUCTION

A recent concern is the limited reserves and the rapid depletion of high-grade iron ore, which is utilized in the ironmaking process, due to an increase in steel demand in emerging countries. In addition, high-grade ore becomes higher in gangue (Si, Al, and P) and lower in Fe contents, year by year. For this reason, in the future, the iron and steel-making industry must actively use low-grade iron ore, such as limonite, which has a large amount of goethite ($\alpha$-FeOOH) or gangue components. However, limonite has a large amount of combined water, and its low strength is not suitable for utilization in a blast furnace; the increasing gangue in the iron ore is directly related to the increase in production of iron and steel-making slag. Therefore, the increasing gangue in iron ore also increases the reducing agent ratio ( coke usage) and decreases the tapping ratio (pig iron amount) for the blast furnace method. In other words, this increases energy consumption, CO$_2$ emissions, and iron production costs and decreases iron productivity for the ironmaking process, which is attributed to the increasing gangue in iron ore. It is therefore essential to develop a technology for an upgrading method for low-grade iron ore, which can be achieved by lowering the gangue content and raising the Fe content, for the sustainable development of the iron and steel industry, and the method has been sought after.

It is well-known that Si, Al, and P in iron ore exist as quartz, alumina, kaolinite, aluminosilicate, chlorite, ferric silicate, fayalite, apatite species (fluoroapatite, hydroxyapatite, apatite etc.),1–6 other P species,7 etc. The gangue removal, especially concerning P, through chemical and physical methods has been investigated by many researchers.7–25 It is revealed that chemical leaching is an effective method for P removal from...
iron ore or calcined/alkali roasted iron ores.\(^{3,7−17}\) However, in the chemical leaching reports described above, there are only a few studies focusing on removal of Si and Al.\(^{14,15}\) In addition, although chemical leaching methods using sulfuric acid, hydrochloric acid, and nitric acid against iron ore or calcined/alkali roasted iron ore are effective for the removal of high P content,\(^{3,10,11,13,15,17}\) there are problems such as low Si and Al removal as well as the loss of Fe. In the above reports of P removal,\(^{1−24}\) the investigations were carried out against only one type of iron ore with high P contents, and statistical data acquisition for the removal of gangue from iron ore with different chemical components, physical properties, and different countries of production has not been done. It is therefore important to develop a technology capable of collectively removing gangue components, in particular the high levels of Si and Al content and P affecting the brittleness of the final product from iron ores; the development of technologies concerning these products, which vary in type and are produced in different countries, is vital for sustainable development in iron and steel-making industries worldwide.

Our research group has been investigating the removal of gangue from several types of iron ore having different chemical compositions and physical properties, which is produced in the different countries, and found that hydrothermal treatment with NaOH is an effective solution for gangue removal.\(^{25}\) The removal extent of Si, Al, and P ranged at 10–92%, 39–70%, and 37–78%, and it depends on the types of iron ore. In the present study, we examine the removal of gangue (Si, Al, and P) from iron ores with a combination of alkali roasting and hydrothermal treatment to attain a higher removal extent of gangue than hydrothermal treatment with NaOH only because it has been reported that a combination of NaOH alkali roasting and water leaching at RT to 100 °C is effective in the removal of gangue.\(^{16}\) The effects of the combination of each treatment (leaching at room temperature and hydrothermal treatments of a roasted sample), type of iron ore, physical properties, and calcination temperature on the removal extent of gangue were investigated to develop an upgrading method for producing high-grade iron from low-grade iron ore (limonite).

## RESULTS AND DISCUSSION

### Removal of Gangue Component during Hydrothermal Treatment with NaOH

Table 1 shows the chemical composition, pore properties, and iron forms of the iron ore used in this study. Table 2 summarizes the yield, gangue removal extent, pore properties, and Fe forms in the iron ores treated with a hydrothermal method using 5 M NaOH at 300 °C.\(^{25}\) The yields ranged from 80 to 87%, and a decrease was observed due to the dehydration of limonite and gangue removal. The removal extent of Si, Al, and P ranged between 10–92%, 39–70%, and 38–78%, respectively, and showed a large trend for BRH, which has the highest Fe content, Fe\(_2\)O\(_3\) form, and the lowest loss of ignition (LOI) in the iron ores used in the present study. When the relationship among the gangue components was investigated, positive and negative correlations were found in Al versus P, Al versus Si, and P versus Si.\(^{25}\) The iron forms (α-FeOOH) in the original iron ore changed to Fe\(_2\)O\(_3\) after the samples had been treated. Both the specific surface area and pore volume values of the original iron ore (2–80 m\(^2\)/g and <0.01 to 0.20 cm\(^3\)/g) decreased to <1 to 15 cm\(^3\)/g and <0.01 to 0.10 cm\(^3\)/g, respectively, for all samples obtained after treatment. This decrease means that the sintering of Fe species after dehydration of α-FeOOH in the iron ores occurs through NaOH hydrothermal treatment, irrespective of the iron ore type, because significantly decrease in specific surface area, pore volume, and changing of Fe forms were not observed in the hydrothermal treatment using distilled water.\(^{25}\) Here, decrease in specific surface area and pore volume for treated samples measured by the N\(_2\) adsorption method shows occurrence of Fe species sintering. Now, although the reason why NaOH causes Fe sintering is not clear, it may be due to the morphological change of Fe species caused by the reaction between Fe species and NaOH. From the equilibrium calculation results, it was estimated that the gangue removal occurs due to a reaction of Si, Al, or P and NaOH solution during the hydrothermal treatment accompanied with a

### Table 1. Chemical Composition, Pore Properties, and Iron Forms of the Iron Ore Used in This Study

| sample  | country | total Fe (%) | total Si (%) | total Al (%) | total P (%) | loss of ignition (%) | specific surface area (m\(^2\)/g) | pore volume (cm\(^3\)/g) | Fe form |
|---------|---------|-------------|-------------|-------------|-------------|--------------------|-------------------------------|----------------|---------|
| INL     | Indonesia | 48          | 2.4         | 3.0         | 0.006       | 14                 | 80                           | 0.20            | α-FeOOH (m) |
| ALY     | Australia | 55          | 2.0         | 1.0         | 0.048       | 12                 | 25                           | 0.12            | α-FeOOH (m) |
| ALR     | Australia | 57          | 3.0         | 1.5         | 0.044       | 11                 | 20                           | 0.04            | α-FeOOH (m) |
| MLL     | Malaysia | 59          | 1.1         | 1.8         | 0.053       | 11                 | 15                           | 0.03            | α-FeOOH (m) |
| ILS     | Indonesia | 60          | 1.0         | 2.3         | 0.060       | 10                 | 20                           | 0.04            | α-FeOOH (m) |
| WAL     | Australia | 63          | 2.4         | 2.1         | 0.083       | 8                  | 10                           | 0.03            | α-FeOOH (m), Fe\(_2\)O\(_3\) (w) |
| BRH     | Brazil   | 67          | 2.3         | 0.5         | 0.029       | 1                  | 2                            | <0.10           | Fe\(_2\)O\(_3\) (m) |

\(^{a}\)Heated at 1000 °C in air. \(^{b}\)Calculated by the BET method. \(^{c}\)Calculated by the BJH method. \(^{d}\)Designated by XRD: w (weak) and m (medium).

### Table 2. Summaries of the Yields, Extent of Gangue Removal, Pore Properties, and Fe Forms in Iron Ores Subjected to 5 M NaOH Hydrothermal Treatment at 300 °C

| sample  | yield (%) | Si removal extent (%) | Al removal extent (%) | P removal extent (%) | specific surface area (m\(^2\)/g) | pore volume (cm\(^3\)/g) | Fe form |
|---------|-----------|-----------------------|-----------------------|----------------------|-------------------------------|----------------|---------|
| INL     | 80        | 10                    | 39                    | 38                   | 10                           | 0.10            | Fe\(_2\)O\(_3\) (m) |
| ALY     | 84        | 58                    | 43                    | 70                   | 10                           | 0.04            | Fe\(_2\)O\(_3\) (m) |
| ALR     | 84        | 57                    | 42                    | 60                   | 15                           | 0.03            | Fe\(_2\)O\(_3\) (m) |
| MLL     | 83        | 43                    | 56                    | 68                   | 5                             | 0.03            | Fe\(_2\)O\(_3\) (m) |
| ILS     | 83        | 30                    | 67                    | 78                   | 5                             | 0.02            | Fe\(_2\)O\(_3\) (m) |
| WAL     | 86        | 42                    | 46                    | 42                   | 2                             | <0.01           | Fe\(_2\)O\(_3\) (m) |
| BRH     | 87        | 92                    | 70                    | 69                   | <1                            | <0.01           | Fe\(_2\)O\(_3\) (m) |

\(^{a}\)Calculated by the BET method. \(^{b}\)Calculated by the BJH method. \(^{c}\)Designated by XRD: m (medium).
rarrangement of the Fe structure. In conclusion, although the NaOH hydrothermal treatment is effective in gangue removal from high-grade iron ore, some are not effective for the low-grade ore.

**Effect of Alkali Roasting on Gangue Removal with Distilled Water Leaching at Room Temperature.**

![Figure 1](image.png)

Figure 1. Extent of gangue removal in iron ores treated with the Roasting/H₂O_RT treatment.

shows extent of gangue removal from NaOH-roasted iron ores prepared at 350 °C, which is the temperature that the dehydration reaction occurs for limonite, and treated with H₂O at room temperature (Roasting/H₂O_RT treatment). The characterization results of Roasting/H₂O_RT samples are listed in Table 3 and Figure 2. The results of the iron ore prepared by calcination up to 350 °C in air are also listed in Table 3 for comparison. The extent of removal of Si, Al, and P were 4−72%, 43−75%, and 32−78%, respectively, and the order of the samples were ILS = MLL < INL < ALY < WAL ≪ BRH for Si, ALR = INL < WAL < ALY < MLL < ILS < BRH for Al, and INL ≪ ALR < BRH = ALY = WAL < MLL = ILS for P. Here, the largest extent of gangue removal was found for BRH, which is classified as a high-grade iron ore in the samples used in the present study. The order of the extent of gangue removal components increased as Si ≪ Al ≪ P. It is therefore revealed that the Roasting/H₂O_RT treatment is effective for gangue removal, especially for Al and P removal. Comparable results have been reported by another research group. Although Roasting/H₂O_RT treatments are effective for gangue removal, the extent of Si and Al removal was lower than that of the 5 M NaOH hydrothermal treatment (Table 2). This difference may show that the gangue removal mechanism is different between both treatments. In addition, this difference occurs due to occurrence of gangue removal by the Roasting/H₂O_RT treatment. On the other hand, for a comparison between the specific surface area of a calcined sample in air at 350 °C and Roasting/H₂O_RT samples (Table 3), the latter samples provided higher values than the former samples, and it tended to increase with the order of increasing LOI values. However, pore volumes were similar for both samples. Although the reason is not clear, the agglomeration of pores may occur during the treatment. It was suggested that the decreasing yield and increasing specific surface area occur due to gangue removal. Figure 2 presents the XRD patterns of the samples before and after H₂O treatment at room temperature for comparison. The distributed peaks of Fe₂O₃ were observed for all calcined samples at 350 °C in air (Table 2). For roasted samples, the peaks that are attributable to NaFeO₂ were detected for all samples (Figure 2, left), and existing Na₂CO₃ was also observed only for BRH and WAL, whose Fe₂O₃ was observed in the original samples before treatment (Table 1). In addition, the SiO₂ peaks and unknown peaks disappeared for roasted samples. The NaFeO₂ and Na₂CO₃ peaks observed for roasted samples almost disappeared after H₂O leaching treatment (Figure 2, right), and these XRD patterns consisted of a broad profile, except for BRH, which provided the Fe₂O₃ peaks. The reason for this was thought to be due to the large amount of unreacted Fe₂O₃ with NaOH during the roasting process. The melting point of NaOH is approximately 320 °C, and NaOH became molten until 350 °C during the NaOH roasting sample preparation. In addition, the dehydration of α-FeOOH in limonite and the development of the pore structure occur until 350 °C. Therefore, it was suggested that the limonite dehydration reaction had occurred, at the same time, as the molten NaOH penetrated the pores produced by dehydration and reacted with the iron ore constituents. The formation of Na₂CO₃ may derive from an exposure of NaOH in the laboratory atmosphere, which is nonreacted NaOH with an iron ore composition. According to the equilibrium calculation results, eq 1 is favorable by a thermodynamic equilibrium calculation at RT to 350 °C.

\[
\text{FeOOH} + \text{NaOH} = \text{NaFeO}_2 + \text{H}_2\text{O(g)} \Delta G_{0-350°C} = -0 \text{ to } -10 \text{ kcal/mol}
\]

\[
\text{Fe}_2\text{O}_3 + 2\text{NaOH} = 2\text{NaFeO}_2 + \text{H}_2\text{O(g)} \Delta G_{0-350°C} = -1 \text{ to } -10 \text{ kcal/mol}
\]

- Calculated by the BET method. *Calculated by the BJH method. Designated by XRD: vw (very weak), w (weak), m (medium), and s (strong). Not detected.

**Table 3. Summaries of the Yields, Pore Properties, and Fe Forms in Iron Ores Treated with the Roasting/H₂O_RT Treatment**

| Sample | Yield (%) | Specific surface area (m²/g)* | Pore volume, cm³/g)* | Fe form | Yield (%) | Specific surface area (m²/g)* | Pore volume, cm³/g)* | Fe form |
|--------|-----------|-------------------------------|----------------------|---------|-----------|-------------------------------|----------------------|---------|
| INL    | 90        | 130                           | 0.19                 | Fe₂O₃ (m) | 82        | 175                           | 0.15                 | n.d.²  |
| ALY    | 90        | 100                           | 0.12                 | Fe₂O₃ (m) | 84        | 155                           | 0.11                 | n.d.²  |
| ALR    | 92        | 80                            | 0.05                 | Fe₂O₃ (m) | 84        | 100                           | 0.04                 | n.d.²  |
| MLL    | 91        | 85                            | 0.04                 | Fe₂O₃ (m) | 85        | 100                           | 0.04                 | n.d.²  |
| ILS    | 91        | 85                            | 0.05                 | Fe₂O₃ (m) | 85        | 100                           | 0.05                 | n.d.²  |
| WAL    | 95        | 50                             | 0.04                 | Fe₂O₃ (m) | 85        | 60                            | 0.03                 | n.d.²  |
| BRH    | 99        | 3                             | <0.01                | Fe₂O₃ (m) | 89        | 15                            | 0.01                 | Fe₂O₃ (s) |

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Gibbs standard free energies (\(\Delta G\)) of eqs 1 and 2 are the same. Therefore, the existing pore may be affecting the formation of NaFeO\(_2\) during the preparation of the roasting samples because for BRH, which has an Fe\(_2\)O\(_3\) form and low pore properties, Fe\(_2\)O\(_3\) and Na\(_2\)CO\(_3\) were observed in roasted samples. For eqs 1 and 2, the produced NaFeO\(_2\) is hydrolyzed by H\(_2\)O addition to the Fe\(_2\)O\(_3\) and NaOH solution. However, the clear distinction peaks of Fe\(_2\)O\(_3\) were not found in Roasting/H\(_2\)O_RT samples, except for BRH. This result shows that the rearrangement of Fe species occurs due to the reaction between NaOH and Fe species during the roasting process because NaFeO\(_2\) and amorphous Fe are observed in Figure 2.

According to previous reports, Si, Al, and P exist in iron ores as quartz (Si\(_2\)O\(_4\)), alumina (Al\(_2\)O\(_3\)), aluminosilicate (e.g., Al\(_2\)O\(_3\)Si\(_2\)O\(_5\)), fayalite (Fe\(_2\)Si\(_2\)O\(_6\)), kaolinite (Al\(_2\)Si\(_2\)O\(_5\)\(\cdot\)2H\(_2\)O), apatite species (e.g., Ca\(_5\)(PO\(_4\))\(_3\)OH or Ca\(_2\)(PO\(_4\))\(_2\)CaF\(_2\)), iron phosphate (Fe\(_2\)PO\(_4\)), etc.\(^{1,9,27,28}\)

Based on these reports, the equilibrium calculation was performed to investigate the gangue removal mechanism through the Roasting/H\(_2\)O_RT treatment. For the calculation, assuming the Si, Al, or P species mentioned above reacts with NaOH according to the eqs 3\textasciitilde19. The Gibbs standard free energies of \(\Delta G\) at 0\textdegree\textasciitilde350 °C for eqs 3\textasciitilde19 are listed in Table 4.

\[
\begin{align*}
\text{SiO}_2 + 2\text{NaOH} & = \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O}(g) \quad (3) \\
\text{Al}_2\text{O}_3 + 2\text{NaOH} & = 2\text{NaAlO}_2 + \text{H}_2\text{O}(g) \quad (4) \\
2\text{SiO}_2 + \text{Al}_2\text{O}_3 + 2\text{NaOH} & = 2\text{NaAlSiO}_4 + \text{H}_2\text{O}(g) \quad (5) \\
6\text{SiO}_2 + \text{Al}_2\text{O}_3 + 2\text{NaOH} & = 2\text{NaAlSiO}_8 + \text{H}_2\text{O}(g) \quad (6) \\
\text{Al}_2\text{O}_3\cdot\text{SiO}_2(A) + 4\text{NaOH} & = \text{Na}_2\text{SiO}_3 + 2\text{NaAlO}_2 + 2\text{H}_2\text{O}(g) \quad (7) \\
\text{Al}_2\text{SiO}_3\cdot2\text{H}_2\text{O} + 6\text{NaOH} & = 2\text{Na}_2\text{SiO}_3 + 2\text{NaAlO}_2 + 5\text{H}_2\text{O}(g) \quad (8) \\
\text{Al}_2\text{Si}_2\text{O}_5\cdot2\text{H}_2\text{O} + 2\text{NaOH} & = 2\text{NaAlSiO}_4 + 3\text{H}_2\text{O}(g) \quad (9) \\
\text{FePO}_4 + 4\text{NaOH} & = \text{NaFeO}_2 + 3\text{NaPO}_4 + 2\text{H}_2\text{O}(g) \quad (10) \\
\text{Fe}_2\text{SiO}_4(F) + 2\text{NaOH} & = \text{Na}_2\text{SiO}_3 + \text{H}_2(g) + \text{Fe}_2\text{O}_3 \quad (11) \\
\text{Ca}_3(\text{PO}_4)_2\text{OH} + 9\text{NaOH} & = 3\text{Na}_2\text{PO}_4 + 5\text{CaSiO}_3 + 5\text{H}_2\text{O}(g) \quad (12) \\
\text{Ca}_3(\text{PO}_4)_2\text{OH} + 3\text{NaOH} & = 3\text{Na}_2\text{PO}_4 + 5\text{CaO} + 2\text{H}_2\text{O}(g) \quad (13) \\
\text{Ca}_3(\text{PO}_4)_2\text{OH} + 9\text{NaOH} & = 3\text{Na}_2\text{PO}_4 + 5\text{CaO} + 5\text{H}_2\text{O}(g) \quad (14) \\
\text{Ca}_3(\text{PO}_4)_2\text{OH} + 3\text{NaOH} + 5\text{SiO}_2 & = 3\text{Na}_2\text{PO}_4 + 5\text{CaSiO}_3 + 2\text{H}_2\text{O}(g) \quad (15) \\
\text{Ca}_3(\text{PO}_4)_2\text{OH} + 3\text{NaOH} + 5\text{SiO}_2 & = 6\text{NaPO}_4 + 2\text{NaF} + 10\text{CaO} + 4\text{H}_2\text{O}(g) \quad (16) \\
\text{Ca}_3(\text{PO}_4)_2\text{OH} + 20\text{NaOH} & = 6\text{NaPO}_4 + 2\text{NaF} + 10\text{CaO} + 10\text{H}_2\text{O}(g) \quad (17) \\
\text{Ca}_3(\text{PO}_4)_2\text{OH} + 8\text{NaOH} & = 6\text{NaPO}_3 + 2\text{NaF} + 10\text{CaSiO}_3 + 4\text{H}_2\text{O}(g) \quad (18)
\end{align*}
\]
The rearrangement reaction for the formation of the insoluble Si form and inherently Si form in iron ore may influence the low removal extent of Si using the Roasting/H2O_RT treatment. According to a previous report, it is well accepted that P in limonite exists as an adsorption form into limonite, this replaced the form with a part of Fe oxide, and apatite species.\textsuperscript{7-9,27} In addition, it is believed that the apatite-type P has been demonstrated to be easily removed by chemical leaching\textsuperscript{12,14,17,29} whereas simple chemical leaching is ineffective for the goethite matrix-associated P.\textsuperscript{10} Some hypothesis has been proposed for P associated with the goethite matrix; P exists in solid solution with goethite,\textsuperscript{30} and P in goethite exists in the form of grattarolaite ([Fe3PO7]) via the replacement of a surface hydroxyl group by a P ligand.\textsuperscript{10,28} Moreover, it is considered that P in goethite has been found to be much less soluble than in hematite, and a heat treatment (such as roasting or alkali roasting) prior to leaching is necessary to obtain a high extent of P removal.\textsuperscript{23} In the present study, the Roasting/H2O_RT treatment provides higher P removal than the NaOH hydrothermal treatment for many of the iron ores used. For P removal in iron ore using a combination of roasting, alkali roasting/chemical leaching, or magnetic separation, it has been reported that an occurrence of structural rearrangement (changing of hematite to goethite for a calcination/reaction in the gangue component to form an acid-soluble form for calcination/reaction with the alkali and gangue mineral during roasting, which then forms an acid soluble form for alkali roasting) produces acid-soluble Si, Al, or Si-Al species containing P and damaging the ore structure, and these treatments promote the removal of P\textsuperscript{10,24,31} by using acid leaching. As shown in Table 4, the Fe, Si, Al, and P rearrangement reactions occur easily in NaOH roasting conditions. The high gangue extents of removal from roasted samples were achieved through H2O treatment because watersoluble Al and P are produced by NaOH roasting. Figure 3.

Here, FePO4 was used instead of Fe3PO7 because the latter species does not exist in the HSC Chemistry 5.1 (Outokumpu Research Oy) database, and eqs 12–15 were a referenced equation from ref.\textsuperscript{11} The reactions of eqs 3–12 and 19 (denoted as rearrangement reactions) are supported by thermoequilibrium calculations, and the produced Na-Si, Na-Al, and Na-P compounds have the property of being watersoluble at room temperature. Therefore, a high removal extent of Al and P for the Roasting/H2O_RT treatment may be observed by the rearrangement of gangue components. On the other hand, the extent of Si removal was low for all samples, except for BRH. This reason may be due to a large portion of Si exists in an iron ore other than SiO2 or kaolinite. Furthermore, low extent of Si removal may be caused by a production of water-insoluble Si species, such as CaSiO3. Although, eq 20 is favorable by thermoequilibrium, the water solubility of the produced CaSiO3 is exceptionally low being 0.01 g/100 mL H2O at 20 °C. Equation 21 is also supported by thermoequilibrium for calculation at 150–350 °C, but at a lower temperature (20–150 °C), the reaction of eq 20 occurs easier than eq 21.

\[
\text{CaO} + \text{SiO}_2 = \text{CaSiO}_3 \Delta G_{0-350^\circ C} = -21.4 \text{ to } -21.6 \text{ kcal/mol (20)}
\]

\[
2\text{NaOH} + \text{CaSiO}_3 = \text{Na}_2\text{SiO}_4 + \text{CaO} + \text{H}_2\text{O(g)} \Delta G_{0-350^\circ C} = 3 \text{ to } -5.1 \text{ kcal/mol (21)}
\]
Table 3, the specific surface area increases significantly from the original values (2−80 m²/g) or calcined sample values (3−130 m²/g) to 15−175 m²/g. Figure 4 shows the comparison between the specific surface area of the original sample calcined at 350 °C in air and Roasting/H₂O_RT samples. The specific surface area in Roasting/H₂O_RT samples is larger than those of calcined samples. It is considered that the increasing specific surface area occurs due to the removal of gangue for Roasting/H₂O_RT and the rearrangement of the Fe species. Thus, it is necessary for the method of high Fe crystallization and low pore properties of iron ores to completely develop an upgrading method.

Removal of Gangue by Combination of Alkali Roasting and H₂O Hydrothermal Treatments. In this section, a hydrothermal treatment with H₂O against NaOH roasting samples was carried out because relatively significant extent of gangue removal was observed by using the NaOH hydrothermal treatment and Roasting/H₂O_RT treatment as shown in Table 2 and Figure 1. H₂O was used for the hydrothermal treatment of the roasted sample, and the mixture was heated at 300 °C for 30 min (denoted as Roasting/H₂O_SC). Here, as is mentioned above, it was thought that NaFeO₂ or nonreacted Na species (Na₂CO₃ and NaOH) in roasted samples are hydrolyzed to Fe₂O₃ and NaOH solutions by the addition of H₂O to the roasting samples. In other words, the hydrothermal treatment of roasted samples was carried out in a Na-containing solution containing a water-soluble gangue component at room temperature. The results are shown in Figure 5. The extent of Si, Al, and P removal ranged between 16−95%, 39−80%, and 30−90%, respectively, and the extent of P removal from all samples reached above 60%, except for INL. The order in which the extent increased is INL < ILS < MLL = WAL < ALR = ALY ≪ BRH for Si, INL = ALR < WAL < ALY < MLL < ILS < BRH for Al, and INL ≪ WAL < BRH < ALR < MLL < ILS = ALY for P, and BRH showed a large tendency of removal extent in all samples. The orders to which the extent of removal among the gangue components examined increased as Si < Al < P, and it was found that this treatment method is more effective for Al and P removal than the Roasting/H₂O_RT treatment. Figure 6 illustrates the relationship between Si, Al, and P removal amounts. Although there is some scattering, the negative and positive correlations were observed for Si versus Al, Si versus P, and Al versus P in all samples, except for INL. The correlation constant between properties, and Fe forms in Roasting/H₂O_SC samples. The yield decreased to 80−89%, and the order closely corresponded with that of LOI. The specific surface area decreased from 15−175 m²/g of Roasting/H₂O_RT samples to <1 to 15 m²/g for Roasting/H₂O_SC samples treated at 300 °C. Similar decreases were observed for the pore volume and NaOH hydrothermal treatment (Table 2). Although the amorphous Fe was observed from almost all Roasting/H₂O_RT samples, the Fe form was Fe₂O₃ for all Roasting/H₂O_SC samples. These results show that sintering Fe species and crystallization

![Figure 4](image-url) Extent of increasing specific surface area of the iron ores after the Roasting/H₂O_RT treatment.

![Figure 5](image-url) Extent of gangue removal in iron ores treated with the Roasting/H₂O_SC treatment.

![Figure 6](image-url) Relationship between the amounts of gangue removal of Si, Al, and P with the Roasting/H₂O_SC treatment.

| sample | yield (%) | specific surface area (m²/g) | pore volume (cm³/g) | Fe form |
|--------|-----------|-----------------------------|--------------------|---------|
| NL     | 80        | 15                          | 0.07               | Fe₂O₃ (m) |
| ALY    | 81        | 10                          | 0.08               | Fe₂O₃ (m) |
| ALR    | 84        | 14                          | 0.06               | Fe₂O₃ (m) |
| MLL    | 82        | 10                          | 0.05               | Fe₂O₃ (m) |
| ILS    | 84        | 10                          | 0.04               | Fe₂O₃ (m) |
| WAL    | 85        | 5                           | 0.02               | Fe₂O₃ (m) |
| BRH    | 89        | <1                          | <0.01              | Fe₂O₃ (m) |

*Calculated by the BET method. †Calculated by the BJH method. Designated by XRD: m (medium).
were also occurring during hydrothermal treatment with a Na-containing solution. Figure 7 shows the difference between the extent of gangue removal from Roasting/H₂O_SC and Roasting/H₂O_RT samples to investigate the effect of hydrothermal treatment on gangue removal. As seen in Figure 7, the extent of Si removal tended to increase for Roasting/H₂O_SC samples, and a slight increase in the extent of P removal was found for all samples, except for WAL and INL. The slight decrease of the Al extent occurs due to analytical errors. In conclusion, this combination of treatment can improve Si and P removal in the Roasting/H₂O_RT treatment. It is considered that the removal of Si and P by a Na-containing solution occurs due to a reaction between Si or P species and Na species to form a water-soluble species during hydrothermal treatment.25

In the present work, the hydrothermal treatment temperature of 300 °C was mainly used because the NaOH solution damages (causes corrosion) the SUS reactor in repeating experimental trials. However, it is important to clarify the effect of temperature on the behavior of gangue removal in the Roasting/H₂O_RT treatment. Therefore, the ALY roasted sample was made for hydrothermal treatment at each temperature to clarify the effect of hydrothermal temperature on gangue removal. Figure 8 presents the temperature dependency on the extent of gangue removal from an ALY roasted sample against temperature. The extent of Al and P removal at room temperature (Roasting/H₂O_RT treatment) was as high as 60 and 70%, respectively, whereas that of Si was as low as 15%. When the temperature was raised to 100 °C, the extent of P removal reached 85%, whereas those of Al and Si were constant with those of room temperature. Although the extent of P and Al removal did not change up to 300 °C, that of Si increased along with increasing temperature and reached 70% at 350 °C. In addition, the removal of Al increased at 300–350 °C and attained 75% at 350 °C. These results mean that Roasting/H₂O_SC treatment above 300 °C is more effective for further gangue removal than for temperatures below 300 °C if it is possible to use a corrosion-resistant reactor. Although the relationship between the amounts of Si, Al, and P removal was investigated, clear correlations were not found as seen in Figures 3 and 6. Table 6 summarizes the yields, pore properties, and Fe forms corresponding with the result of Figure 8. In addition, the changes in XRD patterns of the Roasting/H₂O_SC samples against hydrothermal temperature are shown in Figure 9 and summarized in Table 6. The yield of Roasting/H₂O_SC of ALY ranged from 80 to 84% and decreased with increasing temperature. This decreasing occurs

Table 6. Summaries of the Yields, Pore Properties, and Fe Forms in ALY Treated with the Roasting/H₂O_SC Treatment at Different Temperatures

| temperature (°C) | yield (%) | specific surface area (m²/g)b | pore volume (cm³/g)b | Fe formc |
|------------------|-----------|-----------------------------|----------------------|---------|
| RT               | 84        | 155                         | 0.11                 | n.d.⁵   |
| 100              | 84        | 150                         | 0.10                 | n.d.⁵   |
| 150              | 84        | 150                         | 0.10                 | n.d.⁵   |
| 200              | 83        | 130                         | 0.13                 | Fe₂O₃ (w) |
| 250              | 82        | 110                         | 0.14                 | Fe₂O₃ (m) |
| 300              | 81        | 15                          | 0.16                 | Fe₂O₃ (s) |
| 350              | 80        | 15                          | 0.16                 | Fe₂O₃ (s) |

⁵Calculated by the BET method. ⁶Calculated by the BJH method. ⁷Designated by XRD measurement: w (weak), m (medium), and s (strong). ⁸Not detected.

Figure 7. Difference of the extent of gangue removal from the Roasting/H₂O_SC to the Roasting/H₂O_RT treatment.

Figure 8. Temperature dependency on the extent of gangue removal from ALY during the Roasting/H₂O_SC treatment.

Figure 9. Changes in the XRD pattern of the Roasting/H₂O_RT-treated ALY samples during the Roasting/H₂O_SC treatment. (a) Room temperature, (b) 100 °C, (c) 150 °C, (d) 200 °C, (e) 250 °C, (f) 300 °C, and (g) 350 °C.
due to the removal of gangue. Although the specific surface area (155 m²/g) of the Roasting/H₂O_RT ALY sample was constant until 200 °C, a drastic decrease was observed at 250–350 °C, and these values were lowered to 15 m²/g. On the other hand, the amorphous Fe form observed in Roasting/H₂O_RT was changed to Fe₂O₃ above 250 °C due to the crystallization effect of the NaOH and hydrothermal treatment, and the peak intensity increased with increasing temperature. Therefore, it is concluded that this combination of treatments above 300 °C is effective for gangue removal, crystallization of Fe, and decreasing pore of porous and amorphous Fe in iron ores obtained using the Roasting/H₂O_RT treatment.

Effect of Calcination and Roasting Temperatures on Gangue Removal. To clarify the effect of calcination/roasting temperatures on gangue removal, each treatment (NaOH hydrothermal, Roasting/H₂O_RT, and Roasting/H₂O_SC treatment) was carried out against ALY samples (calcined and NaOH roasted at 350, 600, and 900 °C, respectively). The result is shown in Figure 10. The specific surface area decreased from 25–100 to 10–20 m²/g. For the Roasting/H₂O_RT treatment, all the extent of gangue removal tended to increase with increasing NaOH roasting temperature, as seen in Figure 10b. The peaks of attributable NaFeO₂ completely disappeared in all samples after the Roasting/H₂O_RT treatment (Figure 11c,d). In addition, the specific surface area increased to 80–155 m²/g, compared to calcined samples (25–100 m²/g), respectively. A slight increase in the extent of Si and Al removal was observed for the Roasting/H₂O_SC treatment with NaOH roasting temperature, as shown in Figure 10c. The amorphous Fe form obtained in the Roasting/H₂O_RT sample was changed to Fe₂O₃ by the Roasting/H₂O_SC treatment (Figure 11e), and the specific surface area (80–155 m²/g) of the Roasting/H₂O_RT-treated samples decreased to 10–15 m²/g. According to previous work, it is believed that a calcination/alkali roasting treatment is effective for the transformation of leaching solvent-insoluble gangue in an iron ore form to a soluble form by a reaction in the gangue component or alkali compound during heat treatment, resulting in an increased extent of removal during the leaching process. In this study, the increasing Si, Al, and P extent of removal with calcination and roasting temperature were observed. It is, therefore, through the transformation (rearrangement of the structure) of gangue with calcination and the roasting treatment, which also occurs similar to the report mentioned above in the present study, and the resulting extent of gangue removal increased during each of these methods. On the other hand, it may be determined that the effect of pore properties on gangue removal is smaller than that of the calcination/roasting temperature for rearrangement because the specific surface area of the sample prepared at 900 °C, which showed the highest extent of removal for almost all treatments, is low.

Figure 10. Effect of (a) calcination and (b, c) roasting temperatures on the extent of gangue removal from ALY with NaOH hydrothermal (a), Roasting/H₂O_RT (b), and Roasting/H₂O_SC (c) treatments at 300 °C.

Table 7. Summaries of the Yields, Pore Properties, and Fe Forms in Calcined or Roasted ALY Treated with the 5 M NaOH Hydrothermal, Roasting/H₂O_RT, or Roasting/H₂O_SC Treatments at Different Temperatures

| pretreatment | treatment of gangue removal | temperature (°C) | yield (%) | specific surface area (m²/g)ᵃ | pore volume (cm³/g)ᵇ | Fe formᶜ |
|--------------|----------------------------|-----------------|-----------|-------------------------------|---------------------|---------|
| calcination  | none                       | 350             | 90        | 100                           | 0.12                | Fe₂O₃ (m) |
|              |                             | 600             | 89        | 55                            | 0.14                | Fe₂O₃ (s) |
|              |                             | 900             | 88        | 25                            | 0.10                | Fe₂O₃ (s) |
| NaOH hydrothermal |                      | 350             | 81        | 10                            | 0.04                | Fe₂O₃ (m) |
|              |                             | 600             | 84        | 20                            | 0.10                | Fe₂O₃ (s) |
|              |                             | 900             | 83        | 15                            | 0.07                | Fe₂O₃ (s) |
| NaOH roasting| none                       | 350             | n.aᵈ      | n.aᵈ                          | n.aᵈ                | NaFeO₂ (w) |
|              |                             | 600             | n.aᵈ      | n.aᵈ                          | n.aᵈ                | NaFeO₂ (s) |
|              | leaching by H₂O (Roasting/H₂O_RT) | 350         | 82        | 155                           | 0.11                | n.d.⁵    |
|              |                             | 600             | 81        | 125                           | 0.07                | n.d.⁵    |
|              |                             | 900             | 81        | 80                            | 0.05                | n.d.⁵    |
| H₂O hydrothermal (Roasting/H₂O_SC) |                    | 350             | 81        | 10                            | 0.08                | Fe₂O₃ (m) |
|              |                             | 600             | 79        | 15                            | 0.06                | Fe₂O₃ (s) |
|              |                             | 900             | 79        | 10                            | 0.05                | Fe₂O₃ (s) |

ᵃCalculated by BET method.ᵇCalculated by BJH method.ᶜDesignated by XRD : w (weak), m (medium), s (strong).⁴Not analysis.⁵Not detected.
as well as the original ALY. Although it is concluded that nonalkali and alkali roasting treatments are effective for the removal of gangue from iron ore, a dramatic improvement with calcination/roasting at 600 and 900 °C was not found in this case. The low-temperature treatment is more favorable than the high-temperature treatment for the actual process; therefore, we used 350 °C as the main treatment temperature in this study.

**Removal of Gangue by Combination of Alkali Roasting and NaOH Hydrothermal Treatments.** As shown in Figure 5, the extent of Si removal was as low as below 50% by using the Roasting/H₂O_RT at 300 °C treatment, and that of Al also was below 70%. Therefore, in this section, the effect of the combination of alkali roasting and 5 M NaOH hydrothermal treatments (Roasting_H₂O_RT/NaOH_SC) on gangue removal was investigated to attain a high gangue removal. Figure 12 shows the gangue removal extent of iron ores used by Roasting_H₂O_RT/NaOH_SC at 300 °C treatment. This combination provided 65−97% of Si and Al removal extents, and the extent of P removal also reached above 80% for all samples, except for INL, which has the lowest P content and the largest LOI. The highest removal extent was observed for BRH, which has a high Fe content, Fe₂O₃ form, low LOI, and low pore properties of iron ores used in this study. Figure 13 illustrates the relationship between the amounts of Si, Al, and P removal by the Roasting_H₂O_RT/NaOH_SC treatment at 300 °C.

![Figure 11. XRD patterns of ALY samples obtained after the NaOH hydrothermal, Roasting/H₂O_RT, and Roasting/H₂O_SC treatments at 300 °C corresponding to the results of Figure 10. ALY at 350 °C (left), 600 °C (center), and 900 °C (right). (a) Calcination in air, (b) 5 M NaOH hydrothermal-treated sample, (c) Roasted sample, (d) Roasting/H₂O_RT sample, and (e) Roasting/H₂O_SC sample.](image1)

![Figure 12. Extent of gangue removal of iron ores treated with the Roasting_H₂O_RT/NaOH_SC treatment at 300 °C.](image2)

![Figure 13. Relationship between the amounts of gangue removal of Si, Al, and P with the Roasting_H₂O_RT/NaOH_SC treatment at 300 °C.](image3)
surface area was lower than the original iron ores. Therefore, it is concluded that the low-grade ores used were upgraded using the Roasting_H2O_RT/NaOH_SC treatment. Figure 15 presents the effect of the 5 M NaOH hydrothermal treatment on gangue removal calculated by the difference between the extent of gangue removal for the Roasting_H2O_RT/NaOH_SC treatment and the Roasting/H2O_RT treatment. From the difference between the Roasting_H2O_RT/NaOH_SC treatment and the Roasting/H2O_RT treatment (Figure 15a), the removal extent of Si, Al, and P increased by 25−75%, 15−45%, and 10−30%, respectively. This increase may occur by the increasing contact area between the Na-containing solution and iron ore compositions during hydrothermal treatment because the specific surface area increased due to the dehydration reaction of α-FeOOH and gangue removal for the Roasting/H2O_RT treatment. On the other hand, from the difference of the extent of gangue removal from the Roasting_H2O_RT/NaOH_SC treatment to that of the Roasting/H2O_SC treatment (Figure 15b), the extent of Si, Al, and P removal increased by 5−50%, 10−50%, and 2−20%, respectively, for the Roasting/H2O_RT/NaOH_SC treatment. For the latter difference (Figure 15b), the increase in the extent of P removal was lower than that of former (Figure 15a). These results show that the Roasting_H2O_RT/NaOH_SC treatment is more effective for Si and Al removal than that of the Roasting/H2O_RT and Roasting/H2O_SC treatments. Now, although the reason why the extent of gangue removal increased by using the Roasting_H2O_RT/NaOH_SC treatment compared with the Roasting/H2O_SC treatment at 300 °C, the secondary reaction among gangue components removed by the H2O treatment at room temperature of NaOH roasting samples, which remained in the solvent during the Roasting_H2O_RT/H2O_SC treatment at 300 °C, may occur during hydrothermal treatment of the Roasting/H2O_SC treatment. On other words, it may be important to positively remove the gangue eluted by the water treatment of the roasted ore and then perform a hydrothermal treatment by adding a fresh NaOH solution again, such as the use of a flow-type reactor. The clarity of the detail will be the subject of future work.

■ CONCLUSIONS

In the present study, we have examined the removal of gangue (Si, Al, and P) from iron ores by a combination of alkali roasting and hydrothermal treatments to attain a higher extent of gangue removal than hydrothermal treatment with NaOH only. The effects of the combination of each treatment (leaching at room temperature and hydrothermal treatments of

Table 8. Summaries of the Yields, Pore Properties, and Fe Forms in AYL Treated with the Roasting_H2O_RT/NaOH_SC Treatment at 300 °C

| sample | yield (%) | specific surface area (m²/g) | pore volume (cm³/g) | Fe form<sup>c</sup> |
|--------|----------|-----------------------------|-------------------|-------------------|
| INL 79 | 70       | 30                          | 0.11              | Fe₂O₃ (m)        |
| ALY 80 | 20       | 20                          | 0.12              | Fe₂O₃ (m)        |
| ALR 83 | 20       | 20                          | 0.07              | Fe₂O₃ (m)        |
| MLL 82 | 15       | 15                          | 0.03              | Fe₂O₃ (m)        |
| ILS 83 | 15       | 15                          | 0.06              | Fe₂O₃ (m)        |
| WAL 82 | 15       | 15                          | 0.01              | Fe₂O₃ (m)        |
| BRH 88 | 8        | 8                           | 0.01              | Fe₂O₃ (m)        |

<sup>a</sup>Calculated by the BET method. <sup>b</sup>Calculated by the BJH method. <sup>c</sup>Designated by XRD measurement: m (medium).
the roasted sample), iron type, physical properties, calcination temperature on the extent of gangue removal were investigated to develop an upgrading method for producing high-grade iron from low-grade iron ore (limonite). Some findings are listed below.

(1) When the iron ores used in the present study were roasted with NaOH at 350 °C, α-FeOOH in limonite transferred to NaFeO₂. On the other hand, for roasted iron ores, which inherently contained Fe₂O₃ in iron ore, Fe₃O₄ and Na₂CO₃ were observed after the roasting treatment.

(2) The higher extent of Al and P removal than NaOH hydrothermal treatment was observed in H₂O leaching at room temperature of the prepared roasted samples (Roasting/H₂O_RT), whereas that of Si was low for all samples, except for BRH. After H₂O leaching, the Fe form was amorphous for all samples, except for BRH.

(3) The specific surface area significantly increased after the Roasting/H₂O_RT treatment for all samples due to the dehydration of α-FeOOH during the roasting treatment and gangue removal during H₂O leaching.

(4) When roasted samples were supplied for the hydrothermal treatment of H₂O at 300 °C (Roasting/H₂O_SC), the extent of Si and P removal increased compared to the Roasting/H₂O_RT treatment.

(5) The calcination and roasting temperatures influenced the extent of gangue removal more during the NaOH hydrothermal, Roasting/H₂O_RT, and Roasting/H₂O_SC treatments, and the effect on the pore properties of the iron ores is lower than those of the pretreatments above.

(6) When the NaOH hydrothermal treatment was carried out against the samples after the Roasting/H₂O_RT treatment, an extent gangue removal of above 70% was reached, except for P in INL.

### EXPERIMENTAL SECTION

#### Sample
Seven types of iron ore (BRH, WAL, ILS, MLL, ALR, ALY, and INL) produced in various countries (Brazil, Indonesia, Malaysia, and Australia) were used. The fraction size is <150 μm. Table 1 shows the chemical and physical composition and Fe forms of iron ores used. In X-ray diffraction analysis for iron ores, Fe forms were α-FeOOH for all samples, except for BRH and WAL, and the peaks of SiO₂ and nonidentified species were also detected for BRH, ILS, MLL, ALR, and ALY.²⁵

**Hydrothermal Treatment.** The hydrothermal treatment was carried out with an SUS316 made batch reactor (length, 100 mm; d.Ø., 24 mm; thickness, 2 mm). The details of the experimental procedure have been reported in ref 25. About 2.5 g of a sample and 7 mL of solvent were first added into the reactor, the reactor was then pressurized with high-purity He (99.99995%) to check for leakage and to replace the atmosphere in the reactor. After the atmosphere in the reactor was replaced with enough He, the reactor was heated to 150–350 °C in a fluidized sand bath for 30 min. The change of pressure in the SUS reactor corresponded with the general vapor pressure curve of water. After a holding period of 30 min, the reactor was rapidly quenched in a water bath. The solid and liquid phases were separated using the filtrate method, and the former was repeatedly washed with distilled water until the pH of the filtrate becomes neutral. The yield of the treated samples was calculated based on the weight loaded into the reactor, and finally, the treated weight was obtained after each treatment and listed by iron ore basis (original sample basis). The distilled water or 5 M NaOH was used for the hydrothermal treatment. Here, a slight loss of solid phase occurs due to the sintering of the Fe species, which is strongly adhered to the inner wall and the Fe of the reactor, during hydrothermal treatment. In addition, almost no elution of iron was observed in all treatment.

**Alkali Roasting.** A NaOH fraction <150 μm, crushed and sieved, was used for the alkali roasting of the iron ores. NaOH (1.44 g) was physically mixed with the iron ores at room temperature, and the mixture was then heated at 10 °C/min up to 350, 600, or 900 °C in air. It is well-known that dehydration of α-FeOOH in limonite occurs above 300 °C, and the maximum specific surface area is observed at 350 °C.²⁵,²⁶ When the temperature was raised to 600 °C, the highest pore volume is found, whereas the specific surface area decreases, and at 900 °C, both values decrease.²⁵ In this study, the above temperatures were selected to investigate the effect of pore properties on gangue removal. The leaching and hydrothermal treatments of the prepared NaOH roasted samples were carried out as follows: (1) the sample was leached with 7 mL of distilled water at room temperature for 30 min under a N₂ atmosphere. The recovery of the solid phase was the same as that in Hydrothermal treatment section. (2) The sample and 7 mL of H₂O were added into the SUS reactor, and the mixture was heated with the same conditions as mentioned in Hydrothermal treatment section. Here, the NaOH solution concentration in the SUS reactor with the addition of H₂O was adjusted to 5 M NaOH. (3) The sample was first leached with distilled water in the same manner as (1) mentioned above. Following this, the sample, which was recovered and dried at 108 °C for 12 h in N₂ and 7 mL of 5 M NaOH were added into the SUS reactor, and the reactor was then heated in the same manner as that in Hydrothermal treatment section. In the present study, treatments of (1), (2), and (3) were denoted as Roasting/H₂O_RT, Roasting/H₂O_SC (subcritical), and Roasting_H₂O_RT/NaOH_SC, respectively.

**Characterization.** The characterization was carried out by using the N₂ adsorption analysis (Quantachrome, Nova1200e) and conventional powder diffraction (Shimadzu, XRD6000) methods. The detail of the measurement condition has been described in our previous report.²⁵ Each element (Fe, Si, Al, and P) content in the sample before and after treatment was measured by an alkaline fusion method according to the Japanese Industrial Standard method (JIS M8214), which employs the inductively coupled plasma optical emission spectroscopy (Thermo Scientific, iCAP 6300 Duo) method.²⁵,²⁶

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**Notes**

The authors declare no competing financial interest.
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