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ABSTRACT

CN-deficient Prussian blue analogues (PBAs), $[M^N(H_2O)_x]_y[Fe^{II}(CN)_5(NH_3)]$ (M^N = Cu^{II}, Co^{II} or Ga^{III}), were synthesized and examined as a new class of heterogeneous catalysts for hydrolytic decomposition of organophosphates often used as pesticides. The active species of the CN-deficient PBAs were mainly C-bound Fe^{II} ions with exactly single open sites generated by liberation of the NH_3 ligand during the catalytic reactions. $[Cu^{II}(H_2O)_{8/3}]_{3/2}[Fe^{II}(CN)_5(NH_3)]$ showed higher catalytic activity than $[Co^{II}(H_2O)_{8/3}]_{3/2}[Fe^{II}(CN)_5(NH_3)]$ and $[Ga^{III}(H_2O)][Fe^{II}(CN)_5(NH_3)]$ although N-bound Cu^{II} species has been reported as less active than Co^{II} and Ga^{III} species in conventional PBAs. IR measurements of a series of the CN-deficient PBAs after the catalytis reactions clarified that a part of NH_3 ligands remained on $[Co^{II}(H_2O)_{8/3}]_{3/2}[Fe^{II}(CN)_5(NH_3)]$ and hydrogen phosphate formed as a product strongly adsorbed on the Fe^{II} ions of $[Ga^{III}(H_2O)][Fe^{II}(CN)_5(NH_3)]$. Hydrogen phosphate also adsorbed but weakly on the Fe^{II} ions of $[Cu^{II}(H_2O)_{8/3}]_{3/2}[Fe^{II}(CN)_5(NH_3)]$. These results suggest that heterogeneous catalysis of the Fe^{II} ions with single open sites were tuned by the M^N ions through metal-metal interaction.

INTRODUCTION

Utilization of defective coordination polymers as heterogeneous catalysts attracts much attention, because active species with open sites can be intentionally created, resulting in showing unique catalysis contrast to metals or metal oxides.[1–5] In the defective coordination polymers, active species are metal ions with open sites usually formed by the liberation of extra ligands bound to the metal ions.[6–23] For example, the number of open metal sites in coordination polymers composed of ruthenium(II) ion (Ru^{II}) and 1,3,5-benzenetricarboxylate trianion was

regulated by adding isophthalate or pyridine-3,5-dicarboxylate dianion as a second ligand, because a certain amount of extra ligand such as chloride coordinated to the Ru^{II} ions.[22,23] The extra ligands are liberated to provide open sites on the Ru^{II} ions acting as catalytic active species. The average number of open sites on Ru^{II} ions can be controlled by changing the ratio of tri- and dianion ligands.

Another example is Prussian blue analogues (PBAs) composed of a hexacyanometallate anion ($[M^C(CN)_6]^{n-}$) and a metal ion (M^N) to form a M^C–CN–M^N framework.[24–27] Catalysis of PBAs has been studied for various reactions including photocatalytic water oxidation and hydrolysis of organophosphates often used as pesticides.[28–47] Usually, open sites acting as catalytic active sites are selectively formed on the M^N ions by liberation of the extra ligand such as water, because the number of M^N ions in a PBA is larger than that of $[M^C(CN)_6]^{n-}$ anions to maintain charge balance, indicating that M^N ions have extra ligands to satisfy the octahedral coordination structure (Figure 1a). The catalytic properties of M^N ions can be modulated by the electronic interaction between M^N and M^C ions, resulting in the enhancement of heterogeneous catalysis. Average number of open sites formed on M^N ions can be theoretically calculated under the consideration of the valence of $[M^C(CN)_6]^{n-}$ and M^N. However, the exact number of open sites formed on each M^N ion has yet to be precisely controlled.

We report herein the intentional creation of an open site on the C-bound Fe^{II} ions in PBAs by using $[Fe^{II}(CN)_5L]^{3-}$ (L = NH_3 or H_2O) instead of $[Fe^{II}(CN)_6]^{4-}$ as a building unit (Figure 1b). The resulting CN-deficient PBAs possess exactly single open sites on the Fe^{II} ions. The catalysis of a series of CN-deficient PBAs composed of $[Fe^{II}(CN)_5L]^{3-}$ and various M^N ions (Cu^{II}, Co^{II} or Ga^{III}) are examined for organophosphate hydrolysis, because Fe^{II} ions have been reported to show high activity for the hydrolysis reaction (Figure 1c).[28] The correlation between catalytic

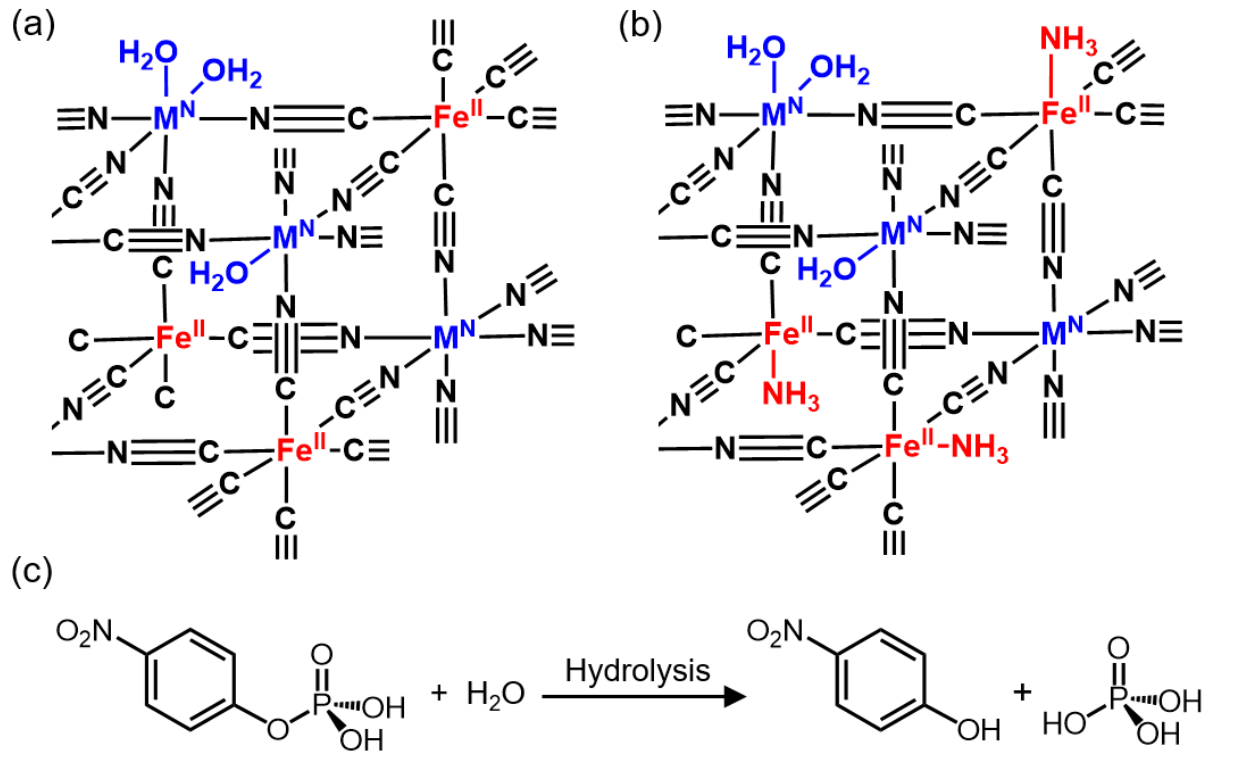

Figure 1. Partial structures of (a) $[M^N(H_2O)_x]_y[Fe^{II}(CN)_6]$ (**M^NFe**) and (b) $[M^N(H_2O)_x]_y[Fe^{II}(CN)_5(NH_3)]$ (**M^NFe-NH_3**) complexes. (c) The hydrolysis of *p*-nitrophenyl phosphate (*p*-NPP).

behavior and adsorbed species on the surfaces of the CN-deficient PBAs composed of various M^N ions is scrutinized.

EXPERIMENTAL SECTION

Materials. Potassium ferrocyanide trihydrate, sodium pentacyanoammineferroate(II) hydrate, copper(II) nitrate trihydrate, cobalt(II) nitrate hexahydrate, gallium(III) nitrate hydrate, disodium *p*-nitrophenyl phosphate hexahydrate, *p*-nitrophenol, concentrated hydrochloric acid, concentrated nitric acid, sodium chloride, trisodium phosphate and sodium hydroxide were purchased from FUJIFILM-Wako Pure Chemical Industries Corporation. Potassium hexacyanoferrate(II) trihydrate and 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid

(HEPES) were obtained from Sigma-Aldrich Co. LLC. All chemicals were used without further purification. Purified water was provided by a water purification system, Advantec RFD210TA, where the electronic conductance was 18.2 MΩ cm.

Synthesis of $[Cu^{II}(H_2O)_x]_y\{[Fe^{II}(CN)_5(NH_3)]_n[Fe^{II}(CN)_6]_{1-n}\}$ complexes (n = 0, 0.50, 0.83 or 1). An aqueous solution (3.0 mL) containing sodium pentacyanoammineferroate(II) ($Na_3[Fe^{II}(CN)_5(NH_3)]$, 0–0.10 M) and potassium hexacyanoferrate(II) ($K_4[Fe^{II}(CN)_6]$, 0–0.10 M) was slowly added to an aqueous solution of copper(II) nitrate (0.13 M, 4.5 mL) with vigorous stirring for 17.5 h. The formed brown precipitates were collected by centrifugation and washed with distilled water a few times. The precipitates were dried *in vacuo* for 12 h. The dried precipitates were milled using a mortar to obtain fine powder of $[Cu^{II}(H_2O)_x]_y\{[Fe^{II}(CN)_5(NH_3)]_n[Fe^{II}(CN)_6]_{1-n}\}$ complexes.

Synthesis of $[Co^{II}(H_2O)_3]_2[Fe^{II}(CN)_6]$ (CoFe) and $[Ga^{III}(H_2O)_{3/2}]_{4/3}[Fe^{II}(CN)_6]$ (GaFe). **CoFe** and **GaFe** was synthesized according to the literature procedure with a slight modification.[28] An aqueous solution of $K_4[Fe^{II}(CN)_6]$ (0.10 M, 8 mL) was slowly added to an aqueous solution of cobalt(II) nitrate or gallium(III) nitrate (0.10 M, 16 mL) with vigorous stirring for 17.5 h. The formed brown precipitates were collected by centrifugation and washed with distilled water a few times. The precipitates were dried *in vacuo* for 12 h. The dried precipitates were milled using a mortar to obtain fine powder of **CoFe** and **GaFe**.

Synthesis of $[Co^{II}(H_2O)_{8/3}]_{3/2}[Fe^{II}(CN)_5(NH_3)]$ (CoFe-NH_3) and $[Ga^{III}(H_2O)][Fe^{II}(CN)_5(NH_3)]$ (GaFe-NH_3). An aqueous solution of sodium pentacyanoammineferroate(II) ($Na_3[Fe^{II}(CN)_5(NH_3)]$, 0.10 M, 8 mL) was slowly added to an aqueous solution of cobalt(II) nitrate or gallium(III) nitrate (0.10 M, 12 mL) with vigorous stirring for 17.5 h. The formed brown precipitates were collected by centrifugation and washed

with distilled water a few times. The precipitates were dried *in vacuo* for 12 h. The dried precipitates were milled using a mortar to obtain fine powder of **CoFe-NH_3** and **GaFe-NH_3**.

Synthesis of $[Cu^{II}(H_2O)_{8/3}]_{3/2}\{[Fe^{II}(CN)_5(H_2O)]_{3/4}[Fe^{II}(CN)_5(NH_3)]_{1/4}\}$ (CuFe-H_2O). Sodium pentacyanoaquaferroate(II) ($Na_3[Fe^{II}(CN)_5(H_2O)]$) was synthesized according to the reported procedure with a slight modification.[48] $Na_3[Fe^{II}(CN)_5(NH_3)]$ (25 mM) in a deaerated 4-(2-hydroxyethyl)-1-piperazineethanesulfonate (HEPES) buffer solution (pH 7.2, 100 mM, 40 mL) containing 0.87 M sodium chloride was allowed to stand for 15 min under N_2 atmosphere with vigorous stirring. The ratio of $[Fe^{II}(CN)_5(H_2O)]^{3-}$ and $[Fe^{II}(CN)_5(NH_3)]^{3-}$ in the resulting solution was 3:1, as determined by IR absorption using the ATR technique, however, $[Fe^{II}(CN)_5(H_2O)]^{3-}$ cannot be further purified by either recrystallization or chromatography due to its instability. Then, the solution containing $[Fe^{II}(CN)_5(H_2O)]^{3-}$ was slowly added to an aqueous solution of copper(II) nitrate (0.3 M, 7.5 mL) with vigorous stirring for 17.5 h. The formed brown precipitates were collected by centrifugation and washed with distilled water a few times. The precipitates were dried *in vacuo* for 12 h. The dried precipitates were milled using a mortar to obtain fine powder of **CuFe-H_2O**.

Physical measurements. Ultraviolet−visible (UV−vis) absorption spectra were recorded on a JASCO V−770 spectrometer. Infrared (IR) spectra were obtained on a JASCO FT/IR−6200 spectrometer with an attenuated total reflectance unit using a diamond window. The amount of ammine ligand and ammonium ion in the PBAs were calculated according to a literature procedure with slight modifications.[49] Powder X-ray diffraction patterns were recorded on a Shimadzu XD−3A. Incident X-ray radiation was produced by an Fe X-ray tube operating at 40 kV and 15 mA with Fe Kα radiation (λ = 1.94 Å). The scan rate was 1° min^{-1} from 2θ = 20−60°. The atomic ratio of PBAs was determined using a Shimadzu EDX−730 X-ray fluorescence

spectrometer. Inductively coupled plasma optical emission spectroscopy (ICP-OES) analyses were performed on a Shimadzu ICPE-9810. Prior to the analyses, PBAs (ca. 1 mg) were dispersed in a mixed solution of nitric acid and sulfuric acid (v/v = 1/1, 1.0 mL). The dispersion was ultrasonicated for several minutes to dissolve the PBAs. The obtained clear solutions were then diluted by adding a certain amount of 2 M nitric acid and purified water to obtain the sample solutions in the optimum concentration range for ICP-OES analyses. Inductively coupled plasma mass spectrometry (ICP-MS) analyses were performed on a PerkinElmer NexION 300D. Prior to the analyses, PBAs (5.0 mg) were dispersed in a mixed solution of nitric acid and hydrochloric acid (v/v = 1/1, 6.0 mL). The dispersion was heated using a PerkinElmer Multiwave 3000 system (1200 W) for 10 min followed by holding at the temperature for 15 min to dissolve the PBAs. The obtained clear solutions were then diluted by adding a certain amount of 2% nitric acid and purified water to obtain the sample solutions in the optimum concentration range for ICP-MS analyses. Scanning electron microscope (SEM) images of the PBAs were obtained using a JEOL JSM-6500F operated at 15 kV. X-ray photoelectron spectroscopy (XPS) analyses were performed using a Shimadzu ESCA-3400HSE. An incident radiation was Mg Kα X-ray (1253.6 eV) at 200 W. The samples were mounted on a stage with a double-sided carbon tape. The binding energy of each element was corrected by the C 1s peak (284.6 eV) from the carbon tape.

Nitrogen (N_2) adsorption-desorption isotherms at −196 °C were obtained with a MicrotracBEL Belsorp-mini II. Weighed samples (~100 mg) were used for adsorption analysis after pretreatment at 150 °C for 1 h *in vacuo*. The samples were exposed to N_2 within a relative pressure range from 0.01 to 101.3 kPa. Adsorbed amount of N_2 was calculated from the pressure change in a cell after reaching equilibrium at −196 °C. The total surface area was calculated from

the Brunauer–Emmett–Teller (BET) plot. Size of mesopores and micropores were calculated by the Barrett−Joyner−Halenda (BJH) method and microporous (MP) method, respectively.

Catalysis evaluation for the hydrolysis of organophosphates. A typical procedure for catalysis measurements is as follows: a HEPES buffer solution (750 μL, 100 mM, pH 6.0 or 8.3) containing disodium *p*-nitrophenyl phosphate (*p*-NPP, 25 mM) and a catalyst (0.063 mmol of Fe) in a sealed microtube was shaken at 900 rpm at 50 °C using an a Block Bath Shaker (MyBL-100S, As One, Japan). An aliquot (10 μL) of the reaction mixture periodically sampled was diluted with a HEPES buffer solution (2,490 μL, 100 mM, pH 8.3) and analyzed by a UV−vis spectrophotometer. The conversion ratio of *p*-NPP at a certain reaction time was determined by the absorbance change at 400 nm ascribed to the formed *p*-nitrophenolate ion (*p*-NP, $\varepsilon = 1.57 \times 10^4\ M^{-1}$ cm). Recycling performance was evaluated by adding a buffer solution containing *p*-NPP to a catalyst taken out from the reaction solution by centrifugation.

RESULTS AND DISCUSSION

Structure of $[M^N(H_2O)_x]_y[Fe^{II}(CN)_5(NH_3)]$ (M^NFe-NH_3) complexes. Cu^{II}, Co^{II} and Ga^{III} ions were chosen as M^N ions of the CN-deficient PBAs because of different valence and catalytic behavior of each meal ion as reported previously. Cu^{II} ion is divalent ion with low activity for hydrolysis of *p*-nitrophenyl phosphate (*p*-NPP), Co^{II} ion is also divalent but catalytically active, and Ga^{III} is trivalent and catalytically active.[28] $[Cu^{II}(H_2O)_{8/3}]_{3/2}[Fe^{II}(CN)_5(NH_3)]$ (**CuFe-NH_3**), $[Co^{II}(H_2O)_{8/3}]_{3/2}[Fe^{II}(CN)_5(NH_3)]$ (**CoFe-NH_3**) and $[Ga^{III}(H_2O)][Fe^{II}(CN)_5(NH_3)]$ (**GaFe-NH_3**) were obtained by the reaction of $Na_3[Fe^{II}(CN)_5(NH_3)]$ with Cu^{II}, Co^{II} and Ga^{III} ions, respectively. Similarly, $[Cu^{II}(H_2O)_3]_2[Fe^{II}(CN)_6]$ (**CuFe**), $[Co^{II}(H_2O)_3]_2[Fe^{II}(CN)_6]$ (**CoFe**) and $[Ga^{III}(H_2O)_{3/2}]_{4/3}[Fe^{II}(CN)_6]$ (**GaFe**) were synthesized by the reaction of $K_4[Fe^{II}(CN)_6]$ with the corresponding metal ions. The scanning electron microscope (SEM) images showed that the

particles size of each PBA was 50 μm at the largest and most of particles were less than 20 μm (Figure S1). No shape-controlled particles were observed even at smaller particles. Insignificant contamination of Na^+ and K^+ ions in the PBAs was assured by inductively coupled plasma optical emission spectroscopy (ICP-OES) and X-ray fluorescence spectroscopy, where the molar ratios of Na/Fe and K/Fe are lower than 0.0035 and 0.026, respectively (Figure S2 and Table S1).

X-ray photoelectron spectroscopy (XPS) measurements of **CuFe-NH$_3$** and **CuFe** were performed for the energy regions of Cu 2p, Fe 2p, O 1s and N 1s (Figure S3). The values for binding energy of Cu $2p_{3/2}$ of **CuFe-NH$_3$** and **CuFe** were 933.8 eV and 933.2 eV, respectively, which are close to the typical values for the Cu^{II} species (933.5 eV).[50] The binding energy of Fe $2p_{3/2}$ peaks were found at 708.7 eV and 709.1 eV for **CuFe-NH$_3$** and **CuFe**, respectively, which are also comparable to the typical binding energy of Fe^{II} species (709.1 eV).[50] These results suggest that the involvement of NH_3 ligands hardly affected the oxidation states of Cu^{II} and Fe^{II} ions. The binding energy of O 1s in **CuFe-NH$_3$** was 532.5 eV, which is virtually the same to that of **CuFe** (532.2 eV). The binding energy of N 1s in **CuFe-NH$_3$** (397.9 eV) was also similar to that in **CuFe** (398.3 eV) even in the presence of NH_3 ligands, because the peaks for N 1s in CN^- and NH_3 ligands (397.7 and 399.0 eV, respectively, according to the literature) are overlapped, but the peak was hardly deconvoluted.[51]

The bridging structures of Fe^{II}–CN–M^N in **M^{N}Fe-NH$_3$** complexes were confirmed by infrared (IR) spectroscopy. The CN-stretching bands (ν_{CN}) of **CuFe-NH$_3$**, **CoFe-NH$_3$** and **GaFe-NH$_3$** appeared at 2094, 2084 and 2106 cm^{-1}, respectively, which were shifted from that of $K_3[Fe^{II}(CN)_5(NH_3)]$ (2038 cm^{-1}) in the higher wavenumber region (Figure 2). Such higher wavenumber shift evidenced the formation of Fe^{II}–CN–M^N structures, because the electron density of an antibonding orbital of CN ligand was reduced by the additional coordination to M^N

ions.[52] Also, the wavenumbers of ν_{CN} similar to those of corresponding **CuFe**, **CoFe** and **GaFe** appeared at 2096, 2084 and 2117 cm^{-1}, respectively, supported the Fe^{II}–CN–M^N formation without ligand isomerization (Figure 2).[52] The wavenumber of ν_{CN} of **GaFe-NH$_3$** (2106 cm^{-1}) lower than that of **GaFe** (2117 cm^{-1}) by 11 cm^{-1} resulted from a partial oxidation of Fe ions in **GaFe** as reported previously,[53] indicating that the valence of Fe ions is +2 in **GaFe-NH$_3$**. Also, ammine ligand coordination in **CuFe-NH$_3$**, **CoFe-NH$_3$** and **GaFe-NH$_3$** was confirmed by the peaks at 1344, 1269 and 1270 cm^{-1}, respectively, assigned to H–N–H bending vibration (δ_{HNH}), which were not observed for **CuFe**, **CoFe** and **GaFe**.[54] The peaks at around 1400 cm^{-1} observed for **CuFe-NH$_3$**, **CoFe-NH$_3$** and **GaFe-NH$_3$** can be assigned to δ_{HNH} of ammonium ion (NH_4^+) trapped in the interstitial sites of PBAs.[54] NH_4^+ could be formed by partial replacement of NH_3 to H_2O ligands during synthesis in an aqueous solution (*vide infra*).

Nitrogen (N_2) adsorption-desorption isotherms of PBAs were performed to investigate their porous structures (Figure S4). The total surface areas were calculated from the Brunauer–Emmett–Teller (BET) method (Table 1). Homogeneous distribution of micropores (0.5–0.7 nm) formed by the cubic lattice structure of PBAs were determined by the microporous (MP) method. Type IV isotherms observed for a series of PBAs suggest the presence of mesopores in the sizes of 3−10 nm as determined by the Barrett−Joyner−Halenda (BJH) method. The mesopores in this size range are formed by the gaps among PBA particles, as reported previously.[28]

The powder X-ray diffraction (PXRD) patterns obtained for **M^NFe-NH$_3$** complexes were assignable to cubic structure (Figure 3a, c, e). The cell parameters obtained for M^N = Cu, Co and Ga were a = 10.00, 9.94 and 10.04 Å, respectively. The a values were comparable to those of corresponding **M^NFe** complexes without open sites on Fe^{II} ions, where a = 9.95, 10.10 and 10.02 Å for M^N = Cu, Co and Ga, respectively (Figure 4b, d, f). Broader peaks observed for

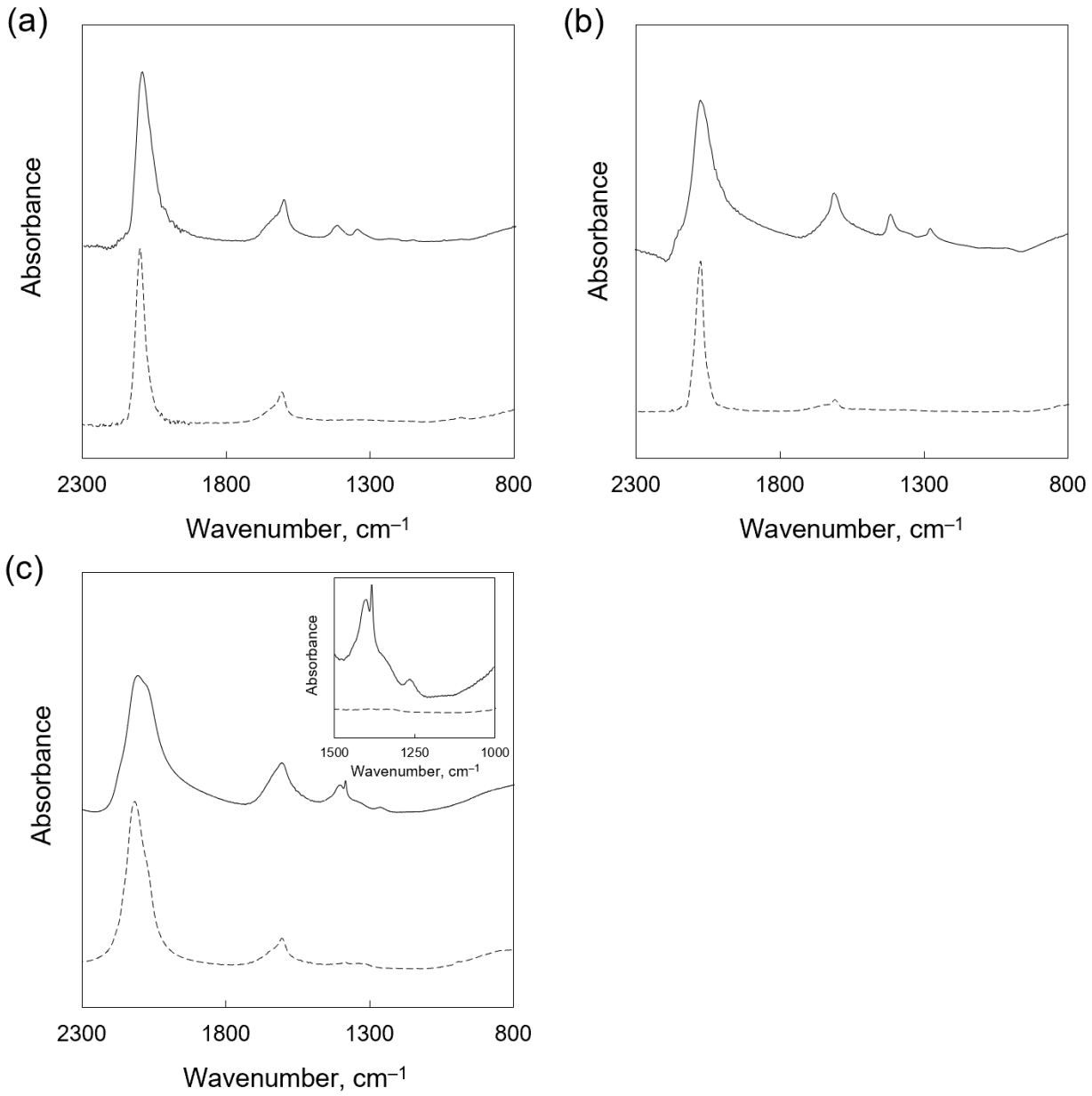

Figure 2. Infrared spectra of (a) $[Cu^{II}(H_2O)_{8/3}]_{3/2}[Fe^{II}(CN)_5(NH_3)]$ (**CuFe-NH3**, solid line) and $[Cu^{II}(H_2O)_2]_{3/2}[Fe^{II}(CN)_6]$ (**CuFe**, broken line), (b) $[Co^{II}(H_2O)_{8/3}]_{3/2}[Fe^{II}(CN)_5(NH_3)]$ (**CoFe-NH3**, solid line) and $[Co^{II}(H_2O)_2]_{3/2}[Fe^{II}(CN)_6]$ (**CoFe**, broken line), and (c) $[Ga^{III}(H_2O)][Fe^{II}(CN)_5(NH_3)]$ (**GaFe-NH3**, solid line) and $[Ga^{III}(H_2O)_{3/2}]_{4/3}[Fe^{II}(CN)_6]$ (**GaFe**, broken line). Magnified views of δ_{HNH} region (1000−1500 cm^{-1}) are shown in the insets.

Table 1. Total surface areas obtained by the Brunauer−Emmett−Teller (BET) method, pore diameters obtained by the Barrett−Joyner−Halenda (BJH) method and the microporous (MP) method of a series of PBAs calculated from their N_2 adsorption-desorption isotherms

PBA	Total surface area, $m^2\ g^{-1}$	Mesopore diameter, nm	Micropore diameter, nm
CuFe-NH$_3$	77	7.0	0.7
CuFe	101	10.2	0.7
CuFe-H$_2$O	32	4.6	0.7
CoFe-NH$_3$	50	5.3	0.7
CoFe	284	10.8	0.7
GaFe-NH$_3$	179	3.2	0.6
GaFe	393	3.5	0.8

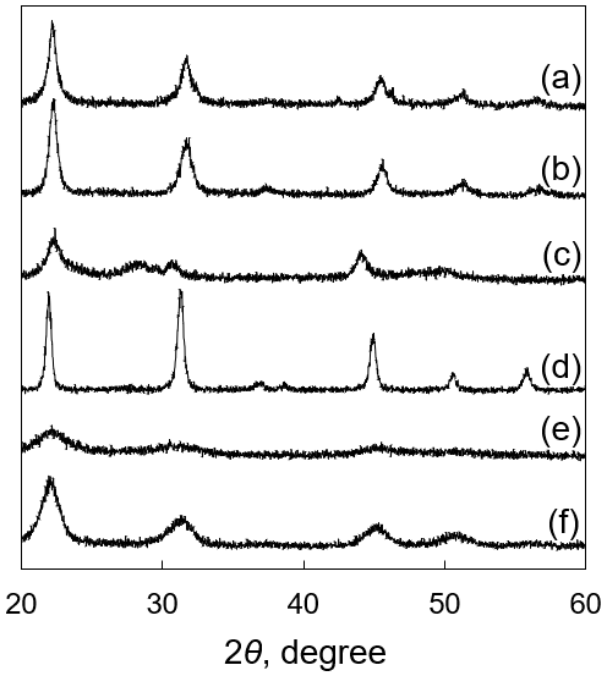

Figure 3. Powder X-ray diffraction patterns of (a) $[Cu^{II}(H_2O)_{8/3}]_{3/2}[Fe^{II}(CN)_5(NH_3)]$ (**CuFe-NH$_3$**), (b) $[Cu^{II}(H_2O)_2]_{3/2}[Fe^{II}(CN)_6]$ (**CuFe**), (c) $[Co^{II}(H_2O)_{8/3}]_{3/2}[Fe^{II}(CN)_5(NH_3)]$ (**CoFe-NH$_3$**), (d) $[Co^{II}(H_2O)_2]_{3/2}[Fe^{II}(CN)_6]$ (**CoFe**), (e) $[Ga^{III}(H_2O)][Fe^{II}(CN)_5(NH_3)]$ (**GaFe-NH$_3$**) and (f) $[Ga^{III}(H_2O)_{3/2}]_{4/3}[Fe^{II}(CN)_6]$ (**GaFe**).

M^NFe-NH_3 complexes, especially for **GaFe-NH_3**, than those of **M^NFe** complexes resulted from the low crystallinity of **M^NFe-NH_3** complexes due to the local disorder originated from partial deficiencies of CN^- ligands. However, the shift of ν_{CN} and microporous structures determined by the N_2 adsorption-desorption isotherms indicate the formation of **M^NFe-NH_3** complexes having cubic lattice structures without extended defects.

Catalysis of $[M^N(H_2O)_x]_y[Fe^{II}(CN)_5(NH_3)]$ complexes for Hydrolysis of *p*-Nitrophenyl Phosphate. Catalytic activity of **M^NFe** and **M^NFe-NH_3** complexes for hydrolysis of *p*-nitrophenyl phosphate (*p*-NPP) was examined at 50 °C in a 4-(2-hydroxyethyl)-1-piperazineethanesulfonate (HEPES) buffer solution (100 mM, pH 8.3, 0.75 mL) containing metal complexes (0.063 mmol of Fe) and *p*-NPP (25 mM). The yield of the hydrolysis product, *p*-nitrophenolate ion (*p*-NP), was determined by characteristic absorbance change at 400 nm (Figure S5). No catalytic activity was observed for $[Fe^{II}(CN)_6]^{4-}$ and $[Fe^{II}(CN)_5(NH_3)]^{3-}$ dissolved in the buffer solutions (Figure 4). The IR spectrum of an aqueous solution containing $[Fe^{II}(CN)_5(NH_3)]^{3-}$ reacted with hydrogen phosphate indicates the absence of δ_{HNH} peak at 1255 cm^{-1}, suggesting that the open Fe^{II} sites formed during the reaction (Figure S6). However, the peaks at 1078 cm^{-1} assignable to the PO stretching vibration (ν_{PO}) appeared, suggesting the coordination of hydrogen phosphate to the Fe^{II} ions.[55,56] Thus, tuning of electronic properties of Fe^{II} ions by M^N ions through CN^- ligand is essential to suppress the product inhibition by hydrogen phosphate.

The higher conversion ratios and initial reaction rates for 1 h (ν_0) were observed for the reaction solutions containing **CoFe** (28% for 24 h and 0.3×10^{-3} mol L^{-1} h^{-1}) and **GaFe** (26% for 24 h and 0.3×10^{-3} mol L^{-1} h^{-1}) compared with those containing **CuFe** (5% for 24 h and 0.1×10^{-3} mol L^{-1} h^{-1}), indicating that the N-bound Co^{II} and Ga^{III} ions act as the active species,

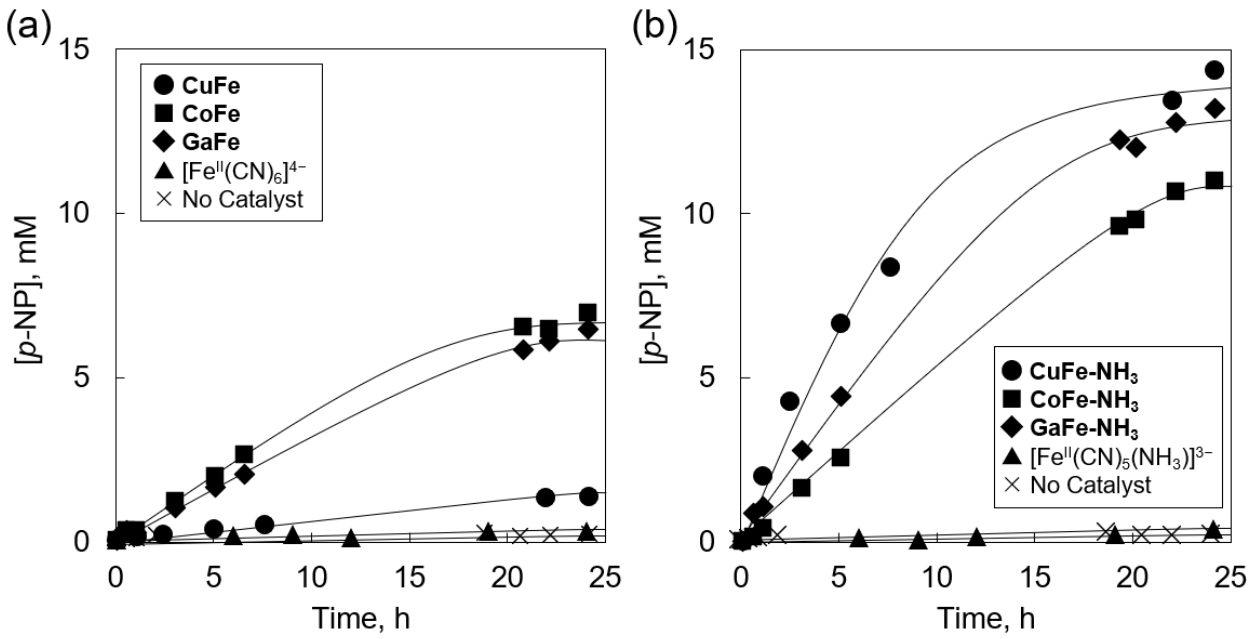

Figure 4. Time profiles of the *p*-nitrophenolate ion (*p*-NP) formation in a HEPES buffer solution (100 mM, 0.75 mL, pH 8.3, 50 °C) containing disodium *p*-nitrophenyl phosphate (*p*-NPP, 25 mM) in the presence of (a) $[Cu^{II}(H_2O)_3]_2[Fe^{II}(CN)_6]$ (**CuFe**), $[Co^{II}(H_2O)_2]_{3/2}[Fe^{II}(CN)_6]$ (**CoFe**), $[Ga^{III}(H_2O)_{3/2}]_{4/3}[Fe^{II}(CN)_6]$ (**GaFe**) and hexacyanoferrate ion ($[Fe^{II}(CN)_6]^{4-}$), or (b) $[Cu^{II}(H_2O)_{8/3}]_{3/2}[Fe^{II}(CN)_5(NH_3)]$ (**CuFe-NH3**), $[Co^{II}(H_2O)_{8/3}]_{3/2}[Fe^{II}(CN)_5(NH_3)]$ (**CoFe-NH3**), $[Ga^{III}(H_2O)][Fe^{II}(CN)_5(NH_3)]$ (**GaFe-NH3**) and pentacyanoammineferrate ion ($[Fe^{II}(CN)_5(NH_3)]^{3-}$).

however, Cu^{II} ions are inactive (Figure 4a). **CuFe-NH3** showed the higher catalytic activity compared with **CuFe**. The conversion ratio and v_0 value observed for **CuFe-NH3** were 58% for 24 h and 2.0×10^{-3} mol L^{-1} h^{-1}, respectively, suggesting that the open Fe^{II} sites were successfully created during the catalytic reaction. The conversion ratios and v_0 values observed for **CoFe-NH3** (44% for 24 h and 0.4×10^{-3} mol L^{-1} h^{-1}) and **GaFe-NH3** (53% for 24 h and 1.0×10^{-3} mol L^{-1} h^{-1}) were higher than those for **CoFe** and **GaFe**, suggesting that the Fe^{II} ions contribute to *p*-NPP hydrolysis (Figure 4b). However, the conversion ratios and v_0 values for

CoFe-NH$_3$ and **GaFe-NH$_3$** were lower than those of **CuFe-NH$_3$**. These results imply that the catalytic properties of open Fe^{II} sites of **CuFe-NH$_3$**, **CoFe-NH$_3$** and **GaFe-NH$_3$** were not the same.

Repetitive catalysis experiments using **CuFe-NH$_3$** indicated that the conversion ratios (24 h) obtained for the reactions were 42, 13, 12 and 11% at the 1st to 4th runs, respectively (Figure S7). The conversion ratio at the 2nd run was lower than that at the 1st run. No further decrease in conversion ratios were observed at the 3rd and 4th runs. A possible reason for the deceleration was structural deformation of **CuFe-NH$_3$**, however, virtually the same PXRD patterns of **CuFe-NH$_3$** before and after catalytic hydrolysis strongly support no degradation of **CuFe-NH$_3$** (Figure S8). Thus, product inhibition of the Fe^{II} ions would be a reason for deceleration.

Adsorbed Species on Open Sites of Fe^{II} Ions in $[M^N(H_2O)_x]_y[Fe^{II}(CN)_5(NH_3)]$ Complexes After the Reaction. The liberation of NH_3 ligands from **CuFe-NH$_3$** during the catalytic reaction was confirmed by ex situ IR spectroscopy. The IR measurement of **CuFe-NH$_3$** after the reaction clarified that the strength of the most characteristic peak at 1348 cm^{-1} ascribed to δ_{HNH} decreased by ~85% compared with that of fresh **CuFe-NH$_3$**, suggesting that open Fe^{II} sites successfully formed during the catalytic reaction (Figure 5a).[28] Instead, the peaks at 1014 cm^{-1} and around 989 cm^{-1} assignable to ν_{PO} appeared for **CuFe-NH$_3$** after the reaction, indicating the adsorption of hydrogen phosphate.[55,56] The adsorbed hydrogen phosphate in **CuFe** and **CuFe-NH$_3$** after the reactions were more directly quantified by inductively coupled plasma mass spectrometry (ICP-MS). The molar ratio of P and Fe in **CuFe-NH$_3$** after the catalytic hydrolysis was 0.12, which was six times higher than that in **CuFe** (0.021, Table S2). These results suggest that hydrogen phosphate formed by the *p*-NPP hydrolysis preferably bound to the open Fe^{II} sites in **CuFe-NH$_3$** (Figure 6).

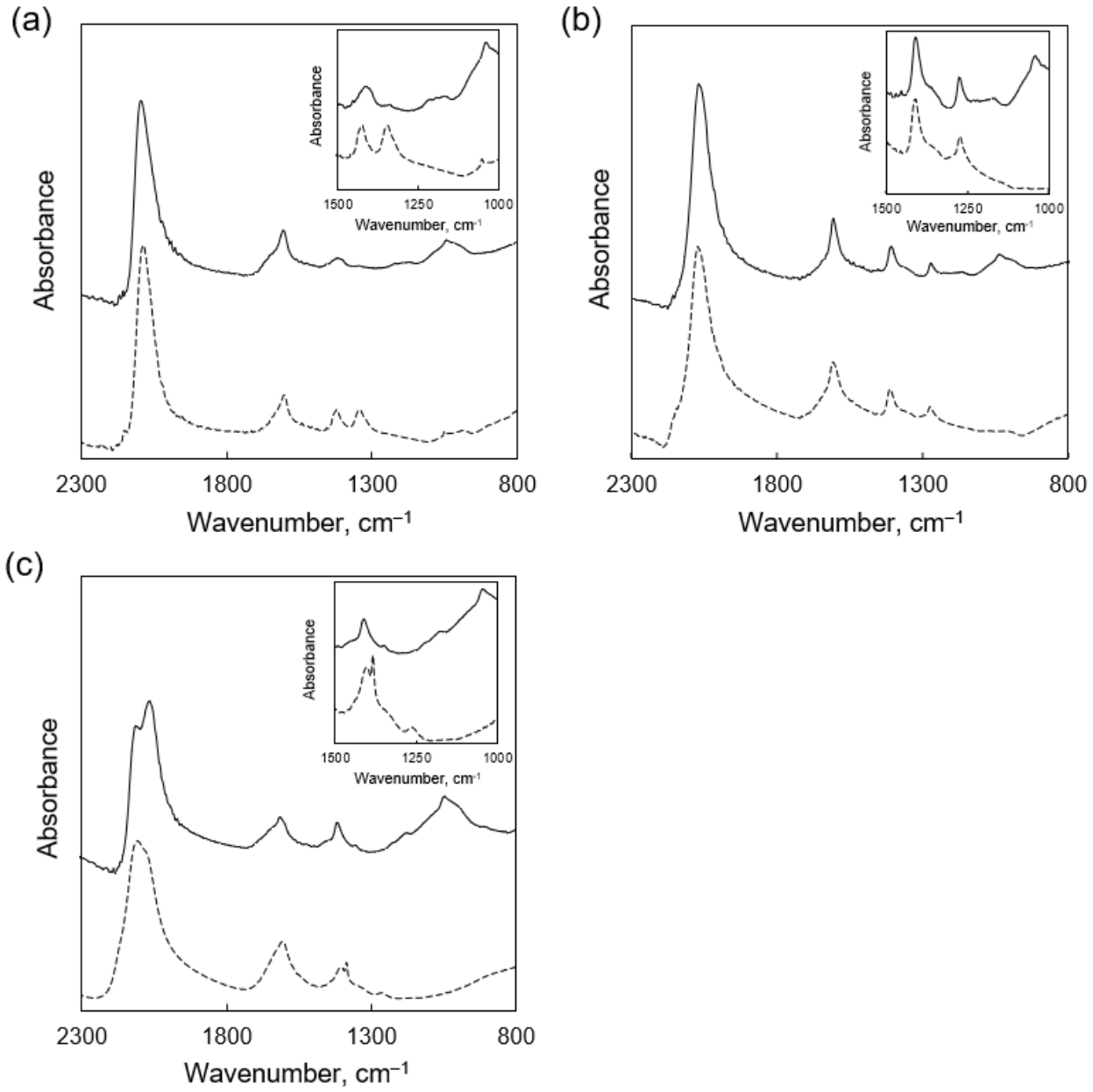

Figure 5. Infrared (IR) spectra of (a) $[Cu^{II}(H_2O)_{8/3}]_{3/2}[Fe^{II}(CN)_5(NH_3)]$ (**CuFe-NH$_3$**), (b) $[Co^{II}(H_2O)_{8/3}]_{3/2}[Fe^{II}(CN)_5(NH_3)]$ (**CoFe-NH$_3$**) and (c) $[Ga^{III}(H_2O)][Fe^{II}(CN)_5(NH_3)]$ (**GaFe-NH$_3$**) before (broken lines) and after (solid lines) catalytic hydrolysis of disodium *p*-nitrophenyl phosphate (*p*-NPP, 25 mM) in a HEPES buffer solution (100 mM, 0.75 mL, 50 °C) for 24 h. Magnified views of δ_{HNH} and ν_{PO} region (1000−1500 cm^{-1}) are shown in the insets.

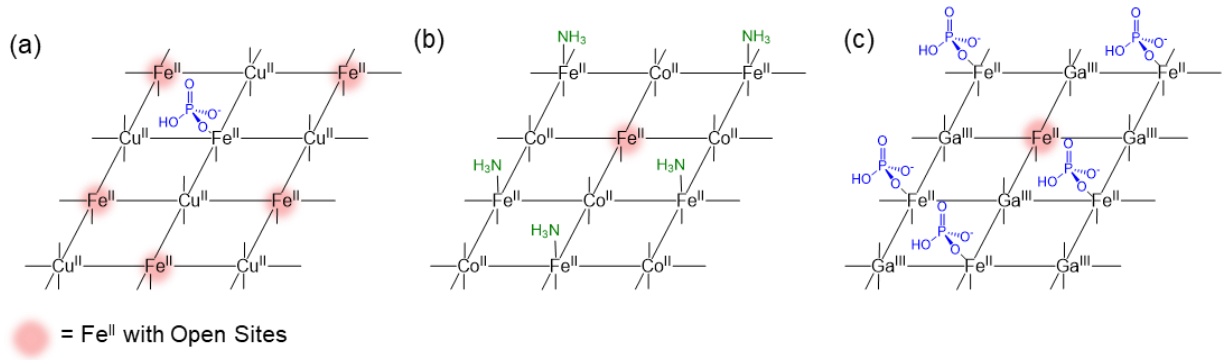

Figure 6. Schematic drawing of difference of adsorbed species on $[M^{N}(H_2O)_x]_y[Fe^{II}(CN)_5(NH_3)]$ (**M^{N}Fe-NH_3**) complexes (M^{N} = (a) Cu^{II},(b) Co^{II} or (c) Ga^{III})..

Adsorbed species on the surfaces of **CoFe-NH_3** and **GaFe-NH_3** after the reaction were also investigated by IR spectroscopy. The IR spectrum of **CoFe-NH_3** after the catalytic hydrolysis showed that the δ_{HNH} and ν_{PO} peaks appeared at 1262 cm^{-1} and 1038 cm^{-1}, respectively (Figure 5b), however, no peak assignable to ν_{PO} was observed for **CoFe** after the reaction (Figure S9a). Thus, limited liberation of NH_3 ligand in **CoFe-NH_3** suppressed the interaction with substrates, resulting in low catalytic activity. The IR spectrum of **GaFe-NH_3** after the reaction showing strong ν_{PO} peak appeared at 1037 cm^{-1} indicated the adsorption of hydrogen phosphate bond (Figure 5c). On the other hand, much weaker ν_{PO} peak observed for **GaFe** after the reaction indicated that hydrogen phosphate mainly adsorbed on the Fe^{II} not Ga^{III} ions of **GaFe-NH_3** (Figure S9b). The ν_{CN} peak of **GaFe-NH_3** appeared at 2066 cm^{-1} after the reaction is attributed to a contaminant, as reported previously.[51] The Fe^{II} ions with enhanced Lewis acidity by Co^{II} and Ga^{III} ions favors interaction with hydrogen phosphate and/or ammonia, which decelerate the catalytic reactions (Figure 6).[28] Thus, the metal ions coupled with Fe^{II} ions with single open sites in CN-deficient PBAs precisely regulated the catalysis and adsorption properties of the Fe^{II} ions.

Lability of NH_3 Compared with That of H_2O at Different pH values. Open Fe^{II} sites formed during the catalytic reaction are active sites, thus, liberation of NH_3 ligands is important

to achieve high catalytic activity. Lability of NH_3 ligand in **CuFe-NH$_3$** was confirmed by catalysis comparison with **CuFe-H$_2$O** which mainly possesses H_2O as the extra ligand instead of NH_3. **CuFe-H$_2$O** was prepared by mixing an aqueous solution of $Na_3[Fe^{II}(CN)_5(H_2O)]$, which was prepared from $Na_3[Fe^{II}(CN)_5(NH_3)]$ according to reported procedure, with that of copper(II) nitrate.[48] Insignificant contamination of Na^+ ions was confirmed by the ICP-OES analysis, in which the molar ratio of Na/Fe was 0.021 (Table S1). The IR spectra of obtained precipitate indicated that nearly 75% of NH_3 was replaced with water to provide $[Cu^{II}(H_2O)_{8/3}]_{3/2}\{[Fe^{II}(CN)_5(H_2O)]_{3/4}[Fe^{II}(CN)_5(NH_3)]_{1/4}\}$ (Figure S10).[48] On the other hand, the ν_{CN} peak of **CuFe-H$_2$O** appeared at 2094 cm^{-1}, which is comparable to those of **CuFe-NH$_3$** and **CuFe** (2094 and 2096 cm^{-1}, respectively), supports the formation of bridging structures of Fe^{II}–CN–M^N with cubic lattice structure. However, slightly broader PXRD peaks assignable to cubic structure (Figure S11) and smaller total surface areas calculated from the N_2 adsorption-desorption measurements (Table 1) compared with those of **CuFe-NH$_3$** suggests the low crystallinity of **CuFe-H$_2$O**.

The catalytic hydrolysis of *p*-NPP (25 mM) was examined at 50 °C in a HEPES buffer solution (100 mM, pH 8.3, 0.75 mL) containing **CuFe-NH$_3$** or **CuFe-H$_2$O** (0.063 mmol of Fe). **CuFe-NH$_3$** and **CuFe-H$_2$O** showed very similar reaction profiles in the reaction solutions of both pH 6.0 and 8.3 (Figure 7). These results suggest that open Fe^{II} ions acting as catalytic active species were successfully created on **CuFe-NH$_3$** and **CuFe-H$_2$O** irrespective of their crystallinity and solution pH.

Concentration Effect of Fe^{II} ions with Single Open Sites on Catalysis. The concentration of Fe^{II} ions with open sites were precisely tuned by concomitant use of $[Fe^{II}(CN)_5(NH_3)]^{3-}$ and $[Fe^{II}(CN)_6]^{4-}$ as building blocks. $[Cu^{II}(H_2O)_x]_y\{[Fe^{II}(CN)_5(NH_3)]_n[Fe^{II}(CN)_6]_{1-n}\}$ complexes (n =

0, 0.50, 0.83 or 1) were synthesized by mixing an aqueous solution containing the various ratios of $[Fe^{II}(CN)_5(NH_3)]^{3-}$ and $[Fe^{II}(CN)_6]^{4-}$ and that containing copper(II) nitrate. Similar PXRD patterns of $[Cu^{II}(H_2O)_x]_y\{[Fe^{II}(CN)_5(NH_3)]_n[Fe^{II}(CN)_6]_{1-n}\}$ complexes are ascribed to the cubic structure (Figure S12).

Catalytic hydrolysis of *p*-NPP was examined in a HEPES buffer solution (100 mM, pH 6.0, 0.75 mL) containing $[Cu^{II}(H_2O)_x]_y\{[Fe^{II}(CN)_5(NH_3)]_n[Fe^{II}(CN)_6]_{1-n}\}$ complexes (0.063 mmol of

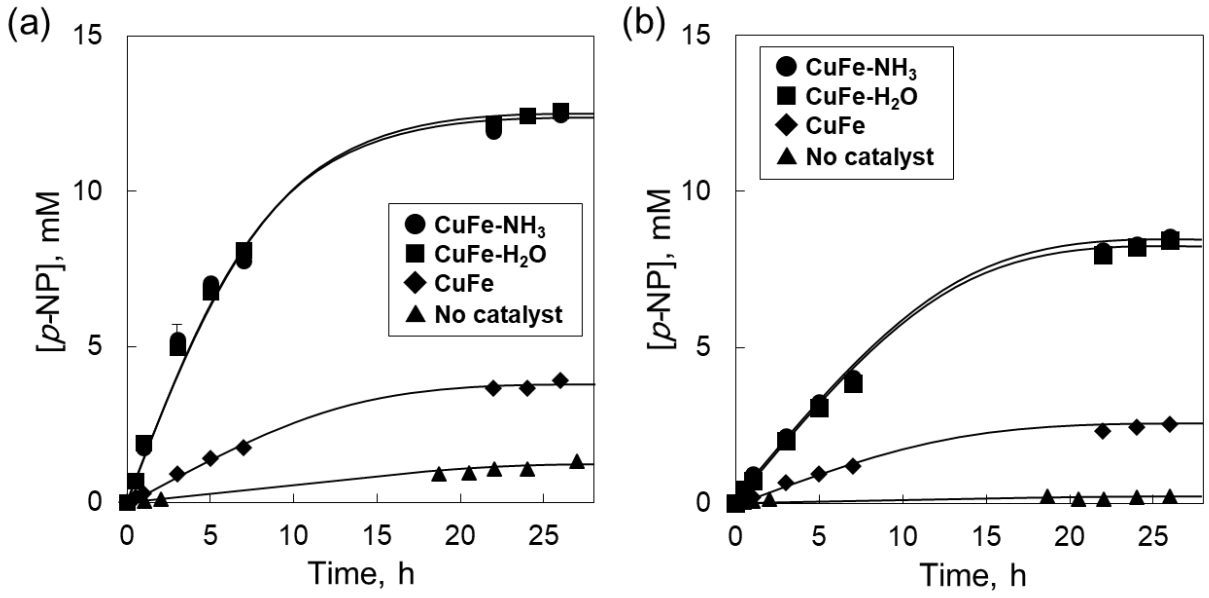

Figure 7. Time profiles of the *p*-nitrophenolate ion (*p*-NP) formation in a HEPES buffer solution (100 mM, 0.75 mL, 50 °C) containing disodium *p*-nitrophenyl phosphate (*p*-NPP, 25 mM) in the absence and presence of $[Cu^{II}(H_2O)_{8/3}]_{3/2}[Fe^{II}(CN)_5(NH_3)]$ (**CuFe-NH$_3$**), $[Cu^{II}(H_2O)_{8/3}]_{3/2}\{[Fe^{II}(CN)_5(H_2O)]_{3/4}[Fe^{II}(CN)_5(NH_3)]_{1/4}\}$ (**CuFe-H$_2$O**) and $[Cu^{II}(H_2O)_3]_2[Fe^{II}(CN)_6]$ (**CuFe**) at (a) pH 6.0 and (b) pH 8.3.

Fe) and *p*-NPP (25 mM). The conversion ratios in 24 h and v_0 values for $[Cu^{II}(H_2O)_x]_y\{[Fe^{II}(CN)_5(NH_3)]_n[Fe^{II}(CN)_6]_{1-n}\}$ complexes (22% and 0.4×10^{-3} mol L^{-1} h^{-1} for n = 0.50, and 34% and 1.2×10^{-3} mol L^{-1} h^{-1} for n = 0.83) were higher than those for **CuFe** (n = 0)

but lower than those for **CuFe-NH$_3$** (n = 1), suggesting that increasing the number of Fe^{II} ions with single open sites in the PBAs is important to achieve high catalytic activity (Figure 8).

CONCLUSION

CN-deficient Prussian blue analogues (PBAs), $[M^N(H_2O)_x]_y[Fe^{II}(CN)_5(NH_3)]$ (**MFe-NH$_3$**, M^N = Cu^{II}, Co^{II} or Ga^{III}), were synthesized to examine C-bound Fe^{II} ions with single open sites as

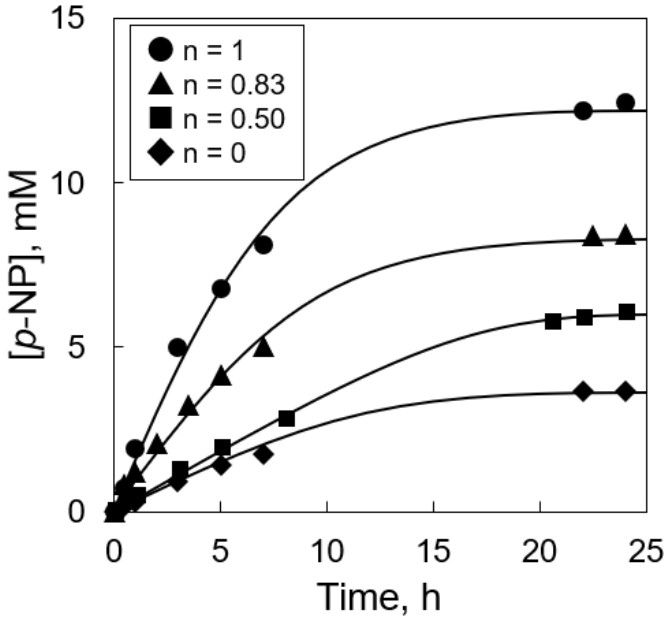

Figure 8. Time profiles of the *p*-nitrophenolate ion (*p*-NP) formation in a HEPES buffer solution (100 mM, 0.75 mL, pH 6.0, 50 °C) containing disodium *p*-nitrophenyl phosphate (*p*-NPP, 25 mM) in the presence of $[Cu^{II}(H_2O)_x]_y\{[Fe^{II}(CN)_5(NH_3)]_n[Fe^{II}(CN)_6]_{1-n}\}$ complexes (n = 0, 0.50, 0.83 or 1).

precisely controlled active species for hydrolysis of *p*-nitrophenyl phosphate. Liberation of NH_3 from the Fe^{II} ions during the catalytic reactions resulted in the formation of exactly single open site on each Fe^{II} ion, different from conventional PBAs. High catalytic activity of Fe^{II} ions with open sites coupled with catalytically inert Cu^{II} ions as the M^N ions clearly indicated the direct

involvement of the Fe^{II} ions as the active species in the catalytic hydrolysis. Then, heterogeneous catalysis of the CN-deficient PBAs employing Co^{II} and Ga^{III} ions, which are catalytically active species in conventional PBAs, instead of Cu^{II} ions was examined. However, no catalysis enhancement was observed for the CN-deficient PBAs containing Co^{II} and Ga^{III}, because Lewis acidity of the Fe^{II} ions enhanced by the M^{N} ions favors interaction with hydrogen phosphate and/or ammine ligand. These results suggest that heterogeneous catalysis of metal ions with precisely controlled open sites can be tuned by interaction between coupled metal ions in CN-deficient PBAs, leading to rational design of active sites for highly sophisticated heterogeneous catalysis.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website. Scanning electron microscope (SEM) images, X-ray fluorescence spectra, X-ray photoelectron spectra (XPS), nitrogen (N_2) adsorption-desorption isotherms, infrared (IR) spectra, ultraviolet-visible (UV-Vis) spectra, powder X-ray diffraction (PXRD) patterns, reaction profiles, elemental analyses data.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interests.

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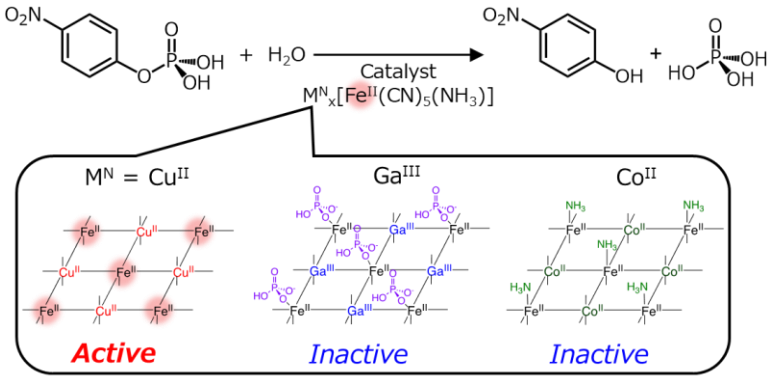
TOC graphic



Synopsis

Single open sites were created on Fe^{II} ions of CN-deficient Prussian blue analogues, ($[M^N(H_2O)_x]_y[Fe^{II}(CN)_5(NH_3)]$; M^N = Cu^{II}, Co^{II} or Ga^{III}) by liberation of NH_3 ligand. Lewis acidity of the Fe^{II} ions tuned by the M^N ions through metal-metal interaction affected interaction between the Fe^{II} ions and HPO_4^- or NH_3 ligands, resulting in enhancement of heterogeneous catalysis for hydrolysis of toxic organophosphates.