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Oxidation activity of iron phosphate and its characters

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Abstract

Iron phosphate catalysts possess a unique selectivity to oxidative dehydrogenation. Unlike ordinary catalysts consisting of molybdenum and/or vanadium, they have no double-bond oxygen species (M=O) that are considered to be responsible for the oxygen insertion function and, as a result, for the degradation by C–C bond fission. The defect of iron phosphate catalysts is a lack of oxidation activity. Addition of a very small amount of molybdenum into iron phosphate enhances markedly the oxidation activity without modifying the high selectivity originated from iron phosphate. The marked increase in the activity is ascribable to an increase in the reducibility of iron phosphate, because the reoxidizability of iron phosphate is high enough. It is proposed that the reaction over a Mo-doped iron phosphate is promoted by redox cycle of iron phosphate but not by that of molybdenum phosphate.

Keywords: Iron phosphate; Vanadium phosphate; Molybdenum phosphate; Oxidative dehydrogenation; Reducibility; Reoxidizability

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1. Functions required for selective oxidation

It is widely believed that oxidation reactions promoted over a metal oxide catalyst is performed by redox cycle of the metal oxide [1] and, as a result, the oxidation activity is dependent on the redox actions, that is, a pair of reducibility and reoxidizability of metal oxide. For example:

$$\text{M–O} + \text{RH} \rightarrow \text{M} + \text{ROH} \quad \text{(reduction of metal oxide)} \qquad (1)$$

$$\text{M} + 0.5\text{O}_2 \rightarrow \text{M–O} \quad \text{(reoxidation of reduced metal oxide)} \qquad (2)$$

In this regard, it has been proposed [2] that oxidation reaction can proceed selectively when the reducibility of metal oxide is moderate. This proposition is right still now. However, it is hard to understand satisfactorily the selectivity in an oxidation reaction only from the redox function of metal oxide.

We have proposed [3,4] that oxidation reaction is promoted by two different factors of a metal oxide catalyst: (1) activation of oxygen due to redox cycle of metal oxide; (2) activation of reactant molecule according to acid–base-type interaction between the reactant molecules and the metal oxide, that is, basic molecules are activated on the acidic sites of metal oxide, while acidic molecules are activated on the basic sites. Further, it has also been proposed [3,4] that oxidation reaction proceeds selectively when the reaction is governed mainly by the second factor. For example, when the first function (especially reducibility of metal oxide) is strong enough, the oxidation reaction can take place without requiring the second factor and it proceeds non-selectively. On the other

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hand, when the first function is not strong enough, only the reactant molecules which are activated on the metal oxide, can be oxidized and, as a result, the selectivity of reaction is decided by selective activation of reactant molecules on the metal oxide. Accordingly the first requirement for selective oxidation is the possession of reducibility with a moderate strength. This requirement is, however, far from sufficient in many cases.

The second requirement for a selective oxidation catalyst is the activation of reactant molecules without activating the aimed products. However, the requirement is not simple, because selective oxidation reactions are classified into four types in term of the acid–base properties of the reactant and the product. The acid–base properties required for metal oxide catalyst can be summarized in Table 1.

Most of the reactant molecules such as hydrocarbons, aldehydes, ketones, and alcohols are included among basic (electron-donating) molecules. Type 1 is termed “acid formation” and Type 2 is “base formation”.

The requirement for Type 1 is the possession of a strongly acidic property. Indeed, oxides or phosphates of molybdenum and vanadium are widely used as a main component of catalysts used in many selective oxidation reactions, because they possess an eminent function as a solid acid as well as a moderate function of redox cycle.

The formation of dienes and unsaturated aldehydes belongs to Type 2. The requirement for Type 2 is the possession of a moderate character in both acid and base. The presence of an acidic character is desirable in enhancing the activity, but when the acidic character is too high, the reaction cannot stop at the step of the basic product. The catalysts for Type 2 are generally obtained by a combination of acidic oxides and basic oxides. The practical examples are mixed oxides of Bi–Mo and Fe–Sb.

Table 1
Acid–base properties required for oxidation catalyst

Type of reaction	Properties of		Properties required for metal oxide
	Reactant	Product	
1	Base	Acid	Acidic
2	Base	Base	Moderate in both acid and base
3	Acid	Base	Basic
4	Acid	Acid	Acidic

The oxidation of acetic acid to formaldehyde and CO_2 is an example of Type 3. The necessary condition for this reaction is the possession of a sufficient basic property [3].

An example of Type 4 is oxidative hydrogenation of isobutyric acid to form methacrylic acid. Heteropoly acids such as $H_3PMo_{12}O_{40}$ are claimed to be effective. This means that the possession of a sufficient acidic character is required, much as in the case of Type 1.

2. Two types of oxidation reactions

Certainly, possession of both a redox function with a moderate strength and acid–base properties fit the aimed reaction is necessary as a catalyst for every selective oxidation. This is certainly one of the necessary conditions, but this is not always sufficient. Indeed, in many cases, we cannot still explain completely the selectivity even by both the redox and the acid–base properties, because there are other conditions required depending on the nature of reactants and products.

Recently, we have paid attention to the fact that there are two different kinds in oxidation reaction: (1) oxygen insertion reaction; (2) oxidative dehydrogenation [5,6]. In the case of oxides or phosphates of molybdenum and vanadium, they possess catalytic activity for the both oxidation reactions. However we cannot control the selectivity between the two reactions. In some cases they promote the oxygen insertion and in other cases they promote the oxidative dehydrogenation. The selectivity varies depending on the nature of the reactant and the product molecules. For example, Bi–Mo mixed oxide promotes the oxygen insertion into propylene to form acrolein, but it promotes the oxidative dehydrogenation of *n*-butene to form butadiene. Similarly, Mo–P heteropoly compounds (salts of $H_3PMo_{12}O_{40}$) promote the oxygen insertion into methacrolein to form methacrylic acid, while they promote the oxidative dehydrogenation of isobutyric acid to form methacrylic acid.

3. Iron phosphate

Recently we have been interested in iron phosphate ($FePO_4$), because it possesses both the redox

Table 2
Comparison of the catalytic activity for consumption of different reactants

Reactant	Consumption (%)	Temperature required[a] (°C)		
		Fe–P[b]	Mo–P[c]	V–P[d]
1-Butene	50	470	360	340
Methanol	40	480	320	300
Crotonaldehyde	98	420	330	350
Methacrylaldehyde	50	400	340	360
Isobutyric acid	90	400	260	280
Propionic acid	50	360	280	300

[a] Reaction temperature required for a fixed consumption of reactant.

[b] Iron phosphate with a P/Fe atomic ratio of 1.2.

[c] $H_3PMo_{12}O_{40}$ supported on an equal weight of natural pumice.

[d] Vanadium phosphate with a P/V atomic ratio of 1.06 consisting of $(VO)_2P_2O_7$.

and acidic properties as phosphates of molybdenum and vanadium [$H_3PMo12O_{40}$ and $(VO)_2P_2O_7$]. Iron phosphate seems therefore to be promising as a catalyst for selective oxidations belonging to Type 1 and Type 4. However, following conclusions were derived as the characteristics:

(1) Oxidation activity of iron phosphate is much lower than those of $H_3PMo_{12}O_{40}$ and $(VO)_2P_2O_7$ (Table 2).
(2) Selectivity of iron phosphate is much lower than those of $H_3PMo_{12}O_{40}$ and $(VO)_2P_2O_7$ in the cases of many partial oxidation reactions (Table 3) [6,7].
(3) Iron phosphate shows a relatively high selectivity in the oxidative dehydrogenation of reactants with a high reactivity. For example, reactant molecules in which the carbon atom at α-position of electron-attracting group (X = –COOH, –CHO, or CN) is tertiary (Table 4) [8–10]:

$$CH_3\text{–}CH(CH_3)\text{–}X + 0.5O_2 \rightarrow CH_2{=}CCH_3\text{–}X + H_2O \qquad (3)$$

(4) Iron phosphate cannot promote the oxygen insertion reactions, such as –CH_3 → –CHO → –COOH (Table 3) [6,7].
(5) Reduced iron phosphate (amorphous $Fe_2P_2O_7$), that was formed by reduction of $FePO_4$ at a low temperature of 120–220 °C, can be re-oxidized to $FePO_4$ with gaseous oxygen even at a low temperature of 100 °C [11]. This means that the reoxidizability of iron phosphate is very high.
(6) Iron phosphate catalysts show a unique selectivity in the following oxidative dehydrogenation reactions:
    (1) lactic acid to pyruvic acid [12]:

$$CH_3\text{–}CH(OH)\text{–}COOH + 0.5O_2 \rightarrow CH_3\text{–}CO\text{–}COOH + H_2O \qquad (4)$$

    (2) glycolic acid to glyoxylic acid [5]:

$$HOCH_2\text{–}COOH + 0.5O_2 \rightarrow OCH\text{–}COOH + H_2O \qquad (5)$$

    (3) hydroxyacetone to pyruvaldehyde [13]:

$$CH_3\text{–}CO\text{–}CH_2OH + 0.5O_2 \rightarrow CH_3\text{–}CO\text{–}CHO + H_2O \qquad (6)$$

Table 3
Comparison of the selectivity for different reactions

Reaction		Conversion (%)	Selectivities (mol%)		
Reactant	Product		Fe–P[a]	Mo–P[b]	V–P[c]
Propane	Acrylic acid	20	0	10	45
n-Butane	Maleic anhydride	30	0	32	60
Propene	Acrylic acid	80	2	18	32
n-Butene	Maleic anhydride	99	3	33	49
Isobutene	Methacrylic acid	99	1	26	25
Methacrylaldehyde	Methacrylic acid	60	29	50	53
Propionic acid	Acrylic acid	50	5	24	17

[a] Iron phosphate with a P/Fe atomic ratio of 1.2.

[b] $H_3PMo_{12}O_{40}$ supported on an equal weight of natural pumice.

[c] Vanadium phosphate with a P/V atomic ratio of 1.06 consisting of $(VO)_2P_2O_7$.

Table 4
Comparison of the selectivity for oxidative dehydrogenations

Reaction		Conversion (%)	Selectivities (mol%)		
Reactant	Product		Fe–P[a]	Mo–P[b]	V–P[c]
Isobutyric acid	Methacrylic acid	80	81	62	55
Isobutyraldehyde	Methacrylaldehyde	80	82		56
Isobutyronitrile	Methacrylonitrile	85	75		45

[a] Iron phosphate with a P/Fe atomic ratio of 1.2.
[b] $H_3PMo_{12}O_{40}$ supported on an equal weight of natural pumice.
[c] Vanadium phosphate with a P/V atomic ratio of 1.06 consisting of $(VO)_2P_2O_7$.

Table 5
Oxidative dehydrogenations promoted by iron phosphate

Reaction		Conversion (%)	Selectivities (mol%)		
Reactant	Product		Fe–P[a]	Mo–P[b]	V–P[c]
Lactic acid	Pyruvic acid	75	76		37
Glycolic acid	Glyoxylic acid	70	76	22	21
Hydroxy acetone	Pyruvaldehyde	98	78	88	68

[a] Iron phosphate with a P/Fe atomic ratio of 1.2.
[b] $H_3PMo_{12}O_{40}$ supported on an equal weight of natural pumice.
[c] Vanadium phosphate with a P/V atomic ratio of 1.06 consisting of $(VO)_2P_2O_7$.

The results are summarized in Table 5. The characteristics of these reactants are (1) possessing of a high reactivity and (2) susceptibility to decomposition by C–C bond fission.

4. Differences between iron phosphate and vanadium- or molybdenum-based compounds

It is interesting to note the finding that iron phosphate possesses catalytic activity only for oxidative dehydrogenation, but not for oxygen insertion reaction, unlike oxides or phosphates of molybdenum and vanadium. What is the difference between iron phosphate and molybdenum- or vanadium-based compounds?

We noticed the following difference. Oxides or phosphates of molybdenum and vanadium possess double-bond oxygen species (M=O). This M=O species have generally been believed to play a role in liberating oxygen species, which attack the reactant molecules:

$$\mathrm{M{=}O + HRH \rightarrow M + HROH} \quad \text{(oxygen insertion)} \qquad (7)$$

$$\mathrm{M{=}O + HRH \rightarrow M + R + H_2O} \quad \text{(oxidative dehydrogenation)} \qquad (8)$$

However, iron phosphate has no double-bond oxygen species. That is, it cannot liberate oxygen species. This may be the reason why iron phosphate cannot promote the oxygen insertion reaction. The mode of redox cycle of iron phosphate may therefore be different from that of molybdenum and vanadium compounds. The redox cycle is envisaged as follows [7,8]:

$$\mathrm{Fe^{3+} + R{-}H \rightarrow Fe^{2+} + H^+ + R} \quad \text{(reduction)} \qquad (9)$$

$$\mathrm{Fe^{2+} + H^+ + 0.25O_2 \rightarrow Fe^{3+} + 0.5H_2O} \quad \text{(re-oxidation)} \qquad (10)$$

where R is a compound with unsaturated bonding such as C=C or C=O.

It is considered that the main degradation reaction, which is occurred by C–C bond fission, is promoted by the oxygen insertion function of catalyst. Therefore, the oxygen insertion function is quite undesirable in the case of certain oxidative dehydrogenation reactions where the reactant molecules are susceptible to decompose by C–C bond fission.

5. Improvement of iron phosphate catalyst

Iron phosphate shows relatively high oxidation activity at a low temperature of 150 °C in cases where the reactant molecules are susceptible to react, because the re-oxidation of iron phosphate takes place even at a low temperature of 100 °C. However, iron phosphate shows a low catalytic activity for oxidation of molecules that are not susceptible to react. This may be due to a lack of the reducibility, that is, a lack of the function oxidizing the reactant molecules. This may be a defect of iron phosphate as an oxidation catalyst.

In order to improve the catalytic activity, various elements were added into iron phosphate [14]. It was found that the addition of a very small amount of molybdenum (Mo/Fe atomic ratio of 0.001–0.02) increases markedly both the catalytic activity and the selectivity in oxidative dehydrogenation. The level of oxidation activity becomes the same as those of phosphates of molybdenum and vanadium. The addition of a further amount of molybdenum clearly decreases the selectivity.

Owing to the enhancement in catalytic activity, the oxidation becomes possible for reactant molecules with a low reactivity that cannot be oxidized over neat iron phosphate catalysts. For example, the following oxidative dehydrogenation reactions can be performed over molybdenum-doped iron phosphate catalysts:

(1) ethylene glycol to glyoxal [15]:

$$\mathrm{HOCH_2{-}CH_2OH + O_2 \rightarrow HCO{-}CHO + 2H_2O} \qquad (11)$$

(2) propylene glycol to methylglyoxal (pyruvaldehyde) [16]:

$$\mathrm{HOCH_2{-}CHOH{-}CH_3 + O_2 \rightarrow HCO{-}CO{-}CH_3 + 2H_2O} \qquad (12)$$

The results are shown in Tables 6 and 7.

6. Role of molybdenum-doped into iron phosphate

A sample of neat iron phosphate and that of $\mathrm{Mo^{6+}}$-doped iron phosphate with a Mo/Fe atomic ratio of 0.01 were reduced in a stream of nitrogen containing 2.5 mol% of lactic acid for 12 h at a temperature ranging from 160 to 240 °C. The values of extent of reduction, that is, the $\mathrm{Fe^{2+}/(Fe^{2+}+Fe^{3+})}$ ratios, were measured for each sample using the redox titration method [17] (Fig. 1). It is clear that the $\mathrm{Mo^{6+}}$-doped iron phosphate is reduced much more extensively than the neat iron phosphate. This indicates that $\mathrm{Mo^{6+}}$ enhances markedly the reducibility of iron phosphate.

On the other hand, both the neat iron phosphate without doping and the $\mathrm{Mo^{6+}}$-doped iron phosphate with a Mo/Fe atomic ratio of 0.01 were reduced deeply in a stream of nitrogen containing 7.4 mol% of hydroxyacetone (acetol) at 200 °C for 36 h. About 80% of iron ions in the samples were reduced to $\mathrm{Fe^{2+}}$. Then, they were reoxidized in a stream of air for 12 h at a temperature ranging from 120 to 220 °C. The values of extent of reoxidation, that is, the differences

Table 6
Oxidative dehydrogenation of ethylene glycol to form glyoxal[a]

Catalyst	Atomic ratio	T_{50}[b] (°C)	S_{50}[c] (mol%)
Fe–P	1–1	300	10.5
Fe–P–Mo	1–1–0.04	260	40.0
Mo–P	1–0.08	250	12.0
V–P	1–1.06	270	19.2
Mo–Fe	1–0.4	250	8.2

[a] Feed rates: ethylene glycol–oxygen–water–nitrogen = 14.5–25–950–500 mmol/h; amount of catalyst used = 5 g.

[b] Reaction temperature required for the ethylene glycol conversion of 50%.

[c] Selectivity to glyoxal at an ethylene glycol conversion of 50%.

Table 7
Oxidative dehydrogenation of propylene glycol to form pyruvaldehyde[a]

Catalyst	Atomic ratio	T_{50}[b] (°C)	S_{50}[c] (mol%)
Fe–P	1–1	250	5.9
Fe–P–Mo	1–1–0.04	185	52.0
Mo–P	1–0.08	203	3.6
V–P	1–1.06	212	3.0
Mo–Fe	1–0.4	175	5.8
Mo–V	1–0.1	198	16.8

[a] Feed rates: propylene glycol–oxygen–water–nitrogen = 11.7–25–480–500 mmol/h; amount of catalyst used = 10 g.

[b] Reaction temperature required for the propylene glycol conversion of 50%.

[c] Selectivity to pyruvaldehyde at a propylene glycol conversion of 50%.

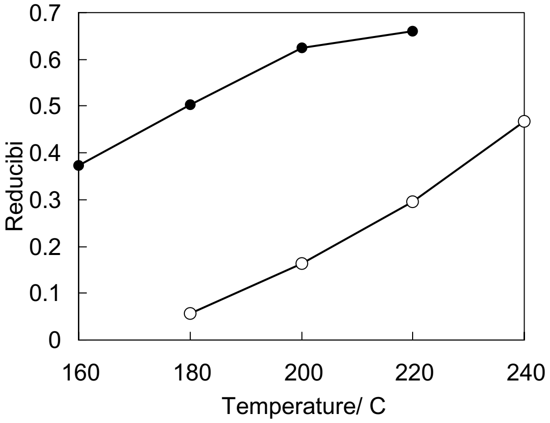

Fig. 1. Reducibility of iron phosphate catalysts. Reducibility: $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio. (○) original iron phosphate; (●) Mo^{6+}-doped iron phosphate (Mo/Fe = 0.01); (△) W^{6+}-doped iron phosphate (W/Fe = 0.01).

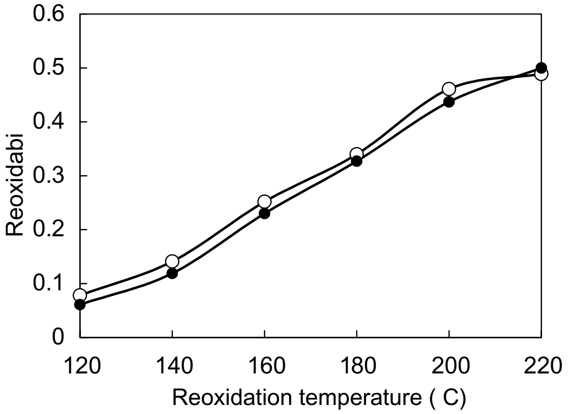

Fig. 2. Reoxidizability of iron phosphate catalysts. Reoxidizability: ($Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio before reoxidation-treatment) − ($Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio after reoxidation-treatment). (○) original iron phosphate; (●) Mo^{6+}-doped iron phosphate (Mo/Fe = 0.01).

in $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratios between before and after the reoxidation treatment, were measured for the two samples (Fig. 2). No difference is found in the extent of reoxidation between the two samples. This means that the reoxidability of catalyst is not affected by the doping of Mo^{6+}.

It is likely that the catalytic activity is controlled by the reducibility, because the reoxidizability of iron phosphate is high enough. This may be the reason why the activity increases as the reducibility increases. It is also proposed that the oxidation reaction is promoted by redox cycle of iron phosphate but not by that of molybdenum phosphate, because the amount of molybdenum is very small. This is the reason why a high selectivity originated from iron phosphate is preserved. However, when the amount of molybdenum is larger than about 4 mol%, the selectivity falls. A part of oxidation reaction may be performed by the redox cycle of molybdenum phosphate as well as by that of iron phosphate.

References

[1] P. Mars, D.W. Van Krevelen, Chem. Eng. Sci. Spec. Suppl. 3 (1954) 41.
[2] W.M.H. Sachtler, N.H. De Boer, in: W.M.H. Sachtler, G.C.A. Schuit, N.H. De Boer (Eds.), Proceedings of the Third International Congress on Catalysis, vol. 1, Amsterdam, North-Holland, Amsterdam, 1965, p. 252.
[3] M. Ai, J. Synth. Org. Chem. Jpn. 35 (1977) 201 (in Japanese).
[4] M. Ai, in: T. Seiyama, K. Tanabe (Eds.), Proceedings of the Seventh International Congress on Catalysis, 1980, Elsevier, Amsterdam, 1981, p. 1060.
[5] M. Ai, in: R.K. Grasselli, S.T. Oyama, A.M. Gaffney, J.E. Lyons (Eds.), Proceedings of the Third World Congress on Oxidation Catalysis, Stud. Surf. Sci. Catal. 110 (1997) 527.
[6] M. Ai, Catal. Today 52 (1999) 65.
[7] M. Ai, E. Muneyama, A. Kunishige, K. Ohdan, Bull. Chem. Soc. Jpn. 67 (1994) 551.
[8] M. Ai, E. Muneyama, A. Kunishige, K. Ohdan, Appl. Catal. A 109 (1994) 135.
[9] E. Muneyama, A. Kunishige, K. Ohdan, M. Ai, J. Mol. Catal. 89 (1994) 371.
[10] E. Muneyama, A. Kunishige, K. Ohdan, M. Ai, Appl. Catal. A 116 (1994) 165.
[11] M. Ai, Shokubai, Catal. Catal. 41 (1999) 477 (in Japanese).
[12] M. Ai, K. Ohdan, Appl. Catal. A 150 (1997) 13.
[13] M. Ai, K. Ohdan, Bull. Chem. Soc. Jpn. 72 (1999) 2143.
[14] M. Ai, Appl. Catal. A 234 (2002) 235.
[15] M. Ai, Bull. Chem. Soc. Jpn. 75 (2002) 375.
[16] M. Ai, Shokubai, Catal. Catal. 44 (2002) 474 (in Japanese).
[17] R.A.J. Day, A.L. Underwood, Quantitative Analysis, 4th ed., Prentice-Hall, Englewood Cliffs, NJ, 1980.