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Acidic cesium salts of molybdovanadophosphoric acids as efficient catalysts for oxidative dehydrogenation of isobutyric acid [1]

Kwan Young Lee *,[2], Syoichi Oishi [3], Hiroshi Igarashi [4], Makoto Misono

Department of Applied Chemistry, Faculty of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

Abstract

Oxidative dehydrogenation of isobutyric acid to methacrylic acid has been studied using Cs salts of 12-molybdovanadophosphoric acids as catalysts ($Cs_nH_{3+x-n}PMo_{12-x}V_xO_{40}$, $n = 0$–$(3+x)$, $x = 0$–2, which will be abbreviated as CsnMo12-xVx). Among them, Cs2.75Mo11V showed remarkably high performance; the highest conversion (97%) and selectivity for methacrylic acid (MAA, 78%) at 623 K. At the same reaction conditions, Mo11V (i.e. $n = 0$, $x = 1$) gave only 40% conversion and 52% selectivity. As for the series of Cs2.75Mo12-xVx, the activity was in the order of $x = 1 > x = 2 > x = 0$ and the MAA selectivity, $x = 1 \geq x = 2 > x = 0$. The nature of Mo11V was confirmed by IR to be partially destroyed during pretreatment in O_2 at 623 K, while Cs2.75Mo11V decomposed only slightly. This fact indicates that the thermal stability afforded this catalyst to make efficient use of the redox ability controlled by incorporation of V, and the enhanced redox ability, high surface area, and high surface acidity of Cs salts would be the main reasons for their effectiveness.

Keywords: Acidic cesium salts; Molybdovanadophosphoric acids; Oxidative dehydrogenation; Isobutyric acid; Methacrylic acid

1. Introduction

Solid heteropolyacids are useful commercial catalysts for acid as well as oxidation catalysis [1]. Mo, V mixed-coordinated heteropolyacids have attracted much attention as catalysts for several kinds of heterogeneous oxidations such as oxygenations of methacrolein to methacrylic acid [2] and acetaldehyde to acetic acid [3], oxidative dehydrogenations of methanol to formaldehyde [4–7] and isobutyric acid to methacrylic acid [2,8,9], and the combination of the two reactions such as n-butane [10–12] or n-pentane [13] to maleic anhydride.

Because of environmental problems, processes to replace for the acetone cyanohydrin process have been demanded for methacrylic acid (MAA) production. Isobutyric acid (IBA) which can be produced by carbonylation of propylene is a good candidate based on C_3 feedstock. The most promising catalysts for the

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* Corresponding author.

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[2] Present address: Department of Chemical Engineering, Korea University, 1, 5-ka, Anam-dong, Sungbuk-ku, Seoul 136-701, Korea.

[3] Present address: Showa Denko Co., Kawasaki 210, Japan.

[4] Present address: Laboratory of Electrochemical Energy Conversion, Yamanashi University, 4-3 Takeda, Kofu 400, Japan.

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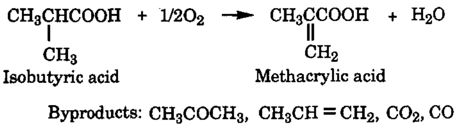


$$\underset{\text{Isobutyric acid}}{CH_3\underset{CH_3}{\underset{|}{C}}HCOOH} + 1/2O_2 \rightarrow \underset{\text{Methacrylic acid}}{CH_3\underset{CH_2}{\underset{\|}{C}}COOH} + H_2O$$

Byproducts: CH_3COCH_3, $CH_3CH=CH_2$, CO_2, CO

Scheme 1.

oxidative dehydrogenation of IBA (Scheme 1) are Fe-P-O and heteropolyacids. Fe-P-O shows a little higher activity than heteropolyacids but an extremely large amount of steam is necessary to achieve high activity [14,15]. Molybdovanadophosphoric acids and their salts which have been studied until now showed fairly high activity but thermal deactivation was the drawback for commercialization [16].

Cs salts of tungstophosphoric acid have been studied widely and it was demonstrated that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ revealed a high activity in acid catalysis [17,18]. The surface area increased from 5 m^2 g^{-1} for $H_3PW_{12}O_{40}$ to 130 m^2 g^{-1} for $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. Cs salts increase the thermal stability as well [1]. On the other hand, the usefulness of Cs salts as oxidation catalysts has been investigated to much less extent. Acidic Cs salts having integer numbers of Cs substitution for H showed no remarkable effects [8,10]. But higher activities were observed for $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ [19,20]. In the present study, the optimum substitution number of Cs has been found to be around 2.75 (vide infra).

Hence, it is the purpose of this study to investigate in more detail the effect of Cs substitution and enhance the yield of MAA from IBA by controlling precisely the Cs content in the salts of molybdovanadophosphoric acids.

2. Experimental

Molybdovanadophosphoric acids ($H_{3+x}PMo_{12-x}V_xO_{40} \cdot mH_2O$, which will be abbreviated as Mo12-*x*V*x*) were supplied by Nippon Inorganic Color and Chemical Co. They were used after the extraction by diethyl ether and the subsequent recrystallization. Their Cs salts were prepared using aqueous solutions of Cs_2CO_3 and heteropolyacid by the same method as the preparation of Cs salts of tungstophosphoric acids [17,18]. IBA (> 98%) was purchased from Wako Pure Chemical Industries. Cs salts of 12-molybdovanadophosphoric acids, $Cs_nH_{3+x-n}PMo_{12-x}V_xO_{40}$, will be abbreviated as Cs*n*Mo12-*x*V*x*.

IBA was fed to a 10 mm o.d. glass reactor by N_2 carrier gas flowing through a saturator which was kept at 328 K. All the flow-lines from the saturator were made of Teflon or glass tubes, which were heated to 373 K in order to prevent adsorption or condensation on the wall of the tubes. The standard reaction conditions were as follows. The composition of the feed gas was IBA 1.8%, O_2 3.8% in N_2 balance. The total flow rate was 70 cm^3 min^{-1} and the reaction temperature was 623 K. Before the reaction, the catalyst was pretreated at 623 K in air for 2 h.

Reactants and products were analyzed by on-line GC with an TCD detector. Packed GC columns used for analyses were 2 m FFAP for IBA and MAA at 373 K, 1.2 m MS-5A for CO at room temperature, and 3 m Porapak Q for CO_2, C_3H_6, and acetone with heating from 323 to 453 K.

Conversion was determined from the percent ratio of IBA converted on the basis of IBA fed. Selectivity was calculated by dividing each product by the sum of the products. Since the formation of acetone and propylene was always accompanied by the equimolar amount of CO or CO_2, the net amounts of CO and CO_2 produced from the destructive oxidation of IBA were determined by deducting acetone + propylene from the amount of CO and CO_2 experimentally determined. Total carbon balance was around 95%.

IR spectra were recorded on a Shimazu FTIR-8600 spectrometer using an in situ IR cell. The catalyst was dispersed on a silicon wafer and set in the IR cell. BET surface area was measured by use of Micromeritics ASAP 2000.

X-ray diffraction patterns were obtained using a Mac Science MXP3 diffractometer (40 kV and 30 mA). Si powder (99.99%) was added to samples as an internal reference. Sampling was carried out by 0.01° and the scan speed was 2° min^{-1}.

3. Results and discussion

Fig. 1 shows the results of IBA oxidation over Mo12-xVx at the steady state at 623 K. All the products, MAA, acetone, propylene, and CO + CO_2 started to be formed from the beginning of the reaction and steady states were reached within 3 h for all the catalysts examined. The IBA conversions and selectivities to those products are shown as a function of the V content in Fig. 1. The conversion of IBA for Mo12 was 50% and decreased with the V content to 30% for Mo9V3. For the selectivity to MAA, Mo11V revealed the maximum value even though it was not very high compared to others. Akimoto et al. have shown that the highest oxidation–reduction potential measured by cyclic voltammetry at 293 K was the highest at Mo11V, which paralleled the catalytic activity for IBA oxidation at 573 K [8]. Such promoting effect of V substitution was not noticeable in the present study; the thermal instability of the Mo12-*x*V*x* at 623 K is the probable reason for the low activity.

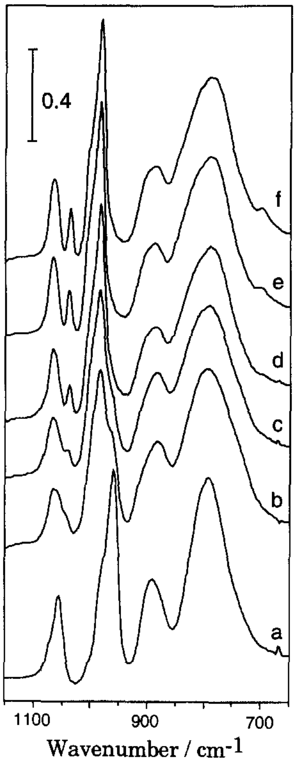


Fig. 2. Changes in in situ IR spectra of $H_4PMo_{11}VO_{40}$ during heating in O_2 at various temperatures: (a) fresh catalyst, (b) 423 K, (c) 473 K, (d) 523 K, (e) 573 K, and (f) 623 K.

The thermal stability of Mo11V was examined by in situ IR measurements heating the catalyst in O_2. The results are shown in Fig. 2. Fresh catalyst showed absorption bands at 1072 cm^{-1} (shoulder), 1055 cm^{-1} (very strong) for ν(P–O), 981 cm^{-1} (shoulder), 961 cm^{-1} (very

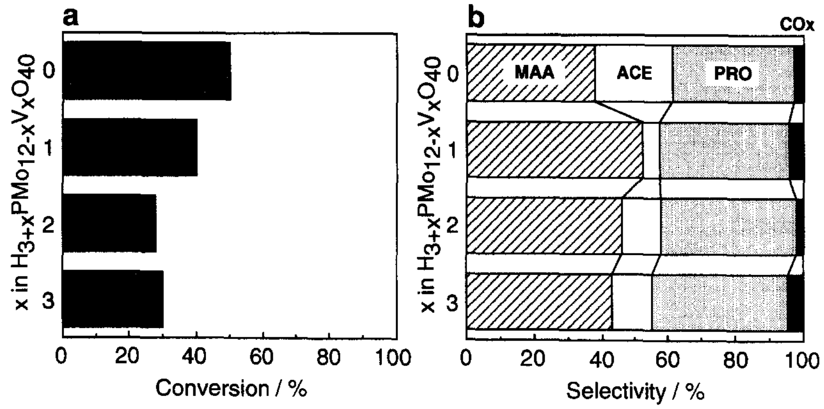


Fig. 1. Effects of V contents, *x*, in $H_{3+x}PMo_{12-x}V_xO_{40}$ catalysts on the conversion (a) and selectivity (b) for oxidative dehydrogenation of isobutyric acid at 623 K. MAA, ACE, and PRO are methacrylic acid, acetone, and propylene, respectively.

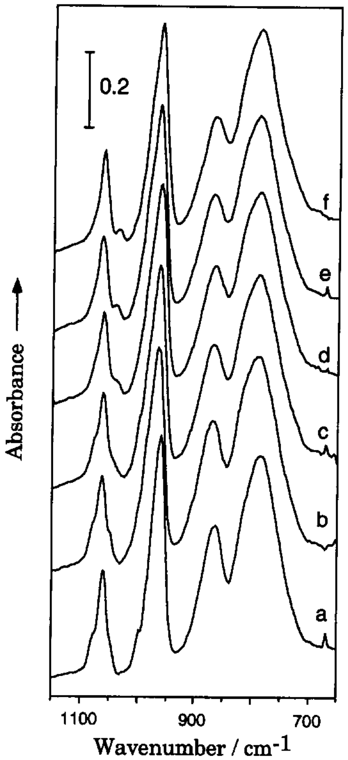


Fig. 3. Changes in in situ IR spectra of $Cs_{2.75}H_{1.25}PMo_{11}VO_{40}$ during heating in O_2: (a) fresh catalyst, (b) 423 K, (c) 473 K, (d) 523 K, (e) 573 K, and (f) 623 K.

strong) for ν(M = O), and 890 cm^{-1} (medium), 792 cm^{-1} (very strong) for ν(M–O–M) at room temperature. These bands coincided with those reported by Rocchiccioli-Deltcheff et al. [21], supporting the formation of Mo, V mixed-coordinated heteropolyanion. From 473 K, a new band appeared at 1040 cm^{-1}. Its intensity increased with temperature and became remarkable at 623 K, while the rest of the spectra remained very similar to that of Mo12. The band at 1040 cm^{-1} has been assigned to vanadophosphate by Rocchiccioli-Deltcheff et al. [21], while the assignment remained still controversial. So, it is concluded that the Keggin anion was decomposed during the pretreatment at 623 K even in air, and this decomposition explains the small effect of V substitution shown in Fig. 1.

In order to improve the thermal stability of molybdovanadophosphoric acids, Cs salts of the above heteropolyacids were utilized. The IR spectra of Cs2.75Mo11V are shown in Fig. 3. In contrast to Mo11V (Fig. 2), the band at 1040 cm^{-1} was suppressed noticeably. It appeared from 523 K which was higher than that for Mo11V and its intensity was much smaller than Mo11V. The intensity did not change by a further heating at 623 K for over 5 h. These facts indicate that the formation of Cs salts stabilized the anion structure at high temperature.

The dependencies on the Cs contents of the conversion and selectivity of IBA oxidation for CsnMo11V are shown in Fig. 4. Both conversion and selectivity for MAA increased sharply at $n = 2$ and reached a high maximum at $n = 2.75$, where the conversion was 98% and MAA selectivity 77%. Further increase of Cs contents

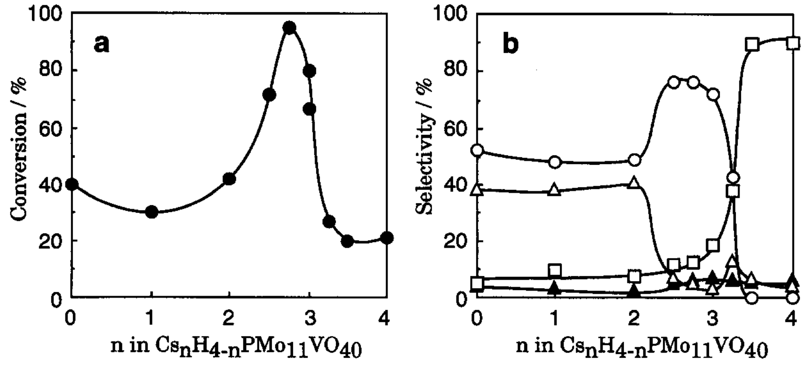


Fig. 4. Effects of Cs contents, n, in $Cs_nH_{4-x}PMo_{11}VO_{40}$ catalysts on the conversion (a) and selectivity (b) for oxidative dehydrogenation of isobutyric acid at 623 K: ○, methacrylic acid; □, acetone; △, propylene; ▲, CO_x.

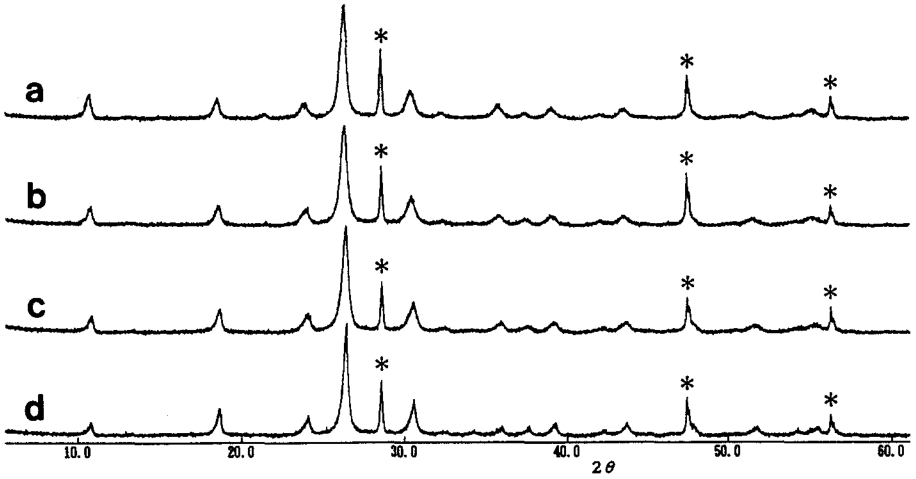


Fig. 5. XRD patterns of $Cs_nH_{4-x}PMo_{11}VO_{40}$: (a) $n = 2$, (b) $n = 2.75$, (b) $n = 3$, (c) $n = 4$. Asterisks represent XRD patterns of Si powder used as an internal reference.

above $n = 3$ decreased the activity substantially. It is likely that there is little acidity above $n = 3$ since excess Cs ions exist on the surface (vide infra). MAA formation was not observed at $n = 3.5$ and 4, suggesting that the presence of both Brönsted acidity and redox ability was necessary in order to produce MAA, which has been pointed out by other research groups as well [16,22,23] and also observed for the oxidation of methacrolein to MAA [24]. Formation of propylene decreased from $n = 2$, while acetone increased from $n = 3$.

XRD patterns of Cs*n*Mo11V for $n = 2$, 2.75, 3, and 4 are shown in Fig. 5. Little differences were observed among the XRD patterns, which were the same bcc pattern as $H_3PW_{12}O_{40} \cdot 6H_2O$ and $Cs_3PW_{12}O_{40}$ [25]. Considering the bcc structure and the size of Cs^+ ion, up to three Cs^+ ions per Keggin anion are possible to be incorporated into the stable bcc structure [25]. Therefore, the excess Cs ions above $n = 3$ cannot exist in the bulk. They are probably dispersed as thin films or fine particles on the surface since no other peaks other than those for heteropolyacid were detected by XRD for $n > 3$. For $n < 3$, the Cs salts are most probably the solid solutions and/or mixtures of Mo11V and Cs3Mo11V, similarly to the case of $Cs_nH_{3-n}PW_{12}O_{40}$ (Cs*n*W12) [17,18].

Fig. 6 shows the BET surface areas of Cs*n*Mo11V ($n = 0$–4). From $n = 2$, the surface area increased sharply, and reached 170 $m^2\ g^{-1}$ above $n = 3$. This change was similar to that reported for Cs*n*W12 [17,18]. The high surface area would be one of the main reasons of the high activity of acidic Cs salts of molybdovanadophosphoric acids. However, additional chemical effects should be considered since the patterns of the surface area was not the same with that of activity. From the surface area and the total H^+ amount for each acidic Cs salt, surface acidity can be estimated as in the case

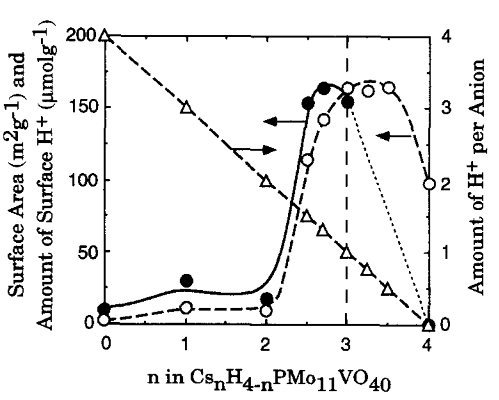
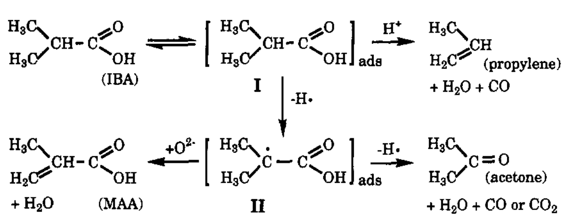


Fig. 6. BET surface areas and calculated surface acidity (amount of surface H^+) of $Cs_nH_{4-x}PMo_{11}VO_{40}$: ○, surface area; △, amount of H^+ per anion; ●, amount of surface H^+ per gram (see text).



Scheme 2. Overall reaction scheme for the oxidative dehydrogenation of IBA proposed by Akimoto et al. [8].

of Cs*n*W12 [17,18] as shown in Fig. 6. Here, the surface acidity was evaluated only up to $n=3$, since H^+ (or Cs^+) is very likely not dispersed uniformly in the solid bulk for $n>3$ from the XRD results as described above. The surface acidity (Fig. 6) reflects the pattern of activity (Fig. 4) very well below $n=3$. This close correspondence and the similar behavior between Cs*n*W12 [17,18] and Cs*n*Mo11V for $n \leqslant 3$ indicate that the surface acidity thus estimated is reasonable for $n \leqslant 3$.

IBA decomposition to propylene in the absence of O_2 is typical acid catalysis [8,26]. The formation of propylene, however, was not directly correlated with the surface acidity and even was suppressed at around $n=2.75$ (Fig. 4), although the surface acidity must be high. Ernst et al. have suggested the different active sites for the formations of propylene and MAA or acetone [27]. However, the present results indicate that the active sites for the two reactions are not independent. The following facts also suggest that the two reactions are related: (1) The fully neutralized Cs salt of the heteropolyacid was catalytically inert for the production of not only propylene but also MAA as shown in the present study and by others [16,22,23]. (2) As oxygen feed was stopped during the reaction, propylene decreased with other oxidation products [27].

Akimoto et al. have suggested a reaction mechanism such as Scheme 2 [8]. According to them, there is a common adsorbed IBA intermediate (**I**) for propylene and MAA or acetone. MAA is formed via the consecutive homolytic abstraction of hydrogen from **I**, while propylene is produced through decomposition of **I** by the attack of acidic proton. Their idea that there is a common intermediate for the formations of propylene and MAA is interesting. The present study indicates as discussed above that common intermediate for propylene and MAA is formed, this step being accelerated by high surface acidity. When the catalyst has high oxidizing ability, this intermediate is preferably transformed to MAA in the presence of O_2, for example, by steps in Scheme 2. In consequence, MAA could be produced very selectively due to high oxidizing ability and surface acidity around $n=2.75$.

The selective acetone formation above $n=3$ is noticeable even though the activity was low. Surface basicity caused by the Cs species (possibly oxides or carbonates) on the surface as discussed above may be responsible for the selective acetone formation above $n=3$. Further efforts would be devoted to clarify the

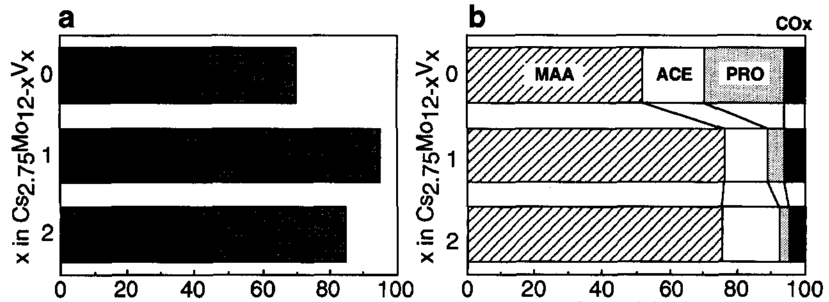


Fig. 7. Effect of V-contents, *x*, in $Cs_{2.75}H_{x+0.25}PMo_{12-x}V_xO_{40}$ catalysts on the conversion (a) and selectivity (b) for oxidative dehydrogenation of isobutyric acid at 623 K. MAA, ACE, and PRO are methacrylic acid, acetone, and propylene, respectively.

precise chemical effects for activity, selectivity and the mechanism. Anyway, the high conversion and selectivity of Cs2.75Mo11V which obtained here is one of the best records which have been reported so forth using heteropoly compounds as catalysts. It may be notable that it was achieved without the presence of water.

Then, the effect of V substitution for the relatively stable Cs2.75Mo11V was investigated (Fig. 7). Among Cs2.75Mo12-xVx, the activity was in the order of $x = 1 > x = 2 > x = 0$ and the MAA selectivity, $x = 1 \geq x = 2 > x = 0$. This effect of V coincided in general with the oxidizing activity or the redox potential which has been determined for Mo12-xVx at 293 K [8]. This indicates that the thermal stability afforded sufficient use of redox ability modified by the incorporation of V to polyanion. Thus, the enhanced redox ability due to the thermal stability, the high surface area, and the high surface acidity, which were brought about by the formation of acidic Cs salts, would be the main reasons for the high performance of this catalyst. It has been reported that the V atoms leave the polyanion structure under reaction conditions and play roles in oxidation catalysis [28]. The present study does not provide any direct information on this subject. However, it was shown at least in the present study that the Cs salts of V-containing heteropolymolybdates exhibited significantly smaller decomposition and higher catalytic performance when the contents of V and Cs were well controlled.

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