

## Remarkable Effect of Iron-Substitution for Molybdenum in Phosphododecamolybdate on Oxidative Dehydrogenation of 2-Propanol

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Cesium hydrogen salt of mono-iron-substituted phospho-undecamolybdate,  $\text{Cs}_{2.8}\text{H}_{1.2}\text{PMo}_{11}\text{FeO}_{39}$ , was synthesized and the catalyst showed intrinsically higher selectivity to acetone for the title reaction compared with the iron-impregnated  $\text{Fe}^{3+}$  (1.2–5.0 wt%)/ $\text{Cs}_{3.0}\text{PMo}_{12}\text{O}_{40}$ .

Polyoxometalates provide a good basis for the molecular design of mixed oxide catalysts because the redox and acidic properties can be controlled at atomic/molecular levels by changing the constituent elements. Among polyoxometalates, the catalysis by Keggin-type anions has most extensively been investigated because of their rather high thermal stabilities and ease of synthesis.<sup>1–7</sup> During the past decade, there has been a great interest in the synthesis and oxidation catalysis of transition metal-substituted polyoxometalates due to their unique and remarkable influences on the catalytic performances.<sup>3,6,8–10</sup> For the synthesis of transition metal-substituted polyoxometalates, lacunary (or defect) polyoxometalates are important synthetic intermediates, and the vacancy provides a pentadentate ligand for the transition metals. 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 hydrocarbon and molecular oxygen.<sup>11–16</sup> It has recently been reported that the addition (“not substitution”) of Fe enhanced the catalytic performance of  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PMo}_{12}\text{O}_{40}$  or  $\text{Cs}_{2.5}\text{H}_{1.5}\text{PVMo}_{11}\text{O}_{40}$  for the selective oxidation of light alkanes<sup>11,12,17</sup> and that  $\text{Fe}^{3+}$  promoted the H abstraction from alkanes by  $\text{O}^{2-}$  neighboring  $\text{Mo}^{6+}$ .<sup>17</sup> It is expected that the introduction of  $\text{Fe}^{3+}$  into the polyoxometalate can result in a large enhancement of catalytic performance. Therefore, the synthesis of iron-substituted molybdophosphate and the demonstration of the effectiveness of the  $\text{Fe}^{3+}\text{--O--Mo}^{6+}$  for the selective oxidation are important from the standpoint of the development of heterogeneous catalysts. However, little is known of the oxidation catalysis by iron-substituted molybdophosphates because there is no reliable, reproducible, and selective method of their synthesis.<sup>18–20</sup> In this work, we report the synthesis of mono-iron-substituted phospho-undecamolybdate and demonstrate the remarkable effect of the iron-substitution on the selectivity for the oxidative dehydrogenation of 2-propanol.

Cesium hydrogen salt of mono-iron-substituted phospho-undecamolybdate was synthesized as follows. Phosphododecamolybdic acid ( $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ) was commercially obtained from Nippon Inorganic Color and Chemical Co., Ltd. and recrystallized from water.  $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 28\text{H}_2\text{O}$  (2.0 mmol) was dissolved in water (0.1 mol·dm<sup>−3</sup>), and the pH of the solution was adjusted to 4.3 with lithium carbonate. Only one signal was observed at −0.9 ppm (vs 85%  $\text{H}_3\text{PO}_4$ ) for the <sup>31</sup>P NMR spectrum, showing the presence of highly pure lacunary species,  $\text{PMo}_{11}\text{O}_{39}^{7-}$ . Then, ferric nitrate  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  (2.2 mmol)

was added to the solution and the solution was filtered. To the reddish yellow filtrate was added cesium chloride (6.0 mmol) to yield a yellow precipitate. The precipitate was filtered off, washed with water, and aspirated to dryness (yield 55%, yellow). Elemental analysis: Found: Cs, 16.43; P, 1.34; Mo, 46.37; Fe, 2.03%. Calcd for  $\text{Cs}_{2.8}\text{H}_{1.2}[\text{PMo}_{11}\{\text{Fe}(\text{H}_2\text{O})\}\text{O}_{39}]\cdot 6\text{H}_2\text{O}$ : Cs, 16.43; P, 1.37; Mo, 46.58; Fe, 2.46%. No changes in the anion structure were observed by IR and TG/DTA analyses after the thermal treatment at 473 K and after the reaction at the same temperature. More characterization was carried out for the phenyltrimethylammonium salt since  $\text{Cs}_{2.8}\text{H}_{1.2}\text{PMo}_{11}\text{FeO}_{39}$  was insoluble in any solvents without the decomposition of the anion structure. Phenyltrimethylammonium salt of mono-iron-substituted phospho-undecamolybdate was prepared by adding phenyltrimethylammonium chloride to the acetonitrile solution of tetra-*n*-butylammonium salt.<sup>21</sup> Elemental analysis: Found: C, 22.05; H, 2.96; N, 3.52; P, 1.20; Mo, 41.50; Fe, 2.15; Cl, 1.35%. Calcd for  $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_5[\text{PMo}_{11}\{\text{Fe}(\text{Cl})\}\text{O}_{39}]\cdot 1\text{CH}_3\text{CN}\cdot 1\text{H}_2\text{O}$ : C, 22.21; H, 2.98; N, 3.31; P, 1.22; Mo, 41.52; Fe, 2.20; Cl, 1.39%. The UV-vis spectrum in v/v 7/3 acetonitrile/dimethylsulfoxide at 296 K showed a broad absorption bands at 307 nm ( $\epsilon$  29000 M<sup>−1</sup>cm<sup>−1</sup>) characteristic of O→Mo charge transfer bands of  $\alpha$ -Keggin structure.<sup>22</sup> No signal was observed for the <sup>31</sup>P NMR spectrum in acetonitrile at 295 K because of the presence of P–O–Fe<sup>3+</sup> (paramagnetic species) bond in the polyoxometalate structure in agreement with reports.<sup>23,24</sup> The cesium salt of  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  ( $\text{Cs}_{3.0}\text{PMo}_{12}\text{O}_{40}$ ) was prepared with aqueous solution of cesium carbonate and  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  as reported previously.<sup>17</sup>  $\text{Fe}^{3+}$  (1.2–5.0 wt%)/ $\text{Cs}_{3.0}\text{PMo}_{12}\text{O}_{40}$  was prepared by impregnating  $\text{Cs}_{3.0}\text{PMo}_{12}\text{O}_{40}$  with an aqueous solution of ferric nitrate. The iron content of 2.5 wt% corresponded to that in  $\text{Cs}_{2.8}\text{H}_{1.2}\text{PMo}_{11}\text{FeO}_{39}$ . It was confirmed by IR and XRD spectroscopy that the primary and secondary structures of phosphododecamolybdate were kept before and after the impregnation.

Reactions were carried out with a flow reactor (Pyrex tube, 10 mm internal diameter) at 453 K under atmospheric pressure. The feed gas consisted of 17 vol% of 2-propanol, 35 vol% of O<sub>2</sub>, and N<sub>2</sub> balance. Total flow rates were 24 cm<sup>3</sup>·min<sup>−1</sup>. All the flow lines were heated at 393 K to prevent adsorption of 2-propanol and products. Prior to the reaction, 0.8 g of each catalyst was treated in an O<sub>2</sub> stream (48 cm<sup>3</sup>·min<sup>−1</sup>) for 1 h at 473 K. The gases at the outlet of the reactor were taken out intermittently with the aid of sampler directly connected to the system and analyzed by a gas chromatograph with FFAP (1.0 m), Porapak-Q (4.0 m), and Molecular Sieve 5A (1.2 m) columns. Selectivities were fractions of the sum of the products and calculated on the C<sub>3</sub>(2-propanol)-basis. Carbon balance was usually more than 90%. The conversion and selectivity for the oxidative dehydrogenation of 2-propanol catalyzed by  $\text{Cs}_{2.8}\text{H}_{1.2}\text{PMo}_{11}\text{FeO}_{39}$  reached an almost constant level after 2 h;

the conversions were 15, 14, 14, and 14% after 0.5, 1.0, 1.5, and 2.0 h, respectively. The products were acetone, propene, di-isopropyl ether (DIPE), and CO<sub>2</sub>.

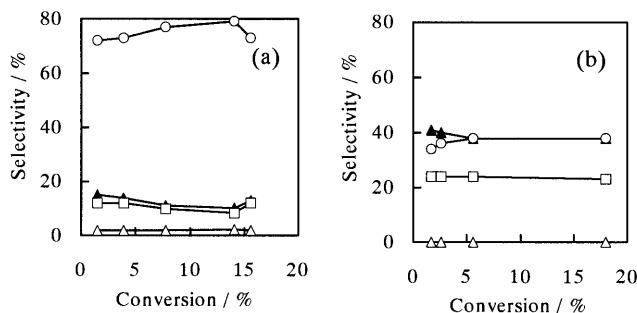
**Table 1.** Oxidative dehydrogenation of 2-propanol at 453 K

Catalyst	Acidity <sup>a</sup>	Conv. / %	Selectivity / %		
			Acetone	Propene	DIPE
Cs <sub>2.8</sub> H <sub>1.2</sub> PMo <sub>11</sub> FeO <sub>39</sub> <sup>b</sup>	165	14	80	10	8
Fe/Cs <sub>3.0</sub> PMo <sub>12</sub> O <sub>40</sub>	151	18	38	38	23
Cs <sub>3.0</sub> PMo <sub>12</sub> O <sub>40</sub>	trace	6	16	32	52

<sup>a</sup>Amount of ammonia desorbed in the range 373 – 1273 K / μmol g<sup>-1</sup>.

<sup>b</sup>The selectivity to CO<sub>2</sub> was 2 %.

Table 1 summarizes the results for oxidative dehydrogenation of 2-propanol catalyzed by Cs<sub>2.8</sub>H<sub>1.2</sub>PMo<sub>11</sub>FeO<sub>39</sub>, Fe<sup>3+</sup>(2.5wt%)/Cs<sub>3.0</sub>PMo<sub>12</sub>O<sub>40</sub>, and Cs<sub>3.0</sub>PMo<sub>12</sub>O<sub>40</sub> at 453 K. The respective selectivities to acetone were 80, 38, and 16%, and that observed for iron-substituted Cs<sub>2.8</sub>H<sub>1.2</sub>PMo<sub>11</sub>FeO<sub>39</sub> was much higher than that of iron-impregnated Fe<sup>3+</sup>(2.5wt%)/Cs<sub>3.0</sub>PMo<sub>12</sub>O<sub>40</sub>, while the activities were close to each other. The acid amounts are also shown in Table 1 and decreased in the same order as that of selectivities to acetone. This fact shows that the highest selectivity to acetone for Cs<sub>2.8</sub>H<sub>1.2</sub>PMo<sub>11</sub>FeO<sub>39</sub> does not result from the suppression of the production of propene and DIPE catalyzed by acidic sites, but the iron-substitution. Figure 1 shows changes in selectivities with percent conversion of 2-propanol. The conversion was changed by changing W/F, where W is the weight of catalyst and F is the total flow rate. The selectivity to acetone almost unchanged with an increase in conversion for Cs<sub>2.8</sub>H<sub>1.2</sub>PMo<sub>11</sub>FeO<sub>39</sub>. Similar dependencies of selectivities to propene and CO<sub>2</sub> on conversions were observed. The selectivities to acetone extrapolated to 0% conversion for Cs<sub>2.8</sub>H<sub>1.2</sub>PMo<sub>11</sub>FeO<sub>39</sub> and Fe<sup>3+</sup>(2.5 wt%)/Cs<sub>3.0</sub>PMo<sub>12</sub>O<sub>40</sub> catalysts were ca. 73% and 30%, respectively. These facts show that the selectivity to acetone for Cs<sub>2.8</sub>H<sub>1.2</sub>PMo<sub>11</sub>FeO<sub>39</sub> is intrinsically much higher than that of Fe<sup>3+</sup>(2.5 wt%)/Cs<sub>3.0</sub>PMo<sub>12</sub>O<sub>40</sub>. The selectivities to acetone were in the range of 26–38% and did not much increase when amounts of iron loaded changed in the range of 1.2–5.0 wt%. Thus, it is clearly demonstrated that the incorporation of iron into molybdophosphate much more increases the selectivity for the oxidative dehydrogenation of 2-propanol (to acetone) com-



**Figure 1.** Changes in selectivities with conversions for oxidative dehydrogenation of 2-propanol at 453 K. (a) Cs<sub>2.8</sub>H<sub>1.2</sub>PMo<sub>11</sub>FeO<sub>39</sub>. (b) Fe<sup>3+</sup>(2.5 wt%)/Cs<sub>3.0</sub>PMo<sub>12</sub>O<sub>40</sub>. ○, ▲, □, and △ represent selectivities to acetone, propene, DIPE, and CO<sub>2</sub>, respectively.

pared with the traditional impregnation of iron. It was confirmed that Cs<sub>2.8</sub>H<sub>1.2</sub>PMo<sub>11</sub>FeO<sub>39</sub> showed higher selectivity to methacrolein than Cs<sub>3.0</sub>PMo<sub>12</sub>O<sub>40</sub> for the oxidation of isobutane. Further experiments of oxidation of isobutane are in progress and will be reported in due course. The strategy of the catalyst design and synthesis would be very important for the development of new solid catalysts.

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