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Iron as an effective additive for enhancement of catalytic performance of cesium hydrogen salt of molybdophosphoric acid for selective oxidation of isobutane, propane, and ethane under oxygen-rich and -poor conditions and the catalyst design

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Abstract

The effects of iron addition and substitution on the catalytic performance of heteropoly compounds for selective oxidation were studied. The addition of iron to heteropoly compounds effectively enhanced the catalytic performance for the selective oxidation of light alkanes of ethane, propane, and isobutane under oxygen-rich and -poor conditions. Furthermore, on the basis of above results, it was attempted to synthesize mono-iron-substituted molybdophosphate, and a remarkable enhancement of catalytic performance was demonstrated for the oxidative dehydrogenation of 2-propanol. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Selective oxidation; Oxidative dehydrogenation; Alkane; Iron; Catalyst design

1. Introduction

The catalytic function of heteropoly compounds in the solid state has attracted much attention because their redox and acidic properties can be controlled by changing the constituent elements [1–6]. Functionalization of light alkanes to the valuable chemicals by selective oxidation is also of great interests since the price and availability of light alkanes are substantially more favorable than those of alkenes [7–9].

It has been reported that heteropoly compounds can catalyze the oxidation of light alkanes [10–14] and the catalytic performance is much enhanced by the addition of transition metals [15–19]. The effects of addition of transition metals are much influenced by the reaction conditions. For example, copper enhances the catalytic performance under oxygen-poor conditions by promoting the reoxidation of the catalyst [20–22] and did not enhance the catalytic performance under oxygen-rich conditions [17,18,23–35]. Iron has been one of the most widely used additives for enhancing catalytic activity of heteropoly compounds in the patent literature [22,26–29]. However, the effect of iron to the catalytic performance is still ambiguous because iron was added with many kinds of metals under various reaction conditions. Therefore, the clarification of the effect of iron on the catalytic performance of heteropoly compounds is interesting.

The transition-metal-substituted polyoxometalates have brought about considerable research due to their unique and remarkable influences on the catalytic performances [3,6,30–32] as well as the industrial use [33]. It has been reported that the transition metals play significant roles in the redox processes as reservoirs for electrons and active sites for the activation of hydrocarbons and molecular oxygen [34–37]. Therefore, the

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oxidation catalysis by the transition-metal-substituted polyoxometalate is interesting, while there are no reliable and reproducible reports for the synthesis of iron-substituted molybdophosphate.

Here, we attempt to demonstrate the effectiveness of iron addition to molybdophosphates on the selective oxidation of lower alkanes, and to synthesize mono-iron-substituted molybdophosphate for the catalyst design.

2. Experimental

$H_3PMo_{12}O_{40}$ and $H_4PVMo_{11}O_{40}$ heteropolyacids were commercially obtained from Nippon Inorganic Colour and Chemical and used after the purification with ether extraction. The cesium- and iron-containing catalysts were prepared according to the previous reports [17,18].

The other reagents were analytical grade and used without further purification. Cesium hydrogen salt of mono-iron-substituted molybdophosphate ($Cs_{2.8}H_{1.2}PMo_{11}FeO_{39}$) was synthesized as follows. $H_3PMo_{12}O_{40}28H_2O$(2.0 mmol) was dissolved in 20 ml of water (0.1 mol dm^{-3}), and the pH of the solution was adjusted to 4.3 with lithium carbonate [38]. Then, ferric nitrate (0.9 g, 2.2 mmol) was added to the solution and the solution was filtered. To the reddish-yellow filtrate was added cesium chloride (1.0 g, 6.0 mmol) to yield a yellow precipitate. The precipitate was filtered off, washed with water, and aspirated to dryness. The catalyst prepared was characterized by FT-IR spectroscopy, elemental analysis, BET surface area, XRD, and TG/DTA. Infrared spectrum (cm^{-1}): 1063 (s), 1044 (m) ν (P–O), 963 (vs) ν(Mo=O), 858 (s), 787 (vs) ν(Mo–O–M (M=Mo, Fe)). The atomic ratios of Cs/P, Fe/P, and Mo/P were 2.8, 1.0, and 10.2, respectively, by ICP analysis. BET surface area after drying at 300°C for 1 h in N_2 was 174 m^2/g. XRD pattern showed the signal at 10.5°, 18.3°, 23.8°, 26.1° and 30.3°, assignable to cubic phase ($a = 11.8$ Å), and no signals of iron oxide were observed.

The reactions were performed in a flow reactor (Pyrex tube, 12 mm ID) at an applied temperature under an atmospheric pressure. Prior to the reaction, 1 g each of as-prepared catalyst was mixed with SiC (1.5 g) to prevent an undesirable temperature rise and treated in an O_2 stream (60 cm^3 min^{-1}) for 1 h at 300–425°C. The gases at the outlet of the reactor were taken out intermittently with the aid of a sampler directly connected to the system and analyzed by a gas chromatograph with FFAP, Porapak-Q, and Molecular Sieve 5A columns. The oxidative dehydrogenation of 2-propanol was performed after the pretreatment of catalysts in O_2 at 200°C. The conversion and selectivity data were collected after 2–5 h of reaction, when nearly steady state conversion and selectivity were obtained for each catalyst. Selectivities were calculated on the C_n-basis (n in C_nH_{2n+2}; $n = 2$–4). Carbon balance was more than 90% for each reaction.

3. Results and discussion

3.1. Oxidation of light alkanes

Fig. 1 shows the results for the oxidation of isobutane catalyzed by $Cs_{2.5}Fe_xH_{0.5-3x}PMo_{12}O_{40}$ at 340°C under oxygen-rich conditions. The products were methacrylic acid, methacrolein, acetic acid, CO and CO_2. The yields of methacrylic acid and methacrolein increased from $x = 0$ to 0.08 while the conversion little decreased. It follows that the sum of yields of methacrylic acid and methacrolein reached a maximum at $x = 0.08$ and then decreased. Similar changes in conversions and selectivities were observed for the oxidation of isobutane catalyzed by Ni added $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$, and the decrease in activity above $x = 0.08$ is explained by the decrease in Brønsted acidity [18].

Table 1 shows the results of the oxidation of isobutane catalyzed by $Cs_{2.5}Fe_xH_{0.5-3x}PMo_{12}O_{40}$ under oxygen-poor conditions. The products were methacrolein, isobutene, acetic acid, CO and CO_2. Methacrylic acid was not observed under oxygen-poor conditions. The conversion and selectivity to methacrolein were increased by the addition of iron ($x = 0.08$). Further addition of iron much decreased the selectivity to methacrolein in a similar way to Fig. 1.

Table 2 shows the results of the oxidation of propane catalyzed by $Cs_{2.5}Fe_xH_{0.5-3x}PMo_{12}O_{40}$ at 360°C under oxygen-rich conditions. The content of iron was kept 0.08, where the highest sum of yields of methacrylic acid and methacrolein was obtained for the oxidation of isobutane in Fig. 1. The addition

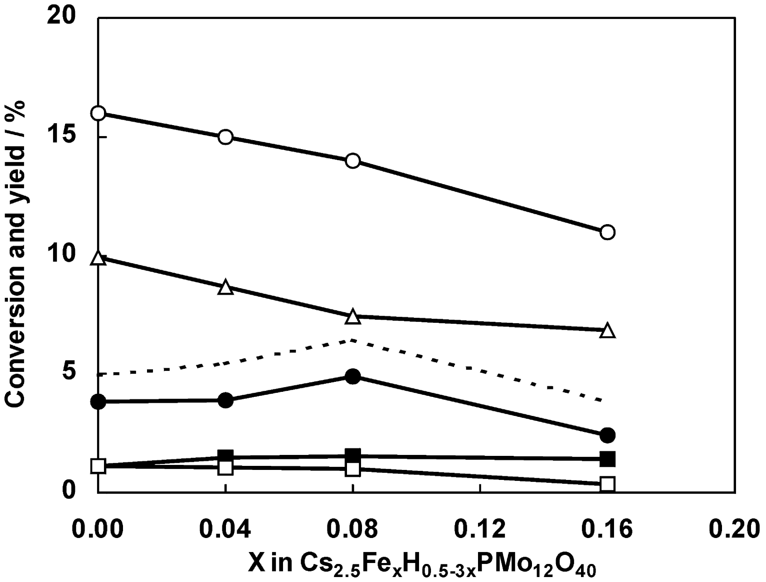

Fig. 1. Oxidation of isobutane catalyzed by $Cs_{2.5}Fe_xH_{0.5-3x}PMo_{12}O_{40}$ at 340°C. Reaction conditions: 17% Isobutane, 33 vol.% O_2, N_2 (balance); catalyst weight, 1.0 g; total flow rate, 30 $cm^3\,min^{-1}$. (○), (●), (■), (□), and (△) represent conversion of isobutane and yields of methacrylic acid, methacrolein, acetic acid, and CO_x, respectively. Broken line indicates the sum of yields of methacrylic acid and methacrolein.

Table 1
Effect of addition of iron to $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ on oxidation of isobutane at 340°C under oxygen-poor conditions[a]

M^{n+}[b]	Conversion (%)	Yield (selectivity)[c] (%)					
		Methacrolein	Isobutene	Acetone	Acetic acid	CO	CO_2
$H^+ (x = 0)$	10	1.5 (15)	1.2 (12)	3.0 (30)	0.1 (1)	3.0 (30)	1.2 (12)
$Fe^{3+} (x = 0.08)$	15	4.5 (30)	0.3 (2)	3.8 (25)	0.3 (2)	4.2 (28)	1.8 (12)
$Fe^{3+} (x = 0.16)$	13	0.9 (7)	0.0 (0)	2.0 (15)	0.5 (4)	7.0 (54)	2.6 (20)

[a] Isobutane, 33 vol.%; O_2, 13 vol.%; N_2, balance; catalyst, 1.0 g; total flow rate, 15 $cm^3\,min^{-1}$.
[b] Catalyst, $Cs_{2.5}M_x^{n+}H_{0.5-nx}PMo_{12}O_{40}$ ($x = 0$, 0.08, 0.16).
[c] Calculated on the C_4 (isobutane)-basis.

Table 2
Effect of addition of iron to $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ on oxidation of propane at 360°C under oxygen-rich conditions[a]

M^{n+}[b]	Conversion (%)	Yield (selectivity)[c] (%)						Sum of yields of acrylic acid+acrolein (%)
		Acrylic acid	Acrolein	Propene	Acetic acid	CO	CO_2	
H^+	12	1.0 (8)	0.1 (1)	0.7 (6)	1.0 (8)	7.4 (62)	1.8 (15)	1.1
Fe^{3+}	13	2.3 (18)	0.3 (2)	1.2 (9)	1.4 (11)	6.5 (50)	1.3 (10)	2.6

[a] Propane, 30 vol.%; O_2, 40 vol.%; N_2, balance; catalyst, 1.0 g; total flow rate, 30 $cm^3\,min^{-1}$.
[b] Catalyst, $Cs_{2.5}M_x^{n+}H_{0.5-nx}PMo_{12}O_{40}$ ($x = 0$, 0.08).
[c] Calculated on the C_3 (propane)-basis.

Table 3
Effect of addition of iron to $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ on oxidation of ethane at 425°C under oxygen-rich conditions[a]

M^{n+}[b]	Conversion (%)	Yield (selectivity)[c] (%)		
		C_2H_4	CO	CO_2
H^+	10	3.4 (35)	5.2 (54)	1.1 (11)
Fe^{3+}	10	3.9 (39)	4.2 (42)	1.8 (18)

[a] Ethane, 33 vol.%; O_2, 33 vol.%; N_2, balance; catalyst, 1.0 g; total flow rate, 15 cm^3 min^{-1}.

[b] Catalyst, $Cs_{2.5}M_x{}^{n+}H_{0.5-nx}PVMo_{11}O_{40}$ ($x = 0$, 0.08).

[c] Calculated on the C_2 (ethane)-basis.

of iron to $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ resulted in an increase in selectivities to acrylic acid and acrolein, while the conversion little changed.

Tables 3 and 4 show the effects of addition of iron to $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ on the selective oxidation of ethane at 425°C under oxygen-rich and -poor conditions, respectively. The products were ethene, CO and CO_2 under both conditions. Selectively oxygenated products of acetic acid and acetaldehyde were not observed under the conditions. Under oxygen-rich conditions, the addition of iron increased the selectivity to ethene from 35 to 39%, while the conversion did not change. On the other hand, under oxygen-poor conditions, the addition of iron increased the conversion from 4 to 6% without much change in the selectivity. Thus, it was clearly demonstrated that iron is an effective additive for the selective oxidation of light alkanes both under oxygen-rich and -poor conditions in contrast with the fact that copper is an effective additive only under oxygen-poor conditions. Under oxygen-rich conditions, the addition of iron increased selectivities without an increase in conversions. Iron may suppress the complete oxidation of alkenes (propene, ethene), aldehydes (methacrolein, acrolein), and carboxylic acids (methacrylic acid, acrylic acid). Under oxygen-poor conditions, conversions were increased by the addition of iron. A similar increase in conversion was observed for the addition of copper and the role is the acceleration of the reoxidation of catalysts [20,21]. Iron would also promote the reoxidation of catalyst.

Table 4
Effect of addition of iron to $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ on oxidation of ethane at 425°C under oxygen-poor conditions[a]

M^{n+}[b]	Conversion (%)	Yield (selectivity)[c] (%)		
		C_2H_4	CO	CO_2
H^+	4	2.4 (61)	0.8 (21)	0.7 (18)
Fe^{3+}	6	3.7 (58)	1.7 (26)	1.0 (16)

[a] Ethane, 57 vol.%; O_2, 9 vol.%; N_2, balance; catalyst, 1.0 g; total flow rate, 15 cm^3 min^{-1}.

[b] Catalyst, $Cs_{2.5}M_x{}^{n+}H_{0.5-nx}PVMo_{11}O_{40}$ ($x = 0$, 0.08).

[c] Calculated on the C_2 (ethane)-basis.

3.2. Synthesis of iron-substituted molybdophosphate and the oxidative dehydrogenation of 2-propanol

On the basis of above results, the synergistic effect is expected upon the incorporation of iron into $PMo_{12}O_{40}{}^{3-}$ anion structure. The lacunary molybdophosphate, $PMo_{11}O_{39}{}^{7-}$, was first prepared by controlling pH. The purity was confirmed by ^{31}P NMR. Only one peak was observed at −0.9 ppm (vs. 85% H_3PO_4) for ^{31}P NMR spectrum, showing the presence of highly pure lacunary species, $PMo_{11}O_{39}{}^{7-}$. The cesium hydrogen salt of mono-iron-substituted molybdophosphate was prepared by adding ferric nitrate and then cesium chloride to the solution as described in experimental section. The FT-IR spectrum of the prepared catalyst showed the splitting of P–O asymmetric stretch (1063 and 1044 cm^{-1}), a characteristic of transition-metal-substituted α-Keggin structure. The ^{31}P MAS NMR (298 K) showed no signals. The disappearance of signals of P atom is attributed to the paramagnetic effect caused by the presence of paramagnetic species (Fe^{3+}) in the anion structure [39,40]. These facts suggest that an iron atom occupies the vacant site of the anion structure.

Table 5 summarizes the results for oxidative dehydrogenation of 2-propanol catalyzed by $Cs_{2.8}H_{1.2}$-$PMo_{11}FeO_{39}$, Fe^{3+}(2.5 wt.%)/$Cs_{3.0}PMo_{12}O_{40}$, and $Cs_{3.0}PMo_{12}O_{40}$ at 180°C. The products were acetone, propene, di-isopropylether (DIPE), and CO_2. The selectivities to acetone were 80, 38, and 16%, respectively. The selectivity to acetone for iron-substituted molybdophosphate ($Cs_{2.8}H_{1.2}PMo_{11}FeO_{39}$) was much higher than that for iron-impregnated Fe^{3+} (2.5 wt.%)/$Cs_{3.0}PMo_{12}O_{40}$ with the conversions being close to each other. In addition, the selectivity to acetone almost unchanged with an increase in conversion by changing *W* (weight of catalyst)/*F* (flow rate) for $Cs_{2.8}H_{1.2}PMo_{11}FeO_{39}$. The selectivities to acetone

Table 5
Oxidative dehydrogenation of 2-propanol at 180°C[a]

Catalyst	Conversion (%)	Selectivity[b] (%)			
		Acetone	Propene	DIPE	CO_2
$Cs_{2.8}H_{1.2}PMo_{11}FeO_{39}$	14	80	10	8	2
Fe(2.5 wt.%)/$Cs_{3.0}PMo_{12}O_{40}$	18	38	38	23	0
$Cs_{3.0}PMo_{12}O_{40}$	6	16	32	52	0

[a] 2-Propanol, 17 vol.%; O_2, 33 vol.%; N_2, balance; catalyst, 1.0 g; total flow rate, 30 $cm^3\ min^{-1}$.
[b] Calculated on the C_3 (2-propanol)-basis.

for Fe^{3+}(2.5 wt.%)/$Cs_{3.0}PMo_{12}O_{40}$ were in the range of 26–38% and did not much increase in the range of loading amounts of 1.2–5.0 wt.%. These facts clearly show that the iron-substitution more promotes the oxidative dehydrogenation (of 2-propanol to acetone) than the impregnation of iron. No changes were also observed by IR, XRD and TG/DTA analyses after the reaction at 180°C.

In conclusion, the addition of iron to heteropoly compounds enhanced the selective oxidation of light alkanes (ethane, propane, and isobutane) under oxygen-rich and -poor conditions. The effectiveness of the incorporation of iron into molybdophosphate was also demonstrated for the oxidative dehydrogenation of 2-propanol. The present results suggest a novel way of catalyst design.

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