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Effects of Methods of Preparing Iron Phosphate and P/Fe Compositions on the Catalytic Performance in Oxidative Dehydrogenation of Isobutyric Acid

Methacrylic acid is a raw material for various polymers. It is currently produced by oxidation of isobutylene. Attempts have also been made to produce it by oxidative dehydrogenation of isobutyric acid:

$$CH_3\text{–}CH(CH_3)\text{–}COOH + 0.5O_2 \rightarrow CH_2{=}C(CH_3)\text{–}COOH + H_2O.$$

It is known in patents that both iron phosphates and heteropoly compounds based on $H_3PMo_{12}O_{40}$ are effective as catalysts. It was also reported that catalysts based on $(VO)_2P_2O_7$ exhibit a performance comparable to that of heteropoly compounds (*1*). The catalytic action of heteropoly compounds have been extensively studied. On the other hand, as for the action of iron phosphates, there have been a limited number of reports (*2–5*). In this study, we attempt to gain more insight into the action of iron phosphates.

Eight series of iron phosphates with different P/Fe atomic ratios were prepared according to the following procedures.

Method A. Powder of $FePO_4 \cdot nH_2O$ was kneaded with an aqueous solution containing a desired amount of 85% H_3PO_4 and a small amount of "Snowtex O" (Nissan Chem. Co.) colloidal silica, Si/Fe atomic ratio of about 0.1, yielding a paste-like compound.

Method B. $NH_4H_2PO_4$ was used instead of 85% H_3PO_4 in 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 precipitate was filtered and the obtained gel was mixed with desired amounts of 85% H_3PO_4 and the colloidal silica. The mixture was boiled slowly for 1–2 h and then excess water was evaporated to yield a paste.

Method C'. $NH_4H_2PO_4$ was used instead of 85% H_3PO_4 in Method C.

Method D. $Fe(NO_3)_3 \cdot 9H_2O$, 85% H_3PO_4, and the colloidal silica were mixed in a solution and excess water was evaporated.

Method E. $NH_4H_2PO_4$ was used instead of 85% H_3PO_4 in Method D.

Method F. Powder of $Fe(C_2O_4) \cdot 2H_2O$ was kneaded with a solution containing desired amounts of 85% H_3PO_4 and the colloidal silica.

Method G. Powder of $Fe_4(P_2O_7)_3 \cdot 9H_2O$ was kneaded with a solution containing desired amounts of $NH_4H_2PO_4$ and the colloidal silica.

The obtained paste-like compounds were dried at 120°C for 6 h and the resulting solids were broken up and sieved to a 7–20 mesh size. Finally, they were calcined at a fixed temperature for 4 h. For convenience, the catalysts were designated by a number giving the P/Fe atomic ratio followed by a letter designating the preparation method.

The X-ray powder diffraction (XRD) patterns were studied using a Rigaku–Denki Model RAD-RB diffractometer with CuK_α radiation. The results obtained from the samples calcined at 500°C are summarized in Table 1. The crystallinity of all the samples with a P/Fe ratio of 1.0–1.2 was very low, and an unidentified compound characterized with three peaks at 2θ = 20.00°, 20.95°, and 22.50° was observed in the 1.0 D, 1.2 C, 1.2 D, and 1.2 E samples. Clear peaks corresponding to $NH_4FeP_2O_7$ were

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TABLE I

Main and Minor Structures of the Iron Phosphate Catalysts

Method	P/Fe ratio					
	1.0		1.2		1.5	
	Main	Minor	Main	Minor	Main	Minor
A	amo	—	amo	—	$FeH_2P_2O_7$	—
B	amo	—	amo	—	$NH_4FeP_2O_7$	—
C	amo	—	amo, X	$NH_4FeP_2O_7$	amo, X	$NH_4FeP_2O_7$
C′			amo	—		
D	amo, X	$Fe(PO_3)_3$	amo, X	$Fe(PO_3)_3$	amo, X	$FeH_2P_2O_7$
E			amo, X			
F	amo	—	amo	—	$NH_4FeP_2O_7$	—
G					amo	—

Note. amo, amorphous compound; X, compound characterized by three peaks at $2\theta = 20.00°$, $20.95°$, and $22.50°$ in XRD spectra.

observed in the 1.5 B, 1.5 C, and 1.5 E which were prepared in the presence of ammonium ions. On the other hand, small peaks corresponding to $FeH_2P_2O_7$ were observed in the 1.5 A and 1.5 D samples which were prepared in the absence of ammonium ions.

The 1.2 C sample was calcined at temperatures from 300–700°C. No clear peaks were observed in the samples calcined below 480°C. The unidentified compound was observed in the samples calcined at 500°C, though the crystallinity was low, and small peaks corresponding to $FePO_4$ were also observed. In the samples calcined at 550°C, $FePO_4$ was the sole phase observed, and no clear change was observed in the XRD spectra with a further elevation of calcination temperature.

The thermal transformations of the P/Fe = 1.0–1.2 samples are considered as amorphous compounds $\xrightarrow{500°C}$ unidentified phase $\xrightarrow{550°C}$ $FePO_4$ phase. The differential thermal analysis (DTA) and thermogravity (TG) studies indicated that these transformations are not accompanied with any clear change in both heat and mass. Probably, they are a kind of agglomeration or sintering.

The 1.7 C samples were also calcined at different temperatures. The sample calcined at 300°C showed peaks corresponding to $NH_4FeP_2O_7$. $1.5H_2O$. The sample calcined at 500°C showed clear peaks corresponding to $NH_4FeP_2O_7$, and the sample calcined at 700°C showed clear peaks corresponding to $FePO_4$. The DTA and TG studies indicated that a clear endothermic peak with a decrease in mass is observed at 450–550°C. This may be ascribed to the decomposition of $NH_4FeP_2O_7$. It is inferred that in the cases where iron phosphates are prepared in the presence of ammonium ions, the excess of phosphorus with respect to the stoichiometry of $FePO_4$, viz., P/Fe = 1.0, forms $NH_4FeP_2O_7 \cdot 1.5H_2O$. The transformations are $NH_4FeP_2O_7 \cdot 1.5H_2O \xrightarrow{450°C} NH_4FeP_2O_7 \xrightarrow{500-550°C} FePO_4 + NH_3 +$ polycondensed phosphates.

To check for the presence of ammonium ions in the samples, elementary analysis was performed. The 0.8 C, 1.0 C, and 1.2 C samples calcined at 500°C contain no nitrogen, while the 1.2 C calcined 400°C and the 1.6 C calcined at 500°C contain 0.7 and 2.3 wt% nitrogen, respectively. This indicates that 60% $NH_4FeP_2O_7$ remains in the 1.2 C sample after the calcination of 400°C and 70% $NH_4FeP_2O_7$ remains in the 1.6 C sample

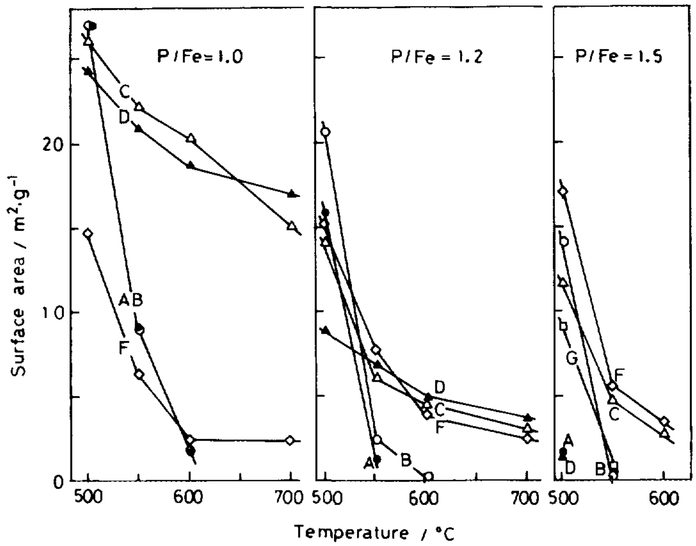

FIG. 1. Effects of the method of preparation, the P/Fe ratio, and the temperature of calcination on the surface area. Letters designate the preparation methods (see text).

after the calcination at 500°C. It is therefore concluded that almost all of $NH_4FeP_2O_7$ in the P/Fe = 1.0–1.2 samples is decomposed by the calcination at 500°C, while a large amount of $NH_4FeP_2O_7$ remains in the samples with a higher phosphorus content, i.e., P/Fe > 1.5, even after the calcination at 500°C.

The surface areas of the samples were measured by the BET method using nitrogen as adsorbate at − 196°C. The results are summarized in Fig. 1. The samples with a low phosphorus content, i.e., P/Fe < 1.2, calcined at a temperature below 500°C, possess a large surface area of 10–30 m^2/g. However, the surface area decreases with an increase in the phosphorus content and, moreover, falls sharply as the calcination temperature is raised. This may be induced by the thermal transformations of iron phosphates and by the formation of polycondensed phosphates having a low melting point. It should be noted that the surface areas of the samples with a high phosphorus content, i.e., P/Fe > 1.5, are very small when they were prepared in the absence of ammonium ions. Possibly, $NH_4FeP_2O_7$ which is formed in the presence of ammonium ions prevents, to a certain extent, the formation of the polycondensed phosphates with a low melting point.

The catalytic performances in the oxidative dehydrogenation of isobutyric acid were tested according to the procedures described previously (*1*). The typical results are shown in Fig. 2. Regardless of the variation in the method of preparation, the samples with a P/Fe ratio of less than unity are clearly less active than those with a P/Fe ratio of 1.0–1.2, though they possess a larger surface area. However, the activity falls as the P/Fe ratio is increased to more than unity and with increased calcination temperature, much as the surface area falls. Indeed, it seemed difficult to discover some clear correlation between activity and the method of preparation.

The selectivity to methacrylic acid was 75–80 mol% with the isobutyric acid conversion of up to 90% over the catalysts with a P/Fe ratio of 1.0 to 1.5, and it remained unchanged regardless of variations in the method of preparation. However, the samples with a P/Fe ratio of less than unity or more than 1.6 showed a clearly lower selectivity.

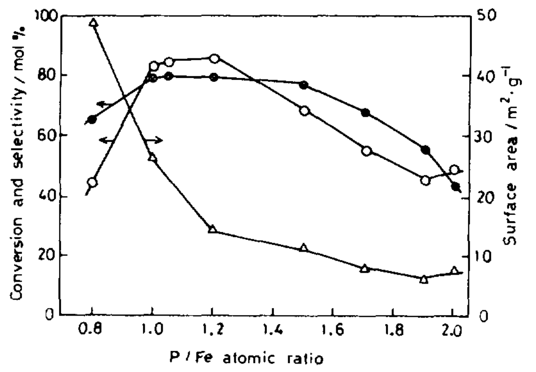

FIG. 2. Conversion of isobutyric acid, selectivity to methacrylic acid, and surface area obtained from the iron phosphates prepared by Method C and calcined at 500°C as a function of the P/Fe ratio. Reaction temperature, 380°C; contact time, 2.0 s; feed rates of isobutyric acid–oxygen–steam–nitrogen, 21.5–16.5–324–350 mmol/h. (○) conversion, (●) selectivity, and (△) surface area.

The highest activities are obtained from the iron phosphates with a P/Fe ratio of unity or a little higher than unity. This reveals that species with a P/Fe ratio of unity are responsible for catalytic action.

Taking into account the fact that iron phosphates with a P/Fe ratio of 1.0–1.2 are reduced in the presence of isobutyric acid but in the absence of oxygen, to $Fe_2P_2O_7$ (P/Fe = 1.0), whose XRD patterns were reported by Von Royen and Korinth (*6*), it is very likely that the active species with a P/Fe ratio of unity keep the P/Fe ratio unchanged at unity during the redox cycle, much as in the case of $(VO)_2P_2O_7$ catalysts where the P/V ratio is generally believed to be kept constant at unity during the redox cycle (*7*, *8*).

Besides $NH_4FeP_2O_7$ and $FeH_2P_2O_7$, no other compounds with a P/Fe ratio of more than unity were observed in the XRD spectra, except for a small amount of $Fe(PO_3)_3$ in the 1.0 D and 1.2 D samples. The 2.0 C and 2.0 E samples, which show clear peaks corresponding only to $NH_4FeP_2O_7$ in the XRD spectra, were much lower in both activity and selectivity to methacrylic acid than the samples with a P/Fe ratio of 1.0–1.2, and the 1.5 A and 1.5 D samples containing $FeH_2P_2O_7$ were very low in activity. These findings indicate that the compounds with a P/Fe ratio of more than unity scarcely affect catalytic action. Indeed, selectivity remains almost unchanged with variations in the P/Fe ratio from 1.0–1.5, though activity varies markedly due to variation in the surface area. However, with an increase in the P/Fe ratio to greater than 1.6, the selectivity falls. Possibly, this may be ascribed to the difference in the reaction conditions, because more severe conditions are required to achieve a fixed level of conversion of isobutyric acid due to a marked decrease in activity.

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M. AI*,[1]
E. MUNEYAMA†
A. KUNISHIGE†
K. OHDAN‡

**Research Laboratory of Resources Utilization*
Tokyo Institute of Technology
4259 Nagatsuta, Midori-ku
Yokohama 227, Japan

†UBE Scientific Analysis Laboratory, Inc.
1978-5 Kogushi
Ube 755, Japan

‡Ube Laboratory, UBE Industries, Ltd.
1978-5 Kogushi
Ube 755, Japan

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[1] To whom correspondence should be addressed.