Effects of valence states of iron in iron phosphates on the catalytic activity in oxidative dehydrogenation of isobutyric acid

Mamoru Ai [a,1], Etsuhiro Muneyama [b], Atsuhiro Kunishige [b] and Kyoji Ohdan [c]

[a] *Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan*
[b] *UBE Scientific Analysis Laboratory Inc., 1978-5 Kogushi, Ube 755, Japan*
[c] *Ube Laboratory, UBE Industries Ltd., 1978-5 Kogushi, Ube 755, Japan*

Received 8 July 1993; accepted 28 October 1993

Oxidative dehydrogenation of isobutyric acid to methacrylic acid was studied over an iron phosphate catalyst with a P/Fe atomic ratio of 1.2. The freshly prepared catalyst consisting of Fe^{3+} is reduced with isobutyric acid to iron(II) pyrophosphate [$Fe_2P_2O_7$] via a bluish black intermediate. Under the reaction conditions, the fresh catalyst is reduced gradually to the intermediate and the $Fe_2P_2O_7$ is also reoxidized to the intermediate. However, both the catalytic activity and the selectivity were scarcely affected with a large variation in the valence states of iron in the bulk of iron phosphate. On the other hand, the studies on the reaction in the absence of oxygen revealed that the reaction is promoted by the redox cycle of iron phosphate.

Keywords: Valence states of iron; iron phosphate; methacrylic acid; isobutyric acid

1. Introduction

Both iron phosphates and heteropoly compounds based on 12-molybdophosphoric acid [$H_3PMo_{12}O_{40}$] are known in patents to be effective as catalysts for the oxidative dehydrogenation of isobutyric acid to methacrylic acid:

$$CH_3{-}CH(CH_3){-}COOH + \tfrac{1}{2}O_2 \rightarrow CH_2{=}C(CH_3){-}COOH + H_2O\,.$$

It was also reported that vanadyl pyrophosphate [$(VO)_2P_2O_7$], which exhibits an excellent performance in the oxidation of *n*-butane to maleic anhydride, exhibits a performance comparable to that of heteropoly compounds in the reaction of isobutyric acid, too [1].

The catalytic action of the heteropoly compounds has been extensively studied

[1] To whom correspondence should be addressed.

[2–5]. However, as for the action of iron phosphates, there have been very few detailed studies [6–8].

The present study was undertaken to clarify the effects of variation in the valence states of iron on the catalytic performance, for a better understanding of the action of iron phosphates.

2. Experimental

An iron phosphate catalyst with a P/Fe atomic ratio of 1.2 was prepared with the following procedures. Iron nitrate [$Fe(NO_3)_3 \cdot 9H_2O$] (122 g, 0.3 mol) was dissolved in about 5 ℓ of water and dilute ammonia solution was added to precipitate iron hydroxide gel. The precipitate was filtered and the obtained wet gel was mixed with 41.5 g of 85% orthophosphoric acid [H_3PO_4] and 9.0 g of colloidal silica "Snowtex O" (Nissan Chem. Co.) containing 20% of silica. Then, the mixture was boiled slowly for 1–2 h yielding a slightly brownish white precipitate. Excess water was evaporated and the obtained paste-like compound was dried in an oven at 120°C for 6 h. The resulting solid was broken and sieved to a 7–20 mesh size. Finally, it was calcined in a stream of air for 4 h at 500°C, unless otherwise indicated.

XRD patterns of powder samples were studied using a Rigaku-Denki, model RAD-RB diffractometer with Cu K_α radiation. The spectra of XPS were recorded on a V.G. Scientific, Escalab-200X spectrometer with Mg K_α radiation. The surface areas were measured with the BET method using nitrogen as adsorbate at −196°C. The amounts of Fe^{2+} and Fe^{3+} in the bulk of catalyst were determined by the redox titration method [9].

The oxidative dehydrogenation of isobutyric acid was conducted with a continuous-flow system at atmospheric pressure as described in the previous study [1]. The feed rates of isobutyric acid, oxygen, water, and nitrogen were 21.5, 16.5, 324, and 350 mmol/h, respectively, unless otherwise indicated.

3. Results

3.1. PERFORMANCE OF CATALYST

The reaction was conducted at 400°C with different contact times. The main products were methacrylic acid, acetone, propylene, and carbon oxides [CO_x], as in the case of the reaction over heteropoly compounds and vanadyl pyrophosphate [1–5]. The results are summarized in table 1. The selectivity to methacrylic acid is 79–81 mol% up to the isobutyric acid conversion of about 90%. With a further increase in the conversion, the selectivity falls and, instead, that to CO_x increases.

Table 1
Catalytic performances of the iron phosphate catalyst [a]

Catalyst used (g)	Contact time (s)	IBA conversion (%)	Selectivity (mol%) to			
			MAA	acetone	propylene	CO_x
0.5	0.09	63.0	80.5	10.2	1.0	8.0
0.7	0.13	72.5	80.8	9.6	0.9	8.4
1.0	0.19	82.7	80.3	9.0	0.8	9.9
1.5	0.28	89.6	78.7	9.6	0.7	11.1
2.0	0.38	96.5	77.5	9.5	0.7	12.4
2.5	0.47	95.6	77.2	9.9	0.7	11.9

[a] Reaction temperature, 400°C. IBA, isobutyric acid; MAA, methacrylic acid.

3.2. EFFECTS OF THE REDUCTION OF CATALYST

The catalyst samples calcined at 500°C, which consist only of Fe^{3+}, were reduced in a stream of hydrogen. After 4 h on stream, 75, 90, and 96% of Fe^{3+} were reduced to Fe^{2+} at 400, and 450, and 500°C, respectively. The color of the catalyst before the reduction is slightly brownish white. With an increase in the extent of reduction, the bluish black color became deep, and after reaching its maximum at a $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio of about 0.5, it disappeared. The color of the samples with $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio of more than 0.9 is grayish white.

In the XRD spectra of the freshly calcined samples, $NH_4FeP_2O_7$ and an unknown phase with three peaks at $2\theta = 20.00$, 20.95, and 22.50° were observed, though the crystallinity was low. Clear peaks in the spectra obtained from the fully reduced samples were assigned to $Fe_2P_2O_7$ [10]. The spectra obtained from the bluish black intermediate samples showed two clear peaks at $2\theta = 19.96$ and 21.24°, but they are not yet identified.

Table 2 shows the effects of the temperatures of calcination and reduction on the valence states of iron in the bulk and the catalyst performance. With rising temperatures, longer contact times are required to achieve a fixed level of conversion; that is, the activity falls, because of the decrease in the surface area. However, the selectivity is scarcely affected with the variation in the temperatures. It should be noted that both the activity and selectivity are scarcely affected with a large variation in the valence states of iron in the bulk.

3.3. EFFECTS OF THE TIME-ON-STREAM

The gaseous reaction feed was passed over a 1.5 g portion of catalyst at 400°C (the contact time was 0.28 s). The variations in the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio, conversion and selectivity to methacrylic acid are shown in fig. 1. As the time-on-stream increased, the extent of catalyst reduction increases and the bluish black

Table 2
Effects of the temperatures of calcination and reduction [a]

Temp (°C)	Surface area (m^2/g)	$Fe^{2+}/(Fe^{2+}+Fe^{3+})$		Catalyst used (g)	Contact time (s)	IBA conv. (%)	Selectivity to MAA (mol%)
		before [b]	after [c]				
calcination							
400	25.3	0	0.28	1.5	0.28	89	79
				2.5	0.47	93	76
500	14.0	0	0.15	1.5	0.28	78	76
				2.5	0.47	92	79
600	5.1	0	0.03	2.5	0.47	50	72
700	3.0	0	0.02	2.5	0.47	36	75
				27.0	5.0	97	75
reduction							
500	8.0	0.92	0.73	2.5	0.47	86	80
				4.5	0.84	94	78
600	3,7	0.96	0.94	5.0	0.93	88	81
700	2.5	0.98	0.97	5.0	0.93	78	79
				10.0	1.85	95	78

[a] Reaction temperature, 400°C. IBA, isobutyric acid; MAA, methacrylic acid.
[b] Before, before the reaction.
[c] After, after the reaction for 1.5 h.

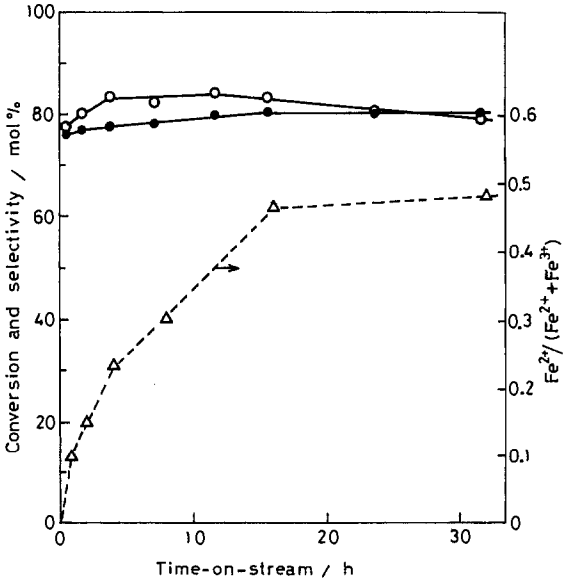

Fig. 1. Variation in the activity and selectivity and the $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio as a function of the time-on-stream. Catalyst: freshly calcined catalyst. (○) Conversion of isobutyric acid; (●) selectivity to methacrylic acid; (△) $Fe^{2+}/(Fe^{2+}+Fe^{3+})$.

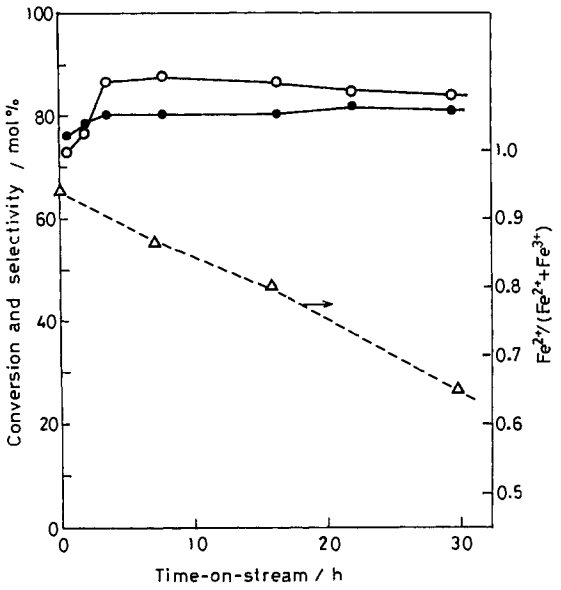

Fig. 2. Variation in the activity and selectivity and the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio as a function of the time-on-stream. Catalyst: reduced catalyst. (○) Conversion of isobutyric acid; (●) selectivity to methacrylic acid; (△) $Fe^{2+}/(Fe^{2+} + Fe^{3+})$.

color becomes deep. After 32 h on stream, the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio reaches 0.48. However, the variations in both the activity and selectivity are small.

Clear peaks at $2\theta = 19.96$ and 21.24° which are not identified, and small peaks corresponding to $Fe_2P_2O_7$ and $FePO_4$ were observed in the XRD spectra obtained from the samples used in the reaction for 16 h.

The reaction was also conducted over a 1.5 g portion of reduced catalyst with a $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio of 0.95. Fig. 2 shows the variations in the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio, conversion, and selectivity. As the time-on-stream increased, the catalyst is reoxidized gradually and the bluish black color becomes deep (the color of the reduced catalyst was grayish white). After 32 h on stream, the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio reaches 0.64. However, the variations in both the activity and selectivity are small.

3.4. REACTION IN THE ABSENCE OF OXYGEN

The reaction feed without oxygen was passed at 400°C over a 3 g portion of freshly calcined catalyst (the contact time was 0.56 s). The variations in the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio and one-pass yields of methacrylic acid, acetone, and propylene are shown in fig. 3. With increasing time-on-stream, the extent of catalyst reduction increases; the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio reaches 0.85 after 2 h on stream, and the yields of methacrylic acid and acetone decrease markedly, while that of propylene increases. After 2 h on stream, propylene was almost the sole product.

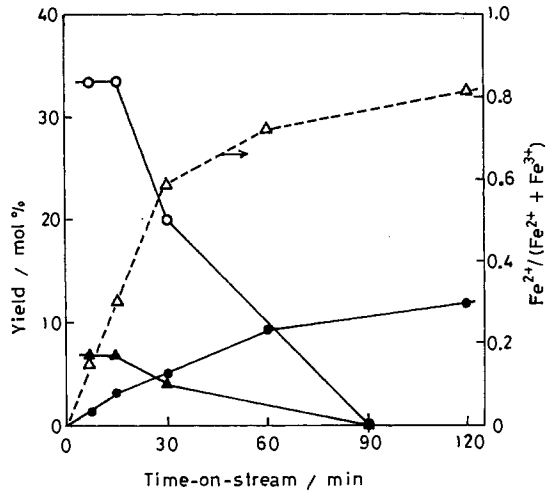

Fig. 3. Reaction of isobutyric acid in the absence of oxygen. Reaction temperature, 400°C; contact time, 0.56 s; feed rates of isobutyric acid/water/nitrogen = 21.5/324/350 mmol/h. (△) $Fe^{2+}/(Fe^{2+}+Fe^{3+})$. Yield: (○) methacrylic acid; (▲) acetone; (●) propylene.

Another series of experiments were performed using large amounts (15 g) of catalyst. During the first 1 h on stream, 98% of isobutyric acid fed was consumed and the one-pass yields of methacrylic acid, acetone, propylene, and CO_x were 63, 12, 15, and 9 mol%, respectively. The selectivities to methacrylic acid and acetone are close to those obtained in the presence of oxygen (tables 1 and 2), though the selectivity to propylene is markedly higher. After 8 h on stream, the consumption of isobutyric acid decreased to 35% and propylene was the sole product.

3.5. XPS MEASUREMENTS

The XPS measurements were performed with respect to the following four samples: sample 1, catalyst calcined at 600°C in air for 4 h; sample 2, the sample 1 used in the reaction at 400°C for 3 h; sample 3, catalyst calcined at 500°C for 4 h followed by reduction in a stream of a hydrogen–steam mixture (H_2O/H_2 molar ratio of 0.7) at 600°C for 4 h; sample 4, the sample 3 used in the reaction at 400°C for 3 h.

The binding energies for Fe $2p_{3/2}$ are listed in table 3, together with the $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratios of each sample. And the XPS spectra for Fe 2p are also shown in fig. 4. As shown in table 3 and fig. 4, the binding energies for Fe $2p_{3/2}$ with respect to the samples 1 and 3 are 713 and 711 eV, respectively. These values are believed to be the binding energies corresponding to Fe^{3+} and Fe^{2+}, respectively, in agreement with the results of previous studies [7,11]. Interestingly, the binding energy for sample 2 is the same as that for sample 1, and moreover that for sample 4 is the same as that for sample 3. This finding suggests that the valence states of iron on the surface are almost the same as those in the bulk.

Table 3
Comparison of the characters of iron phosphate catalysts before and after use in the reaction [a]

Catalyst sample	$Fe^{2+}/(Fe^{2+}+Fe^{3+})$	Fe $2p_{3/2}$ BE [b] (eV)
1 (before)	0	713
2 (after)	0.051	713
3 (before)	0.98	711
4 (after)	0.93	711

[a] At 400°C for 1.5 h.
[b] Binding energy.

4. Discussion

The freshly prepared iron phosphates consisting only of Fe^{3+} ions with a low crystallinity are reduced with hydrogen or isobutyric acid in the presence of water to form iron(II) pyrophosphate [$Fe_2P_2O_7$] via a bluish black intermediate with a $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio of around 0.5, which is characterized with two clear peaks in the XRD spectra at $2\theta = 19.96$ and 21.24°. Under the reaction conditions used in this study, the fresh iron phosphate is reduced gradually to the bluish black intermediate. On the other hand, the $Fe_2P_2O_7$ is also reoxidized to the same intermediate under the reaction conditions.

It seems therefore very likely that the species with a P/Fe ratio of unity in the bulk keep the P/Fe ratio at unity during the redox cycle, much as in the case of vanadyl pyrophosphate [$(VO)_2P_2O_7$] where the P/V ratio is generally believed to be kept constant at unity during the redox cycle [12,13].

It is important to note that both the activity and selectivity are scarcely affected with a large variation in the valence states of iron in the bulk (figs. 1 and 2 and table 2).

Unexpectedly, the XPS measurements performed for cooled catalyst samples indicate that the valence states of iron on the surface are the same as those in the bulk. This suggests that there is rapid equilibrium between surface and bulk. How-

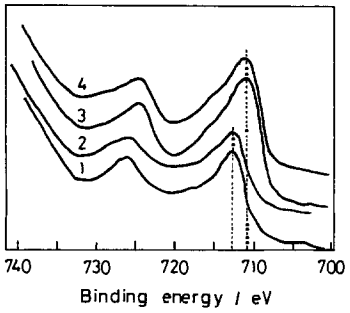

Fig. 4. XPS spectra of iron phosphate. Figures indicate the sample numbers shown in table 3.

ever, these results seem to be doubtful, because surface–bulk exchange reaction should take place during the time between the sample preparation and the XPS measurement; especially, during the cooldown. Therefore, further studies performed for catalyst samples at working states, if possible, are needed to resolve this problem.

On the other hand, the results obtained from the reaction performed in the absence of oxygen (fig. 3) reveal that methacrylic acid and acetone are formed by the reduction of iron phosphate with almost the same selectivities as those obtained in the presence of oxygen. This finding indicates that the reaction is promoted by redox cycle of iron phosphate catalyst as generally observed in many other mild-oxidation reactions over many catalysts containing vanadium oxide or molybdenum oxide.

At present, we cannot yet explain the reason why the activity and selectivity are scarcely affected with a large variation in the valence states of iron. Further studies are needed to know the reason.

References

[1] M. Ai, J. Catal. 98 (1986) 401.
[2] M. Akimoto, Y. Tsuchida, K. Sato and E. Echigoya, J. Catal. 72 (1981) 83.
[3] O. Watzenberger, G. Emig and D.T. Lynch, J. Catal. 124 (1990) 247.
[4] G.B. McGarvey and J.B. Moffat, J. Catal. 132 (1991) 100.
[5] M.J. Bartoli, Monceaux, E. Bordes, G. Hequet and P,. Courtine, Stud. Surf. Sci. Catal. 72 (1992) 81.
[6] C. Virely, O. Fabregue and M. Forissier, Bull. Soc. Chim. France (1988) 457.
[7] Y. Barbaux, M. Dekiouk, D. Le Maguer, L. Gengembre, D. Huchette and J. Grimblot, Appl. Catal. 90 (1992) 51.
[8] M. Dekiouk, N. Boisdron, S. Pietrzyk, Y. Barbaux and J. Grimblot, Appl. Catal. 90 (1992) 61.
[9] R.A.Jr. Day and A.L. Underwood, *Quantitative Analysis*, 4th Ed. (Prentice-Hall, Englewood-Cliffs, 1980).
[10] P. Von Royen and J. Korinth, Z. anorg. all. Chem. Band. 291 (1976) 227.
[11] A.V. Annapragada and E. Gulari, J. Catal. 123 (1990) 130.
[12] E. Bordes and P. Courtine, J. Catal. 57 (1976) 236.
[13] E. Bordes and P. Courtine, J. Chem. Soc. Chem. Commun. (1985) 294.
[14] F. Garbassi, J. Bart, R. Tassinari, G. Vlaic and P. Labarde, J. Catal. 98 (1986) 317.
[15] J. Haas, C. Plog, W. Maunz, K. Mittag, K. Gollmer and B. Kloppriers, in: *Proc. 9th Int. Congr. on Catalysis*, Vol. 4, Calgary 1988, eds. M.J. Phillips and M. Ternan (Chem. Inst. Canada, Ottawa, 1988) p. 1632.
[16] L.M. Cornaglia, C. Caspani and E.A. Lombardo, Appl. Catal. 74 (1991) 15.