

Oxidation by iron phosphate catalyst

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Abstract

Iron phosphates are effective as catalysts for oxidative dehydrogenation of lactic acid to pyruvic acid and that of glycolic acid to glyoxylic acid unlike phosphates of vanadium and molybdenum. The structure of iron(III) orthophosphate is transformed into a new phase having crystalline water during the use in these reactions. This induces a marked increase in the catalytic performances. The formation, characteristics, and catalytic properties of the new crystalline phase were studied. © 2000 Elsevier Science B.V. All rights reserved.

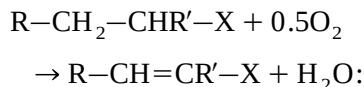
Keywords: Iron phosphate; Oxidative dehydrogenation; Lactic acid; Pyruvic acid; Glycolic acid; Glyoxylic acid

1. Introduction

As catalysts for partial oxidation reactions for producing acidic compounds such as carboxylic acids and anhydrides, possession of a strong acid function is required as well as the redox function [1,2]. Oxides of vanadium and molybdenum possess both acid–base and redox functions. Acidic properties of these oxides can be improved further by an incorporation of phosphorus. Indeed, phosphates of vanadium and molybdenum, such as $(\text{VO})_2\text{P}_2\text{O}_7$ and $\text{H}_3\text{-PMo}_{12}\text{O}_{40}$, are known to be effective as catalysts for producing acidic compounds. Accordingly, a great number of studies concerning them have already been reported [3,4]. On the

other hand, relatively little attention has been paid to iron phosphate, which possesses both acidic and redox functions like $(\text{VO})_2\text{P}_2\text{O}_7$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, though iron phosphate catalysts have been known to be effective for the oxidative dehydrogenation of isobutyric acid to form methacrylic acid [5].

It was found in our previous studies [6–8] that iron phosphates show a high selectivity in the oxidative dehydrogenation of compounds in which the carbon atom at the α -position of an electron-attracting group (X), such as COOH , CHO , or CN , is tertiary; for example, isobutyric acid, isobutyraldehyde, and isobutyronitrile.



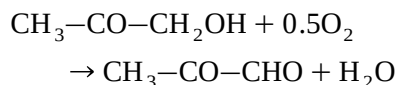
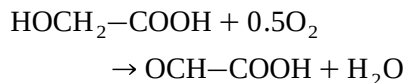
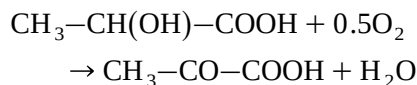
X = CHHO , CHO , or CN

Recently, it was found that iron phosphate showed a unique catalytic performance for several oxidative dehydrogenation, such as the for-

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mation of pyruvic acid from lactic acid [9], glyoxylic acid from glycolic acid [10], and pyruvaldehyde (2-oxopropanal) from hydroxyacetone (acetol) [11].



It is interesting to note that iron phosphate catalysts are effective only for the oxidative dehydrogenation, but not for oxygen insertion reaction, unlike phosphates of vanadium and molybdenum.

More recently, it was also found that iron(III) orthophosphate (FePO_4) was transformed into a new crystalline phase during its use as catalyst in the oxidative dehydrogenation of both lactic acid [12] and glycolic acid, and that the performances of catalyst were markedly enhanced by the change in structure. XRD patterns of the new phase were found to be very similar to those of clay minerals such as kaolinite, halloysite, dickite, and nacrite. From the studies on DTA/TG, FT-IR, elementary analysis, the chemical composition of the new phase was estimated as $\text{FePO}_4 \cdot 0.5\text{H}_2\text{O}$ or $\text{Fe}_2\text{P}_2\text{O}_7(\text{OH})_2$; an iron phosphate phase with crystalline water [13].

The aim of this study is to get more insight into the new crystalline phase concerning the formation and the physical and catalytic properties.

2. Experimental

2.1. Catalyst

The original iron phosphate catalyst sample was prepared according to the procedures described previously [11,14,15]. The P/Fe atomic

ratio was in the range of 1.05–1.2. It was calcined in a stream of air at 400°C for 8 h. It consisted of tridymite-type FePO_4 [16] and the presence of the quartz-type FePO_4 [17] was not detected in the XRD patterns. The BET surface area was 9.6 m²/g.

2.2. Reaction procedures

The reaction was carried out with a continuous-flow system at atmospheric pressure. 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. The iron phosphate sample (0.5–60 g) was placed near the bottom of the reactor and porcelain cylinder, 3 mm long and 1.5 mm i.d./3.0 mm o.d., were placed both under and above the sample. Air, a mixture of oxygen and nitrogen, nitrogen, oxygen, hydrogen, or helium was fed in from the top of the reactor; an aqueous solution containing a fixed amount of an organic compound was introduced into the preheating section of the reactor by a syringe pump. The effluent gas from the reactor was led successively into four chilled scrubbers to recover the water-soluble compounds. The products were analyzed by GC and LC.

2.3. Characterization of iron phosphate

XRD patterns were studied using a Shimadzu 6000 diffractometer with Cu K_α radiation. Surface areas were measured by the BET method using nitrogen as adsorbate at -196°C . The amount of Fe^{2+} and Fe^{3+} ions in the bulk were determined by the redox titration method [18].

3. Results

3.1. Formation and properties of new iron phosphate crystalline phase

The effects of reaction variables on the formation of the new iron phosphate crystalline

phase were studied. The typical procedures were as follows. A 5-g portion of the tridymite-type FePO_4 sample was placed in the stainless steel reactor and a mixture of nitrogen and oxygen was fed in with feed rates of 200 and 5.0 ml/min, respectively. An aqueous solution containing around 10 wt.% of an organic compound was introduced with a feed rate of 35 ml/h. The reaction temperature was in range of 210–240°C and the reaction time was 24 h.

3.1.1. Effect of organic compound

In order to know the effect of organic compounds on the formation of the new phase, vapors of various kinds of organic compounds were passed over the tridymite-type FePO_4 sample in the presence of a large amount of steam and a limited amount of oxygen. The results are summarized in Table 1.

The best results were obtained from oxalic acid; the new phase was the sole crystalline compound observed in the XRD patterns. The next best results were obtained from lactic acid; a small amount of $\text{Fe}_2\text{P}_2\text{O}_7$ was always formed

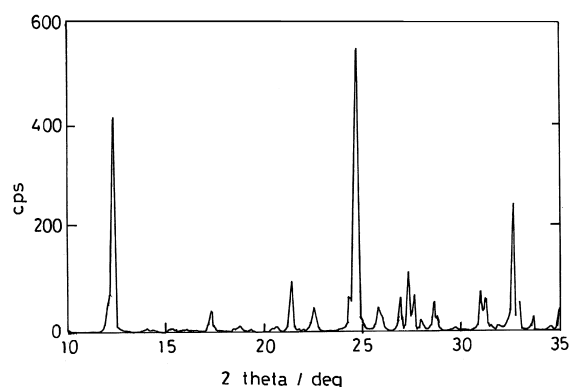


Fig. 1. XRD patterns of new phase.

together with the new phase. The third best results were obtained from glycolic acid; a mixture of $\text{Fe}_2\text{P}_2\text{O}_7$ and the new phase was obtained. In the case of hydroxyacetone (acetol), the iron phosphate sample was reduced totally to $\text{Fe}_2\text{P}_2\text{O}_7$ and the new phase was not obtained. On the other hand, the new phase was scarcely obtained from *n*-propanol, propylene glycol, formic acid, isobutyric acid, and pyruvic acid. The transformation from the tridymite-type FePO_4 to quartz-type FePO_4 is not ascribable to the organic compounds used, but to the steam [19].

Typical XRD patterns of the new phase obtained using oxalic acid are shown in Fig. 1. The relative intensities of the three main peaks at 2θ of 12.2°, 24.5°, and 32.4° were 60, 100, and 65, respectively [13]. No clear peaks assigned to any known iron phosphate crystalline phases were detected in the XRD patterns.

3.1.2. Effect of reaction temperature

The effect of reaction temperature on the formation of the new phase was studied using oxalic acid as the organic compound. The optimum temperature was found to be in the range of 210–240°C. At a temperature below 200°C, the vaporization of oxalic acid became difficult. On the other hand, at a temperature above 300°C, the FePO_4 sample was not transformed into the new phase.

Table 1

Effects of organic compound on the formation of new phase
Quartz = quartz-type FePO_4 ; Tridymite = tridymite-type FePO_4 ;
(vs) = very small amount; (s) = small amount.
Reaction conditions: sample = 5 g [$\text{P}/\text{Fe} = 1.15$]; feed rates
(mmol/h), organic compound/oxygen/water/nitrogen = 10–
20/10–20/1880/500; temperature = 210–240°C; reaction period
= 24 h.

Reactant	Phase observed in XRD	$\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratio
<i>n</i> -Propanol	Quartz + New phase (vs)	0.00
Propylene glycol	Quartz + New phase (vs)	0.01
Formic acid	Quartz + New phase (vs)	0.00
Isobutyric acid	Quartz + New phase (s)	0.01
Pyruvic acid	Tridymite + New phase (s)	0.10
Oxalic acid	New phase	0.28
Lactic acid	New phase + $\text{Fe}_2\text{P}_2\text{O}_7$ (s)	0.27
Glycolic acid	New phase + $\text{Fe}_2\text{P}_2\text{O}_7$	0.28
Acetole	$\text{Fe}_2\text{P}_2\text{O}_7$	0.82

3.1.3. Effect of oxygen concentration

The effect of oxygen in the feed gas was studied by changing the concentration from zero to 20 mol% using oxalic acid as the organic compound. In the absence of oxygen, a small amount of crystalline $\text{Fe}_2\text{P}_2\text{O}_7$ was obtained besides the new phase at 220°C. While at 200°C the new phase was the sole phase observed in XRD patterns. Moreover, when the concentration of oxygen was more than 1 mol%, the new phase was the sole phase observed even at 220°C.

3.1.4. Thermal stability

The new phase was found to be stable enough up to 300°C in nitrogen or in air. The crystalline water is not removed up to 300°C. It decomposed gradually at 400°C; within 4 h the majority was decomposed to form amorphous phase with a small amount of either $\text{Fe}_2\text{P}_2\text{O}_7$ (in nitrogen) or Y-phase (in air). The Y-phase is known to be obtained by reoxidation of $\text{Fe}_2\text{P}_2\text{O}_7$ by air at a temperature above 400°C [20,21].

3.2. Catalytic activity

Catalytic performances of the new phase were studied in both the oxidative dehydrogenation of lactic acid to pyruvic acid and that of glycolic acid to glyoxylic acid.

3.2.1. Oxidation of lactic acid to pyruvic acid

The oxidation of lactic acid was carried out both at 225°C and 230°C. The feed rates of lactic acid, air, and water vapor were 19.2, 350, and 962 mmol/h, respectively. The contact time was fixed at 1.6 s. The catalytic performances of the new phase were compared with those obtained from various other iron phosphate catalysts, which are prepared from the original tridymite-type FePO_4 . The $\text{Fe}_2\text{P}_2\text{O}_7$ sample was obtained by reducing the tridymite-type FePO_4 with hydrogen at 550°C for 12 h [22,23]. The $\text{Fe}_3(\text{P}_2\text{O}_7)_2$ sample was obtained by reducing the tridymite-type FePO_4 with a P/Fe atomic ratio of 1.2 with hydrogen at 400°C for 4 h [24]. The Y-phase was obtained by reoxidizing the $\text{Fe}_2\text{P}_2\text{O}_7$ sample with air at 500°C for 6 h [20,21]. The results are shown in Table 2.

The catalyst consisting of the new phase was clearly higher than that consisting of the original tridymite-type FePO_4 in both the activity and selectivity. The $\text{Fe}_3(\text{P}_2\text{O}_7)_2$ and Y-phase iron phosphate show a higher activity than the new phase, but the new phase is higher in both the yield and selectivity to pyruvic acid than the $\text{Fe}_3(\text{P}_2\text{O}_7)_2$ and Y-phase iron phosphate.

3.2.2. Oxidation of glycolic acid to glyoxylic acid

The oxidation of glycolic acid was carried out using the original tridymite-type FePO_4 un-

Table 2

Comparison of the catalytic performances of various iron phosphates in the oxidation of lactic acid to form pyruvic acid^a
Conv = conversion of lactic acid; Yield = yield of pyruvic acid; Selct = selectivity to pyruvic acid.

Iron phosphate catalyst	Temperature = 225°C			Temperature = 230°C		
	Conv/%	Yield/%	Selct/%	Conv/%	Yield/%	Select/%
Tridymite-type FePO_4	29.5	19.6	66	41.1	25.5	62
New phase	53.2	40.0	75	62.3	45.0	72
Y-phase	58.0	34.8	60	67.0	35.5	53
$\text{Fe}_3(\text{P}_2\text{O}_7)_2$	61.0	37.8	62	78.0	42.1	54
$\text{Fe}_2\text{P}_2\text{O}_7$	32.4	25.0	77	42.2	31.5	75

^a Feed: lactic acid/air/steam = 1902/350/962 mmol/h; contact time = 1.6 s.

der the following reaction conditions; feed rates of glycolic acid, oxygen, water vapor, and nitrogen were 12.3, 25, 480, and 500 mmol/h, respectively; reaction temperature of 240°C; amount of catalyst used of 5.0 g (contact time of 1.25 s).

The structure of iron phosphate changed during the use in the reaction like in the case of the oxidation of lactic acid [12]. After 20 h on stream, the original tridymite-type FePO_4 was transformed into quartz-type FePO_4 , probably this transformation is ascribable to the action of water vapor [19], and after 100 h on stream all of the quartz-type FePO_4 was transformed into the new phase. The variations in the XRD patterns are shown in Fig. 2.

Fig. 3 shows the variations in the conversion of glycolic acid and the oxidation states of iron in the bulk as a function of the time-on-stream. As the time-on-stream increases, the catalytic activity increases, shows a maximum at around 20 h on stream, and then falls with a further increase in the reaction time. After about 110 h on stream, the catalyst was calcined in a stream of air at 400°C for 1 h. It was found that the

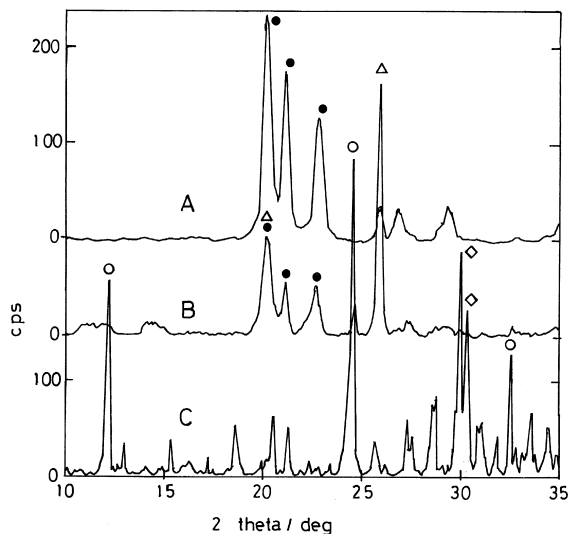


Fig. 2. Variation of the structure during the oxidation of glycolic acid. (A) Initial, (B) after 20 h on stream, (C) after 100 h on stream. (●) tridymite-type FePO_4 , (Δ) quartz-type FePO_4 , (○) $\text{Fe}_2\text{P}_2\text{O}_7$, (◊) new phase.

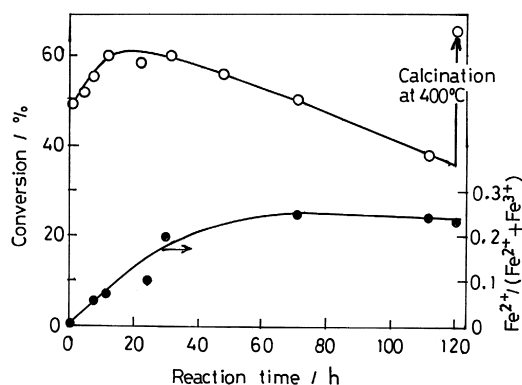


Fig. 3. Variation of the catalytic activity and the oxidation states of iron phosphate during the oxidation of glycolic acid.

calcined catalyst, which still consisted of the new phase, showed a markedly higher catalytic activity.

4. Discussion

During the use of FePO_4 as catalyst in the oxidation of lactic acid or glycolic acid, the FePO_4 is transformed into the new phase having crystalline water. This finding indicates that crystalline water is incorporated into FePO_4 , when the FePO_4 sample is exposed to vapors of water and organic compound, such as oxalic acid, lactic acid, and glycolic acid, at a temperature in the range of 200–240°C.

The presence of water vapor should be indispensable for the formation of new phase. Indeed, in the cases of lactic acid [12], the presence of water vapor was found to be indispensable. On the other hand, in the cases of oxalic acid and glycolic acid, the effects of water vapor cannot be checked because these acids are solid.

FePO_4 is insoluble in water, interestingly, the solubility increases as increasing the concentration of oxalic acid or glycolic acid in the water. Further, lactic acid dissolves FePO_4 . From these findings, it is likely that the organic acids such as oxalic acid, lactic acid, and glycolic acid play

a role in dissolving partially FePO_4 and inserting water molecule in the crystalline phase.

It is considered that oxygen plays a role in suppressing the reduction of FePO_4 to $\text{Fe}_2\text{P}_2\text{O}_7$ with the organic compound and that the variation of the role of oxygen depends on the reducing force of the organic compound. For example, the presence of oxygen is not important in the case of oxalic acid, but there exists an optimum concentration of oxygen in the case of lactic acid [12] and glycolic acid. In the case of hydroxyacetone, however, the formation of $\text{Fe}_2\text{P}_2\text{O}_7$ cannot be suppressed even in the presence of oxygen.

Temperatures below 200°C should be beneficial to the equilibrium for the water incorporation, but they may not be beneficial to the rate of crystalline transformation and to the vaporization of organic compound; at temperatures higher than 250°C , the incorporation of water may become difficult. Accordingly, the optimum temperature becomes about 220°C .

The presence of a large amount of water vapor is indispensable to promote selectively oxidative dehydrogenation reactions performed with iron phosphate catalysts [24–26]. From this evidence and consideration of the finding that the new phase having crystalline water shows a performance better than that of the iron phosphate without crystalline water, it is likely that the crystalline water takes part in the oxidative dehydrogenation reactions. A similar view has been proposed in the case of the oxidative dehydrogenation of isobutyric acid by Millet et al. [27].

As is common in oxidation reactions performed at low temperatures, the catalytic activity for oxidation of glycolic acid falls gradually as the time-on-stream increases. It is likely that the catalyst is deactivated due to the deposit of some nonvolatile products on the surface. Possibly, iron phosphate catalyst cannot burn out the nonvolatile products at low temperature used in

the reaction. This may be the reason why the catalytic activity is totally regenerated after the calcination in air at a higher temperature of 400°C .

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