Synthesis of iron-exchanged Na-P1 zeolites with different iron release properties

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Abstract. Iron-exchanged zeolites are used as iron nutrient source to plants. To develop materials which allow an effective supply of iron, we prepared iron-exchanged Na-P1 zeolites using ferric chloride (FeChl-Z) and ferric citrate (FeCit-Z) solutions via a cation exchange method, and evaluated the chemical form and release property of the iron. The content of iron in FeChl-Z and FeCit-Z was 199 and 225 mmol kg\textsuperscript{-1}, respectively. FeChl-Z mainly contained highly polymerized hydroxy-iron species, whereas FeCit-Z contained mainly monomeric to oligomeric hydroxy-iron species. 1 M ammonium acetate solution (pH 4.5) extracted 68\% and 17\% iron from FeCit-Z and FeChl-Z, respectively. This suggests that the different iron form retained by the methods using different iron solutions influenced iron release properties of the iron-exchanged zeolites.

1. Introduction
Zeolites are porous aluminosilicates with negative charges in their framework structure resulting from isomorphous substitution mainly of Al to Si, and the negative charges are electrostatically compensated by exchangeable cations such as Na\textsuperscript{+} and Ca\textsuperscript{2+}. Iron-exchanged zeolites retaining iron species as exchangeable cations are useful materials as catalyst, adsorbent, and iron nutrient sources for plants \cite{1-6}. Some methods have been proposed for the preparation of iron-exchanged zeolites, and the chemical form of the retained iron species affect the properties of the iron-exchanged zeolites such as the activity of catalytic decomposition of N\textsubscript{2}O \cite{7}.

One of the preparation methods of the iron-exchanged zeolites is a cation exchange method in which a solution of inorganic iron salt such as ferric chloride is mixed with a zeolite \cite{7-9}. This method is easy and often used in the preparation of iron-exchanged zeolites to supply iron nutrient for plants. However, in this process, iron species retained on the zeolites are mainly highly polymerized hydroxy-iron cations, especially when zeolites with low Si/Al or high cation exchange capacity (CEC) are used. Because the polymerization of hydroxy-iron cations tends to be accelerated with increasing pH, and the increase in pH is greater for zeolites with higher CEC when ferric solutions are mixed with zeolites \cite{9-11}. On the other hand, the use of organic iron salt solutions is proposed for the inhibition of hydrolysis reaction of iron at the surface of high Si/Al zeolites with low CEC \cite{12-14}.
The iron species of the iron-exchanged zeolites prepared using organic iron salts are expected to be released more easily than those of the iron-exchanged zeolites prepared using inorganic iron salts. In this study, to develop materials which effectively supply iron to plants, we prepared iron-exchanged Na-P1 zeolites by using ferric chloride and ferric citrate as inorganic and organic iron salts, respectively. Na-P1 has gismondine framework structure and belongs to P-type zeolites. A kind of P-type zeolites was chosen here because P-type zeolites have relatively high CEC [15,16] and can easily be synthesized from not only reagents but also waste materials such as coal fly ash and paper sludge [17-19]. The iron species adsorbed on the Na-P1 zeolite were characterized including their release property.

2. Experimental

2.1. Synthesis of Na-P1 zeolite
For the synthesis of Na-P1 zeolite, 4.0 g of sodium aluminate (Nacalai Tesque) was dissolved in a 50.6 mL of 1.3 M NaOH solution in a polytetrafluoroethylene conical flask, and 20.6 g of sodium silicate (Grade 3, Fuji Chemicals) was added and mixed. The mixture was heated on a hotplate with a cooling tube at 100 °C for 6 h. After cooling to room temperature, the product was washed with distilled water and dried at 40 °C for 24 h.

2.2. Preparation of iron-exchanged Na-P1 zeolites
Iron-exchanged Na-P1 zeolites were prepared by using solutions of ferric chloride hexahydrate (nacalai tesque) and ferric citrate n-hydrate (nacalai tesque). In a plastic bottle, 1 g of the synthesized Na-P1 zeolite was added to a 100 mL of 25 mM ferric chloride or ferric citrate solution adjusted to the pH of 2.0 by using dilute NaOH solution. The mixture was then shaken for 2 h at room temperature. After washing with distilled water, the product was dried at 40 °C for 24 h. Hereafter, the product prepared with the ferric chloride solution is referred to as FeChl-Z, and the product prepared with the ferric citrate solution is referred to as FeCit-Z.

2.3. NaOH treatment
To dissolve amorphous materials in the samples, 0.1 g of the samples were boiled in a 10 mL of 0.5 M NaOH solution for 30 min [20]. Then, the samples were washed with distilled water and dried at 40 °C for 24 h.

2.4. Extraction of iron species
The release properties of iron species retained by FeChl-Z and FeCit-Z were determined by two extraction methods: citrate-bicarbonate-dithionite (CBD) method [21] and 1 M ammonium acetate method [22] at the pH of 4.5.

2.5. Characterization
Powder X-ray diffraction (XRD) patterns were obtained by an X-ray diffractometer equipped by monochromator (Ultima IV, Rigaku) with Cu-Kα radiation (40 kV, 40 mA). FT-IR spectra were measured by an FT-IR spectrophotometer (FT/IR-4000, JASCO) with KBr pellets. Differential thermal analysis (DTA) was carried out by using a differential thermal analyzer (Thermo plus, Rigaku). UV-visible diffuse reflectance spectra were measured by using an UV-Vis spectrophotometer (V-670, JASCO) with an integrating sphere (ISN-723, JASCO). The contents of Fe, Na, Al, and Si in the samples were determined by an atomic absorption spectrophotometer (Z-5000, Hitachi High-Technologies) after dissolving them in a mixed solution of hydrogen fluoride, aqua regia and boric acid. The value of CEC of the Na-P1 was determined by measuring the amount of Na⁺ extracted by NH₄⁺ from Na⁺-saturated Na-P1 using the atomic absorption spectrophotometer.
3. Results and Discussions

3.1. Characterization of Na-P1

XRD pattern of the product shown in Figure 1 agreed with that of Na-P1 type zeolite reported by International Zeolite Association [23], suggesting that Na-P1 type zeolite was successfully synthesized in this study. The value of CEC of the product was determined as 4.526 mol kg\(^{-1}\). The Na/Al ratio of the synthesized Na-P1 was 0.97, close to 1.0, and the ratio did not change after the NaOH treatment. This indicates that the product contains few amorphous materials. The Si/Al ratio of the NaOH-treated Na-P1 was determined as 1.96 and the ratio was within the range reported previously [15, 16, 24].

![Figure 1. XRD pattern of the product in the synthesis of Na-P1 zeolite](image)

3.2. Characterization of iron-exchanged Na-P1

The contents of iron in the iron-exchanged Na-P1 zeolites were 199 mmol kg\(^{-1}\) (1.11 wt%) for FeChl-Z and 225 mmol kg\(^{-1}\) (1.26 wt%) for FeCit-Z, and their Fe/Al ratios were about 0.05. The atomic ratios of the exchangeable cations to aluminum, (Na+Fe)/Al, were 0.52 for FeChl-Z and 0.57 for FeCit-Z, and they were much smaller than 1.0. However, after the NaOH treatment, the (Na+Fe)/Al ratios increased to 0.94 for both FeChl-Z and FeCit-Z. These results indicated that Na-P1 particles were partially dissolved and precipitated as amorphous materials during the iron-exchange treatment. In the next step, the preparation method of iron-exchanged zeolites should be improved to prevent the dissolution of zeolites.

To observe the presence of citrate species remaining in FeCit-Z, DTA was carried out. The DTA curves of Na-P1 and FeCit-Z are shown in Figure 2 together with those of the mixtures of Na-P1 and ferric citrate. The curve of the mixture of Na-P1 (95 wt%) and ferric citrate (5 wt%) (Figure 2d), showed clear exothermic peaks at around 216 and 309 °C that are attributed to organic compounds [25]. Also in the curve of the mixture of Na-P1 (99 wt%) and ferric citrate (1 wt%) (Figure 2d), similar exothermic peaks were slightly recognized, but in the DTA curve of FeCit-Z (Figure 2b), such peaks were not observed. In addition, FT-IR spectrum of FeCit-Z showed no peaks ascribed to organic compounds (not shown). These results indicate that citrate species are not contained in FeCit-Z, and major iron species in FeCit-Z is not associated with ferric citrate.
Figure 2. DTA curves of (a) Na-P1, (b) FeCit-Z, (c) mixture of Na-P1 (99 wt%) and ferric citrate (1 wt%), (d) mixture of Na-P1 (95 wt%) and ferric citrate (5 wt%), and (e) ferric citrate

Figure 3 shows UV-Visible diffuse reflectance spectra of the samples. The spectra of FeChl-Z (Figure 3b) and FeCit-Z (Figure 3c) showed absorption bands in the range of 200–700 nm. In previous studies on iron-exchanged zeolites [10,11,26], the bands below 300 nm were ascribed to isolated Fe(III) species, the bands between 300 and 400 nm were ascribed to oligomeric Fe(III)$_x$O$_y$ clusters on the internal or external surface of zeolites, and the bands above 400 nm were attributed to Fe$_2$O$_3$ nanoparticles on the external surface of the zeolites. The absorption bands above 300 nm of FeCit-Z were smaller than those of FeChl-Z, and in the spectrum of FeChl-Z the band at near 480 nm was similar to that of goethite (α-FeOOH) and ferrihydrite (Fe$_5$HO$_8$•4H$_2$O) [27]. These results suggest that FeChl-Z contains much more amount of highly polymerized oxyhydroxide/oxide clusters of iron while FeCit-Z contains much isolated Fe(III) species.

Figure 3. UV-Visible diffuse reflectance spectra of the samples and iron minerals. (a) Na-P1, (b) FeChl-Z, (c) FeCit-Z, (d) goethite, (e) ferrihydrite. The spectra of (d) and (e) were obtained after diluting 10 times by mixing with BaSO$_4$.

The release properties of iron from FeChl-Z and FeCit-Z are shown in Figure 4. The CBD extractable iron (CBD-Fe) corresponds to the amount of free iron oxides and exchangeable iron
retained on the surface of Na-P1 zeolite particles [21], and ammonium acetate extractable iron (NH$_4$-Fe) corresponds only to the amount of cation-exchangeable iron available to plants [22]. For FeChl-Z, the ratio of CBD-Fe to the amount of total iron in the sample (Total-Fe) was about 97%, indicating that about 3% of iron existed in the pore region of the Na-P1 particles where the CBD reagents could not reach. In contrast, the ratio of NH$_4$-Fe to total-Fe was about 17%, indicating that most of iron species in FeChl-Z were highly polymerized hydroxy-iron which were strongly adsorbed on the surface of Na-P1 particles and were not easily exchanged by NH$_4^+$. For FeCit-Z, the ratio of NH$_4$-Fe to total-Fe was about 68%, meaning that much more iron was available to plants as compared to FeChl-Z. For FeCit-Z, however, the ratio of CBD-Fe to total-Fe was about 68%, much smaller than that of FeChl-Z of 97%, suggesting that some iron species existed inside of the zeolite channels. The presence of iron species in FeCit-Z after CBD treatment was also indicated by its light yellow color contrary to white color of FeChl-Z after the treatment (Figure 5). Because the size of highly polymerized hydroxyl-iron cations are larger than the pore opening size of Na-P1 (0.31 nm×0.45 nm [100], 0.28 nm×0.48 nm [010]) [28, 29], only the isolated Fe(III) species (and oligomeric Fe(III)$_2$O$_3$ clusters) are included inside of FeCit-Z, and gave the light yellow color.

**Figure 4.** The amounts of total iron and extractable iron by CBD and ammonium acetate in the products

**Figure 5.** Color of the samples: (a) the synthesized Na-P1, (b) FeChl-Z, (c) FeCit-Z, (d) CBD treated Na-P1, (e) CBD treated FeChl-Z, (f) CBD treated FeCit-Z
4. Conclusions
FeChl-Z retains mostly iron species with lower release property. On the other hand, FeCit-Z retains much iron species with higher release property. By mixing different iron sources such as FeChl-Z and FeCit-Z, the supply period of iron nutrient to plants might be controlled. Furthermore, it should be noted that the different preparation methods of iron-exchanged zeolites affect the supply property of iron nutrient of the products for plants.

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