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Formation of Pyruvaldehyde (2-Oxopropanal) by Oxidative Dehydrogenation of Hydroxyacetone

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Various mixed oxides were tested as catalysts for oxidative dehydrogenation of hydroxyacetone to form pyruvaldehyde (2-oxopropanal). The best results were obtained from an iron phosphate with a P/Fe atomic ratio of 1.05. The yield of pyruvaldehyde reached 88%. The next best results were obtained from a supported heteropoly acid ($H_3PMo_{12}O_{40}$). The other molybdenum- and vanadium-based oxide catalysts were not suitable. The effects of the composition and structure of iron phosphate and the effects of reaction variables on the formation of pyruvaldehyde were also studied.

Pyruvaldehyde (2-oxopropanal) is a raw material of various medical and agricultural chemicals. In industry, it is generally produced by a gas phase oxidation of 1,2-propanediol over silver-based catalysts at about 600 °C, like the oxidation of ethylene glycol to form glyoxal. However, the selectivity is still not high enough; about 65%. On the other hand, a large amount of hydroxyacetone (1-hydroxy-2-propanone) is formed as a by-product in the liquid-phase oxidation of 1,2-propanediol to form lactic acid, in the gas phase oxidation of 1,2-propanediol to form pyruvaldehyde, and in the production of acetone and phenol by the cumene-process.

As catalysts for partial oxidation reactions, iron phosphates are known to be clearly lower in activity than phosphates of vanadium and molybdenum, such as divanadium(IV) dioxide diphosphate [$(VO)_2P_2O_7$] and heteropoly compounds based on dodecamolybdophosphoric acid [$H_3PMo_{12}O_{40}$],[1] while they 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,[2] isobutyraldehyde,[3] and isobutyronitrile.[4]

$$R\text{–}CH_2\text{–}CHR'\text{–}X + 0.5O_2 \rightarrow R\text{–}CH{=}CR'\text{–}X + H_2O$$

Recently, it was found that iron phosphate catalysts show a uniquely high selectivity in the oxidative dehydrogenation of lactic acid to pyruvic acid[5] and also in that of glycolic acid to glyoxylic acid.[6]

$$CH_3\text{–}CH(OH)\text{–}COOH + 0.5O_2 \rightarrow CH_3\text{–}CO\text{–}COOH + H_2O$$

$$HOCH_2\text{–}COOH + 0.5O_2 \rightarrow OHC\text{–}COOH + H_2O$$

These findings led us to study the catalytic performance of iron phosphates in a similar reaction, that is, oxidative dehydrogenation of hydroxyacetone to form pyruvaldehyde.

$$CH_3\text{–}CO\text{–}CH_2OH + 0.5O_2 \rightarrow CH_3\text{–}CO\text{–}CHO + H_2O$$

The effects of the composition and structure of iron phosphate and the effects of reaction variables on the formation of pyruvaldehyde were also studied. Finally, the catalytic activity was discussed on the basis of the redox property of iron phosphate.

Experimental

1. Catalysts. Iron(III) phosphates with a P/Fe atomic ratio of 1.0, 1.05, and 1.15 were prepared according to the procedures described in the previous studies.[6] The calcination was performed in air at 400 °C for 12 h. The three catalysts obtained consist of tridymite-type $FePO_4$.[7] A V–P oxide catalyst with a P/V atomic ratio of 1.06 consisting of $(VO)_2P_2O_7$ was prepared according to a patent.[8] An $H_3PMo_{12}O_{40}$ catalyst was prepared by supporting $H_3PMo_{12}O_{40}$ on an equal weight of natural pumice between 10—20 in mesh size. The other mixed oxide catalysts used were the same as those used in previous studies.[9—12]

The amounts of Fe^{2+} and Fe^{3+} ions in the bulk of iron phosphates were determined by the redox titration method.[13] X-Ray powder diffraction (XRD) patterns were studied using a Shimadzu 6000 diffractometer with a Cu $K\alpha$ radiation.

2. Reaction Procedures. The vapor-phase contact oxidation of hydroxyacetone was done 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 catalyst was placed near the bottom of the reactor and porcelain cylinders, 3 mm long and 1.5 mm i.d./3.0 mm o.d., were placed both under and above the catalyst bed. Air was fed in from the top of the reactor with a feed rate of 200 ml min^{-1}; an aqueous solution containing 200 g of hydroxyacetone (purity of 90%) in 1000 ml was introduced into the preheating section of the reactor with a syringe pump. Unless indicated otherwise, the feed rates of hydroxyacetone, air, and water were 23.3, 500, and 491 mmol h^{-1}, respectively, and the amount of catalyst used was 10 g. The reaction temperature was in the range of 140 to 280 °C. The effluent gas from the reactor was led successively into four chilled scrubbers to recover the water soluble compounds. The products were analyzed by both GC and LC.

The conversion of hydroxyacetone was defined as: 100×[1−(moles of unreacted hydroxyacetone)/(moles of hydroxyacetone fed)]. The yields and selectivities were defined as:

yield of pyruvaldehyde = 100×(moles of pyruvaldehyde)/(moles of hydroxyacetone fed);

yield of CO_x = 33.3×(moles of CO_x)/(moles of hydroxyacetone fed);

selectivity = 100×(yield)/(conversion).

Results

1. Performances of Various Metal Oxide Catalysts. Since little information has been reported on the oxidative dehydrogenation from hydroxyacetone to pyruvaldehyde, it seems necessary to make a character sketch of the catalytic function for this reaction. Therefore, a series of experiments were done under the conditions described under Experimental using various kinds of single- and binary-oxide catalysts. In general, data were taken 1 to 2 h after the start of each run. The results are listed in Table 1.

The results may be summarized as follows:

(1) The best performance in the yield of pyruvaldehyde is obtained with the Fe–P oxide with P/Fe atomic ratio of 1.05. The yield reaches 88%.

(2) The next best catalyst is the Mo–P oxide consisting of $H_3PMo_{12}O_{40}$.

(3) The other Mo-based oxides are lower in both activity

Table 1. Activity of Metal Oxides for the Formation of Pyruvaldehyde

Catalyst Metal oxide	Atomic ratio	Reaction temp/°C	Conversion[a] %	Yield[b] %	Selectivity[c] %
None		160	13.0	4.7	36
		180	22.0	8.8	39
		200	32.0	20.0	63
Mo		160	23.0	10.5	46
		200	50.0	34.7	69
Mo–P[d]	12–1	160	61.7	51.5	84
		180	88.1	76.8	87
		200	98.6	85.8	87
Mo–V	9–1	160	30.0	15.2	51
		200	55.4	40.3	73
Mo–Sn	7–3	180	75.7	42.5	57
Mo–Fe	7–3	160	28.5	14.5	51
		200	69.0	48.1	69
Mo–Bi	5–5	200	45.3	20.0	44
V		200	59.3	39.8	67
V–P[e]	1–1	160	71.5	40.0	56
		200	90.0	61.5	68
V–Mo	8–2	160	61.9	41.6	67
V–W	9–1	180	74.0	54.4	74
V–Ti	5–5	160	64.3	44.8	70
Fe		160	46.2	30.5	66
		180	69.0	46.0	67
		200	95.2	65.6	69
Fe–P	9–1	180	98.5	68.2	69
	7–3	180	97.2	72.8	75
	4.9–5.1	160	80.0	70.8	88
		180	87.8	77.4	88
		200	96.6	88.0	91
Fe–Mo	9–1	200	98.7	74.1	75
	8–2	200	71.1	48.3	68
Fe- W	7–3	200	99.0	71.8	73
Fe–K	9–1	200	44.7	28.0	63
Sn–Mo	7–3	200	67.5	38.5	57
Bi		200	45.3	16.1	36
Co		200	43.0	24.6	57
Ni		200	38.5	21.6	56
Ni–P	5–5	200	43.4	16.7	39
Cr		200	40.0	21.0	52
Mn		200	43.4	21.5	50
Cu		200	44.7	28.4	63

a) Conversion of hydroxyacetone, b) yield of pyruvaldehyde, c) selectvity to pyruvaldehyde, d) $H_3PMo_{12}O_{40}$, e) $(VO)_2P_2O_7$.

and selectivity.

(4) The V-based oxides are lower in both activity and selectivity.

(5) Among the single oxides tested, the Fe oxide shows the highest activity.

(6) The activity of Fe oxide increases with a combination of an acidic oxide such as oxides of P, Mo, and W, while it falls sharply with addition of an oxide of K.

(7) The basic oxides, such as oxides of Sn, Bi, Co, Ni, Cr, Mn, and Cu are not active.

2. Performance of Iron Phosphate Catalyst. The study in the preceding section has revealed that the best results are obtained with the iron phosphate with a P/Fe atomic ratio of 1.05. Thus, the performance of iron phosphate was studied in more detail using this catalyst.

Several series of experiments were done at a temperature ranging from 160 to 200 °C using a 0.5 to 20 g portion of catalyst. Figure 1 shows the yields of pyruvaldehyde as a function of the conversion of hydroxyacetone. The selectivity is given from the slope through the origin.

The yield of pyruvaldehyde reaches 88% at the conversion of 96% (selectivity of 91%). The selectivity increases as the conversion of hydroxyacetone increases up to about 95%. This suggests that pyruvaldehyde is stable enough under the conditions used and that it is produced consecutively via certain intermediate compounds.

Besides pyruvaldehyde, the assigned products were lactic acid, pyruvic acid, acetic acid, and carbon oxides. The discrepancy between the amount of consumed hydroxyacetone and that of the sum of the assigned products was defined as unidentified products. The product distributions are shown in Table 2. The formation of pyruvic acid is below 1.5%. This finding suggests that consecutive oxidation of pyruvaldehyde to form pyruvic acid is very small. It is interesting to find that a small amount of lactic acid is obtained from hydroxyacetone. The amount of carbon oxides increases nearly in proportion to the conversion of hydroxyacetone. This finding suggests that carbon oxides are formed from hydroxyacetone in parallel with pyruvaldehyde, but not from consecutive decomposition of the produced pyruvaldehyde. The increase in the selectivity to pyrualdehyde as increasing the conversion of hydroxyacetone (Fig. 1) suggests that some of the unidentified compounds are the intermediates in the reaction from hydroxyacetone to pyruvaldehyde.

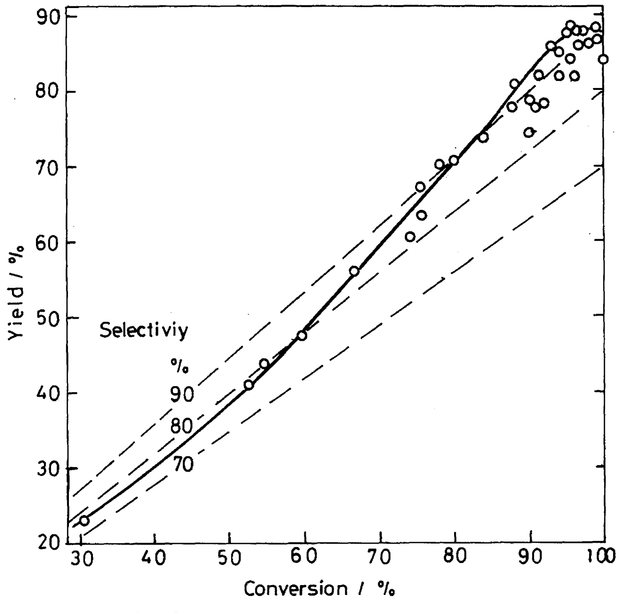

Fig. 1. Yield of pyruvaldehyde with the iron phosphate catalyst with a P/Fe atomic ratio of 1.05 as a function of the conversion of hydroxyacetone.

Table 2. Product Distributions Obtained from Iron Phosphate Catalyst[a)]

Conversion[b)]	Yield / %				
%	Pyruvald[c)]	Pyru. acid[d)]	Lactic acid	CO_x	UIP[e)]
30.0	23.4	0.5	0.8	1.3	4.5
54.6	44.0	1.0	1.0	2.1	6.5
66.6	56.2	1.2	2.3	2.7	4.2
73.9	60.5	1.0	2.0	2.7	7.7
80.0	70.8	1.2	1.9	3.0	4.1
87.8	77.4	1.3	1.9	3.7	3.5
91.4	82.0	1.1	2.0	3.7	2.6
96.7	87.0	1.2	2.3	4.0	2.2
98.1	88.2	1.5	2.3	3.7	2.4
99.0	88.0	1.5	2.6	4.0	2.9

a) P/Fe atomic ratio of 1.05, b) conversion of hydroxyacetone, c) pyruvaldehyde, d) pyruvic acid, e) unidentified product.

3. Stability of Catalytic Activity. Figure 2 shows the variation of conversions of hydroxyacetone as a function of the elapse of time. At a temperature above 200 °C, the catalytic activity is relatively stable. But at a lower temperature of 160 °C, the activity falls markedly. The deactivated catalysts were fully regenerated by a calcination at 400 °C in air. Possibly, at the low temperature the catalysts cannot oxidize and remove the by-products deposited on the surface.

4. Effects of P/Fe Composition. The effects of the

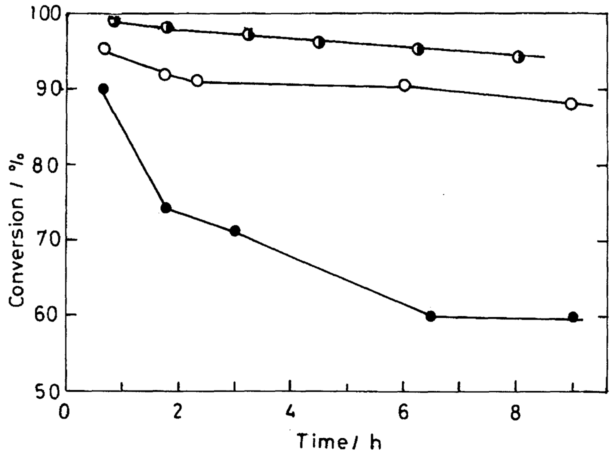

Fig. 2. Variation of the conversion of hdroxyacetone as a function of the elapse of time. Reaction conditions: (○) catalyst used of 2.5 g, 220 °C, (◑) catalyst used of 10 g, 200 °C, (●) catalyst used of 15 g, 160 °C.

P/Fe composition on the formation of pyruvaldehyde were studied using the following three catalysts; P/Fe = 1.0, 1.05, and 1.15. The results obtained with a 10 g portion of each catalyst are shown in Table 3.

It is concluded that the P/Fe = 1.05 catalyst is lower in the activity than those of the P/Fe = 1.00 and 1.15 catalysts, but it shows a higher selectivity than the latter.

5. Effects of Structure of Iron Phosphate. The effects of the difference in the structure of iron phosphate on the formation of pyruvaldehyde were studied using the following three catalysts with a P/Fe atomic ratio of 1.05:

(1) Iron phosphate freshly calcined at 400 °C and consisting of tridymite-type $FePO_4$.[7] The $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio was zero.

(2) Y-phase iron phosphate obtained by reoxidation of $Fe_2P_2O_7$; it is characterized with only one clear peak at $2\theta = 29.5$ in the XRD spectra and it was proposed by Millet and Vedrine[14] as $Fe_3(P_2O_7)_2$. However, we designated this compound as Y-phase,[15] because another compound had been assigned to be $Fe_3(P_2O_7)_2$.[16] The $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio was 0.31.

(3) $Fe_2P_2O_7$ obtained by full reduction of $FePO_4$.[17,18] The $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio was 0.92.

The results obtained with a 10 g portion of each catalyst are compared in Table 4. It is sure that the catalytic activity falls as the extent of reduction of iron ions increases, though no clear variation is observed in the selectivity to pyruvaldehyde.

The catalyst consisting of tridymite-type $FePO_4$ was transformed into amorphous phase and the $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio increased from zero to 0.13—0.17 with the use in the oxidation of hydroxyacetone for about 10 h. In the cases of the catalysts consisting of Y-phase and $Fe_2P_2O_7$, however, no changes in either the structure or the $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio were observed by the use in the reaction.

6. Effects of Reaction Variables. For understanding of the characteristics of the reaction, the effects of reaction variables such as temperature and concentrations of both oxygen and hydroxyacetone were studied using freshly calcined iron phosphate catalyst with a P/Fe atomic ratio of 1.05 consisting of tridymite-type $FePO_4$.

Table 3. Effects of P/Fe Composition on the Formation of Pyruvaldehyde

P/Fe Atomic ratio	Reaction temp/°C	Conversion %	Yield %	Selectivity %
1.00	140	95.4	70.3	74
	170	97.9	80.2	82
1.05	140	68.1	51.3	75
	160	80.0	70.8	88
	180	87.8	77.4	88
	200	96.7	87.0	90
1.15	140	81.9	62.1	76
	160	95.6	78.5	82
	180	97.8	79.8	82

Table 4. Effects of Structure of Iron Phosphate on the Formation of Pyruvaldehyde

Structure of iron phosphate	Reaction temp/°C	Conversion %	Yield %	Selectivity %
Tridymite-type	140	68.1	51.3	75
$FePO_4$	160	80.0	70.8	88
	180	87.8	77.4	88
	200	96.7	87.0	90
Y-phase	140	67.0	49.1	73
	160	83.0	70.0	84
	180	96.9	85.2	88
	200	99.1	85.9	87
$Fe_2P_2O_7$	140	39.2	28.9	74
	160	59.4	51.8	87
	180	77.3	69.8	90
	200	91.6	80.3	88
	220	98.3	87.0	89
	240	99.7	91.0	91

The initial rates of hydroxyacetone consumption were measured from several series of runs conducted at 140, 160, and 180 °C using small amounts of catalyst in the range from zero to 5 g. From the plot of the logarithm of the initial rates against the reciprocal of reaction temperature expressed by absolute temperature (Kelvin), the apparent activation energy was calculated to be 46 kJ (11 kcal) mol^{-1}. It should be noted that the activation energy is very low.

The effects of reaction temperature on the selectivity to pyruvaldehyde were also studied. Since the selectivity changes generally with a variation in the extent of conversion, the selectivity should be compared at the same level of conversion. The results obtained at a conversion in the range of 94 to 98%, are compared in Table 5. It is clear that the selectivity is independent of the temperature in a wide range of 180 to 280 °C.

To study the effects of oxygen concentration on the reaction rate, the reaction was done with a 10 g portion of catalyst at 140 °C under the conditions described in Experimental, while the volume concentration of oxygen in the feed was changed from 0.5 to 50%. The variations in the yield of pyruvaldehyde are shown in Fig. 3. The reaction order with respect to oxygen concentration was calculated to be about 0.3.

To study the effects of concentration of hydroxyacetone

Table 5. Effects of Reaction Temperature on the Selectivity to Pyruvaldehyde

Reaction temp/°C	Amount of catalyst/g	Conversion %	Yield %	Selectivity %
180	20	96.7	86.0	89
200	10	96.6	86.3	89
220	2.5	94.0	82.0	87
240	2.5	97.9	86.5	88
280	0.3	95.2	82.2	82

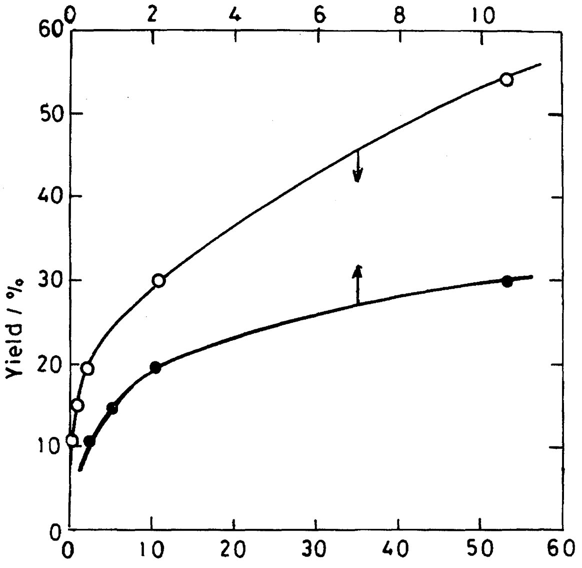

Fig. 3. Yield of pyruvaldehyse at 140 °C as a function of the volume concentration of oxygen in the feed gas.

on the reaction rate, another series of experiments were performed with a 1.0 g portion of catalyst at 140 °C under the conditions described in Experimental, while the concentration of hydroxyacetone in the feed gas was changed from 0.77 to 4.5%. The variation in the rate of pyruvaldehyde formation is shown in Fig. 4. The effect of hydroxyacetone concentration on the reaction rate is found to be very small.

Discussion

Iron phosphate catalyts had been known to be much lower in activity than Mo- or V-based mixed oxide catalysts in the cases of oxidation performed at a temperature above 300 °C,[1] whereas the results shown in Table 1 reveal that Fe-based oxide catalysts, notably iron phosphate catalysts, were markedly higher in the oxidation activity than Mo- or V-based mixed oxide catalysts at a low temperature in the range of 140 to 200 °C. Indeed, the oxidative dehydrogenation of hydroxyacetone to pyruvic aldehyde takes place rapidly enough even at a low temperature of 140 °C over the iron phosphate catalysts. This finding suggests that reduction and reoxidation of the iron phosphates can take place during the oxidation of hydroxyacetone even at the low temperature.

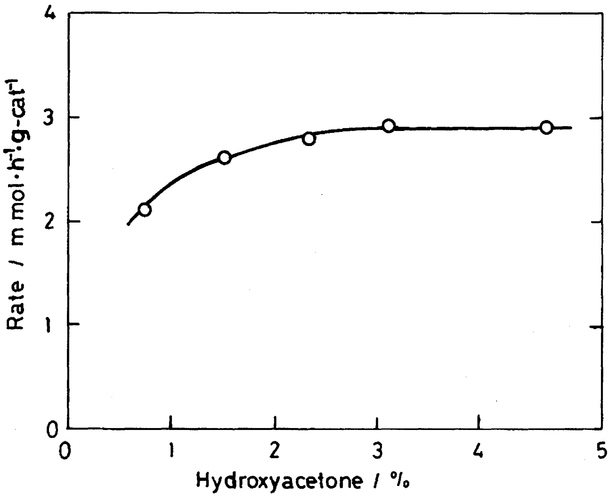

Fig. 4. Rate of pyruvaldehyde formation at 140 °C as a function of the concentration of hydroxyacetone in the feed.

Interestingly, it was actually found that the iron phosphate catalysts consisting of tridymite-type $FePO_4$ are reduced deeply by hydroxyacetone at 140 °C in the absence of oxygen to form an amorphous compound with a $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio of 0.7—0.8. The IR spectra of the amorphous compound were similar to those of crystalline $Fe_2P_2O_7$. These findings suggest that the amorphous compound consists of $Fe_2P_2O_7$. It is at least evident that the reducing function of hydroxyacetone is great and, as a result, the iron ions in the bulk of iron phosphate are reduced at a low temperature.

On the other hand, it was also found that a reduced and amorphous iron phosphate with a $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio of 0.8, which was obtained by the reduction of tridymite-type $FePO_4$ with hydroxylacetone in a nitrogen medium at 140 °C, was reoxidized by air even at at a low temperature of 140 °C to form another amorphous phase with a $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio of 0.15. The IR spectra of the amorphous compound were similar to those of crystalline quartz- and tridymite-tyope $FePO_4$. This suggests that the amorphous compound consists of $FePO_4$. It is at least evident that reoxidation of iron ions by air can take place in the bulk of iron phosphate even at a low temperature of 140 °C.

These results strongly support the conclusion that reduction and reoxidation of iron phosphate can take place even at low temperature during the oxidation of hydroxyacetone. This may be the reason why the iron phosphate catalysts show a high activity at low temperature.

As for the selectivity, an excellent selectivity to form pyruvldehyde is obtained only from the iron phosphate and $H_3PMo_{12}O_{40}$ catalysts. It is interesting to note that an excellent selectivity in the oxidative dehydrogenation of isobutyric acid to form methacrylic acid is also obtained only from these two catalysts.[1,2] It is still difficult to explain clearly the reason why, but it is at least evident that these two catalysts possess eminent functions in both redox and acid. Possibly, the balance between the redox and acidic properties plays an important role in the selectivity. We would like to ascribe a part of the excellent selectivity of iron phosphates to the absence of metal–oxygen double bond species, too.[6]

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