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Characteristics of Iron Phophate as a Catalyst for Partial Oxidation

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The catalytic performances of iron phosphate were compared with those obtained from the phosphates of vanadium and molybdenum in the partial oxidation of various compounds, such as 1-butene, crotonaldehyde, methacrylaldehyde, propinaldehyde, butyraldehyde, isobutyraldehyde, propionic acid, butyric acid, and isobutyric acid. Iron phosphate showed excellent performance for only the oxidative dehydrogenation of isobutyraldehyde and isobutyric acid to form methacrylaldehyde and methacrylic acid, respectively.

Both molybdenum phosphates based on 12-molybdophosphoric acid [$H_3PMo_{12}O_{40}$] and iron phosphates have been known in patents to be effective as catalysts for the oxidative dehydrogenation of isobutyric acid to methacrylic acid. Indeed, there have been a number of studies concerning the catalytic action of these phophates in the oxidative dehydrogenation of isobutyric acid.1—11) Recently, it was also reported that vanadium phosphates based on divanadium (IV) dioxide diphosphate [$V_2O_2(P_2O_7)$], which exhibit excellent performance in the oxidation of *n*-butane to maleic anhydride, exhibit a performance comparable to those obtained by molybdenum phsophate catalysts in the oxidative dehydrogenation of isobutyric acid.12,13)

It has been found in previous studies12—17) that the molybdenum phosphates and vanadium phosphates show similar catalytic performances under several mild oxidation reactions, and that this can be ascribed mainly to their strongly acidic character with a redox function.

In this study we attempted to compare the catalytic performances of iron phosphate with those of molybdenum and vanadium phosphated in different kinds of partial oxidation reactions and to clarify the characteristics of iron phosphate as a catalyst for partial oxidation.

Experimental

Catalyts. Iron phosphate with a P/Fe atomic ratio of 1.2 was prepared according to the following procedures. Iron(III) nitrate [$Fe(NO_3)_3\cdot 9H_2O$] (122 g, 0.3 mol) was dissolved in about 5 dm^3 of water, and a dilute ammonia solution was added to precipitate iron(III) 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. The mixture was then slowly boiled for 1 to 2 h, yielding a slightly brownish-white precipitate. Excess water was evaporated by means of a hot air current; the obtained paste-like compound was dried in an oven at 120 °C for 6 h. The resulting solid was broken up and sieved to a 7—20-mesh size. Finally, it was calcined in a stream of air at 500 °C for 4 h.

The iron phosphate catalyst had a BET surface area of 15 $m^2\,g^{-1}$. From an X-ray diffraction study it was found that the fresh catalyst, which is not used in the reaction, consists only of Fe^{3+} ions and contains both the $FePO_4$ phase and an unidentified phase characterized by three main peaks at $2\theta=20.00°$, 20.95°, and 22.50°, though the crystallinity is low.18) In the presence of water, the catalyst is reduced to iron(II) diphosphate [$Fe_2P_2O_7$] via another unidentified intermediate phase characterized by peaks at $2\theta=19.98°$ and 21.24° and having an $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio of around 0.5.

A vanadium phosphate with a P/V atomic ratio of 1.06 used in this study was the same as that which was prepared in a previous study19) form V_2O_5 and 98% orthosphosphoric acid by using a mixture of benzyl and isobutyl alcohols as a reducing solvent, according to patent,20) and was known from an X-ray diffraction study to consist of divanadium(IV) dioxide diphosphate.21)

Reaction Procedures. The vapor-phase contact oxidation of 1-butene, methanol, crotonaldehyde, methacrylaldehyde, propinaldehyde, butyraldehyde, isobutyraldehyde, propionic acid, butyric acid, and isobutyric acid was conducted with a continuous-flow system at atmospheric pressure. The reactor was made of a stainless-steel tube with a 50 cm long and 1.8 cm in i. d., mounted vertically and immersed in a lead bath. Air or a mixture of oxygen and nitrogen was fed in from the top of the reactor with liquid reactant samples and water being introduced into a preheating section of the reactor by two syringe pumps. The produced formaldehyde was analyzed by iodometry and the other compounds were analyzed by gas chromatographs: a 1-m column of molecular sieve 13X for CO; a 12-m column of propylenecarbonate for CO_2, propylene, and butenes; a 2-m column of PEG 20M at 100 °C for aldehydes, ketones, and alcohols; and a 1-m column of ST-1200+H_3PO_4 at 100 °C for acids. The detailed procedures were almost the same as those described in previous studies.12,14—17)

Results

1-Butene. The oxidation of 1-butene was conducted at 400 °C and a contact time of 8.5 s with feed rates of 1-butene, water, and air of 25, 324, and 350 $mmol\,h^{-1}$, respectively. The results are summarized in Table 1 together with the results obtained previously with a vanadium phosphate and a molybdenum phosphate. It was found that the iron phosphate is markedly less active and less selective than the phosphates of

Table 1. Oxidation of 1-Butene

Catalyst	Temp °C	O_2/C_4H_8 ratio	Contact time/s	Conv. %	Selectivity to MA/mol%	Ref.
P/Fe=1.2	400	0.7	8.5	8	4	
	400	10.	8.5	10	5	
	450	10.	8.5	23	4	
P/V=1.1	400	9.	2.0	99	45	19
$H_3PMo_{12}O_{40}$	350	9.	13.0	98	33	17

MA=maleic anhydride.

vanadium and molybdenum in the oxidation of 1-butene to maleic anhydride.

Methanol. The oxidation of methanol was conducted at temperatures from 400 to 480 °C and a contact time of 4.2 s with feed rates of methanol, oxygen, water, and nitrogen of 33.7, 20 or 70, 324, and 350 mmol h^{-1}, respectively. The results are summarized and compared with those obtained from a vanadium phosphate and a molybdenum phosphate catalyst in Table 2. The iron phosphate is markedly less active and less selective than the phosphates of vanadium and molybdenum in the oxidation of methanol to formaldehyde.

Crotonaldehyde. The oxidation of crotonaldehyde was conducted at temperatures from 340 to 420 °C and a contact time of 2.2 s with feed rates of crotonaldehyde, oxygen, water, and nitrogen of 24.9, 16.5 or 70, 324, and 350 mmol h^{-1}, respectively. The results were compared with those obtained previously from a vanadium phosphate and a molybdenum phosphate (Table 3). As shown in Table 3, crotonaldehyde has a relatively high reactivity and, as a result, a high conversion of more than 90% is achieved with the iron phosphate catalyst. However, the iron phosphate is less selective than the phosphates of vanadium and molybdenum in the oxidation of crotonaldehyde to furan or maleic anhydride.

Methacrylaldehyde. The oxidation of methacrylaldehyde was conducted at 400 or 425 °C and a contact time of 2.2 s with feed rates of methacrylaldehyde, oxygen, water, and nitrogen of 24.4, 20 or 70, 324, and 350 mmol h^{-1}, respectively. The results were compared with those obtained previously from a vanadium phosphate and a molybdenum phosphate. The iron phosphate is less active and less selective than the phosphates of vanadium and molybdenum in the oxidation of methacrylaldehyde to methacrylic acid (Table 4).

Propionaldehyde. The oxidation of propinaldehyde was conducted at 400 °C over the iron phosphate and a vanadium phosphate with a P/V atomic ratio of 1.06 with feed rates of propinaldehyde, oxygen, water, and nitrogen of 28.4, 20, 324, and 350 mmol h^{-1}, respectively. The results are summarized in Table 5. As for the oxidative dehydrogenation of propinaldehyde to acrylaldehyde, the iron phosphate is slightly more selective than the vanadium phosphate. However, regarding the oxidation of propinaldehyde to propionic acid, the iron phosphate is much less selective than the vanadium phosphate.

Butyraldehyde. The oxidation of butyraldehyde was conducted at 400 °C over the iron phosphate and a vanadium phosphate with a P/V atomic ratio of 1.06 with feed rates of butyraldehyde, oxygen, water, and nitrogen of 22.8, 20, 1060, and 350 mmol h^{-1}, respectively. The results are summarized in Table 6. Much as in the case of the oxidation of propinaldehyde, the iron phosphate is slightly more selective than the vanadium phosphate in the oxidative dehydrogenation of butyraldehyde to methacrylaldehyde, but it is less selective for the oxidation of butyraldehyde to butyric acid.

Propionic Acid. The oxidation of propinic acid was conducted at temperatures from 360 to 400 °C and a contact time of 2.2 s with feed rates of propionic acid, oxygen, water, and nitrogen of 27.6, 20, 324, and 350 mmol h^{-1}, respectively. The results are compared with those obtained previously from a vanadium phosphate and a molygdenum phosphate in Table 7.

The main products besides carbon oxides were acetaldehyde and acrylic acid, which were formed by C–C fission and oxidative dehydrogenation, respectively. It was found that iron phosphate is less selective than the phosphates of vanadium and molybdenum for the formation of acrylic acid.

Butyric Acid. The oxidation of butyric acid was conducted at 360 and 400 °C with feed rates of butyric acid, oxygen, water, and nitrogen of 23.2, 20, 324, and 350 mmol h^{-1}, respectively. The results are summarized in Table 8. The main products besides carbon oxides were propinaldehyde and acrylaldehyde, which were formed by the C–C bond fission of butyric acid and by oxidative dehydrogenation of the produced propionaldehyde, respectively. The formation of crotonic acid, which is formed by the oxidative dehydrogenation of butyric acid, is very small.

Isobutyraldehyde. The oxidation of isobutyric acid was conducted at 400 °C over the iron phosphate and a vanadium phosphate with a P/V atomic ratio of 1.06 with feed rated of isobutyraldehyde, oxygen, water, and nitrogen of 22.5, 20, 1060, and 350 mmol h^{-1}, respectively. The results are summarized in Table 9. The main products besides carbon oxides were methacrylaldehyde and methacrylic acid. It was found that

Table 2. Oxidation of Methanol

Catalyst	Temp °C	O_2/CH_3OH ratio	Contact time/s	Conv. %	Selectivity to HCHO/mol%	Ref.
P/Fe=1.2	400	0.4	4.2	9	67	
	400	1.4	4.2	9	45	
	450	0.4	4.2	31	28	
	480	0.4	4.2	40	30	
P/V=1.1 (on TiO_2)	340	2.0	10.0	98	95	22
$H_3PMo_{12}O_{40}$	365	8.0	1.0	55	90	23

Table 3. Oxidation of Crotonaldehyde

Catalyst	Temp °C	O_2/C_4H_6O ratio	Contact time/s	Conv. %	Select.(mol%) to furan	MA	Ref.
P/Fe=1.2	400	0.67	2.2	38	10	12	
	450	0.67	2.2	58	10	9	
	340	2.8	2.2	73	18	23	
	380	2.8	2.2	89	17	19	
	420	2.8	2.2	97	15	14	
P/V=1.6	400	22.	1.0	92	9	40	24
$H_3PMo_{12}O_{40}$	330	4.0	1.7	95	40	14	25

MA=maleic anhydride.

Table 4. Oxidation of Methacrylaldehyde

Catalyst	Temp °C	O_2/C_4H_6O ratio	Contact time/s	Conv. %	Selectivity to MAA/mol%	Ref.
P/Fe=1.2	400	0.8	2.2	10	53	
	425	0.8	2.2	15	48	
	400	2.9	2.2	50	29	
P/V=1.06	340	9.2	7.0	48	53	16
	370	9.2	7.0	80	40	
$H_3PMo_{12}O_{40}$	320	9.0	7.0	57	50	16
	360	9.0	7.0	80	40	

MAA=methacrylic acid.

Table 5. Oxidation of Propionaldehyde

Catalyst	Temp °C	O_2/C_3H_6O ratio	Contact time/s	Conv. %	Selectivity (mol%) to Acrylald.	Acids
P/Fe=1.2	400	0.7	2.1	31	24	20
	400	0.7	8.2	40	18	20
P/V=1.06	400	0.7	2.1	30	17	48

Acrylald.=acrylaldehyde; Acids=propionic acid and small amounts of acrylic acid and acetic acid.

iron phosphate is more selective for the formation of methacrylaldehyde and, as a result, is much less selective for the formation of methacrylic acid than vanadium phosphate.

Isobutyric Acid. The oxidation of isobutyric acid was conducted at 400 °C with feed rates of isobutyric acid, oxygen, water, and nitrogen of 21.5, 16.5, 324, and 350 $\mathrm{mmol\,h^{-1}}$, respectively. The results are compared with those obtained previously from a vanadium phosphate and a molybdenum phosphate in Table 10. It was found that the iron phosphate is more selective for the formation of mehtacrylic acid than the phosphates of vanadium and molybdenum.

Discussion

The partial oxidation reactions tested in this study contain different types of oxidation, such as oxidative dehydeogenetion, oxygen insertion, and oxidative C–C bond fission. The last reaction is usually an undesirable side-reaction.

Table 6. Oxidation of Butyraldehyde

Catalyst	Temp	O_2/C_4H_8O	Contact	Conv.	Selectivity (mol%) to	
	°C	ratio	time/s	%	Crotonald.	Acids
P/Fe=1.2	400	0.9	1.0	32	10	27
	400	0.9	2.1	44	5	18
P/V=1.06	400	0.9	2.1	42	4	51

Crotonald. = crotonaldehyde; Acids = butyric acid and small amounts of acetic acid and acrylic acid.

Table 7. Oxidation of Propionic Acid

Catalyst	Temp	$O_2/C_3H_6O_2$	Contact	Conv.	Select. (mol%)		Ref.
	°C	ratio	time/s	%	to AcH	AA	
P/Fe=1.2	360	0.75	2.2	62	71	5.2	
	380	0.75	2.2	67	74	6.9	
	400	0.75	2.2	73	75	11.0	
P/V=1.06	300	10.	12.	50	43	24.	17
$H_3PMo_{12}O_{40}$	280	10.	12.	50	43	24.	17

AcH = acetaldehyde; AA = acrylic acid.

Table 8. Oxidation of Butyric Acid

Catalyst	Temp	$O_2/C_4H_8O_2$	Contact	Conv.	Select. (mol%) to		
	°C	ratio	time/s	%	C acid	P ald	Acryl
P/Fe=1.2	400	0.9	0	0	—	—	—
	360	0.9	0.5	32	0	35	6
	400	0.9	0.5	50	0	21	9
	400	0.9	2.2	52	3	22	12

C acid = crotonic acid; P ald = propionaldehyde; Acryl = acrylaldehyde.

Table 9. Oxidation of Isobutyraldehyde

Catalyst	Temp	O_2/C_4H_8O	Contact	Conv.	Select. (mol%) to	
	°C	ratio	time/s	%	M acry	Acids
P/Fe=1.2	400	0.9	0	29	50	3
	400	0.9	0.35	64	76	2
	400	0.9	0.6	72	79	1
	400	0.9	1.0	82	82	1
P/V=1.06	400	0.9	0.2	34	58	15
	400	0.9	0.6	55	67	16
	400	0.9	1.0	59	68	18
	400	0.9	2.1	72	56	25

M acry = methacrylaldehyde; Acids = methacrylic acid and acetic acid.

Table 10. Oxidation of Isobutyric Acid

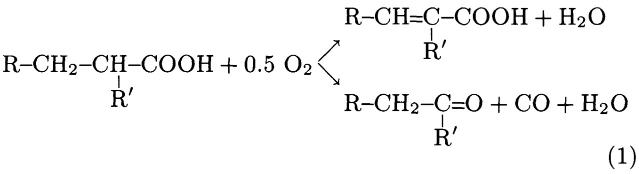
Catalyst	Temp	$O_2/C_4H_8O_2$	Contact	Conv.	Select. (mol%) to				Ref.
	°C	ratio	time/s	%	MAA	Aceton	C_3H_6	CO_x	
P/Fe=1.2	400	0.8	0.1	63	80.5	10.2	1.0	8.0	
	400	0.8	0.2	83	80.3	9.0	0.9	9.9	
	400	0.8	0.4	97	77.5	9.5	0.7	12.4	
P/V=1.06	265	14.5	4.6	60	55.0	19.0	24.0	8.0	12
	275	14.5	4.6	80	50.0	16.0	25.0	11.0	
$H_3PMo_{10}V_2O_{40}$	245	14.5	2.5	60	60.0	29.0	3.0	11.0	12
	260	14.5	2.5	80	60.0	25.0	2.0	12.0	

MAA = methacrylic acid; C_3H_6 = propylene.

It is clear from the results that iron phosphate is markedly less active as an oxidation catalyst than the phosphates of vanadium and molybdenum. It was also found that iron phosphate shows excellent performance only for the oxidative dehydeogenetion of isobutyraldehyde and isobutyric acid.

Interestingly, iron phosphate cannot promote oxygen insertion reactions, such as the formation of maleic anhydride from 1-butene and crotonaldehyde and the formation of a carboxyl group [–COOH] from an aldehyde group [–CHO], unlike in the case of the phosphates of vanadium and molybdenum. Accordingly, iron phosphate is undesirable as a catalyst for the production of carboxylic acids from aldehydes. However, when the oxidative dehydrogenetion and oxidation of aldehyde to acid take place in competition with each other, for example, the oxidations of propionaldehyde, butyraldehyde, and isobutyraldehyde, the iron phosphate suppresses the formation of acid.

In the oxidation of carboxylic acids, oxidative dehydeogenation and oxidative C–C bond fission take place in competition with each other:



$$\mathrm{R{-}CH_2{-}\underset{\displaystyle R'}{\underset{|}{CH}}{-}COOH + 0.5\ O_2} \begin{cases} \nearrow\ \mathrm{R{-}CH{=}\underset{\displaystyle R'}{\underset{|}{C}}{-}COOH + H_2O} \\ \searrow\ \mathrm{R{-}CH_2{-}\underset{\displaystyle R'}{\underset{|}{C}}{=}O + CO + H_2O} \end{cases} \qquad (1)$$

The results lead to the following general trend. When the carbon atom at the α-position is secondary, such as isobutyric acid, the reaction proceeds mainly to oxidative dehydrogenation, while when the carbon atom is primary, such as propionic acid or butyric acid, the reaction proceeds mainly to the C–C bond fission. This may be ascribed to the difference in the reactivity of the hydrogen attached to the carbon atom at the α-position; that is, the hydrogen attached to the secondary carbon atom is more reactive than that attached to the primary carbon atom.

Iron phosphate is more favorable than the phosphates of vanadium and molybdenum for the oxidative dehydrogenation of isobutyric acid, but is less favorable for the oxidative dehydrogenation of propionic aicd and scarcely promotes the oxidative dehydeogenation of butyric acid.

It should be noted that iron phosphate is also not desirable as a catalyst for the oxidative dehydeogenation of 1-butene, methanol, crotonaldehyde, propinaldehyde, and butyraldehyde. The results seem to indicate that the hydrogen-abstracting function of iron phosphate is so weak that the side-reactions, such as C–C bond fission, take place in preference to oxidative dehydrogenation, when the reactivity of hydrogen in the reactant is low.

On the other hand, all of the catalysts studied in this study (phosphates of iron, vanadium, and molybdenum) are typical of solid acids, though they surely possess a certain extent of basic and redox functions, too.

From a study on the catalytic activities for dehydration of 2-propanol.[26] it was found that iron phosphate is markedly lower in the acidic property than the phosphates of vanadium and molybdenum. However, further information is needed to fully explain the difference in the selectivities between iron phosphate and the phosphates of vanadium and molybdenum from the viewpoint of the acidic and basic properties of catalysts.

As for the redox of metal ions, both divanadium dioxide diphosphate [$V_2O_2(P_2O_7)$] and molybdophosphoric acid [$H_3PMo_{12}O_{40}$] possess oxygen atoms which are not linked with the phosphorus atom, that is, double-bond oxygen [V=O and Mo=O]. Therefore, these phosphates can liberate an oxygen atom by the reduction of metal ions. However, in the case of iron phosphate, it may be impossible to liberate an oxygen atom by the reduction of Fe^{3+} ions to Fe^{2+} ions, because the oxygen atoms in iron phosphate are linked with at least one phosphrous atom. This may be the reason why the iron phosphate cannot promote oxygen insertion reactions, unlike the phosphates of vanadium and molybdenum.

As for oxidative dehydrogenetion over the phosphates of vanadium and molybdenum, it is generally believed that hydrogen is abstracted by lattice oxygen:

$$\mathrm{R{-}H + O \rightarrow R + OH.} \qquad (2)$$

On the other hand, in the case of iron phosphate, which cannot liberate an oxygen atom, we are led to the following consideration. The reduction of Fe^{3+} ions in iron phosphate is performed by the abstraction of a hydrogen atom from a hydrogen-donating compound [R–H], such as isobutyric acid or isobutyraldehyde, to form a hydrogen phosphate:

$$\mathrm{Fe^{3+} + R{-}H \rightarrow Fe^{2+}H^{+} + R.} \qquad (3)$$

Fe^{3+} ions are regenerated by the reoxidation of hydrogen phosphate by molecular oxygen,

$$\mathrm{Fe^{2+}H^{+} + 0.25\ O_2 \rightarrow Fe^{3+} + 0.5\ H_2O.} \qquad (4)$$

This may be the reason why iron phosphate promotes only oxidative dehydrogenations, but not oxygen insertion reactions.

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