Comparison of catalytic properties for partial oxidation between heteropolyacids and phosphates of vanadium and iron

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Abstract

The catalytic properties of heteropoly compounds such as 12-molybdophosphoric acid [$H_3PMo_{12}O_{40}$] and its derivatives for gas-phase partial oxidation of various organic compounds were compared with those of phosphates of transition metals such as vanadium phosphate and iron phosphate. The characteristics of catalysts consisting of heteropoly compounds were elucidated.

Keywords: Molybdophosphoric acid; Vanadyl pyrophosphate; Iron phosphate: Oxidation of alkanes; Oxidation of alkenes: Oxidation of methacrolein; Oxidation of acrolein; Oxidation of crotonaldehyde: Oxidation of isobutyric acid; Oxidation of propionic acid; Oxidation of methanol; Formation of furan

1. Introduction

It is well known that catalysts consisting of heteropolyacids such as 12-molybdophosphoric acid [$H_3PMo_{12}O_{40}$] and its derivatives show an excellent selectivity in the gas-phase oxidation of methacrolein to methacrylic acid. Indeed, this process is commercialized. The same catalysts are also known to show a high selectivity in the oxidative dehydrogenation of isobutyric acid to methacrylic acid. For this reason, the majority of studies on partial oxidation using heteropoly compounds as solid catalysts was limited to these two reactions.

It has been reported that $H_3PMo_{12}O_{40}$ and its derivatives are eminent as an oxidizing agent as well as an acid [1–3]. The possession of these two properties should be responsible for achieving a high selectivity in the formation of methacrylic acid.

It should be noted that the possession of both acidic and redox properties is not unique to the compounds consisting of $H_3PMo_{12}O_{40}$ and its derivatives. For example, phosphates of transition metals and mixed oxides containing molybdenum and/or vanadium also possess these two properties.

It is doubtless that the possession of redox properties is indispensable to a catalyst for promoting any partial oxidation reactions [4]. It has been proposed that in the case of partial oxidations, only the reactants which are activated on the surface of catalyst, should be selectively oxidized [5–7]. For

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example, acidic sites on catalysts play a role in activating only basic reactants due to an acid–base type interaction between the reactant and catalyst. That is, only basic reactants are oxidized on acidic catalysts. On the other hand, acidic reactants are not activated on acidic catalysts. As a result, they are not oxidized and liberated from the catalyst surface to the gas phase. The possession of acidic properties is indispensable for achieving a high selectivity in any 'acid-formation-type partial-oxidations' [8–10]. Further, it should also be noted that the redox property is closely related to the basic property of the catalyst [5–7,11,12]. It is therefore concluded that the possession of two sorts of sites with opposite properties, that is, both acidic and basic sites, is required for catalysts for 'acid-formation-type partial-oxidations'.

According to the above-mentioned view, it seems to be interesting and useful to clarify and generalize the characteristic properties of compounds consisting of $H_3PMo_{12}O_{40}$ and its derivatives as catalysts for various kinds of partial oxidation reactions. We attempted in this study to compare the catalytic properties for many kinds of oxidation reactions between catalysts consisting of heteropoly compounds and those consisting of metal phosphates, basing on the experimental results obtained recently in our laboratory.

As the metal phosphates, vanadium phosphate and iron phosphate were chosen. These two compounds are also known to possess acidic and redox properties [13,14]. Vanadium phosphate consisting of vanadyl pyrophosphate $((VO)_2P_2O_7)$ (abbreviated hereafter to V-P) is known as an excellent catalyst for production of maleic anhydride in the oxidation of n-butane. This process is also commercialized. Iron phosphates with a P/Fe atomic ratio of near to unity (abbreviated hereafter to $FePO_4$) are known as good catalysts for oxidative dehydrogenation of isobutyric acid to methacrylic acid as well as catalysts consisting of heteropoly compounds. Recently, it is also reported that $FePO_4$ catalysts are effective for oxidative dehydrogenation of many other compounds in which the carbon atom at the α-position of an electron-attracting group such as –COOH, –CHO, and –CN is tertiary [15].

2. Experimental

2.1. Catalysts

A $FePO_4$ catalyst with a P/Fe atomic ratio of 1.2 was prepared according to the procedures described in previous reports [14–16].

V-P catalysts with a P/V atomic ratio of 1.0 to 1.05 were prepared according to patented procedures [17].

Catalysts based on $H_3PMo_{12}O_{40}$ and its derivatives were prepared according to the procedures described in previous reports [18–22].

As an index of the acidic properties of the catalysts, the rates of an acid-catalyzed reaction, that is, dehydration of 2-propanol, are shown in Table 1.

Table 1
Rates of 2-propanol dehydration at 180°C

Catalyst	$(mol/g \cdot h) \times 10^4$
$FePO_4$	7.1
V-P	106
$H_5PV_2Mo_{10}O_{40}$	280

Concentration of 2-propanol in air = 7.7 mol%.

2.2. Reaction procedures

The vapor-phase contact oxidations were conducted 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 containing a fixed concentration of reactant molecules is introduced from the top of the reactor. 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 GC's.
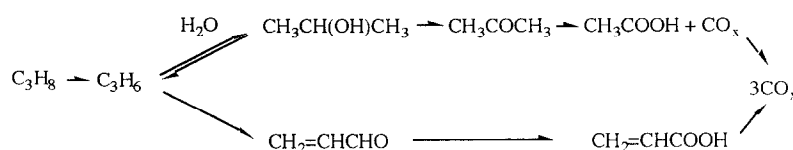
3. Results and discussion

3.1. Oxidation of alkane

3.1.1. Propane

The oxidation of propane was conducted using both a V-P catalyst with a P/V atomic ratio of 1.0 and another V-P catalyst containing $H_3PMo_{12}O_{40}$ with a Mo/P/V ratio of 0.2/1.02/1 [23]. The feed rates of propane, water vapor, and oxygen were 7.8, 130, and 260 ml/min, respectively, and the contact time was 9 s. The main products were acrylic acid, acetic acid and carbon oxides. The results are summarized in Table 2.

By analogy with the oxidation of n-butane [13], the oxidation of propane proceeds through the following reaction pathway [24]:

$$C_3H_8 \rightleftharpoons C_3H_6 \overset{H_2O}{\underset{}{\rightleftharpoons}} CH_3CH(OH)CH_3 \rightarrow CH_3COCH_3 \rightarrow CH_3COOH + CO_x \searrow 3CO_x$$

$$C_3H_6 \searrow CH_2{=}CHCHO \longrightarrow CH_2{=}CHCOOH \nearrow$$

Since the hydration of propene to 2-propanol is considered to be in equilibrium during the reaction, the selectivity is decided by the competition between the allylic oxidation of propene and the oxidative dehydrogenation of 2-propanol followed by the C–C bond fission. The yield of acrylic acid from propane is much lower than that of maleic anhydride in the oxidation of n-butane [13], because

Table 2
Oxidation of propane

Catalyst	Temp. (°C)	Conversion (%)	Selectivity (mol%) to		
			AA	AcOH	CO_x
V-P	375	23	29	22	49
	380	34	22	15	63
	390	39	20	13	67
V-P + $H_3PMo_{12}O_{40}$	355	22	15	45	40
	365	34	11	40	49
	375	40	10	35	55

AA = acrylic acid, AcOH = acetic acid.

Table 3
Oxidation of n-butane

Catalyst	Temp.	C.t.	Conv.	Selectivity (mol%) to			
	(°C)	(s)	(%)	MA	AA	AcOH	CO_x
V-P	360	9.7	11.0	72	0	3	25
	420	9.7	33.8	60	0	2	38
	455	9.7	70.1	54	0	3	43
	475	9.7	99.0	50	0	3	47
$H_3PMo_{12}O_{40}$	360	5.7	3.1	33	12	20	35
$Cs_2HPMo_{12}O_{40}$	360	5.7	11.1	30	14	18	28
$H_5PMo_{10}V_2O_{40}$	360	5.7	15.3	32	15	19	33
$Cs_2H_3PMo_{10}V_2O_{40}$	360	5.7	20.7	35	19	17	29
$H_3PMo_{12}O_{40} + 2VO^{2+}$	360	5.7	27.0	23	7	14	56
$Bi_3PMo_{12}O_{40} + 2VO^{2+}$	360	5.7	31.8	32	14	17	37

MA = maleic anhydride, AA = acrylic acid, AcOH = acetic acid, c.t. = contact time, conv. = n-butane conversion.

(i) suppression of the dehydrogenation of 2-propanol is more difficult than that of 2-butanol, and (ii) acrylic acid is much less stable than maleic anhydride.

It is found that the incorporation of $H_3PMo_{12}O_{40}$ into the V-P increases both the oxidation activity and the selectivity to acetic acid, while it decreases the selectivity to acrylic acid. This finding suggests that the incorporated $H_3PMo_{12}O_{40}$ plays a role in promoting the oxidative dehydrogenation of 2-propanol to acetone in preference to the allylic oxidation of propene.

3.1.2. n-butane

Oxidation of n-butane was done at an n-butane concentration of 2.2 mol% in air using both the V-P catalyst and catalysts consisting of $H_3PMo_{12}O_{40}$ and its derivatives [13,19,20]. The results are summarized in Table 3. $H_3PMo_{12}O_{40}$ by itself is scarcely active for oxidation of n-butane. The addition of certain cations, notably Cs^+ and Bi^{3+}, and of vanadium compounds, e.g., VO^{2+}, enhances markedly the activity. It should be noted that the oxidation activities of catalysts consisting of heteropoly compounds are of comparative order with that of the V-P catalyst. As for the selectivity to maleic anhydride, the heteropoly compounds are lower than the V-P catalyst. The selectivities to acrylic acid and acetic acid obtained over the heteropoly compounds are clearly higher than those obtained over the V-P catalyst.

Maleic anhydride is considered to be formed by the following consecutive steps: butane $\rightarrow$ butene $\rightarrow$ butadiene $\rightarrow$ furan $\rightarrow$ maleic anhydride [13]. On the other hand, acrylic acid and acetic acid are formed by another consecutive route: butane $\rightarrow$ butene $\leftrightarrow$ 2-butanol $\rightarrow$ methyl ethyl ketone $\rightarrow$ acrylic acid and acetic acid [13]. The hydration of butene to 2-butanol may be in equilibrium during the reaction. Much as the case of oxidation of propane, the selectivity should be decided by the competition between the allylic oxidation of butene and the oxidative dehydrogenation of 2-butanol. It is concluded that the dehydrogenation of 2-butanol is promoted more largely over the heteropoly compounds.

3.2. Alkene

3.2.1. Propene

Oxidation of propene was done over the catalysts consisting of heteropoly compounds and the V-P catalyst [25,26]. The concentrations of propene and water were 2.5 and 16.2 mol% in air, respectively.

Table 4
Oxidation of propene

Catalyst	Temp.	C.t.	Conv.	Selectivity (mol%) to			
	(°C)	(s)	(%)	AA	Acrol	AcOH	CO_x
V-P	420	1.0	39	30	14	24	32
	440	1.0	55	32	8	13	47
	460	1.0	82	32	5	8	55
$H_3PMo_{12}O_{40}$	370	4.5	51	22	4	34	40
$Cs_2HPMo_{12}O_{40}$	360	4.5	76	20	6	42	32
$Cs_3H_2PMo_{10}V_2O_{40}$	360	4.4	41	20	10	38	32

AA = acrylic acid, acrol = acrolein, AcOH = acetic acid, c.t. = contact time, conv. = propene conversion.

The results are shown in Table 4. The heteropoly compounds show a lower selectivity to acrylic acid and a higher selectivity to acetic acid than the V-P catalyst, though the oxidation activities are of the same order of magnitude.

Acrylic acid may be formed from acrolein which is formed by the allylic oxidation of propene. On the other hand, acetic acid is formed by C–C bond fission of acetone which is formed by oxididative dehydrogenation of 2-propanol. Much as the case of oxidation of propane, the oxidative dehydrogenation of 2-propanol is promoted more largely on the catalysts consisting of heteropoly compounds.

3.2.2. 1-butene

The catalytic performances obtained in the oxidation of 1-butene were summarized in Table 5 [13,15,26]. The main products were maleic anhydride, acetic acid, and carbon oxides. The $FePO_4$ catalyst is much less active and selective than the $H_3PMo_{12}O_{40}$ and V-P catalysts. The activities of the $H_3PMo_{12}O_{40}$ and V-P catalysts are of the same order of magnitude. However, the $H_3PMo_{12}O_{40}$ catalyst shows a lower selectivity to maleic anhydride and a higher selectivity to acetic acid than the V-P catalyst. Maleic anhydride is considered to be formed by the following consecutive steps [27,28]: butene → butadiene → furan → maleic anhydride. On the other hand, acetic acid is formed by C–C bond fission of methyl ethyl ketone as follows: butene ↔ 2-butanol → methyl ethyl ketone → acetic acid + carbon oxides. Much as the oxidations of n-butane and propene, the oxidative dehydrogenation of 2-butanol is promoted more largely on the catalysts consisting of $H_3PMo_{12}O_{40}$ than on the V-P catalyst.

3.2.3. Isobutene

The oxidation of isobutene was done using tertiary butyl alcohol as the starting material [29–31]. The feed rates of tertial butyl alcohol, water, and air were 14, 200, and 1,000 ml/h, respectively. The

Table 5
Oxidation of 1-butene to maleic anhydride

Catalyst	Temp.	O_2/C_4H_8	C.t.	Conv.	Selectivity (mol%) to		
	(°C)	ratio	(s)	(%)	MA	AcOH	CO_x
$FePO_4$	400	10	8.5	10	5	5	90
V-P	350	9	4.6	99	45	7	48
$H_3PMo_{12}O_{40}$	350	9	13.0	98	33	18	49

MA = maleic anhydride, AcOH = acetic acid, c.t. = contact time, conv. = 1-butene conversion.

Table 6
Oxidation of isobutene

Catalyst	Temp. (°C)	C.t. (s)	Conversion (%)	Selectivity (mol%) to				
				MAA	Macro	AcOH	Acet	CO_x
V-P	350	4	99	17	8	30	1	44
$H_3PMo_{12}O_{40}$	350	4	99	8	18	22	2	50
$Cs_2HPMo_{10}V_2O_{40}$	340	4	99	17	15	15	1	52

MAA = methacrylic acid, Macro = methacrolein, AcOH = acetic acid, Acet = acetone, c.t. = contact time.

main products were methacrolein, methacrylic acid, acetic acid, acetone, and carbon oxides. The results are shown in Table 6. No clear difference in both oxidation activity and selectivity to methacrylic acid are observed between the heteropoly compounds and V-P catalysts. A very small amount of tertiary butyl alcohol may be formed by the hydration of isobutene, however the tertiary alcohol cannot be oxidized to form a ketone or aldehyde. The hydration may be in equilibrium during the oxidation. Therefore, there exists no competition between the allylic oxidation and the dehydrogenation of alcohol. This may be the reason why the selectivities are similar between the heteropoly compounds and the V-P catalyst.

3.2.4. Butadiene

The oxidation of butadiene was done [18,32]. The main products were maleic anhydride, furan, and carbon oxides. The yield of furan attained a maximum at a butadiene conversion of about 60 to 70%, regardless of the reaction conditions and the catalysts. This finding suggests that furan is formed as an intermediate from butadiene to maleic anhydride. The results are shown in Table 7. The $H_3PMo_{12}O_{40}$ catalyst shows clearly higher yields of furan than the V-P catalyst, though the yields of maleic anhydride at a high butadiene conversion are almost the same.

Since the butadiene conversion corresponding to the maximum yield of furan is independent of the catalyst used, the difference in the yield of furan is not ascribed to the difference in the relative reactivity between butadiene and furan, but to the difference in affinity of catalyst to furan, that is, the affinity of the $H_3PMo_{12}O_{40}$ catalysts to furan may be smaller than that of the V-P catalyst.

Because hydration of butadiene cannot take place unlike in the oxidations of butene and propene, there exists no competition between the allylic oxidation and the oxidative dehydrogenation of alcohol. This may be the reason why the selectivity to maleic anhydride over the $H_3PMo_{12}O_{40}$ is the same as that over the V-P.

Table 7
Oxidation of butadiene

Catalyst	Temp. (°C)	O_2/C_4H_6 ratio	C.t. (s)	Conv. (%)	Yield (mol%) of		
					furan	MA	CO_x
V-P	350	30	0.2	60	7	30	63
	350	30	1.5	99	0	46	54
$H_3PMo_{12}O_{40}$	350	40	0.3	60	12	26	62
	370	40	1.8	99	0	48	52

MA = maleic anhydride, c.t. = contact time, conv. = butadiene conversion.

Table 8
Oxidation of methanol to formaldehyde

Catalyst	Temp. (°C)	O_2/CH_3OH ratio	C.t. (s)	Conversion (%)	Selectivity (mol%)
$FePO_4$	480	0.4	4.2	40	30
V-P	340	2.0	10.0	98	95
$H_3PMo_{12}O_{40}$	360	8.0	1.2	55	90
	370	6.0	2.0	98	63

C.t. = contact time.

3.3. Alcohol

3.3.1. Methanol

Methanol is oxidized to formaldehyde over acidic catalysts, while it is oxidized to CO_2 over basic catalysts [33]. Parallels are found between the catalytic activities and the amount of acidic or basic sites [33]. Over amphoteric oxides such as mixed oxides of Sn–Mo, Sn–W, and Ti–Mo, methanol is oxidized to methyl formate [34]. It is therefore predictable that the main product over acidic catalysts such as $H_3PMo_{12}O_{40}$, V-P, and $FePO_4$, is formaldehyde. The results are shown in Table 8 [15]. The $FePO_4$ catalyst is clearly less active and less selective than the $H_3PMo_{12}O_{40}$ and V-P catalysts. The $H_3PMo_{12}O_{40}$ catalyst shows a lower selectivity than the V-P catalyst, because a relatively large amount of loss was observed over the $H_3PMo_{12}O_{40}$ catalyst. It is considered that polymerization of the produced formaldehyde is promoted more largely by acidic sites on the $H_3PMo_{12}O_{40}$ catalyst.

3.4. Aldehyde

3.4.1. Crotonaldehyde

Furan is formed as an intermediate in the oxidation of crotonaldehyde to maleic anhydride [21,22,35]. The oxidation of crotonaldehyde was done over the $FePO_4$, V-P, and $H_3PMo_{12}O_{40}$ catalysts [15]. The results obtained at a crotonaldehyde conversion of about 90% are compared in

Table 9
Oxidation of crotonaldehyde

Catalyst	Temp. (°C)	O_2/C_4H_6O ratio	C.t. (s)	Conv. (%)	Selectivity (mol%) to		
					furan	MA	CO_x
$FePO_4$	380	2.8	2.2	89	17	19	64
V-P	400	22.0	1.0	92	19	40	41
$H_3PMo_{12}O_{40}$	330	4.0	1.7	95	45	14	41

MA = maleic anhydride, c.t. = contact time.

Table 10
Oxidation of acrolein to acrylic acid

Catalyst	Temp. (°C)	O_2/C_3H_4O ratio	C.t. (s)	Conversion (%)	Selectivity (mol%)
V-P	320	14	2	50	90
$H_3PMo_{12}O_{40}$	380	12	2	40	60

C.t. = contact time.

Table 11
Oxidation of methacrolein to methacrylic acid

Catalyst	Temp.	O_2/C_4H_6O	C.t.	Conv.	Selectivity (mol%) to		
	(°C)	ratio	(s)	(%)	MAA	AcOH	CO_x
$FePO_4$	400	0.8	2.2	10	53	—	—
	400	2.9	2.2	50	29	—	—
V-P	340	9.2	7.0	48	53	25	15
	370	9.2	7.0	80	40	35	23
$H_3PMo_{12}O_{40}$	320	9.0	7.0	57	50	28	18
	360	9.0	7.0	80	35	35	28

MAA = methacrylic acid, AcOH = acetic acid, c.t. = contact time, conv. = methacrolein conversion.

Table 9. As the oxidation of butadiene, the $H_3PMo_{12}O_{40}$ catalyst shows a clearly higher yield of furan than the V-P catalyst. The reason may be the same as in the case of oxidation of butadiene to furan.

3.4.2. Acrolein

Oxidation of acrolein was done. The main product was acrylic acid. The results are shown in Table 10 [36,37]. The $H_3PMo_{12}O_{40}$ catalyst is less selective than the V-P catalyst. It is considered that the $H_3PMo_{12}O_{40}$ catalyst promotes more largely the polymerization of acrolein.

3.4.3. Methacrolein

The results in the oxidation of methacrolein to methacrylic acid [15,26,31,38] are shown in Table 11. The $H_3PMo_{12}O_{40}$ and V-P catalysts show similar performances; the selectivity to methacrylic acid is about 40 mol% at the conversion of 80%. However, the $FePO_4$ catalyst is clearly less active and less selective.

3.5. Carboxylic acid

3.5.1. Propionic acid

The oxidation of propionic acid was done [15,26,31]. The main products were acrylic acid, acetic acid, and carbon oxides. Acetic acid is formed by C–C bond fission. The results are shown in Table 12. The catalysts consisting of heteropoly compounds show a higher selectivity to acrylic acid than the V-P catalyst, though the selectivities to acetic acid are almost the same. It is supposed that decomposition of acidic compounds is promoted by basic sites, and that basic sites of the V-P catalyst are stronger than those of heteropoly compounds. As a result, propionic acid is degraded more largely

Table 12
Oxidation of propionic acid

Catalyst	Temp	$O_2/C_3H_6O_2$	C.t.	Conv.	Selectivity (mol%) to		
	(°C)	ratio	(s)	(%)	AA	AcOH	CO_x
$FePO_4$	360	0.75	2.2	62	5	71	24
V-P	300	10	12	50	17	43	40
$H_3PMo_{12}O_{40}$	280	10	12	50	24	43	33
$Cs_2HPMo_{12}O_{40}$	270	10	12	50	31	37	32
$Cs_2H_3PMo_{10}V_2O_{40}$	240	10	12	50	31	38	31

AA = acrylic acid, AcOH = acetic acid, c.t. = contact time, conv. = propionic acid conversion.

Table 13
Oxidation of isobutyric acid

Catalyst	Temp.	$O_2/C_4H_8O_2$	C.t.	Conv.	Selectivity (mol%) to			
	(°C)	ratio	(s)	(%)	MAA	Acet	C_3H_6	CO_x
FePO$_4$	400	0.8	0.1	63	80.5	10	1.0	8.5
	400	0.8	0.2	83	80.3	9	1.0	8.3
V-P	265	14.5	4.6	60	55.0	19	24.0	2.0
	275	14.5	4.6	80	50.0	16	25.0	9.0
H$_3$PMo$_{12}$O$_{40}$	245	14.5	2.5	60	60.0	29	3.0	8.0
	260	14.5	2.5	80	62.0	25	2.0	11.0
Cs$_2$HPMo$_{12}$O$_{40}$	230	14.5	2.5	50	60.0	30	3.0	7.0
Cs$_2$H$_3$PMo$_{12}$V$_2$O$_{40}$	220	14.5	2.5	50	69.0	25	2.0	9.0

MAA = methacrylic acid, Acet = acetone, c.t. = contact time, conv. = isobutyric acid conversion.

by the V-P catalyst. The FePO$_4$ catalyst is clearly lower in both the activity and the selectivity to acrylic acid.

3.5.2. Isobutyric acid

Table 13 shows the results obtained in the oxidation of isobutyric acid [15]. The main products were methacrylic acid, acetone, propylene, and carbon oxides. It is known that propylene and acetone are formed in parallel with methacrylic acid [39]. The reaction took place at temperatures lower than the oxidation of propionic acid. This may due to the fact that the H–C bond strength at the α position of the –COOH group is weak, because the carbon atom is tertiary. Though the optimum reaction conditions are not the same, the catalysts consisting of heteropoly compound show a higher selectivity to methacrylic acid than the V-P catalyst, much as the case of oxidation of propionic acid. The reason may be the same as in the reaction of propionic acid. On the other hand, the FePO$_4$ catalyst shows a much higher selectivity than the catalysts consisting of heteropoly compounds. This may due to the high reactivity of isobutyric acid and also to a lack of oxygen insertion function in the FePO$_4$ catalyst [15].

4. Conclusions

The results are summarized in Table 14. The following conclusions are derived from them.

(1) Though the oxidation activities of catalysts consisting of H$_3$PMo$_{12}$O$_{40}$ or its derivatives varies largely depending on the difference in the composition, they are about the same order of magnitude as that of the V-P catalyst. The thermal stability of the heteropoly compounds are known to be much lower than the V-P. On the other hand, the oxidation activity of FePO$_4$ is much lower though the thermal stability is relatively high. It is therefore concluded that catalysts consisting of heteropoly compounds and FePO$_4$ are suitable for oxidation of a reactant having a high reactivity. At least, they are not suitable for oxidation of alkanes.

(2) In the oxidation of hydrocabons such as propene, propene, n-butane, and n-butene, the allylic oxidation is in competition with the oxidative dehydrogenation of alcohol which is formed by the hydration of olefin. The heteropoly compounds promote the oxidative dehydrogenation of alcohol which is formed by the hydration of olefin, more largely than the V-P. Therefore, the heteropoly compounds show a lower selectivity in the allylic oxidation than the V-P.

Table 14
Comparison of the selectivities for different oxidations

Reaction	HPA	V-P	FePO$_4$
(1) Propane → acrylic acid	M	G	B
(2) n-butane → maleic anhydride	M	G	B
(3) Propene → arylic acid	M	G	B
(4) n-butene → maleic anhydride	M	G	B
(5) Isobutene → MAA + Macro	M	M	B
(6) Butadiene → furan	G	M	B
(7) Methanol → formaldehyde	M	G	B
(8) Crotonaldehyde → furan	G	M	B
(9) Acrolein → acrylic acid	M	G	B
(10) Methacrolein → methacrylic acid	G	G	B
(11) Propionic acid → acrylic acid	M	M	B
(12) Isobutyric acid → methacrylic acid	M	M	G

G = good, M = middle, B = bad, HPA = heteropoly compounds, MAA = methacrylic acid, Macro = methacrolein.

(3) In the oxidation of butadiene and isobutene, the selectivity in allylic oxidation is not affected by the oxidative dehydrogenation of alcohol, because hydration does not take place in the oxidation of butadiene and tertiary butyl alcohol is not oxidized to a ketone or aldehyde in the oxidation of isobutene. As a result, the heteropoly compounds show the same selectivity for allylic oxidation as the V-P.

(4) In the formation of furan from butadiene and crotonaldehyde, the heteropoly compounds show a clearly higher selectivity than the V-P shows. This may due to the low affinity of heteropoly compounds to furan.

(5) In the oxidation of acrolein to acrylic acid, the V-P shows a higher selectivity than the heteropoly compounds. This may due to the difference in the activities for the polymerization of acrolein. While in the oxidation of methacrolein, the selectivities of heteropoly compounds are the same as that obtained with the V-P.

(6) In the oxidative dehydrogenation of carboxylic acids, the heteropoly compounds show a higher selectivity than the V-P. The degradation of carboxylic acids which is promoted by basic sites of catalyst, may be promoted more largely on the V-P.

(7) As mentioned in Section 1, the FePO$_4$ catalyst is effective only for oxidative dehydrogenation of compounds in which the carbon atom at the α-position of an electron-attracting group is tertiary. This may due to a very high reactivity of the reactants and also to the absence of oxygen insertion function in the FePO$_4$ which has no double-bond oxygen species.

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