Study on a New Iron Phosphate Crystalline Phase

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An iron phosphate having a new crystalline phase was obtained by a partial reduction of iron(III) orthophosphate with a reducing agent, usually oxalic acid, in the presence of oxygen and a large amount of water vapor at a low temperature of 200 to 250 °C. XRD spectra of the new phase (designated as M-phase) are similar to those of clay minerals. The effects of reaction variables, such as reducing agent, reaction period, starting iron phosphate, temperature, and oxygen feed rate, on the formation of M-phase were studied. Some characterizations of this M-phase were also attempted.

Phosphates of vanadium and molybdenum, such as divanadium(IV) dioxide diphosphate [$(VO)_2P_2O_7$] and heteropoly compounds based on dodecamolybdophosphoric acid [$H_3PMo_{12}O_{40}$], which possess both eminent acidic and redox properties, are widely used as oxidation catalysts for production of acidic compounds; carboxylic acids and anhydrides. Indeed, a great number of studies concerning them have already been reported. On the other hand, iron phosphate was well known to be effective only for the oxidative dehydrogenation of isobutyric acid to methacrylic acid.[1] Recently it was found that iron phosphate will show a unique catalytic performance for oxidative dehydrogenation reactions such as formation of pyruvic acid from lactic acid[2,3] and that of glyoxylic acid from glycolic acid.[4,5] However, little is known about iron phosphate as an oxidation catalyst at present.

In the structure diagram of iron(III) orthophosphate [$FePO_4$], quartz-type $FePO_4$[6] which is a low quartz structure (trigonal) characterized with the XRD peaks at 2θ of 25.89° and 20.40°, and tridymite-type $FePO_4$[7] are known besides an amorphous phase. With a rise in the calcination temperature, the structure varies as follows: amorphous → tridymite → quartz.[8] It is also known[9,10] that iron(III) orthophosphate [$FePO_4$] is reduced to iron(II) diphosphate [$Fe_2P_2O_7$][11,12] via an intermediate of $Fe_3(P_2O_7)_2$.[13] Interestingly, the iron(II) diphosphate is not reoxidized to form $Fe_3(P_2O_7)_2$ nor $FePO_4$, but to another phase characterized with only one clear peak at 2θ of 29.5° in the XRD spectra, which was proposed by Millet et al.[14] as $Fe_3(P_2O_7)_2$. But we designated this compound as Y-phase,[9,10] because another compound had been assigned to be $Fe_3(P_2O_7)_2$.[13]

It was found more recently that a part of iron(III) orthophosphate catalyst is transformed into a new crystalline phase during the oxidative dehydrogenation of lactic acid and glycolic acid, and that the performances of catalyst were markedly enhanced by the structure change.[3] The new iron phosphate phase was designated as M-phase.[3] The XRD spectra are very similar to those of clay minerals such as kaolinite, halloysite, dickite, and nacrite, that is, they are characterized with a clear peak at a low 2θ region of about 12° in the XRD spectra.[3,15]

In this paper, we attempted to clarify the formation and the characteristic properties of M-phase.

Experimental

Iron(III) phosphates with a P/Fe atomic ratio of 1.00 and 1.15 were prepared according to the following procedures. Iron(III) nitrate [$Fe(NO_3)_3 \cdot 9H_2O$] (122 g, 0.30 mol) was dissolved in about 5 dm^3 of water, and a dilute ammonia solution was added to precipitate iron(III) hydroxide gel at a pH value of about 8. The precipitate was filtered and the obtained wet gel was mixed with either 34.6 g (0.30 mol) or 39.8 g (0.345 mol) of 85% orthophosphoric acid [H_3PO_4]. The mixture was then slowly boiled for 1 to 2 h, yielding a slightly brownish-white precipitate. Excess water was evaporated by means of a hot air current; the obtained paste-like compound was dried in an oven at 120 °C for 6 h. The resulting solid was broken up and sieved to a 7—10 mesh size. Finally, it was calcined in a stream of air at a desired temperature for 12 h.

Unless otherwise indicated, the studies were performed with the iron(III) phosphate sample with a P/Fe atomic ratio of 1.15 calcined at 400 °C which consisted of tridymite-type $FePO_4$ and had a specific surface area of 15 $m^2 g^{-1}$, because it generally showed better performances than the P/Fe = 1.00 sample as a catalyst for partial oxidation. The P/Fe = 1.00 was used only for studying the characters of the M phases, because it is more convenient for deciding the chemical composition.

The reactor was made of a stainless steel tube, 50 cm long and 1.8 cm inner diameter, mounted vertically and immersed in a lead bath. Near the bottom of the reactor, a 1 to 40 g portion of the iron phosphate sample was placed and porcelain cylinders, 3 mm long and 1.5 mm inner diameter/3.0 mm outer diameter, were packed above the iron(III) phosphate sample. A mixture of oxygen and nitrogen was fed in from the top of the reactor and an aqueous solution of an organic compound was introduced into the preheating section of

the reactor by a syringe pump. The feed rate of gaseous nitrogen was 200 ml min^{-1} (500 mmol h^{-1}) and that of the aqueous solution was about 35 ml h^{-1}.

The amounts of Fe^{2+} and Fe^{3+} ions in the bulk were determined by the redox titration method.[16] The detailed procedures were described in the previous paper.[9]

X-Ray powder diffraction (XRD) patterns were studied using a Shimadzu 6000 diffractometer with Cu K_α radiation. Fourier-transform infrared (FT-IR) spectra were recorded from 4000 to 400 cm^{-1} with a Perkin–Elmer 1700, using the KBr disk technique. Elementary analyses were performed with a Yanagimoto CHN corder MT-5. Surface areas were measured by the BET method using nitrogen as adsorbate at −196°C.

Results and Discussion

1. Effects of Organic Compound on the Formation of M-Phase. The effects of the organic compound on the formation of M-phase was studied by changing the kinds of organic compound fed in. Over a 5 g portion of the iron-(III) phosphate sample, a reaction gas-mixture was passed at a temperature of 210 to 240 °C for 24 to 48 h. The feed rates of organic compound, oxygen, water, and nitrogen were 10—20, 10—20, 1880, and 500 mmol h^{-1}, respectively. The results are summarized in Table 1.

The amounts of products were estimated from the visual inspection of the XRD peak intensities. The best results for the formation of M-phase were obtained when oxalic acid was used as the organic compound. Figure 1 shows the XRD spectra obtained from a treatment performed under the following conditions: amount of sample used = 5 g, feed rates (mmol h^{-1}) of oxalic acid/oxygen/water/nitrogen = 14.0/12.5/1880/500, temperature = 220 °C, and reaction period = 24 h. M-phase is characterized with three clear peaks at 2θ of 12.2°, 24.5°, and 32.4° (the relative intensities were 60, 100, and 65, respectively) in the XRD spectra, as has been reported in the previous papers.[15] No peaks assigned to any known iron phosphate crystalline phases were detected in the spectra. Almost the same XRD spectra were obtained from the iron(III) phosphate sample with a P/Fe atomic ratio

Table 1. Effects of Organic Compounds on the Formation of M-Phase

Reactant	Phase observed in XRD	$Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio
n-Propanol	Quartz+M (vs)	0.00
Propylene glycol	Quartz+M (vs)	0.01
Formic acid	Quartz+M (vs)	0.00
Isobutyric acid	Quartz+M (s)	0.01
Pyruvic acid	Tridymite+M (s)	0.10
Oxalic acid	M	0.28
Lactic acid	M+$Fe_2P_2O_7$ (s)	0.27
Glycolic acid	M+$Fe_2P_2O_7$	0.28
Acetole	$Fe_2P_2O_7$	0.82

Quartz = quartz-type $FePO_4$; Trdymite = tridymite-type $FePO_4$; M = M − phase; (vs) = very small amount; (s) = small amount. Reaction conditions: sample = 5 g [P/Fe = 1.15]; feed rates (mmol h^{-1}), organic compound/oxygen/water/nitrogen = 10—20/10—20/1880/500; temperature = 210—240 °C; reaction period = 24—48 h.

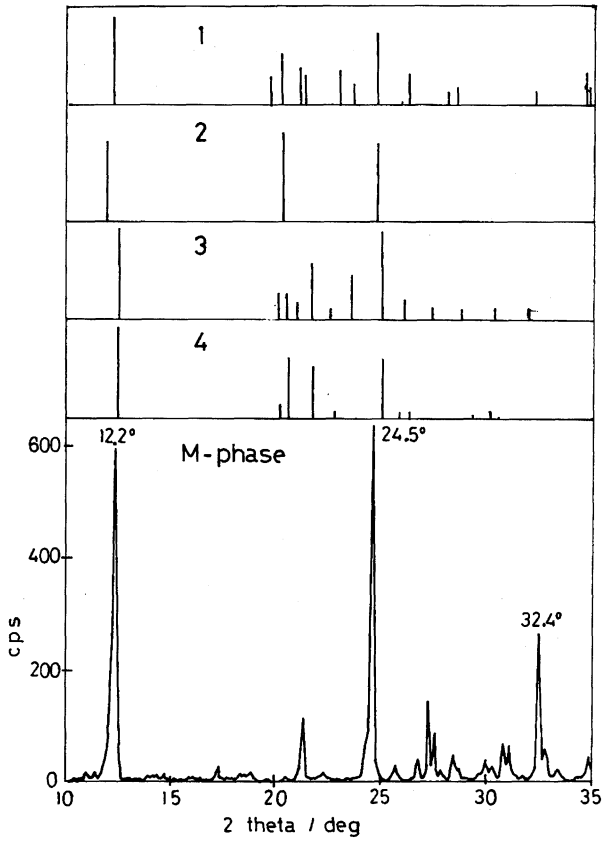

Fig. 1. XRD patterns of M-phase. (1) Kaolinaite, (2) Halloysite, (3) Dickite, and (4) Nacrite.

of 1.00, too. The next best results were obtained with lactic acid, though the formation of a small amount of $Fe_2P_2O_7$ was observed in the XRD spectra. In the case of glycolic acid, iron orthophosphate was transformed into a mixture of M-phase and $Fe_2P_2O_7$. In the case of acetol (hydroxy acetone), the tridymite-type $FePO_4$ is totally reduced to form $Fe_2P_2O_7$. On the other hand, almost no M-phase is formed with *n*-propanol, propylene glycol, formic acid, isobutyric acid, and pyruvic acid. It should be noted that in the last cases the tridymite-type $FePO_4$ was totally transformed into quartz-type $FePO_4$. This low temperature transformation into quartz-type $FePO_4$ was found to be ascribable to the action of water vapor, but not to the action of the reducing agent.[17]

As may be seen in Table 1, when the $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio is low, M-phase is not formed. But when the ratio is high (this is the case of acetol), only $Fe_2P_2O_7$ is formed. It is interesting that the $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratios of the samples consisting mainly of M-phase are about 0.28.

2. Effects of Reaction Period on the Formation of M-Phase. The effects of reaction period on the formation of M-phase were studied using oxalic acid as the organic compound. Over a 3 g portion of the iron phosphate sample, a gas mixture of oxalic acid, oxygen, water vapor, and nitrogen was passed at 210 °C with the feed rates of 14, 12.5, 1880, and 500 mmol h^{-1}, respectively. The variations in both the structure and the extent of reduction, that is, $Fe^{2+}/(Fe^{2+}+$

Fe^{3+}) ratio, are shown as a function of the time on stream in Table 2.

When the amount of sample used was 3 g, the whole sample was transformed into M-phase within 5 h on stream. With further time on stream, no changes in either the structure or the $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio were observed. This means that the produced M-phase is stable enough under the reaction conditions used.

It should also be noted that when the amount of sample used is larger, a longer reaction period is required to convert completely the whole of sample into M-phase. For example, when the amount of sample used was 40 g, a reaction period of more than 24 h was required to convert the sample totally to M-phase.

3. Effects of Starting Iron Phosphate on the Formation of M-Phase. The effects of structure and oxidation state of the starting iron phosphate sample on the formation of M-phase were studied using oxalic acid as the organic compound. The samples of amorphous $FePO_4$, tridymite-type $FePO_4$, and quartz-type $FePO_4$ were prepared by calcining the freshly prepared samples at 350, 450, and 550 °C, respectively. The $Fe_3(P_2O_7)_2$ sample was prepared by reducing the tridymite-type $FePO_4$ with hydrogen at 400 °C for 4 h. The $Fe_2P_2O_7$ sample was prepared by reducing the tridymite-type $FePO_4$ with hydrogen at 550 °C for 12 h. The Y-phase sample was prepared by reoxidizing the $Fe_2P_2O_7$ sample with air at 500 °C for 6 h.

Over a 3 g portion of each sample, a gas mixture of oxalic acid, oxygen, water vapor, and nitrogen was passed at 240 °C for 24 h. The feed rates are 14.0, 12.5, 1880, and 500 mmol h^{-1}, respectively. The results are summarized in Table 3.

Independent of the change in the structure, all of the iron orthophosphate samples can be transformed into M-phase. But when the starting samples are not iron orthophosphate: for example, $Fe_3(P_2O_7)_2$, Y-phase, and $Fe_2P_2O_7$, M-phase cannot be obtained.

4. Effects of Reaction Temperature on the Formation of M-Phase. The effects of reaction temperature on the formation of M-phase were studied. The temperature was changed from 180 to 300 °C, while the the other reaction conditions were fixed as follows: amount of sample used, 3 g; reaction period of 24 h; feed rates of oxalic acid, oxygen, water vapor, and nitrogen of 14.0, 12.5, 1880, and 500 mmol h^{-1}, respectively. As an index of the amount of produced M-phase, the heights of two peaks at 2θ of 12.2° and 24.5° in the XRD spectra are shown in Table 4.

Table 3. Effects of Starting Iron Phosphate on the Formation of M-Phase

Phase observed in XRD	
Starting iron phosphate	After the reaction
Amorphous $FePO_4$	M-phase
Tridymite-type $FePO_4$	M-phase
Quartz-type $FePO_4$	M-phase
$Fe_3(P_2O_7)_2$	$Fe_3(P_2O_7)_2$
Y-phase	Y-phase
$Fe_2P_2O_7$	$Fe_2P_2O_7$

Reaction conditions: sample = 3 g [P/Fe = 1.15]; feed rates (mmol h^{-1}), oxalic acid/oxygen/water/nitrogen = 14.0/12.5/1880/500; temperature = 240 °C; reaction period = 24 h.

It was found that the optimum temperature is in the range of 210 to 240 °C. It was difficult to vaporize satisfactory the oxalic acid under the conditions used at a temperature below 200 °C. It is interesting that the iron(III) phosphate sample was not reduced and did not transform into M-phase at a temperature above 300 °C.

5. Effects of Oxygen Feed Rate on the Formation of M-Phase. The effects of oxygen on the formation of M-phase were studied. The feed rate of oxygen was changed from zero to 100 mmol h^{-1}, while the other conditions were fixed as follows: amount of sample used, 3 g; reaction temperature of 220 °C; reaction period of 24 h; feed rates of oxalic acid, water vapor, and nitrogen of 14, 1880, and 500 mmol h^{-1}, respectively.

The results are shown in Table 5. M-Phase is obtained in a wide range of oxygen feed rate, though about a half of the tridymite-type $FePO_4$ sample is transformed into $Fe_2P_2O_7$ by reduction in the absence of oxygen.

6. Stability of M-Phase. The stability of M-phase was studied by heating the sample consisting of M-phase in an atmosphere of either air or nitrogen. As an index of the amount of M-phase, the heights of the peak at 2θ of 24.5° in the XRD spectra are shown together with the $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratios in Table 6.

It is clear that M-phase is stable enough up to 300 °C in both air and nitrogen, and that the sample is reoxidized, that is, the $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio is decreased to near zero, by

Table 2. Effects of Reaction Period on the Formation of M-Phase

Reaction period (h)	Phase observed in XRD	$Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio
0	Tridymite-type $FePO_4$	0.00
2	Low crystallinity	0.29
5	M-phase	0.36
9	M-phase	0.27
18	M-phase	0.26
21	M-phase	0.27
48	M-phase	0.24

Reaction conditions: sample = 3 g [P/Fe = 1.15]; feed rates (mmol h^{-1}), oxalic acid/oxygen/water/nitrogen = 14.0/12.5/1880/500; temperature = 210 °C.

Table 4. Effects of Reaction Temperature on the Formation of M-Phase

Temp	Peak hights in XRD spectra (arbitary unit)		$Fe^{2+}/(Fe^{2+}+Fe^{3+})$
°C	$2\theta = 12.2°$	$2\theta = 24.5°$	ratio
300	0	10	0.002
280	80	110	0.09
260	100	150	0.30
250	350	480	0.28
240	560	860	0.29
230	520	830	0.29
220	640	1050	0.28
210	520	910	0.27
200	380	580	0.30
180	0	0	0.27

Reaction conditions: sample = 3 g [P/Fe = 1.15]; feed rates (mmol h^{-1}), oxalic acid/oxygen/water/nitrogen = 14.0/12.5/1880/500; reaction period = 24 h.

Table 5. Effects of Oxygen on the Formation of M-Phase

O_2 feed rate (mmol h^{-1})	Phase observed in XRD	$Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio
0	M-phase + $Fe_2P_2O_7$	0.52
7.5	M-phase	0.30
12.5	M-phase	0.26
25.0	M-phase	0.25
50.	M-phase	0.27
100.	M-phase	0.25

Reaction conditions: sample = 3 g [P/Fe = 1.15]; feed rates (mmol h^{-1}), oxalic acid/water/nitrogen = 14.0/1880/500; temperature = 220 °C; reaction period = 24 h.

Table 6. Stability of M-Phase

Heat-treatment			Peak height[a]	$Fe^{2+}/(Fe^{2+}+Fe^{3+})$
Temp (°C)	Period (h)	Medium	at $2\theta = 24.5°$	ratio
Original (without treatment)			780	0.30
300	10	Nitrogen	710	0.30
300	18	Air	720	0.01
400	8	Nitrogen	30	0.29
400	8	Air	50	0.02

a) Arbitrary unit.

air during the heat-treatment at 300 °C. It is interesting that despite a large change in the oxidation states of iron ions, the XRD structure was kept unchanged after the heat-treatment at 300 °C in air. This led us to conclude that M-phase consists of only Fe^{3+} ions, though the presence of a certain amount of Fe^{2+} ions may be required for the formation of M-phase.

It is also clear that M-phase is decomposed gradually at 400 °C both in air and in nitrogen.

7. Decomposition of M-Phase. The decomposition of M-phase was studied at 400 °C in a nitrogen atmosphere by changing the period of heat-treatment. The sample consisting of M-phase was heated in advance at 300 °C for 8 h in nitrogen in order to remove the oxalic acid adsorbed on the sample. Then, the sample was heated at 400 °C. As an index of the amount of M-phase, the heights of two peaks at 2θ of 12.2° and 24.5° in the XRD spectra are shown in Table 7.

It is clear that the majority of M-phase is decomposed to form amorphous phase within 4 h. It is interesting that the oxidation states of iron ions are kept unchanged regardless of the decomposition of M-phase. This also suggests that M-phase is not ascribable to Fe^{2+} ions.

Table 7. Decomposition of M-phase

Treatment	Peak heights in XRD spectra[a]		$Fe^{2+}/(Fe^{2+}+Fe^{3+})$
time (h)	at $2\theta = 12.2°$	at $2\theta = 24.5°$	ratio
0	460	720	0.26
1	180	0	0.35
2	100	1	0.35
4	25	55	0.34
8	0	26	0.29
14	0	0	0.22

a) Arbitrary unit.

8. Regeneration of M-Phase. The regeneration of M-phase was tested according to the following procedures. The sample consisting of M-phase was calcined in nitrogen at 440 °C for 46 h. After the pretreatment, the peaks assigned to M-phase in the XRD spectra were completely disappeared.

Then a gas mixture of nitrogen and water vapor was passed over the iron phosphate sample at 250 °C with the feed rates of 1950 and 500 mmol h^{-1}, respectively.

The XRD spectra of the obtained sample are shown in Fig. 2. It is clear that M-phase is regenerated in part and another unknown phase is formed by the steam-treatment. The unknown phase was characterized with two clear peaks at 2θ of 16.3° and 23.4° in the XRD spectra. As indexes of amounts of M-phase and the unknown phase, the heights of peaks in XRD spectra at 2θ of 12.2°, 24.5°, 16.3°, and 23.4° are shown in Table 8.

9. Characterizations of M-Phase. For convenience of determination of the chemical composition, the M-phase samples used were prepared from iron(III) phosphate with a P/Fe atomic ratio of 1.00 calcined at 400 °C, which consisted of tridymite-type $FePO_4$ and had a specific surface area of 9.0 $m^2 g^{-1}$. A gas mixture of oxalic acid, oxygen, water vapor, and nitrogen was passed over a 20 g portion of the iron phosphate sample at 220 °C for 48 h. The obtained compound was designated as fresh M-phase sample. The $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio was 0.27. A half of the fresh M-phase sample was further calcined in air at 300 °C for 5 h. The resulting compound was designated as heat-treated M-phase sample. The $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio was near zero.

The XRD spectra of the two samples were essentially identical and they were the same as those obtained from the M-phase sample with a P/Fe atomic ratio of 1.15, which is shown in Fig. 1.

Figure 3 shows the results of DTA/TG analyses for both samples. The fresh M-phase sample shows a clear exothermic peak and a weight decrease around 280 °C and another small weight decrease around 480 °C. In the case of the heat-treated M-phase sample, only the second weight decrease around 480 °C was observed. The weight decrease up to 300 °C was 17%, and the weight decrease from 400 to 600 °C was 4.0%.

The results obtained from elementary analyses are listed in Table 9. From the calculation based on the results of elementary analysis, DTA/TG analyses, and analysis of oxidation states of iron ions, the possible chemical compositions for each sample are estimated as follows:

Heat-treated M-phase sample $FePO_4 \cdot 0.5H_2O$ or $Fe_2P_2O_7(OH)_2$
Fresh M-phase sample $FePO_4 \cdot 0.5H_2O \cdot 0.25(COOH)_2$ or $Fe_2P_2O_7(OH)_2 \cdot 0.5(COOH)_2$

The FT-IR spectra of the fresh and heat-treated M-phase samples and another sample prepared by calcining again the heat-treated M-phase sample in air at 600 °C for 5 h are compared in Fig. 4. The spectra of the fresh M-phase sample have absorption peaks at 3300—3500 cm^{-1} (assigned to OH group) and 1700 cm^{-1} (assigned to C=O group), while the spectra of the heat-treated M-phase sample have no absorption peak at 1700 cm^{-1}. The spectra of the sample calcined at 600 °C has no absorption peaks at either 3300—3500 cm^{-1} or 1700

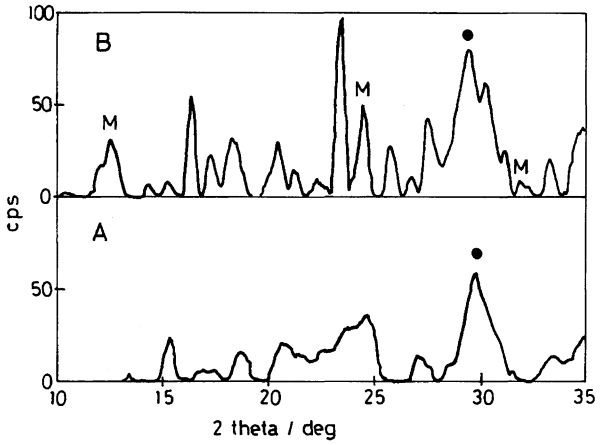

Fig. 2. Effect of the steam-treatment on the XRD patterns. A: before steam-treatment, (B): after steam-treatment. (M): M-phase, (●) $Fe_2P_2O_7$ or Y-phase.

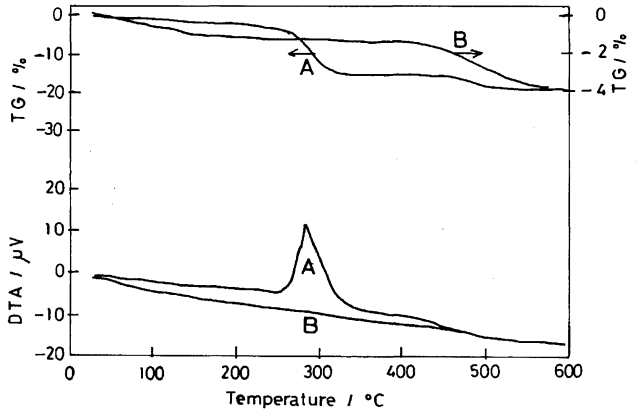

Fig. 3. DTA and TG spectra of M-phase. A: fresh sample, B: heat-treated sample.

Table 8. Regeneration of M-Phase

Treatment time (h)	Peak heights in XRD spectra (arbitrary unit)			
	M-phase		Unknown phase	
	at $2\theta = 12.2°$	at $2\theta = 24.5°$	at $2\theta = 16.3°$	at $2\theta = 23.4°$
0	0	0	0	0
2	10	35	5	10
5	10	45	35	48
23	20	60	45	85
Original[a)]	490	780	0	0

a) Sample consisting of M-phase (sample before the calcination at 440 °C).

Table 9. Results of Elementary Analysis for M-Phase

Sample	Hydrogen (wt%)	Carbon (wt%)	Ash (wt%)
Fresh M-phase sample	0.60	4.34	83
Heat-treated M-phase sample	0.43	0.00	96

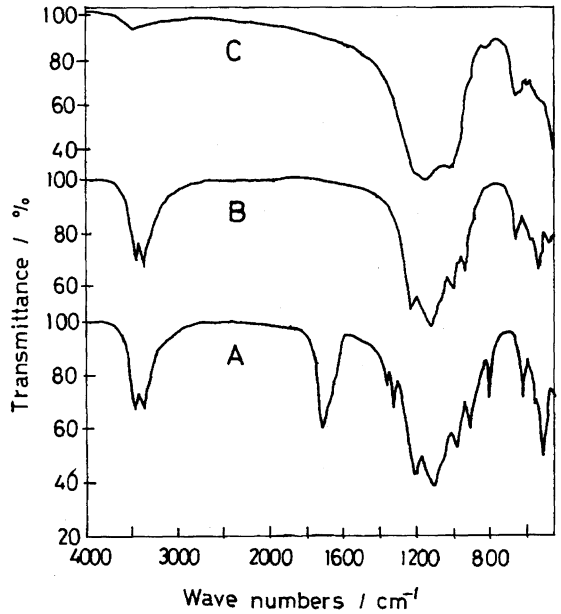

Fig. 4. FT-IR patterns of M-phase. A: fresh sample, B: heat-treated sample, C: fresh sample calcined at 600 °C.

cm^{-1}.

In the light of the results obtained from XRD, elementary analysis, DTA/TG analysis, and FT-IR studies, one may consider that the fresh M-phase sample contains both crystalline water and coordinated oxalic acid. By the heat-treatment at 300 °C, only the coordinated oxalic acid is removed, but the crystalline structure is preserved. However, by the heat-treatment above 400 °C, the crystalline water is removed and the crystalline structure of M-phase is destroyed.

It was found that the presence of water vapor was indispensable for the formation of M-phase in the cases where lactic acid or glycolic acid was used, though the effects of water cannot be checked in the case of oxalic acid, because oxalic acid is solid. It was also found that iron(III) orthophosphate is insoluble in water, but the solubility increases as increasing the concentration of oxalic acid in the water. At present we would like to consider that organic acids play a role in producing Fe^{2+} ions which may take part in the formation of M-phase and also in inserting water molecules into iron phosphate crystalline phase. However, it is still difficult to understand the action of Fe^{2+} ions in the structure and formation of M-phase. Further approaches from different viewpoints are necessary to get more insight into M-phase.

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