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Effects of the method of preparing iron orthophosphate catalyst on the structure and the catalytic activity

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Abstract

Catalytic activity of iron orthophosphate [$FePO_4$] was studied using oxidative dehydrogenation of lactic acid to pyruvic acid as a reaction probe. The structure and surface area are different depending on the differences in the source of starting materials as well as in the preparing methods. However, the specific activity, activity per unit surface area, is little affected with the variation in the structure. By the reduction and reoxidation, the catalytic activity clearly increases. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

It has been shown in previous studies [1–4] that iron phosphate with a P/Fe atomic ratio of 1.15–1.2 shows a unique catalytic performance for oxidative dehydrogenation reactions such as formation of pyruvic acid from lactic acid and formation of glyoxylic acid from glycolic acid:

$$CH_3-CH(OH)-COOH + 0.5O_2 \rightarrow CH_3-CO-COOH + H_2O$$

$$HOCH_2-COOH + 0.5O_2 \rightarrow OHC-COOH + H_2O.$$

However, little is known about iron phosphate as an oxidation catalyst at present. In order to get fundamental information about it, we focused our attention on iron phosphate with a P/Fe atomic ratio of unity, notably iron orthophosphate, $FePO_4$, which is one of the most basic phosphates of iron. In this paper, the effect of the preparing methods, temperature of calcination, and treatments of water-vapor, reduction, and reoxidation on the catalytic functions were studied using the oxidative dehydrogenation of lactic acid to form pyruvic acid as a reaction probe.

2. Experimental

2.1. Catalysts

Three kinds of iron(III) phosphate catalysts were prepared according to the following procedures:

- *Method A*. Powder of iron(III) phosphate [$FePO_4 \cdot nH_2O$] purchased from Wako Pure Che-

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mical Industries, Osaka, was kneaded with a small amount of water, yielding a paste-like compound.

- *Method B*. Powder of iron(III) phosphate [$FePO_4 \cdot 4H_2O$] purchased from Nacalai Tesque, Kyoto, was used as the starting material; the other procedures were the same as those for Method A.
- *Method C*. $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in water and dilute NH_3 solution was added to precipitate iron hydroxide gel. The obtained precipitate was filtered and the resulting cake was mixed with 85% orthophosphoric acid [H_3PO_4]; the amount of orthophosphoric acid was adjusted to a P/Fe atomic ratio of unity. The mixture was boiled slowly for 1–2 h and then the excess water was evaporated to yield a paste.

The obtained paste-like compounds were dried at 120°C for 6 h in a oven, and then the resulting solids were broken up and sieved to a 7–20 mesh size. Finally, they were calcined in flowing air at a fixed temperature (at 400°C unless otherwise indicated) for 8 h. For convenience, the catalysts were represented by a letter designating the preparation method.

The X-ray powder diffraction (XRD) patterns were studied using a Shimadzu 6000 diffractometer with CuK_α radiation.

The amounts of Fe^{2+} and Fe^{3+} ions in the bulk of iron phosphates were determined by the redox titration method [5,6].

The surface areas of the catalyst samples were measured by the BET method using nitrogen as adsorbate at −196°C.

The oxidative dehydrogenation of lactic acid was conducted with a continuous-flow system, as described in the previous studies [1,2]. The reactor was made of a stainless steel tube, 50 cm long and 1.8 cm i.d., mounted vertically and immersed in a lead bath. Air was fed in from the top of the reactor with a fixed rate of 200 ml/min, and an aqueous solution of lactic acid was introduced into the preheating section of the reactor by a syringe pump. The feed rates of lactic acid, air, and water were 20, 500, and 950 mmol/h, respectively. The reaction temperature was in the range of 200–240°C. The conversion of lactic acid was defined as: 100·[1−(moles of unreacted lactic acid)/(moles of lactic acid fed)]. The yields and selectivities were defined as: yields of pyruvic acid, acetic acid, and propionic acid=100·(moles of pyruvic acid, acetic acid, or propionic acid)/(moles of lactic acid fed); yield of citracinic acid=200·(moles of citraconic anhydride)/(moles of lactic acid fed); yield of CO_x=33.3·(moles of CO_x)/(moles of lactic acid fed); selectivity=100·(yield)/(conversion).

3. Results and discussion

3.1. Effects of preparation methods

XRD patterns were studied for the three iron phosphate samples prepared by different methods, while calcined at a fixed temperature of 400°C. The sample prepared from Method A (Sample A) was completely amorphous, though it had a large surface area of 54 m^2/g. The sample prepared from Method B (Sample B) was found to consist of tridymite-type iron orthophosphate [$FePO_4$(T)] [7] with a relatively high crystallinity; the XRD patterns are shown in Fig. 1. The surface area was 7.7 m^2/g. The sample prepared from Method C (Sample C) also consisted of tridymite-type iron orthophosphate [$FePO_4$ (T)], though the crystallinity was lower than that of Sample B. The surface area was 7.0 m^2/g.

The oxidation of lactic acid was performed using the three iron phosphate samples. The main reaction products were pyruvic acid, citraconic anhydride, acetic acid, propionic acid, and CO_x. The product distributions obtained with the Sample A catalyst are shown in Fig. 2.

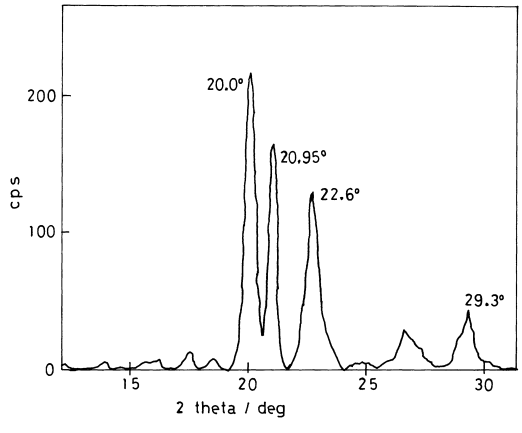

Fig. 1. XRD patterns of sample B calcined at 400°C (tridymite type $FePO_4$).

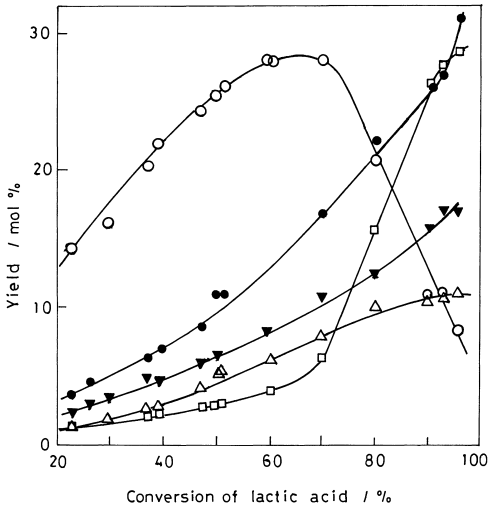

Fig. 2. Product distributions obtained from the reaction over sample A catalyst: (○) pyruvic acid; (△) citraconic anhydride; (▼) propionic acid; (□) acetic acid; (●) CO_x.

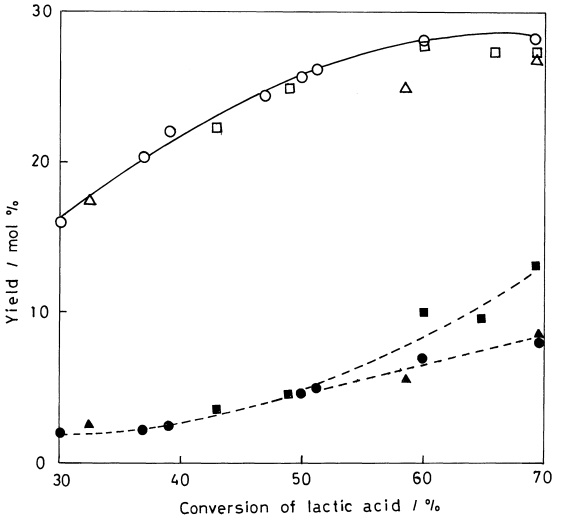

Fig. 3. Effects of the preparing methods on the selectivity: (○, △, □) pyruvic acid; (●, ■, ▲) citraconic anhydride; (○, ●) Sample A; (△, ▲) Sample B; (□, ■) Sample C.

To compare the catalytic activities of the three iron phosphate samples, the reaction was performed at a fixed temperature of 220°C over a 1 or 5 g portion of the catalyst and the yields of pyruvic acid obtained at low conversion levels were measured. The results are summarized in Table 1.

Sample A showed a very high activity and further a high specific activity (yield/surface area). Sample B was low in both activity and specific activity. Sample C showed a little higher specific activity than that of the sample A, though the activity per unit mass was lower due to the lower surface area.

Then the selectivities to pyruvic acid and citraconic anhydride were compared for the three iron phosphates. Since the selectivity varies depending on the variation in the extent of reaction, the yields of both pyruvic acid and citraconic anhydride obtained from the three iron phosphate samples were plotted as a function of the conversion of lactic acid. The results are shown in Fig. 3.

It is concluded from the results that the effects of the method of preparing iron phosphate catalyst on the selectivity of pyruvic acid are small, though a higher selectivity to citraconic anhydride is obtained with Sample C.

Table 1
Catalytic activity of iron phosphate catalysts prepared by different methods

Preparation method	Surface area (m^2/g)	Catalyst used (g)	Yield[a] (mol%)	Yield[a]/area (mol%/m^2)
A	54.0	5	27.0	
		1	11.3	0.21
B	7.7	5	4.2	0.11
C	7.2	5	8.8	0.25

[a]Yield of pyruvic acid obtained at 220°C.

3.2. Effects of the temperature of calcination

Effects of the temperature of calcination on the structure and the catalytic activity are studied. The results were summarized in Table 2. On raising the temperature of calcination, the surface area of the Sample A decreases markedly, while the areas of Sample B and Sample C, which are relatively low, remain unchanged. As for the structures, the variations are different depending on the variation in the method of preparation. In the case of Sample A, it remains amorphous up to 460°C, but at a temperature above 480°C it is transformed into quartz phase without the formation of an intermediate such as tridymite phase. In the cases of Sample B and Sample C, they remain in tridymite phase up to 480°C, but they are transformed into quartz phase at a temperature above 500°C. The

Table 2
Effects of the temperature of calcination

Catalyst preparation method	Calcination temperature (°C)	Structure measured by XRD	Surface area (m^2/g)	Catalyst used (g)	Yield of Pyrvic acid (mol%)	Yield/area (mol%/m^2)
A	400	Amorphous	53.0	1	11.3	0.21
	460	Amorphous	42.0			
	480	Quartz	25.2			
	500	Quartz	21.4	1	4.8	0.26
B	400	Tridymite	7.7	5	4.2	0.11
	450	Tridymite	7.2			
	480	Tridymite	7.5			
	500	Quartz	7.3	5	4.2	0.12
C	400	Tridymite	7.2	5	8.8	0.25
	450	Tridymite	7.3	5	8.6	0.24
	480	Tridymite	7.6			
	500	Quartz	7.2	5	8.8	0.25

XRD patterns of the quartz phase $FePO_4$ are shown in Fig. 4.

The manners of transformation of Sample B and Sample C are consistent with that obtained in the case of iron phosphate with a P/Fe atomic ratio of 1.2 prepared by Method C [8,9], while that of Sample A is different. However, it is evident that either amorphous phase or tridymite phase is transformed into quartz phase at a temperature above 500°C.

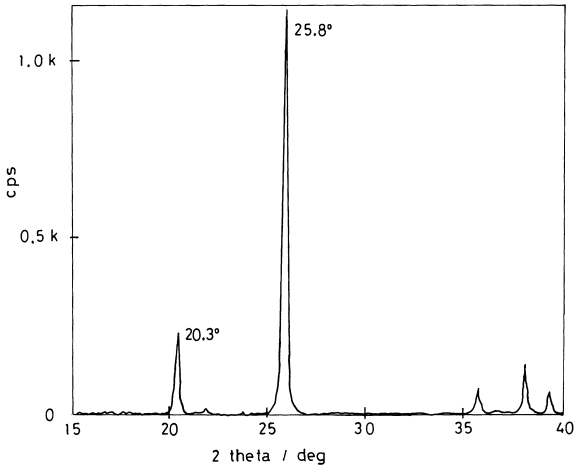

Fig. 4. XRD patterns of the iron phosphate (Sample C) calcined at 500°C (quartz type $FePO_4$).

It should also be noted that both the surface areas and catalytic activities of Sample B and Sample C are not affected by a rise in the calcination temperature. But in the case of Sample A, both the surface area and activity fall with a rise in the temperature, though the specific activity does not change. It is at least evident for each case that the specific activity is independent of the variation in the structure.

3.3. Effects of the water-treatment

A mixture of air and water-vapor was passed over the iron phosphate samples with the rates of 500 and 1000 mmol/h, respectively, at a low temperature 200°C for 6 h. The variations in both structure and surface area due to the water-treatment are shown in Table 3.

Table 3
Effects of the water-vapor treatment on the structure and surface area

Preparation method	Before treatment		After treatment	
	XRD structure	Surface area (m^2/g)	XRD structure	Surface area (m^2/g)
A	Amorphous	53.9	Amorphous	51.5
B	Tridymite	7.7	Quartz	9.1
C	Amorphous	7.2	Quartz	6.8

Table 4
Effects of the water-vapor treatment on the catalytic activity

Preparation method	Treatment	Catalyst used (g)	Yield[a] (mol%)	Yield[a]/area (mol%/m^2)
B	Before treatment	5	4.2	0.11
B	After treatment	5	5.3	0.12
C	Before treatment	5	8.8	0.25
C	After treatment	5	7.6	0.22

[a] Yield of pyruvic acid obtained at 220°C.

Interestingly, after the water-treatment, both Sample B and Sample C consisting of tridymite-type $FePO_4$ are transformed into quartz-type $FePO_4$ even at 200°C, while Sample A consisting of amorphous $FePO_4$ remains unchanged.

The effects of water-treatment on the catalytic activity were studied for Sample B and Sample C catalysts. The results are summarized in Table 4. The catalytic activity is not affected with the variation in the structure due to the water-treatment.

3.4. Effects of reduction and reoxidation of iron phosphate

Hydrogen was passed over each iron phosphate sample at a temperature of 400°C for 6 h. After that, reduced samples were reoxidized by passing a stream of air at a temperature of 400°C for 6 h. The variations in the structure, oxidation states of iron ions, and surface area are compared in Table 5.

All of the three iron orthophosphate samples were transformed into iron pyrophosphate [$Fe_2P_2O_7$] consisting of Fe^{2+} ions by the reduction under the conditions used. The surface area increased a little in the cases of Sample B and Sample C, while it decreased in the case of Sample A.

On the other hand, by the reoxidation performed under the conditions used, all of the reduced samples were transformed into a new phase, which was designated by us as Y-phase [9], while Millet et al. [10] called it α-$Fe_3(P_2O_7)_2$. The XRD patterns of this new phase are shown together with those of $Fe_2P_2O_7$ in Fig. 5.

The variations in structure by the reduction and reoxidation are expressed schematically as follows:

$$FePO_4 \ -(\text{reduction}) \rightarrow Fe_2P_2O_7 \ -(\text{reoxidation}) \rightarrow \text{Y-phase}.$$

The effects of reduction and reoxidation on the catalytic activities were studied for each iron phosphate sample. The results are summarized in Table 6.

It is evident that the catalytic activity is markedly enhanced by the reduction and reoxidation treatments.

Table 5
Effects of the reduction and reoxidation on the structure and surface area

Prepation method	Treatment of catalyst	XRD structure	Ratio of $Fe^{2+}/(Fe^{2+}+Fe^{3+})$	Surface area (m^2/g)
A	Fresh	Amorphous	0.00	53.9
	Reduction	$Fe_2P_2O_7$	0.95	33.4
	Reoxidation	Y-phase	0.16	23.2
B	Fresh	Tridymite	0.00	7.7
	Reduction	$Fe_2P_2O_7$	0.81	12.0
	Reoxidation	Y-phase	0.28	12.8
C	Fresh	Tridymite	0.00	7.2
	Reduction	$Fe_2P_2O_7$	0.68	10.7
	Reoxidation	Y-phase	0.36	9.3

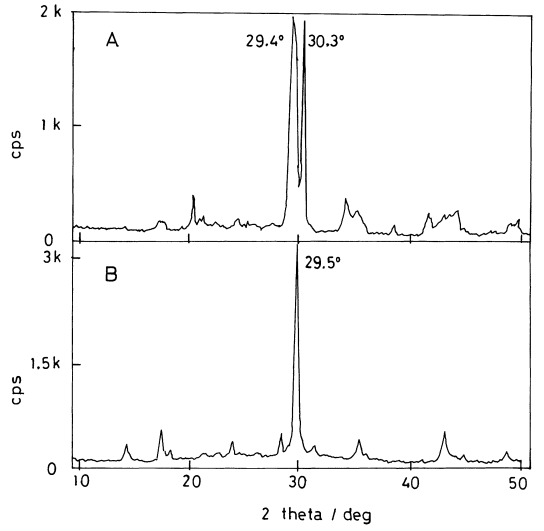

Fig. 5. XRD patterns of $Fe_2P_2O_7$ phase (A) and Y-phase (B).

Table 6
Effects of the reduction and reoxidation on the catalytic activity

Preparation method	Catalyst treatment	Catalyst used (g)	Yield[a] (mol%)	Yield[a]/area (mol%/m^2)
A	Fresh	1	11.3	0.21
	Reduction	1	12.0	0.36
	Reoxidation	1	7.8	0.34
B	Fresh	5	4.2	0.11
	Reduction	5	5.9	0.10
	Reoxidation	5	20.6	0.32
C	Fresh	5	8.8	0.25
	Reduction	5	18.0	0.36
	Reoxidation	5	18.2	0.39

[a]Yield of pyruvic acid obtained at 220°C.

4. Conclusions

The findings obtained in this study are summarized as follows:

1. The structure and surface area of iron phosphate catalysts are different depending on the differences in the sources of starting iron(III) phosphates as well as in the preparing methods.
2. On raising the temperature of calcination up to about 400°C, one obtains tridymite phase in certain cases as an intermediate between amorphous phase and quartz phase.
3. Either amorphous phase or tridymite phase is transformed into quartz phase at a temperature above 500°C.
4. In the presence of water-vapor, the transformation of tridymite phase into quartz phase takes place even at a low temperature of 200°C.
5. The surface area is little affected by the variation in the structure due to the temperature of calcination and the treatment of water-vapor, when it was lower than 8 m^2/g.
6. The specific activity (activity per unit surface area) is not much affected by the variations in the structure.
7. The effect of the difference in the preparing method on the selectivity is small.
8. The catalyst prepared from Method C seems to be best in view of stability of activity and specific activity, though the surface area is not high.
9. The catalyst prepared from Method B is low in both surface area and specific activity, though it shows a higher crystallinity.
10. The catalyst prepared from Method A shows a higher surface area, but it is not stable.
11. By the treatment with reduction and reoxidation, the catalyst prepared from Method A is reduced and reoxidized more easily than those prepared from Method B and Method C.
12. By the treatments of reduction and reoxidation, a clear increase in the activity was observed in the cases of the catalysts prepared from Method B and Method C.

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