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Design of Selective Catalysts for Oxidative Dehydrogenation[1, 2]

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Abstract—Iron phosphate catalysts possess a unique selectivity to oxidative dehydrogenation. Unlike catalysts consisting of molybdenum and/or vanadium, they have no double-bond oxygen species (M=O), which 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 their lack of oxidation activity. The addition of a very small amount of molybdenum to iron phosphate markedly enhances the oxidation activity without modifying the high selectivity that originates from iron phosphate.

It is widely believed that contact oxidation is performed by a redox cycle of metal oxide catalysts [1] and, as a result, the oxidation activity is dependent on the redox action, that is, a pair of reducibility and reoxidizability of metal oxide. In this regard, it has been proposed [2] that an oxidation reaction can proceed selectively when the reducibility of metal oxide is intermediate. This proposition is right still now, while it is hard to understand satisfactorily the selectivity of catalysts in an oxidation reaction only by the redox properties.

It was proposed [3] that an oxidation reaction is promoted by two different factors of a catalyst; (1) activation of oxygen due to the redox action of a metal oxide and (2) activation of reactant molecules according to acid–base-type interaction between the reactant molecules and the catalyst, furthermore, that oxidation reaction proceeds selectively when the reaction is governed mainly by the second factor. For example, when the first function is strong enough, the oxidation reaction can take place without requiring the second factor and it proceeds nonselectively. Accordingly, the selectivity in an oxidation reaction is governed by the selective activation of reactant molecules on the surface of a catalyst, that is, by acid–base-type interaction between the reactant molecule and the catalyst.

Most reactant molecules such as hydrocarbons, aldehydes, ketones, and alcohols are basic (electron-donating) molecules. As a result, catalysts having strongly acidic properties are generally desirable for activation of these basic reactant molecules. Indeed, oxides or phosphates of molybdenum and vanadium are widely used as the main component of catalysts used in many selective oxidation reactions, because they possess eminent functions in both redox and acid.

Certainly, possession of both a moderate redox function and an acid–base function proper to the intended reaction is necessary as a catalyst for every selective oxidation. This is a necessary condition, but this is not always sufficient. Indeed, in many cases, we still cannot completely explain the selectivity even by both the redox and acid–base functions because other conditions are required depending on the nature of the reactants and products.

Recently, we have paid attention to the fact that there are two different kinds of oxidation reactions: (1) oxygen insertion reaction and (2) oxidative dehydrogenation [4, 5]. In the case of oxides or phosphates of molybdenum and vanadium, they possess catalytic activity for both oxidation reactions. However, we cannot control the selectivity between these two reactions. In some cases, they promote oxygen insertion, and in other cases they promote oxidative dehydrogenation. The selectivity varies depending on the nature of the reactant and the product molecules. For example, a Bi–Mo mixed oxide promotes oxygen insertion into propylene to form acrolein, but it promotes oxidative dehydrogenation of *n*-butene to form butadiene. Similarly, Mo–P heteropoly compounds promote oxygen insertion into methacrolein to form methacrylic acid, while they promote the oxidative dehydrogenation of isobutyric acid to form methacrylic acid.

Recently, we have been interested in iron phosphate ($FePO_4$) because it possesses both redox and acidic functions as molybdenum and vanadium phosphates [$H_3PMo_{12}O_{40}$ and $(VO)_2P_2O_7$]. Iron phosphate seems, therefore, to be promising as a catalyst for selective oxidation. However, the following conclusions were derived as the characteristics:

(1) The oxidation activity of iron phosphate is much lower than that of $H_3PMo_{12}O_{40}$, $(VO)_2P_2O_7$, and MoO_3- or V_2O_5-containing mixed oxides (Table 1).

(2) The selectivity of iron phosphate is much lower than that of $H_3PMo_{12}O_{40}$ and $(VO)_2P_2O_7$ in the case of many partial oxidation reactions (Table 2) [5, 6].

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[1] This article was submitted by the author in English.

[2] Paper presented at the 1st International Conference on Highly Organized Catalytic Systems (Chernogolovka, June 24–27, 2003).

Table 1. Comparison of the catalytic activity for oxidation of different reactants

Reactant	Conversion, %	Temperature, °C		
		Fe–P[a]	Mo–P[b]	V–P[c]
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] 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 2. 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

Note: The abbreviations are the same as those in Table 1.

Table 3. Comparison of the selectivity for oxidative dehydrogenations

Reaction		Conversion, %	Selectivity, 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

Note: The abbreviations are the same as those in Table 1.

Table 4. Oxidative dehydrogenations promoted by iron phosphate

Reaction		Conversion, %	Selectivity, 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
Hydroxyacetone	Pyruvaldehyde	98	78	88	68

Note: The abbreviations are the same as those in Table 1.

(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 the α-position of an electron-attracting group (X = –COOH, –CHO, or CN) is tertiary; $CH_3–CH(CH_3)–X + 0.5O_2 \longrightarrow CH_2=CCH_3–X + H_2O$ (Table 3) [7–9].

(4) Iron phosphate cannot promote oxygen insertion reactions such as $–CH_3 \longrightarrow –CHO \longrightarrow –COOH$ (Table 2) [5, 6].

Table 5. Oxidative dehydrogenation of ethylene glycol to form glyoxal. Feed rates: ethylene glycol–oxygen–water–nitrogen = 14.5–25–950–500 mmol/h, amount of catalyst used = 5 g

Catalyst	Atomic ratio	T_{50}, °C[a]	S_{50}, mol %[b]
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] Reaction temperature required for 50% ethylene glycol conversion.

[b] Selectivity to glyoxal at 50% ethylene glycol conversion.

Table 6. Oxidative dehydrogenation of propylene glycol to form pyruvaldehyde. Feed rates: propylene glycol–oxygen–water–nitrogen = 11.7–25–480–500 mmol/h, amount of catalyst used = 10 g

Catalyst	Atomic ratio	T_{50}, °C[a]	S_{50}, mol %[b]
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] Reaction temperature required for 50% propylene glycol conversion.

[b] Selectivity to pyruvaldehyde at 50% propylene glycol conversion.

(5) Reduced iron phosphate can be reoxidized with gaseous oxygen even at a low temperature of 100°C [10]. That is, the reoxidizability of iron phosphate is very high.

It was also found that iron phosphate catalysts show a unique selectivity in the following oxidative dehydrogenation reactions (Table 4):

(1) lactic acid to pyruvic acid [11]

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

(2) glycolic acid to glyoxylic acid [4]

$$HOCH_2\text{–}COOH + 0.5O_2 \longrightarrow OCH\text{–}COOH + H_2O;$$

(3) hydroxyacetone to pyruvaldehyde [12]

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

The characteristics of these reactants are (1) a high reactivity and (2) a susceptibility to decomposition by C–C bond fission.

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

The following difference was observed. Oxides or phosphates of molybdenum and vanadium possess double-bond oxygen species (M=O). It has been suggested that these M=O species play a role in liberating oxygen species, which attack the reactant molecules. 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 oxygen insertion. The mode of the redox cycle of iron phosphate may be different from that of molybdenum and vanadium compounds. The redox cycle is envisaged as follows [6, 7]:

$$Fe^{3+} + R\text{–}H \longrightarrow Fe^{2+}H^+ + R \text{ (reduction)},$$

$$Fe^{2+}H^+ + 0.25O_2 \longrightarrow Fe^{3+} + 0.5H_2O \text{ (reoxidation)}.$$

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

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

In order to improve the catalytic activity, various elements were added to iron phosphate [13]. It was found that the addition of a very small amount of molybdenum (Mo/Fe atomic ratio of 0.001 to 0.02) markedly increases both the catalytic activity and the selectivity in oxidative dehydrogenation. The level of oxidation activity becomes the same as that of molybdenum and vanadium phosphates. The addition of a further amount of molybdenum clearly decreases the selectivity.

Owing to this enhancement in catalytic activity, oxidation becomes possible for reactant molecules with a low reactivity, which 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 [14]

$$HOCH_2–CH_2OH + O_2 \longrightarrow HCO–CHO + 2H_2O;$$

(2) propylene glycol to methylglyoxal (pyruvaldehyde) [15]

$$HOCH_2–CHOH–CH_3 + O_2 \longrightarrow HCO–CO–CH_3 + 2H_2O.$$

The results are shown in Tables 5 and 6.

It is proposed that a very small amount of molybdenum added to iron phosphate plays a role in enhancing the reducibility of iron phosphate. Since the reoxidizability of iron phosphate is high enough, the catalytic activity markedly increases with an increase in the reducibility. It is also proposed that the redox cycle is performed by iron phosphate but not by molybdenum phosphate, because the amount of molybdenum is very small. This is the reason why the high selectivity originating from iron phosphate is preserved. However, when the amount of molybdenum is larger than about 4 mol %, the selectivity falls. Part of the oxidation reaction may be performed by the redox cycle of molybdenum phosphate, as well as by that of iron phosphate.

REFERENCES

1. Mars, P. and Van Krevelen, D.W., *Chem. Eng. Sci. Spec. Suppl.*, 1954, vol. 3, p. 41.
2. Sachtler, W.M.H. and De Boer, N.H., *Proc. 3rd Intern. Congr. Catal.*, Sachtler, W.M.H., Schuit, G.C.A., and De Boer, N.H., Eds., Amsterdam: North-Holland Publ. Co., 1965, vol. 1., p. 252.
3. Ai, M., *Proc. 7th Intern. Congr. Catal.*, Seiyama, T. and Tanabe, K., Eds., Elsevier, Amsterdam: 1981, p. 1060.
4. Ai, M., *Stud. Surf. Sci. Catal.*, 1997, vol. 110, p. 527.
5. Ai, M., *Catal Today*, 1999, vol. 52, p. 65.
6. Ai, M., Muneyama, E., Kunishige, A., *et al.*, *Bull. Chem. Soc. Jpn.*, 1994, vol. 67, p. 551.
7. Ai, M., Muneyama, E., Kunishige, A., *et al.*, *Appl. Catal. A. General*, 1994, vol. 109, p. 135.
8. Muneyama, E., Kunishige, A., Ohdan, K., *et al.*, *Mol. Catal.*, 1994, vol. 89, p. 371.
9. Muneyama, E., Kunishige, A., Ohdan, K., *et al.*, *Appl. Catal. A. General*, 1994, vol. 116, p. 165.
10. Ai, M., *Shokubai* (Catalysts & Catalysis) [in Japanese], 1999, vol. 41, no. 6, p. 477.
11. Ai, M. and Ohdan, K., *Appl. Catal. A. General*, 1997, vol. 150, p. 13.
12. Ai, M. and Ohdan, K., *Bull. Chem Soc. Jpn.*, 1999, vol. 72, p. 2143.
13. Ai, M., *Appl. Catal. A. General*, 2002, vol. 234, p. 235.
14. Ai, M., *Bull. Chem. Soc. Jpn.*, 2002, vol. 75, p. 375.
15. Ai, M., *Shokubai* (Catalysts & Catalysis) [in Japanese], 2002, vol. 44, no. 6, p. 474.