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Characteristics of iron phosphate as a catalyst for partial oxidation

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Abstract

Gas-phase contact oxidation of various organic compounds was carried out using an iron phosphate catalyst with a P/Fe atomic ratio of 1.2. The obtained selectivities were compared with those obtained with catalysts consisting of vanadium phosphate or molybdenum phosphate. The characteristics of iron phosphate as a selective oxidation catalyst were elucidated.

Keywords: Oxidative dehydrogenation; Iron phosphate; Pyruvic acid; Glyoxylic acid; Methacrylic acid; Methyl glyoxal; Citraconic anhydride

1. Introduction

It is generally accepted that possession of redox function which is related to oxidizing function, is required as a catalyst for any oxidation reactions [1]. However, from the redox function, it seems to be impossible to understand the selective function of catalyst in many partial oxidation reactions. Accordingly many attempts have been paid for understanding the selective function of oxidation catalyst.

In this context, an attempt has been made [2,3]. It is based on the following concept. Catalyst plays a role in activating selectively special reactant molecules due to the acid–base-type interaction between reactant molecules and catalyst surface. In addition, only the activated molecules have to be oxidized on the catalyst.

Based on the above-mentioned concept, acidic sites on catalyst activate selectively basic or electron-donating molecules such as olefin, alcohol, aldehyde, and ketone. However, acidic molecules such as carboxylic acid and anhydride are not activated, and as a result, not oxidized on acidic catalysts. On the other hand, basic catalysts activate selectively acidic reactants. That is, acidic compounds are selectively oxidized on the basic sites. It is therefore concluded that the possession of acidic properties is indispensable and that of basic properties is harmful for achieving a high selectivity in any acid-formation-type transformations.

In the case of catalysts used in partial oxidation reactions producing acidic products, the possession of a strongly acidic function is met in many cases by combinations of vanadium or molybdenum with phosphorus. Indeed, phosphates of vanadium and molybdenum, such as vanadyl pyrophosphate [$(VO)_2P_2O_7$] and heteropoly compounds based on dodecamolybdophosphoric acid [$H_3PMo_{12}O_{40}$], are widely used as practical catalysts for production of carboxylic acid and anhydride. Naturally, a great number of studies concerning the phosphates of vanadium and molybdenum, have already been reported [4–7].

On the other hand, iron phosphate was known to be effective for the oxidative dehydrogenation of isobutyric acid to methacrylic acid [8–13].

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In this paper, we focus our attention on the characteristic properties of iron phosphate as an oxidation catalyst, because this point seems to be not fully studied.

2. Experimental

The catalysts used in this study were the following three phosphates; the phosphorus/metal atomic ratios are chosen so as to be the values which are used most widely in practice and are considered to be optimum:

1. an iron phosphate with a P/Fe atomic ratio of 1.2 consisting of a mixture of quartz-type $FePO_4$ and tridymite-type $FePO_4$;
2. a vanadium phosphate with a P/V atomic ratio of 1.06 consisting of $(VO)_2P_2O_7$; and
3. a molybdenum phosphate consisting of $H_3PMo_{12}O_{40}$.

They were the same as those which were prepared in previous studies [14–16].

The vapor-phase contact oxidations were carried out with a conventional continuous-flow system. 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. Air or a mixture of oxygen and nitrogen was led in from the top of the reactor with a fixed rate in the range 140–200 ml/min (350–500 mmol/h). An aqueous solution containing a desired amount of reactant molecules was introduced into the preheating section of the reactor by a syringe pump. The feed rates of the reactant and water vapor were in the range 10–20 and 500–1000 mmol/h, respectively. The contact time was varied by changing the amount of catalyst used from 2 to 20 g while fixing the feed rates. The effluent gas from the reactor was led successively into four chilled scrubbers to recover the water-soluble compounds. The reaction products were analyzed by GCs and LCs.

3. Results

3.1. Comparison of catalytic performances

Oxidation activity of the iron phosphate was mush lower than that of the catalysts consisting of phosphate of either vanadium or molybdenum, though the thermal stability was relatively high. As a result, much severe reaction conditions were required to achieve a fixed level of conversion in the case of the reactions with the iron phosphate catalyst.

The selectivities obtained in several partial oxidation reactions [14,15] at the same levels of conversion are summarized in Table 1. It is clear that the selectivities of iron phosphate are much lower than those obtained from the vanadium phosphate and the molybdenum phosphate in all the reactions tested, except in the case of oxidative dehydrogenation of isobutyric acid to methacrylic acid.

3.2. Oxidative dehydrogenation of compounds similar to isobutyric acid

As mentioned above, the iron phosphate shows a good performance only in the oxidative hydrogenation of isobutyric acid. This led us to test the iron phosphate as a catalyst in the oxidation of other compounds

Table 1
Comparison of the selectivities for different oxidation reactions

Reaction		Conversion (%)	Selectivity (mol%)		
Reactant	Product		V–P	Mo–P	Fe–P
Propane	Acrylic acid	20	45	10	~0
n-Butane	Maleic anhydride	30	60	32	~0
Propene	Acrlic acid	80	32	18	2
n-Butene	Maleic anhydride	99	49	33	3
Isobutene	Methacryl ald+acid	99	25	26	1
Methacrolein	Methacrylic acid	80	53	50	29
Propionic acid	Acrylic acid	50	17	24	5
Isobutyric acid	Methacrylic acid	80	55	62	80

V–P: vanadium phosphate with a P/V atomic ratio of 1.06 consisting of $(VO)_2P_2O_7$; Mo–P: $H_3PMo_{12}O_{40}$ supported on an equal weight of natural pumice; Fe–P: iron phosphate with a P/Fe atomic ratio of 1.2.

Table 2
Performance of iron phosphate catalyst in the oxidation of compounds similar to isobutyric acid

Reaction		Conversion (%)	Selectivity (mol%)
Reactant	Product		
Isobutyric acid	Methacrylic acid	83	81
		96	77
Isobutyraldehyde	Methacriolein	75	80
Isobutyronitrile	Methacrylonitrile	75	70
		86	70

which are similar to isobutyric acid, that is, compounds in which the carbon atom at the α-position of an electron-attracting group (X) is tertiary [17,18]:

$$\mathrm{CH_3{-}CH(CH_3){-}X + 0.5\,O_2 \rightarrow CH_2{=}C(CH_3){-}X + H_2O}$$

where X=COOH, CHO, or CN. The performances are listed in Table 2.

These compounds are easily oxidized even over the iron phosphate catalyst and the selectivities to each reaction are high. It is therefore concluded that iron phosphate is effective as catalyst in oxidative dehydrogenation of compounds in which the carbon atom at the α-position of an electron-attracting group is tertiary.

3.3. *Oxidative dehydrogenation reactions promoted uniquely by iron phosphate*

Catalytic activity of the iron phosphate was also tested in the oxidative dehydrogenation of compounds which have an active hydrogen atom, such as lactic acid, glycolic acid, and hydroxy acetone [16,19,20]. It was found that the iron phosphate catalyst was active enough in the oxidation of these compounds even at a low temperature of about 200°C. The selectivities are shown in Table 3.

For the purpose of comparison, the same reactions were also performed over the vanadium phosphate catalyst consisting of vanadyl pyrophosphate; $(VO)_2P_2O_7$. The selectivities at the same level of conversions as those in the case of iron phosphate catalyst are shown in Table 3.

It is clear that iron phosphate catalyst shows a high selectivity in the oxidative dehydrogenation of these compounds. While the selectivities of vanadium phosphate are clearly lower. The main side reactions over the vanadium phosphate catalyst were oxidative C–C bond fission.

3.4. *Oxidative decarboxy condensation of pyruvic acid to citraconic anhydride*

Recently, it was also found that iron phosphate shows unique performance as a catalyst for another reaction, that is, oxidative decarboxy condensation of pyruvic acid to citraconic anhydride (mono-methyl maleic anhydride; $C_5H_4O_3$) [21]:

$$\mathrm{2CH_3{-}CO{-}COOH + 0.5\,O_2 \rightarrow C_5H_4O_3 + CO_2 + 2H_2O}$$

The performances of the iron phosphate are compared with those obtained with the vanadium phosphate in Table 4. It is clear that citraconic anhydride is

Table 3
Oxidative dehydrogenation reactions promoted uniquely by iron phosphate

Reactant	Product	Conversion (%)	$FePO_4$[a] Selectivity (mol%)	$(VO)_2P_2O_7$[b] Selectivity (mol%)
Lactic acid	Pyruvic acid	50	78	50
CH_3–CH(OH)–COOH	CH_3–CO–COOH	75	66	38
Glycolic acid	Glyoxylic acid	53	77	28
$HOCH_2$–COOH	OHC–COOH	70	76	21
Hydroxy acetone	Methyl glyoxal	98	78	42
CH_3–CO–CH_2OH	CH_3–CO–CHO			

[a] Iron phosphate.

[b] Vanadyl pyrophosphate.

Table 4
Performance in the formation of citraconic anhydride from pyruvic acid

Iron phosphate		Vanadium phosphate	
Conversion (%)	Selectivity (mol%)	Conversion (%)	Selectivity (mol%)
50	71	23	22
98	71	72	7

obtained selectively from pyruvic acid over the iron phosphate catalyst, while it is scarcely obtained over the vanadium phosphate catalyst.

4. Discussion

The characteristics of iron phosphate catalyst seem to be very unique. In the cases of the catalysts consisting of oxides or phosphates of vanadium and/or molybdenum, they possess two functions as partial oxidation catalysts. The one is the function promoting oxygen insertion reaction. The other is oxidative dehydrogenation.

Attention was drawn into the presence of metal–oxygen double bond species in catalyst in order to understand the difference in catalytic function between iron phosphate and phosphates of vanadium and molybdenum. It is generally known that oxides and phosphates of vanadium and molybdenum consist of metal–oxygen double bond species, while iron phosphate has no metal–oxygen double bond species. This led us to the following consideration. The catalyst possessing metal–oxygen double bond species can liberate oxygen atoms, while that without metal–oxygen double bond species cannot liberate any oxygen atoms. As a result, it is likely that the former has a function to insert an oxygen atom into the substrate, while the latter has no such function.

The redox cycle performed by the catalyst possessing metal–oxygen double bond species is generally considered as follows:

$$\mathrm{M{=}O + H{-}R{-}H \rightarrow M + HROH} \quad \text{[oxygen insertion]}$$

$$\mathrm{M{=}O + H{-}R{-}H \rightarrow M + R + H_2O} \quad \text{[dehydrogenation]}$$

$$\mathrm{M + 0.5\,O_2 \rightarrow M{=}O} \quad \text{[reoxidation]}$$

In the case of catalyst without metal–oxygen double bond species as iron phosphate, the redox cycles may be performed in a different manner as follows:

$$\mathrm{Fe^{3+} + RH \rightarrow Fe^{2+}H + R} \quad \text{[dehydrogenation]}$$

$$\mathrm{Fe^{2+}H + 0.25\,O_2 \rightarrow Fe^{3+} + 0.5\,H_2O} \quad \text{[reoxidation]}$$

It is very probable that the degrading side-reactions due to C–C bond fission is promoted by the oxygen insertion function. Therefore, the presence of the oxygen insertion function is harmful especially in the case where only oxidative dehydrogenation is desired. This may be the reason why iron phosphate which has no oxygen insertion function, promotes selectively the oxidative dehydrogenation reactions.

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