Reduction and Reoxidation of Iron Phosphate and Its Catalytic Activity for Oxidative Dehydrogenation of Isobutyric Acid

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The freshly calcined iron phosphate catalysts with a P/Fe atomic ratio of 1.0 ∼ 1.3 consist of amorphous phase, quartz-type $FePO_4$ and/or tridymite-type $FePO_4$ depending on the calcination temperature, though they contain only Fe^{3+} ions. In the absence of oxygen, the P/Fe > 1.2 catalyst samples are reduced with hydrogen or isobutyric acid to form $Fe_2P_2O_7$ via $Fe_3(P_2O_7)_2$. While the P/Fe = 1.0 samples are reduced to $Fe_2P_2O_7$ not passing through $Fe_3(P_2O_7)_2$. $Fe_2P_2O_7$ is oxidized with air to an unknown compound (Y phase), but not to $Fe_3(P_2O_7)_2$ nor $FePO_4$. The Y phase is reduced to $Fe_2P_2O_7$. During the use in the oxidative dehydrogenation of isobutyric acid, the freshly calcined catalysts are reduced to $Fe_3(P_2O_7)_2$, the $Fe_2P_2O_7$ catalysts are in part oxidized to the Y phase, and the Y phase is in part reduced to $Fe_2P_2O_7$, though the rates are very slow. The catalytic activity and selectivity are scarcely affected with the variation in the structure of the iron phosphate catalyst and in the oxidation states of iron ions.   © 1996 Academic Press, Inc.

I. INTRODUCTION

Iron phosphates are known in patents to be effective as catalysts for oxidative dehydrogenation of isobutyric acid (IBA) to methacrylic acid (MAA) similar to heteropoly compounds based on 12-molybdophosphoric acid [$H_3PMo_{12}O_{40}$]. Recently, they were found to be effective also for oxidative dehydrogenation of other compounds in which the carbon atom at the α position of an electron-attracting group such as –CHO and –CN is tertiary; for example, isobutylaldehyde to methacrolein (1, 2) and isobutyronitrile to methacrylonitrile (3).

Indeed, there have been a number of scientific studies concerning the catalytic action of iron phosphate, though there exist some conflicts among them. The structures of iron phosphates with a P/Fe atomic ratio of unity, quartz-type $FePO_4$ [$FePO_4$(Q)] (4), tridymite-type $FePO_4$ [$FePO_4$(T)] (5), and $Fe_2P_2O_7$ (6, 7), are known. $Fe_2P_2O_7$ is generally obtained by reduction of $FePO_4$. Millet et al.

(8) reported the presence of a new phase containing both Fe^{2+} and Fe^{3+} ions and having characteristic peaks in X-ray powder diffraction patterns at $2\theta = 29.53°$ and 29.72°. For determination of the unit cell, they tried to use a calculation method based on the XRD data because it was difficult to grow single crystal. From the calculation, they proposed that the new phase is $Fe_3(P_2O_7)_2$. Further, they proposed that the new phase is associated with the catalytic action. However, $Fe_3(P_2O_7)_2$ was also studied in detail by Ijjaali et al. (9). According to their report (9) the X-ray diffraction (XRD) pattern of $Fe_3(P_2O_7)_2$ is characterized with peaks at $2\theta = 14.48°$, 21.14°, 21.26°, 24.84°, 34.86°, and 35.69°. It is clear that the compound proposed from calculation to be $Fe_3(P_2O_7)_2$ by Millet et al. (8) is different from that assigned by Ijjaali et al. (9).

On the other hand, Barbaux et al. (10) reported that the presence of pyrophosphate groups such as $Fe_3(P_2O_7)_2$ was not proved. Further, they proposed that the reaction is promoted by hydrogen phosphate compounds which are stabilized by the presence of a large amount of water vapor and that there exist zones with a high phosphorus content relative to the iron on both the fresh and used catalyst; that is, a phosphorus gradient exists from the outer layers toward the bulk of the catalyst.

It was found in our recent work (11) that the structure of freshly prepared iron phosphates with a P/Fe atomic ratio close to unity varies with a rise in the calcination temperature as follows; amorphous $\xrightarrow{500°C}$ unidentified phase $\xrightarrow{550°C}$ $FePO_4$(Q) phase. This unidentified phase was later assigned to $FePO_4$(T) phase which is characterized with three main peaks in the XRD spectra at $2\theta = 20.00°$, 20.95°, and 29.35°(5). It was also found (11) that the excess of phosphorus with respect to the stoichiometry of $FePO_4$ or $Fe_2P_2O_7$, viz., P/Fe = 1.0, forms $NH_4FeP_2O_7 \cdot 1.5H_2O$ when the iron phosphate is prepared in the presence of ammonium ions, and that this compound is transformed with a rise in the calcination temperature as follows; $NH_4FeP_2O_7 \cdot 1.5H_2O \xrightarrow{450°C} NH_4FeP_2O_7 \xrightarrow{500-550°C} FePO_4$(Q) + NH_3 + polycondensed phos-

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phates. It was proposed that species with a P/Fe ratio of unity are responsible for catalytic action and that the compounds with a P/Fe ratio of more than unity such as $NH_4FeP_2O_7$, $FeH_2P_2O_7$, and polycondensed phosphates do not have the catalytic action.

It was also found (12) that freshly prepared iron phosphate is reduced to form $Fe_2P_2O_7$ via a bluish black intermediate characterized with two clear peaks in the XRD spectra at $2\theta = 19.96°$ and $21.24°$ and that the catalytic actions such as activity and selectivity are scarcely affected with a large variation in the valence states of iron ions in the bulk.

In this study, we attempted to clarify in more detail the variation in the structure of iron phosphate and the oxidation states of iron ions due to the reduction and reoxidation and also to the use in the oxidative dehydrogenation of isobutyric acid.

EXPERIMENTAL

Catalyst

Iron phosphate catalysts with P/Fe atomic ratios of 1.02, 1.2, and 1.33 were prepared according to the "Method C" procedures described in the previous study (11). Unless otherwise indicated, the studies were performed with the catalyst with a P/Fe ratio of 1.2. The surface area measured by the BET method was 15 m^2/g.

Characterizations

X-ray powder diffraction patterns were studied using a Rigaku-Denki, model RAD-RB diffractometer with $CuK\alpha$ radiation.

The amounts of Fe^{2+} and Fe^{3+} ions in the bulk were determined by the redox titration method (13). The detailed procedures were described in a prevous paper (14). That is, a 1.0 to 1.5 g portion of sample was ground and the resulting powder was added into a solution consisting of about 15 ml of water and 15 ml of concentrated hydrochloric acid. The mixture was boiled slowly for about 1 h to dissolve the iron phosphates. Then, the solution was diluted with about 100 ml of water and it was divided into two parts. One was titrated with 0.033 M potassium dichromate solution using sodium diphenylamine-4-sulfonate as an indicator to determine the amount of Fe^{2+} ions in the solution. The other was heated to about 80 to 90°C and then 0.2 M stannous chloride solution was added so as to convert all of the Fe^{3+} ions to Fe^{2+} ions. The solution was cooled in an ice-water bath and then a small amount of mercury (II) chloride solution was added to eliminate excess stannous ions. Finally, the solution was titrated with 0.33 M potassium dichromate solution to determine the amount of (Fe^{2+} + Fe^{3+}) ions which were present in the initial solution.
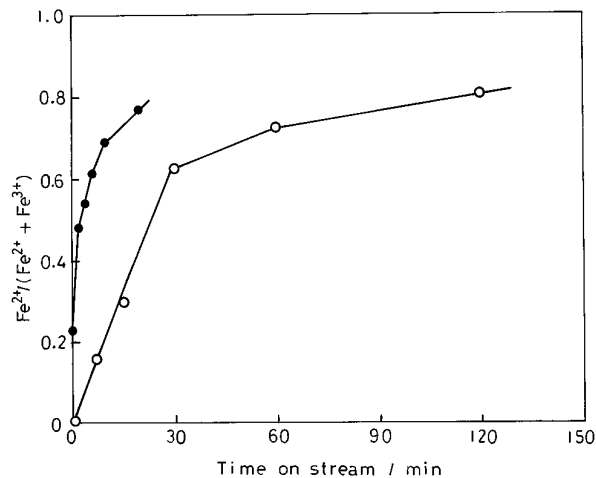

FIG. 1. Reduction of iron phosphate with IBA in the absence of oxygen. (○) Freshly calcined sample; (●) sample consisting of the Y phase.

Fourier-transform infrared (FT-IR) spectra were recorded from 4000 to 400 cm^{-1} with a Perkin-Elmer 1700, using the KBr pressed disk technique.

Reaction Procedures

The vapor phase oxidation of IBA was conducted with a continuous-flow system at atmospheric pressure. The detailed procedures and the definitions were the same as those described in the previous works (1, 14). Unless otherwise indicated, the reaction temperature was 400°C and the feed rates of IBA, oxygen, water, and nitrogen were 21.5, 16.5, 324, and 350 mmol/h, respectively.

RESULTS AND DISCUSSION

Reduction of Freshly Prepared Iron Phosphate

A gaseous mixture of IBA, water, and nitrogen was passed at 400°C with feed rates of 21.5, 324, and 350 mmol/h, respectively, over 1.5 g portions of the iron phosphate with a P/Fe atomic ratio of 1.2 which was previously calcined at 520°C in air for 4 h. The extent of reduction in the bulk, that is, the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio, increased as the time-on-stream increased (open symbol in Fig. 1). XRD spectra of the samples obtained at different times-on-stream are shown in Fig. 2. The freshly calcined iron phosphate contains both $FePO_4(Q)$ and $FePO_4(T)$ with a small amount of $NH_4FeP_2O_7$. It is reduced to $Fe_2P_2O_7$ via a bluish black intermediate compound which is characterized with peaks in the XRD spectra at $2\theta = 19.96°$, $21.24°$, $24.68°$, $35.04°$, $35.54°$, $50.68°$, and $63.12°$. According to the studies by Ijjaali *et al.* (9), this compound was assigned to $Fe_3(P_2O_7)_2$.

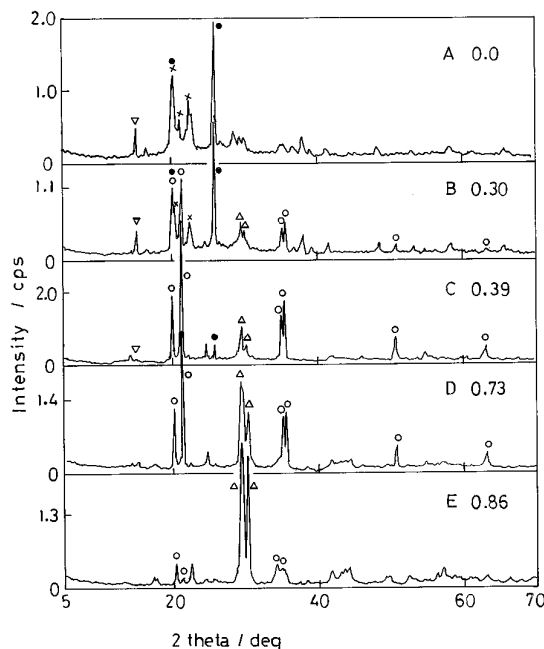The peak heights at $2\theta = 25.8°$, $20.20°$, $21.24°$, and $30.3°$ in

FIG. 2. XRD patterns of iron phosphates reduced by IBA. Reduction time (min): (A) 0; (B) 15; (C) 20; (D) 60; (E) 480. Figures denote the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio. (●) $FePO_4(Q)$; (×) $FePO_4(T)$; (○) $Fe_3(P_2O_7)_2$; (△) $Fe_2P_2O_7$; (▽) $NH_4FeP_2O_7$.

the XRD spectra which reflect the amounts of $FePO_4(Q)$, $FePO_4(T)$, $Fe_3(P_2O_7)_2$, and $Fe_2P_2O_7$, respectively, are plotted as a function of the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio in Fig. 3. It is clear that $Fe_3(P_2O_7)_2$ is an intermediate.

The iron phosphates calcined below 480°C were amorphous, and those calcined above 550°C consisted only of $FePO_4(Q)$ having a good crystallinity, as had been reported

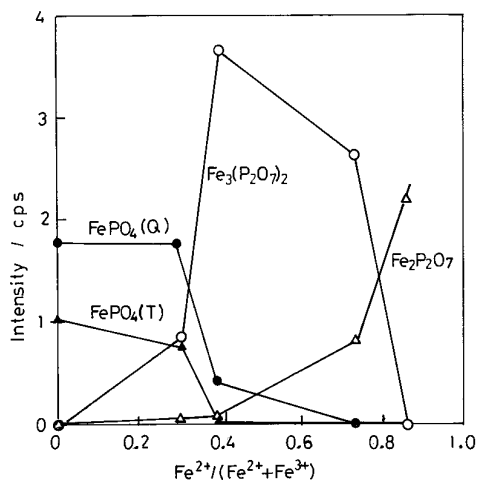**FIG. 3.** Relation between the peak heights in XRD and the extent of reduction. $FePO_4(Q)$ ($2\theta = 25.8°$); $FePO_4(T)$ ($2\theta = 20.20°$); $Fe_3(P_2O_7)_2$ ($2\theta = 21.24°$); $Fe_2P_2O_7$ ($2\theta = 30.3°$).

in the previous study (11). It was found that both the amorphous compound and the nearly pure $FePO_4(Q)$ were reduced to form $Fe_2P_2O_7$ having a good crystallinity, much as the iron phosphate sample calcined at 520°C.

It was also found that the catalyst samples with a P/Fe ratio of 1.33 were reduced to $Fe_2P_2O_7$ via $Fe_3(P_2O_7)_2$, much as the samples with a P/Fe ratio of 1.2.

Interstingly, in the reduction of the catalyst samples with a P/Fe ratio of 1.02, $Fe_2P_2O_7$ was obtained as the product, but $Fe_3(P_2O_7)_2$ was not observed as the intermediate compound.

These findings suggest that the presence of excess phosphorus with respect to the stoichiometry of $FePO_4$ (P/Fe = 1.0) is required to form $Fe_3(P_2O_7)_2$ (P/Fe = 1.33) from $FePO_4$. It is considered that the excess phosphorus exists near to $FePO_4$ as amorphous phase.

Oxidation of $Fe_2P_2O_7$

The samples with a $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio of about 0.9, which consist mainly of $Fe_2P_2O_7$ and have a good crystallinity, were previously prepared by the reduction of freshly calcined iron phosphate (P/Fe = 1.2) in a stream of hydrogen at 480°C for 12 h. Then, a mixture of air and water was passed at 400°C over 1.5 g portions of the reduced samples. With an increase in the time-on-stream, the samples were gradually oxidized and the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio decreased to about 0.22. The color of samples changed from white to dark red-brown.

The XRD spectra obtained at different times-on-stream are shown in Fig. 4. As the extent of oxidation increased, the $Fe_2P_2O_7$ phase was transformed to a new phase in which XRD patterns were similar to those of $Zn_2P_2O_7$ which is isostructural with $Fe_2P_2O_7$ (7); that is, only one clear peak appeared at $2\theta = 29.5°$.

The new phase observed in the oxidation of $Fe_2P_2O_7$ seems to be the same phase which was reported and calculated as $Fe_3(P_2O_7)_2$ by Millet *et al.* (8). However, it is clear that the phase is clearly different in structure from the $Fe_3(P_2O_7)_2$ assigned by Ijjaali *et al.* (9). In order to avoid the confusion between $Fe_3(P_2O_7)_2$ assigned by Ijjaali *et al.* (9) and that proposed from calculation by Millet *et al.* (8), we designate hereafter the phase characterized with $2\theta = 29.5°$ in the XRD spectra as the Y phase.

It was found that $Fe_2P_2O_7$ is oxidized to the Y phase, but not to $FePO_4$ nor $Fe_3(P_2O_7)_2$ under the conditions used. However, the Y phase was transformed slowly to $FePO_4(Q)$ at about 1000°C. The transformation between the Y phase and $Fe_3(P_2O_7)_2$ does not take place under the conditions used.

It was also found that the $Fe_2P_2O_7$ phase, which was obtained by the reduction of the iron phosphates with a P/Fe ratio of 1.02, is also transformed to the Y phase by the oxidation. This finding indicates that the presence of
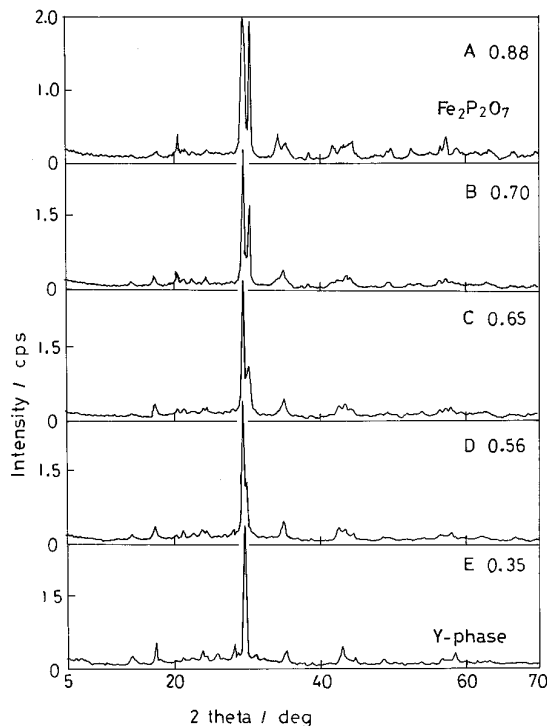
FIG. 4. XRD patterns of samples obtained by oxidation of $Fe_2P_2O_7$ at 400°C. Oxidation time (min): (A) 0; (B) 30; (C) 120; (D) 240; (E) 240 (at 480°C). Figures denote the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratios.

an excess of phosphorus with respect to the stoichiometry of $Fe_2P_2O_7$ (P/Fe = 1.0) is not required to form the Y phase from $Fe_2P_2O_7$.

Reduction of Y-Phase

The iron phosphate sample consisting of the Y phase which had previously been prepared by oxidation of a sample consisting of the $Fe_2P_2O_7$ phase, was reduced again by passing the gaseous mixture of IBA, water, and nitrogen at 400°C. It was found that the Y phase is reduced to form the $Fe_2P_2O_7$ phase much as the freshly calcined sample consisting of $FePO_4$. It is clear that the transformation between $Fe_2P_2O_7$ and the Y phase is reversible. It should be noted that the rate of reduction of the Y phase (closed symbol in Fig. 1) was much faster than that of the freshly calcined sample consisting of $FePO4$ and/or $Fe_3(P_2O_7)_2$ (open symbol in Fig. 1).

Oxidation and Reduction of Iron Phosphate Containing $Fe_3(P_2O_7)_2$

The freshly calcined sample was reduced in a stream of the mixture of IBA, water, and nitrogen at 400°C for 35 min. The XRD spectra of the resulting sample are shown

in Fig. 5A. The sample contained mainly $Fe_3(P_2O_7)_2$ and $Fe_2P_2O_7$. It was then oxidized by air at 480°C for 4 h. The XRD spectra of the resulting samples are shown in Fig. 5B. It was found that the $Fe_2P_2O_7$ phase is transformed to the Y phase, but that the $Fe_3(P_2O_7)_2$ phase remains unchanged. On the other hand, the samples consisting of $FePO_4$ and $Fe_3(P_2O_7)_2$ were obtained by the reduction for a shorter time (for less than 20 min). They were also oxidized by air. It was found that no clear change is observed in the XRD spectra by the oxidation procedures, though the samples are clearly oxidized; the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio decreases from 0.30 to 0.02.

The sample consisting of both $Fe_3(P_2O_7)_2$ and Y phases (Fig. 5B) was reduced in a stream of the mixture of IBA, water, and nitrogen at 400°C for 25 min. The XRD spectra of the resulting samples are shown in Fig. 5C. It was found that the Y phase is transformed to $Fe_2P_2O_7$, but that the $Fe_3(P_2O_7)_2$ phase remained unchanged.

It is concluded from these findings that $Fe_3(P_2O_7)_2$ is formed irreversibly from $FePO_4$, is markedly less oxidizable than $Fe_2P_2O_7$, and is markedly less reducible than the Y phase.

Variation in the Structure and Valence State by the Use in the Oxidation of IBA

The mixture of IBA, oxygen, water vapor, and nitrogen described in Experimental was passed over 1.5-g portions of iron phosphate (P/Fe = 1.2) calcined at 500°C. The extent of reduction is shown as a function of the time-
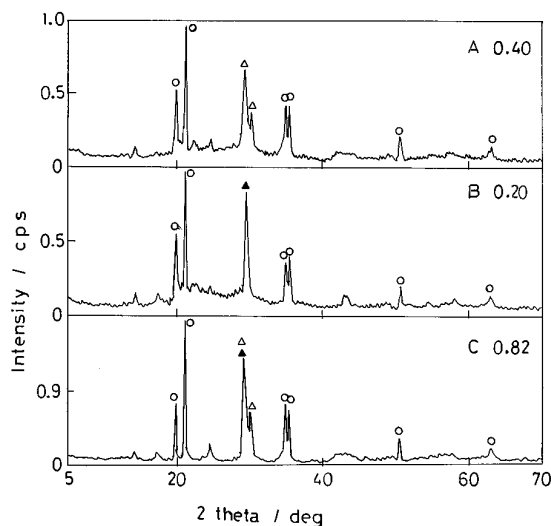

FIG. 5. Change in the XRD patterns due to reduction and reoxidation. (A) Sample obtained by partial reduction of a freshly prepared iron phosphate. (B) Sample obtained by reoxidation of (A). (C) Sample obtained by re-reduction of (B). Figures denote the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratios. (○) $Fe_3(P_2O_7)_2$; (△) $Fe_2P_2O_7$; (▲) Y phase.
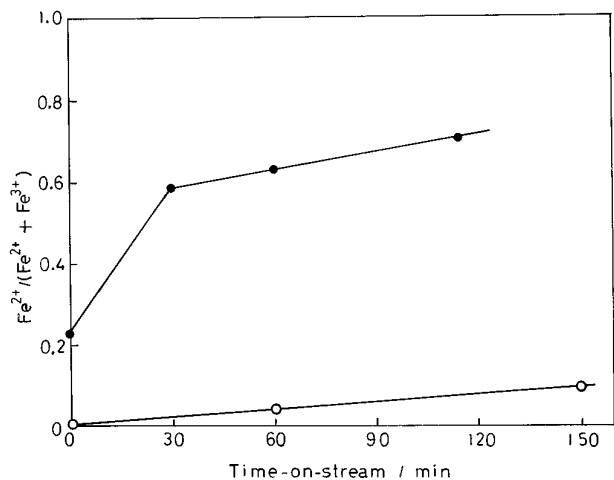
FIG. 6. Reduction of iron phosphate during use in the oxidative dehydrogenation of IBA. (○) Freshly calcined sample; (●) sample consisting of the Y phase.

on-stream in Fig. 6 (open symbol). After 25 h of use in the reaction, the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio increased from zero to 0.40. $Fe_3(P_2O_7)_2$ and a small amount of the $FePO_4$ phase were observed in the XRD spectra. It is therefore concluded that though the rate is very slow, the freshly calcined iron phosphate is reduced to $Fe_3(P_2O_7)_2$ during the use in the oxidation reaction. It should however be noted that the reduction stops at the stage of $Fe_3(P_2O_7)_2$ and, therefore, $Fe_2P_2O_7$ is not formed by the reduction with IBA in the presence of oxygen, unlike by the reduction in the absence of oxygen. It should also be noted that the Y phase is not formed from catalyst samples consisting of $FePO_4$ and/or $Fe_3(P_2O_7)_2$ during use in the oxidation reaction. $Fe_3(P_2O_7)_2$ is formed when the oxidation reaction is performed with catalysts consisting of $FePO_4$. The transformation from $FePO_4$ to $Fe_3(P_2O_7)_2$ is considered to be irreversible.

On the other hand, the mixture of IBA, oxygen, water vapor, and nitrogen were passed at 400°C over 1.5-g portions of catalyst sample consisting of $Fe_2P_2O_7$. The catalysts were reoxidized very slowly during the use in the oxidation of IBA. After 32 h of use in the reaction, the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio decreased from 0.88 to 0.73. It was found from the XRD spectra that a part of the $Fe_2P_2O_7$ phase was transformed to the Y phase, but the presence of $Fe_3(P_2O_7)_2$ and $FePO_4$ was not observed. It is therefore concluded that though the rate is very slow, a part of the $Fe_2P_2O_7$ is reoxidized to the Y phase during the use in the reaction.

Then, the oxidation of IBA was performed over 1.5-g portions of catalyst consisting mainly of Y phase [$Fe^{2+}/(Fe^{2+} + Fe^{3+}) = 0.23$]. The extent of reduction of catalyst, that is, the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio, is shown as a function of the time-on-stream in Fig. 6 (closed symbol). The cata-

lyst sample consisting of the Y phase is reduced much more rapidly than the freshly calcined sample consisting of $FePO_4$ and/or $Fe_3(P_2O_7)_2$. The results conform with those obtained in the reduction by IBA in the absence of oxygen (Fig. 1). It was found from the XRD spectra that a part of the Y phase is reduced to form $Fe_2P_2O_7$ during use in the oxidation of IBA. This indicates that the transformation between the $Fe_2P_2O_7$ and Y phases takes place reversibly during use in the oxidation, when the reaction is performed with catalysts consisting of $Fe_2P_2O_7$ and/or Y phase.

Infrared Study

The infrared (IR) spectra of iron phosphates (P/Fe = 1.2) freshly calcined at 400, 480, and 550°C, consisting of amorphous phase, $FePO_4(T)$, and $FePO_4(Q)$, respectively, are shown in Fig. 7. The spectra are almost the same as those obtained from $FePO_4 \cdot 2H_2O$ (15). This indicates that all of the samples consist of iron (III) orthophosphate ($FePO_4$) though the structures are different.

Figure 8 shows the IR spectra of four iron phosphates (P/Fe = 1.2) consisting of $FePO_4(Q)$, $Fe_3(P_2O_7)_2$ plus a small amount of $FePO_4(Q)$, Y phase, and $Fe_2P_2O_7$. The absorption in the 3000–4000 cm^{-1} range may be ascribed to the adsorption of water vapor during the measurement. The shape of the spectra of the Y phase seems to resemble somewhat that of $Fe_3(P_2O_7)_2$. This led us to feel that the Y phase is a compound which resembles $Fe_3(P_2O_7)_2$ and/or $Fe_2P_2O_7$, though we have no other clear evidence besides that the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio observed for the Y phase (0.2 to 0.5) is near that of $Fe_3(P_2O_7)_2$ (0.33). Further studies on the Y phase seems to be necessary to clarify if the Y phase is an isomer of $Fe_3(P_2O_7)_2$.
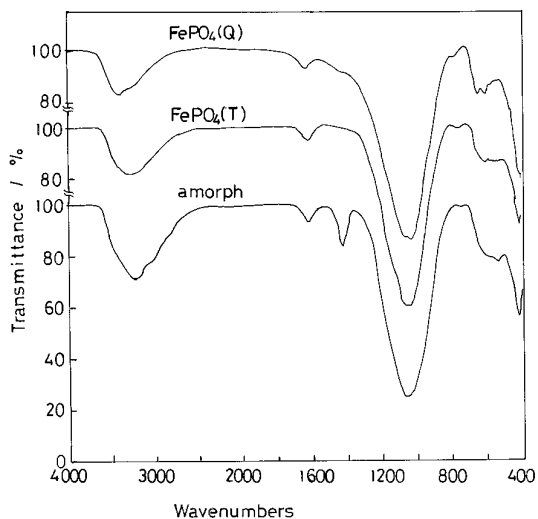

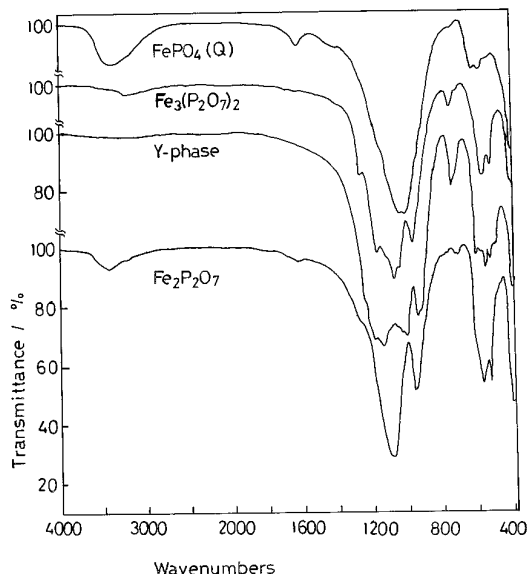**FIG. 7.** IR spectra of freshly calcined iron phosphates.

FIG. 8. IR spectra of iron phosphates.

*Effects of Variation in the Valance States and Structure on the Catalytic Performance*

The catalytic performances of iron phosphates different in both valence states and structures are measured under the fixed reaction conditions described in Experimental. The results are summarized in Table 1. It is clear that both the activity and selectivity are scarcely affected with a large variation in both valence states of iron ions and structures in the bulk in conformity with the previous results (12). It should however be noted by the findings shown in Figs. 1 and 6 that the rate of reduction of the Y phase is much faster than that of $FePO_4$ and $Fe_3(P_2O_7)_2$ and that the rate of reoxi-

dation of $Fe_2P_2O_7$ is much faster than that of $Fe_3(P_2O_7)_2$. These findings reveal that the rate of oxidation–reduction in the bulk does not affect the catalytic action.

It is therefore considered that the catalytic action is ascribable to the functions on the surface rather than those in the bulk. The XPS measurements performed for cooled samples indicate that the valence states of iron on the surface are the same as those in the bulk (12). This suggests that there is rapid equilibrium between surface and bulk. However, these results are doubtful, because a surface–bulk exchange reaction should take place during the time between the sample preparation and the XPS measurement, especially, during the cool down. Therefore, further studies performed for catalyst samples at working states, if possible, are needed to resolve this problem.

CONCLUSIONS

The structural changes due to oxidation–reduction of iron phosphates are summarized schematically as follows.

$FePO_4$ (P/Fe = 1.02) $FePO_4$ (P/Fe = 1.2–1.33)

$Fe_3 (P_2O_7)_2$ Y phase
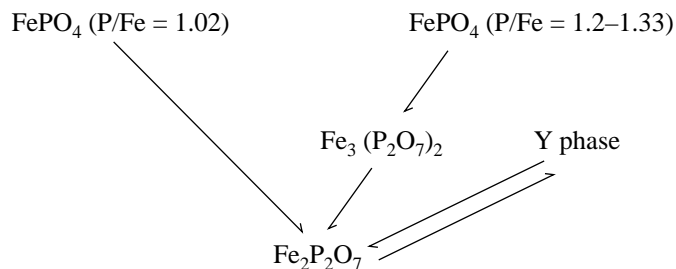
$Fe_2P_2O_7$

(i) As has generally been known, $FePO_4$ without excess phosphorus is reduced directly to $Fe_2P_2O_7$.

(ii) $FePO_4$ with excess phosphorus is reduced to $Fe_2P_2O_7$ via $Fe_3(P_2O_7)_2$.

TABLE 1

Catalytic Performances of Iron Phosphates

Phase observed in XRD spectra		$\left(\dfrac{Fe^{2+}}{Fe^{2+} + Fe^{3+}}\right)$	Conversion of IBA (%)	Selectivity to MAA (mol%)
Main	Minor			
FePO4(Q)	FePO4(T)	0.0–0.1	86.2	78.5
			92.6	77.0
Fe$_3$(P$_2$O$_7$)$_2$	FePO4(Q)	0.4	84.0	82.0
Y phase	—	0.4–0.6	83.0	82.5
			85.0	81.0
Fe$_2$P$_2$O$_7$	Y phase	0.7–0.8	85.0	82.5
			89.0	82.0
Fe$_2$P$_2$O$_7$	—	0.9–0.95	79.0	82.0
			85.0	80.5

Note. Reaction temperature, 400°C; contact time, 0.4 s; feed rates of IBA/oxygen/water/nitrogen = 21.5/16.5/324/350 mmol/h.
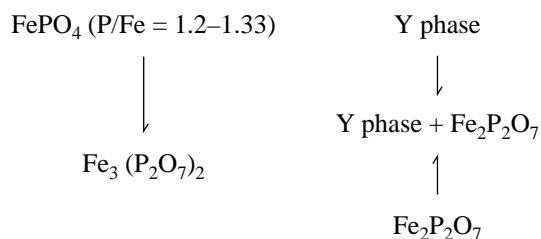
(iii) The Y phase seems to be the same phase which was reported and calculated as $Fe_3(P_2O_7)_2$ by Millet *et al.* (8).

(iv) $Fe_2P_2O_7$ is oxidized to the Y phase, as has been reported by Millet *et al.* (8).

(v) $Fe_2P_2O_7$ is not oxidized to $Fe_3(P_2O_7)_2$ nor to $FePO_4$.

(vi) The Y phase is reduce to $Fe_2P_2O_7$.

On the other hand, the structural changes of iron phosphate during the oxidative dehydrogenation of IBA are summarized schematically as follows.

$$FePO_4 \ (P/Fe = 1.2\text{--}1.33) \qquad\qquad Y \text{ phase}$$

$$\downarrow \qquad\qquad\qquad\qquad\qquad\qquad \downarrow$$

$$\qquad\qquad\qquad\qquad\qquad Y \text{ phase} + Fe_2P_2O_7$$

$$Fe_3 \ (P_2O_7)_2 \qquad\qquad\qquad\qquad \uparrow$$

$$Fe_2P_2O_7$$

(i) $FePO_4$ with excess phosphorus is reduced to $Fe_3(P_2O_7)_2$, but not to $Fe_2P_2O_7$.

(ii) The Y phase is partially reduced to $Fe_2P_2O_7$.

(iii) $Fe_2P_2O_7$ is partially oxidized to the Y phase.

Interestingly, the catalytic performance in the oxidation of IBA is scarcely affected by changes in the structure and valence states of iron in the bulk and also by changes in the oxidation–reduction rates of bulk.

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