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Benzene hydroxylation with hydrogen peroxide catalyzed by vanadium(V)-substituted polyoxomolybdates

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Abstract

Synthesis and ^{31}P and ^{51}V NMR characterization of $Na_5[PMo_{10}V_2O_{40}] \cdot 14H_2O$ **1** as a mixture of five α-Keggin and two β-Keggin divanadium(V)-substituted polyoxomolybdates, recently reported by Pettersson's group, were reproduced. Benzene hydroxylation with hydrogen peroxide catalyzed by **1** was examined under varied conditions: amounts of catalyst precursor, amounts of 30% aqueous H_2O_2, amounts of CH_3CN and different temperature. The turnover vs. time curve has shown a reduced induction period. The NMR characterization revealed that the reaction by **1** was catalyzed by the vanadium(V) species within the Keggin polyoxomolybdates. The traditional vanadium(V)-substituted polyoxomolybdates, "$H_4[PMo_{11}VO_{40}]$" **2**, "$H_5[PMo_{10}V_2O_{40}]$" **3** and "$H_6[PMo_9V_3O_{40}]$" **4**, prepared by the so-called ether-extraction method, consist of Keggin-type $H_4[PMo_{11}VO_{40}]$ and many non-Keggin-type unstable polyoxo species, and do not contain any divanadium(V)-substituted Keggin species like **1**. The reactions by **2–4** were catalyzed by a cationic oxovanadium species $VO(O_2)^+$, directly derived from the contaminated unstable non-Keggin-type species, and, also, indirectly from $H_4[PMo_{11}VO_{40}]$. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Hydroxylation; Benzene; Hydrogen peroxide; Vanadium(V)-substituted polyoxomolybdates; Turnover vs. time curve; Induction period

1. Introduction

There is currently considerable interest in exploiting both the well-defined structure of the catalyst precursor and the multicenter active site to facilitate catalysis by polyoxometalates [1–3]. It has been stressed that it is important to discover more reliable and efficient procedures before the exploration of possible new reactivity patterns [4]. Thus, it is very important to use fully characterized and more reliable catalyst precursors for the catalytic reactions.

Many Keggin- and Dawson-type selectively site-substituted vanadium(V) polyoxotungstates have been well defined. Recently, we have investigated the catalysis by some of them for benzene hydroxylation with hydrogen peroxide [5–7]. We found that this reaction requires a vanadium(V) center and the geometries around it play a significant role [5,6]. Also, it has been recently found that in benzene hydroxylation catalyzed by such polyoxotungstates, the turnover vs. time curve with an induction period

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has suggested the reaction proceeds on the vanadium(V) species within the polyoxotungstates [7]. Further, some of the vanadium(V) atoms incorporated into the polyoxotungstate skeleton can be considered as a model of the solution structure of the vanadate in aqueous solution and, in fact, have shown an insulin-mimetic effect, namely, the effect of normalization of the blood glucose level of streptozotocin-induced diabetes (STZ-mice) [8].

On the contrary, only a few of the corresponding polyoxomolybdates have been known so far. Traditional preparation has been based on the so-called ether-extraction method reported in 1968 by Tsigdinos and Hallada [9], where "$H_4[PMo_{11}VO_{40}]$" **2**, "$H_5[PMo_{10}V_2O_{40}]$" **3** and "$H_6[PMo_9V_3O_{40}]$" **4** have been described. These compounds have been prepared as ether-adducts under H_2SO_4-acidic conditions from the aqueous layers obtained by reactions of different starting molar ratios of Na_2MoO_4, Na_2HPO_4 and $NaVO_3$. Characterization of these compounds has been based on analytical data of P, Mo, V and H_2O, potentiometric titration, UV-vis spectra and TG/DTA. However, ^{31}P and ^{51}V NMR spectroscopic evidences were lacking.

Historically, it was pointed out later that the compound **3** was shown to exist as a mixture of the five Keggin stereoisomers by ^{31}P NMR spectroscopy [10]. Separately, X-ray crystal structures of **3** (with 36 hydrated water) and **4** (with 30 water) were reported by Russian workers to be isostructural, both of which consisted of a distorted "pseudo-Keggin" structure with crystallographic symmetry *4/m* and local symmetry *m3m* [11]. However, these structures were reinterpreted, and it was concluded that they contain normal Keggin molecules disordered as a whole in two positions related by a 90° rotation about the molecular $\bar{4}$ axis [12]. Nevertheless, an extensive work on catalytic reactions using these compounds has been reported so far [1–3], and the ether-extraction preparation of **2–4** has been accepted as standard technique in the field of catalysis. As a matter of fact, these

compounds are commercially available as Keggin-type mono-, di- and trivanadium-substituted polyoxomolybdates. Mechanistic studies of oxidative dehydrogenation using **3** have been discussed based on a definite $[PMo_{10}V_2O_{40}]^{5-}$ species with Keggin structure [13,14].

On the other hand, Pettersson's group has recently achieved the preparation of $Na_5[PMo_{10}V_2O_{40}] \cdot 13.6H_2O$ by a quite different method, completely assigned its ^{31}P and ^{51}V NMR signals and found that it was a mixture of five α-Keggin [1, 2-; 1, 4-; 1, 5-; 1, 6-; 1, 11-positional isomer] and two β-Keggin type [4, 10-; 4, 11-isomer] divanadium(V)-substituted polyoxomolybdates [15]. The polyhedral representation of the polyoxomolybdate with α- and β-Keggin structures, and the positions substituted by vanadium(V) atoms, are shown in Fig. 1. It is noteworthy that all polyoxomolybdates contained in this compound have been clarified to be the positional isomers with α- and β-Keggin structures only, their (^{31}P and ^{51}V) NMR assignment has been completed, and the existence of divanadium(V)-substituted polyoxomolybdates, although only as a mixture, has been evidenced. As to the related polyoxomolybdates, the STM image of Dawson-type monovanadium(V)-substituted polyoxomolybdate $H_7[P_2Mo_{17}VO_{62}]$ has been recently reported [16], in which the sample has been reported to be supplied by an American company. As a matter of fact, although we have made a considerable effort to prepare and isolate a single species of selectively site-substituted vanadium(V) polyoxomolydates with Keggin and Dawson structures including $[P_2Mo_{17}VO_{62}]^{7-}$, almost all attempts have been unsuccessful, except a previously reported isolation of the Keggin-type monovanadium(V)-substituted species $[PMo_{11}VO_{40}]^{4-}$ [6].

In this work, we have reproduced the preparation and ^{31}P and ^{51}V NMR characterization of $Na_5[PMo_{10}V_2O_{40}] \cdot 14H_2O$ **1**, examined an action of **1** and also of **2–4** on benzene hydroxylation with hydrogen peroxide, and studied the species participating in their catalytic reactions
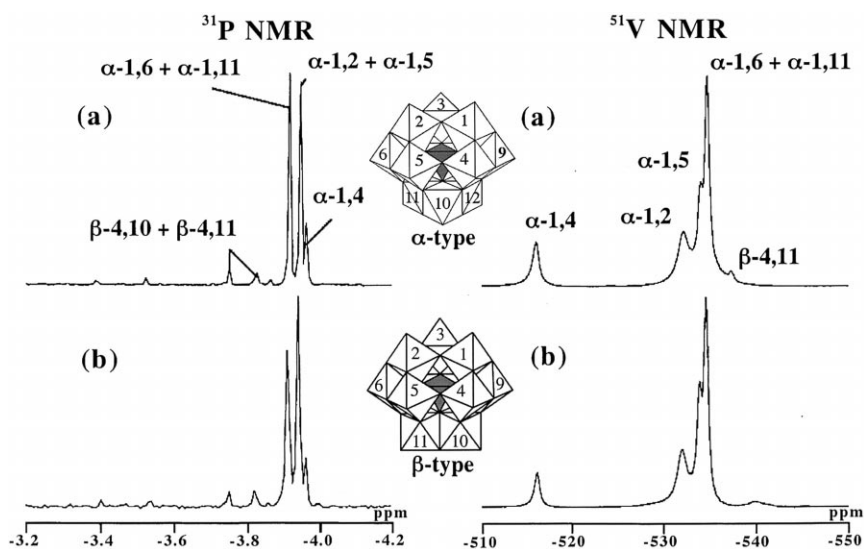
Fig. 1. ^{31}P and ^{51}V NMR spectra in D_2O of the samples (a) before reaction and of the sample (b) recovered after 120-h reaction using $Na_5[PMo_{10}V_2O_{40}] \cdot 14H_2O$ **1** under the following conditions: 0.1 mmol catalyst precursors, 2 ml (25.4 mmol) of 30% H_2O_2, 10 ml (111.6 mmol) benzene and 5 ml of CH_3CN at room temperature. The numbering in ^{31}P and ^{51}V peaks shows the position of the octahedral vanadium atoms substituted in the α- and β-Keggin structures and the assignment is based on the literature [15].

from ^{31}P and ^{51}V NMR measurements of the samples before use and after the reactions, and, also, from the second reaction by the recovered samples after the first reaction. Here, we report benzene hydroxylation catalyzed by **1** under varied conditions, the noteworthy stability as catalyst of **1**, and the fact that the reaction by **1** was catalyzed by the vanadium(V) species within the polyoxomolybdates. Also reported is that the species participating in benzene hydroxylation by **2**–**4** are a cationic oxovanadium species $VO(O_2)^+$ and an indirect $H_4[PMo_{11}VO_{40}]$.

2. Experimental

2.1. Materials

The following were used as received: Na_2CO_3, anhydrous Na_2HPO_4, $Na_2MoO_4 \cdot 2H_2O$, 18 M H_2SO_4, 85% H_3PO_4, benzene, 30% aqueous H_2O_2, CH_3CN, diethyl ether (all from Wako); $NaVO_3$ (Nacalai Tesque); V_2O_5, (Kanto); MoO_3 (Seokawa); D_2O (Isotec). Am-

berlyst® 15(wet) cation-exchange resin (Aldrich), $Na_4[PMo_{11}VO_{40}] \cdot 8H_2O$ [6,7], $(Bu_4N)_4[PMo_{11}VO_{40}]$ [6], ''$H_4[PMo_{11}VO_{40}] \cdot 10H_2O$'' **2** [6,9], ''$H_5[PMo_{10}V_2O_{40}] \cdot 17H_2O$'' **3** [6,9] and ''$H_6[PMo_9V_3O_{40}] \cdot 9H_2O$'' **4** [6,9] were prepared and characterized as reported elsewhere.

2.2. Apparatus and instrumentation

Infrared spectra were recorded on a Jasco 300 FT-IR spectrometer in KBr disks at room temperature. Thermogravimetric (TG) and differential thermal analyses (DTA) were acquired using a Rigaku TG8101D and TAS 300 data-processing system. TG/DTA measurements were run under air with a temperature ramp of 4°C/min between 20°C and 500°C.

^{31}P NMR (161.70 MHz) and ^{51}V NMR (104.95 MHz) were recorded at 25°C in 5-mm o.d. tubes on a JEOL JNM-EX 400 FT-NMR spectrometer and JEOL EX-400 NMR data-processing system. ^{31}P NMR spectra were referenced to an external standard of 25% H_3PO_4 in H_2O in a sealed capillary and the ^{51}V NMR

spectra referenced to an external standard of $VOCl_3$ by a substitution method. The chemical shifts were reported on the δ scale with resonances upfield of H_3PO_4 ($\delta = 0$) as negative, and with resonances upfield of $VOCl_3$ ($\delta = 0$) as negative, respectively.

Gas chromatographic (GC) measurements were carried out on a Shimadzu GC-8APT, which was equipped with an Apiezon grease L glass column (Apiezon grease L 10% on Chromosorb W; column length: 2 m; column temperature: 150°C).

2.3. Preparation and characterization of catalyst precursor $Na_5[PMo_{10}V_2O_{40}] \cdot 14H_2O$ **1**

The preparation of $Na_5[PMo_{10}V_2O_{40}] \cdot 14H_2O$ **1** [15] was reproduced on 1/40 of the scale described in the literature. Over 10 min, 3.18 g (30 mmol) of Na_2CO_3 were added to a suspension of 5.46 g (30 mmol) of V_2O_5 in 50 ml water, which was heated at 50°C in a water bath. The solution was refluxed for 1 h, resulting in a green solution. To it, 25 μl of 30% aqueous H_2O_2 solution was added. After 1-h refluxing of the dark-red solution, the solution was cooled to room temperature. Brown powder formed was filtered off by passing through a folded filter paper (Whatman, No. 5). To the yellow-green filtrate stirred, 43.18 g (300 mmol) of MoO_3 was slowly added, followed by refluxing for 15 min. To the yellow suspension, 4.77 g (45 mmol) of Na_2CO_3 was added over 10 min, and then 3.42 g (30 mmol) of 85% H_3PO_4 was added. The obtained orange suspension was refluxed for 3 h, and the resulting dark-orange clear solution was cooled to room temperature. The solution was evaporated by rotary evaporator to deposit orange crystals. The crystals collected on a fine glass frit were dried thoroughly by suction, and further for 3 h in vacuo. Orange crystals obtained in 15.7-g (26.3%) yield were soluble in water, acetone, acetonitrile, methanol, ethanol and ethyl acetate, but insoluble in benzene, chloroform and dichloromethane.

TG/DTA data: 12.22% weight loss observed below 499°C with endothermic peaks at 82.3, 101.3°C: calc for $Na_5[PMo_{10}V_2O_{40}] \cdot xH_2O$, 12.0%–12.8% ($x = 14$–15). ^{31}P NMR (D_2O, at room temperature): [major peak] -3.92 ppm (α-1,6- and α-1,11-isomers), [minor peaks] -3.96 (α-1,4-isomer), -3.95 (α-1,2- and α-1,5-isomers), -3.82 and -3.75 (β-4,10- and β-4,11-isomers) ppm. ^{51}V NMR (D_2O, at room temperature): [major peak] -534.7 (α-1,6- and α-1,11-isomers), [minor peaks] -537.3 (β-4,11-isomer), -534.0 (α-1,5-isomer), -532.1 (α-1,2-isomer), -515.9 (α-1,4-isomer) ppm. Prominent IR bands (KBr disk): 1076m, 1065m, 1053m, 951s, 870m, 794s cm^{-1}.

2.4. Typical oxidation procedures and products analysis

The oxidation reaction of benzene was carried out at 25°C in a 50-ml round-bottom flask. The reaction system consisted of two liquid phases: an organic layer containing benzene and acetonitrile, and an aqueous layer containing acetonitrile and 30% H_2O_2. In a typical experiment, 0.10 mmol of catalyst precursor, 10 ml (113 mmol) of benzene, 2 ml (25.4 mmol) of aqueous 30% H_2O_2, and 5 ml of acetonitrile in a 50-ml round-bottom flask with a serum cap were employed. A magnetic stirrer was provided to stir the reaction medium. The oxidation reaction at 25°C was monitored at various time intervals by GC analysis (an Apiezon grease L column). For the organic phase in the presence of acetonitrile, 1.5 μl was sampled using a microsyringe and analyzed. The reaction product, phenol, was quantitatively analyzed using the calibration curve based on the relative area of each of authentic samples relative to an acetonitrile. In quantitative analysis of phenol, the amounts contained in the organic layer were actually much greater than those in the aqueous layer; the latter amounts were negligible. Catalytic turnovers were estimated as a ratio of product (mmol)/catalyst precursor (mmol).

3. Results and discussion

3.1. Synthesis and composition of **1**

The molecular formula of **1** written as $Na_5[PMo_{10}V_2O_{40}] \cdot 14H_2O$ was consistent with all data of TG/DTA, FT-IR, ^{31}P and ^{51}V NMR spectra (Fig. 1(a)), and also in good agreement with the literature data [15]. In Fig. 1(a), the assignment of ^{31}P and ^{51}V signals has been based on the literature. Although the synthetic procedure is quite different from a molecular design of the corresponding polyoxotungstates, the formation of **1** and its yield were reproduced in the 1/40 scale of the literature.

3.2. Benzene hydroxylation catalyzed by **1**

Fig. 2(a) shows turnover vs. time curve of benzene hydroxylation with hydrogen peroxide catalyzed by **1** under the following conditions: 0.1 mmol catalyst precursor, 2 ml (25.4 mmol) of 30% aqueous H_2O_2, 10 ml of benzene and 5 ml of CH_3CN at room temperature. After 5-h

reaction, the reaction proceeded catalytically, the catalytic turnover being 0.5 after 3 h, 1.1 after 5 h, 2.3 after 7 h, 8.1 after 24 h and 10.0 after 48 h. Compared with a control experiment (Fig. 2(e)) with the previously reported $(Bu_4N)_4[\alpha-PMo_{11}VO_{40}]$ [6,7], the induction period was much reduced and the catalytic activities were much higher before 72 h.

After 120- and 168-h reactions by **1**, the catalysts were recovered by evaporating the aqueous layer to dryness, washing with ether and collecting the water-soluble species. The recovered catalyst after the 120-h reaction was characterized with FT-IR, ^{31}P and ^{51}V NMR spectra (Fig. 1(b)), and the sample recovered after 168-h reaction was reused for benzene hydroxylation under the same conditions. In the second reaction by the recovered catalyst, where the amount of the recovered catalyst (mmol) was assumed to be 0.1 mmol, the catalytic turnover was 0.8 after 3 h, 1.9 after 5 h, 3.7 after 7 h, 11.0 after 24 h and 11.1 after 48 h. A slight increase of the turnovers is attributed to the fact that true amounts of the recovered
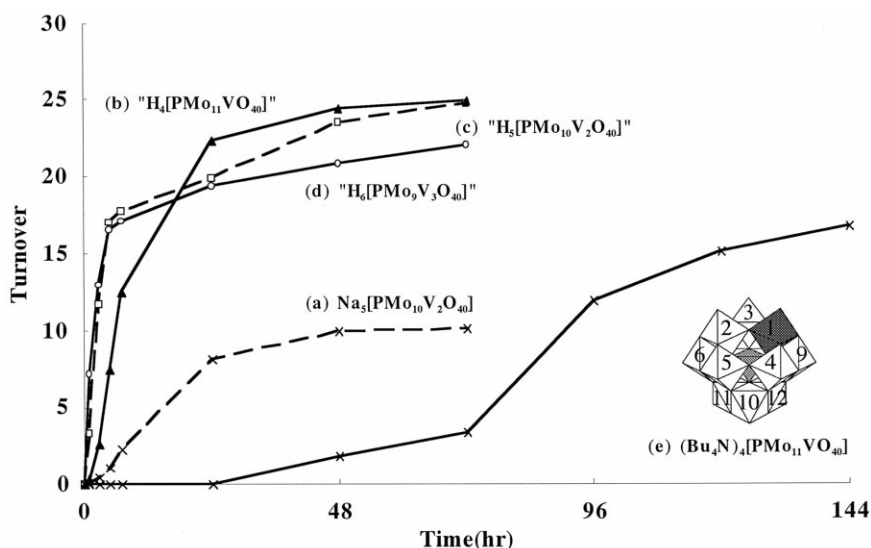

Fig. 2. Benzene hydroxylation catalyzed by (a) $Na_5[PMo_{10}V_2O_{40}]$ **1**, by (b) ''$H_4[PMo_{11}VO_{40}]$'' **2**, (c) ''$H_5[PMo_{10}V_2O_{40}]$'' **3**, (d) ''$H_6[PMo_9V_3O_{40}]$'' **4** and by (e) $(Bu_4N)_4[PMo_{11}VO_{40}]$ under the following conditions: 0.1 mmol catalyst precursors, 2 ml (25.4 mmol) of 30% H_2O_2, 10 ml (111.6 mmol) benzene and 5 ml (for (a)–(d)), 10 ml (for (e)) of CH_3CN at room temperature.

sample are slightly less than 0.1 mmol. We can say that the catalytic activities of the recovered catalyst are almost unchanged and, therefore, **1** is a very stable catalyst precursor. In fact, the ^{31}P and ^{51}V NMR of the recovered sample were almost identical with those of the sample before use (Fig. 1(b)). Thus, it is clear that the reaction by **1** is catalyzed by the vanadium(V) species within this polyoxomolybdate and seven Keggin-type divanadium(V)-substituted polyoxomolybdates included in **1** are stable under the reaction. However, at present, since we have not isolated the respective isomer as a single species, we cannot conclude which isomers participate in the reaction as the true catalysts.

Recently, we have found that, in general, the reaction showing the turnover vs. time curve with an induction period was catalyzed by the vanadium(V) species within the polyoxometalate as observed in the catalysis by $(Bu_4N)_4$-$[\alpha\text{-PMo}_{11}VO_{40}]$ (Fig. 2(e)), and also by $(Bu_4N)_4K[\alpha\text{-}1,2\text{-PW}_{10}V_2O_{40}]$, $K_6H[\alpha\text{-}1,2,3\text{-}SiW_9V_3O_{40}]$ and $K_5[\alpha\text{-}1,2\text{-PW}_{10}V_2O_{40}]$ (only for the first reaction) [7]. The only exception was the reaction catalyzed by the vanadium(V) species within the polyoxometalate, $K_8H[\alpha_2\text{-}P_2W_{15}Mo_2VO_{62}]$, the turnover vs. time curve of which did not show an induction period [7]. On the contrary, the reactions without an induction period as observed in the catalysis by $K_6H[\beta\text{-}1,2,3\text{-SiW}_9V_3O_{40}]$, $K_6[\alpha\text{-}1,2,3\text{-PW}_9V_3O_{40}]$, $Na_4[\alpha\text{-PMo}_{11}VO_{40}]$, $K_4[\alpha\text{-PMo}_{11}VO_{40}]$, $K_6[\alpha\text{-}1,4,9\text{-PW}_9V_3O_{40}]$ and $K_8[\alpha_2\text{-}1,2\text{-P}_2W_{16}V_2O_{62}]$, were catalyzed by the vanadium(V) species generated from the polyoxotungstates. Thus, the reaction by **1** is one of the former examples, although the induction period is much reduced.

Benzene hydroxylation with hydrogen peroxide catalyzed by **1** has been also examined under the following conditions: varied amounts of **1** (0.1, 0.01 mmol), varied amounts of 30% aqueous H_2O_2 (2, 4 ml), and varied amounts of CH_3CN (2, 5 ml) and different temperature (25°C, 45°C and 60°C). The reaction by **1** is also accompanied with decomposition of hydrogen peroxide as observed in the catalysis by

$K_5[\alpha\text{-}1,2\text{-PW}_{10}V_2O_{40}]$ and $(Bu_4N)_4[\alpha\text{-PMo}_{11}\text{-}VO_{40}]$ [7]. Thus, the decreased amounts of **1** and/or the increased amounts of 30% aqueous H_2O_2 lead to the increased turnovers as apparent activities. In fact, under 10 ml of benzene and 5 ml of CH_3CN, when 0.1 mmol of **1** and 4 ml (50.8 mmol) of 30% H_2O_2 were used, the catalytic turnovers were 1.2 after 3 h, 3.4 after 5 h, 5.3 after 7 h, 20.1 after 24 h and 22.1 after 48 h; when 0.01 mmol of **1** and 2 ml (25.4 mmol) of 30% aqueous H_2O_2 were used, the turnovers were 0.6 after 5 h, 2.8 after 7 h, 12.7 after 24 h and 27.1 after 48 h; and when 0.01 mmol of **1** and 4 ml of 30% aqueous H_2O_2 were used, the turnovers were 2.4 after 3 h, 3.4 after 5 h, 4.2 after 7 h, 19.9 after 24 h and 44.9 after 48 h. Further, at elevated temperature, the turnovers were significantly increased, but decomposition of hydrogen peroxide was also promoted and, therefore, the activities rapidly reached the maximum value. Under the following conditions: 0.1 mmol of **1**, 2 ml of 30% H_2O_2, 10 ml of benzene and 5 ml of CH_3CN, the turnovers at 45°C were 0.8 after 30 min, 2.0 after 45 min, 2.8 after 60 min, 6.4 after 90 min, 8.5 after 120 min, and that at 60°C, the turnovers were 8.3 after 30 min, 8.6 after 45 min, 9.6 after 60 min and 10.5 after 90 min. The amount of acetonitrile used (2 and 5 ml) did not influence the activities.

3.3. Benzene hydroxylation catalyzed by three *vanadium(V)-substituted polyoxomolybdates* **2**–**4** obtained by the so-called ether-extraction method

In the reactions by **3** and **4** (Fig. 2(c) and (d)), the turnovers abruptly increased without an induction period. Compared with **1** and $(Bu_4N)_4[\alpha\text{-PMo}_{11}VO_{40}]$, the activities in the early stage of reaction are much higher and their turnover vs. time curves are characteristic of the reactions catalyzed by the vanadium(V) species generated from the polyoxometalates [7]. Since the compounds **3** and **4** are free acid forms and show strong Bronsted acidity, it is likely that a

cationic oxovanadium species such as VO_2^+, generated by decomposition of **3** and **4** with hydrogen peroxide, or a $VO(O_2)^+$ species readily formed by a reaction between VO_2^+ and hydrogen peroxide [17,18], participates in the reactions. The catalytic activity of **2** in the early stage (before 7-h reaction) is much lower than those of **3** and **4**, but that of **2** after 24-h reaction reaches those of **3** and **4** (Fig. 2(b)).

These features probably reflect the actual compositions of such polyoxomolybdates. The ^{31}P and ^{51}V NMR spectra in D_2O reveal that **2** contains $H_4[PMo_{11}VO_{40}]$ as a major species and a few minor species, while **3** and **4** consist of many unidentified minor species plus $H_4[PMo_{11}VO_{40}]$ (Fig. 3). The ^{31}P NMR chemical shifts of many minor species are quite different from those of **1**. On the other hand, the ^{31}P and ^{51}V NMR spectra in D_2O of the samples recovered after 120-h reaction using **2–4** were very simple, and the signals were quite similar to those of separately prepared $Na_4[PMo_{11}VO_{40}]$ as a single species with ^{31}P NMR at -3.84 ppm, ^{51}V NMR at -533.9 ppm [6]. Almost all the initially observed minor peaks disappeared (Fig. 3). Probably, all of the many minor species, other than the $[PMo_{11}VO_{40}]^{4-}$ species contained in **2–4** are not Keggin-type polyoxomolybdates, but a relatively unstable polyoxo species consisting of P, V and Mo atoms, which have tendencies to readily form a highly reactive oxovanadium species by a reaction with hydrogen peroxide. We have so far noticed that such minor species are unstable in the work-up of cation exchange with Bu_4N^+ and Na^+ ions, because some of the ^{31}P signals due to the minor species have disappeared [6]. From the viewpoint of only the reactivity, such minor species may be randomly vanadium(V)-substituted ''pseudo-Keggin'' structure species, initially reported by Russian workers [11], but later reinterpreted by Evans and Pope [12]. If the minor species contain some of the Keggin-type divanadium(V)-substituted polyoxomolybdates, their ^{31}P and ^{51}V NMR peaks should be retained after the reaction, just as observed in **1**.
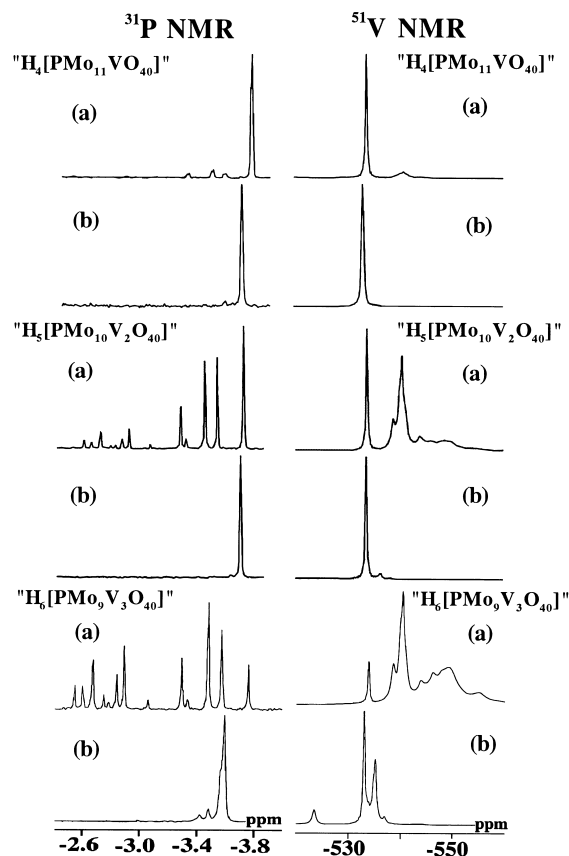

Fig. 3. ^{31}P and ^{51}V NMR spectra in D_2O of the samples (a) before reaction and of the samples (b) recovered after 120-h reaction using ''$H_4[PMo_{11}VO_{40}]$'' **2**, ''$H_5[PMo_{10}V_2O_{40}]$'' **3** and ''$H_6[PMo_9V_3O_{40}]$'' **4** under the conditions: 0.1 mmol catalyst precursors, 2 ml (25.4 mmol) of 30% H_2O_2, 10 ml (111.6 mmol) benzene and 5 ml of CH_3CN at room temperature. The recovery of the sample was performed by evaporating the aqueous layer to dryness, washing with ether, and then collecting water-soluble species.

The ^{51}V NMR spectra of the aqueous layer after the 72-h reaction by **3** showed a major peak at -533.1 ppm due to $H_4[PMo_{11}VO_{40}]$ and a minor peak at -539.4 ppm due to the cationic VO_2^+ or $VO(O_2)^+$ species. In fact, the ^{31}P and ^{51}V NMR in D_2O of the eluate obtained by passing the aqueous layer after 40-h reaction by **3** through the Amberlyst® 15(wet) cation-exchange resin column showed a single species with ^{31}P signal at -3.91 ppm and ^{51}V signal at -533.1 ppm, suggesting that these spectra are due to the pure species of $H_4[PMo_{11}VO_{40}]$.

Also, the FT-IR spectrum of the solid sample recovered after 72-h reaction by **3** confirmed the Keggin polyoxomolybdate.

The second reaction, using the solid sample recovered by passing the aqueous layer after the first 72-h reaction by **3** through the cation-exchange resin, removing any cationic species such as VO_2^+ and $VO(O_2)^+$, and evaporating to dryness, also showed no induction period, the turnovers of which were somewhat lower compared with the first reactions (Fig. 4(b)). The difference in activities between the first and the second reactions, shown in Fig. 4(a) and (b), respectively, should arise from the reactive, cationic species $VO(O_2)^+$, being formed from VO_2^+ under hydrogen peroxide. Thus, the species participating in the first reactions by **3** are cationic oxovanadium species $VO(O_2)^+$ and $H_4[PMo_{11}VO_{40}]$. Fig. 4(c) shows the results from the reaction by freshly prepared $Na_4[PMo_{11}VO_{40}]$ (0.1 mmol). The reactions themselves by $H_4[PMo_{11}VO_{40}]$ and $Na_4[PMo_{11}VO_{40}]$ under aqueous H_2O_2 would also be catalyzed by the vanadium(V) species, $VO(O_2)^+$, generated from these polyoxomolybdates, because of their

turnover vs. time curves without an induction period [7]. The catalytic activity of the intact $[PMo_{11}VO_{40}]^{4-}$ polyoxoanion is, in fact, very low, in particular, in the early stage of the reaction as observed in $(Bu_4N)_4[PMo_{11}VO_{40}]$ (Fig. 2(e)). Although the activities shown in Fig 4(b) include the apparent increments due to a slight loss of the catalyst during the cation exchange and recovering work-up, the difference in activities shown in Fig. 4(b) and (c) may be partly attributed to the effect by Bronsted acidity of $H_4[PMo_{11}VO_{40}]$.

In relation to the discussion here, it has been recently reported that the reaction of the commercially available ''$H_4[PMo_{11}VO_{40}]$'' with H_2O_2 to form $[PMo_{11}O_{39}]^{7-}$ and $VO(O_2)^+$ is fast, and that of $VO(O_2)^+$ with methane is slow and an active species for the selective oxygenation of methane in trifluoroacetic anhydride catalyzed by V-containing catalysts is $VO(O_2)^+$ [19]. Also, for H_2O_2-based epoxidation of alkenes catalyzed by $[PW_9(NbO_2)_3O_{37}]^{6-}$, it has been found that much of the catalytic activity is derived from generation of tungstate under the reaction conditions [20].

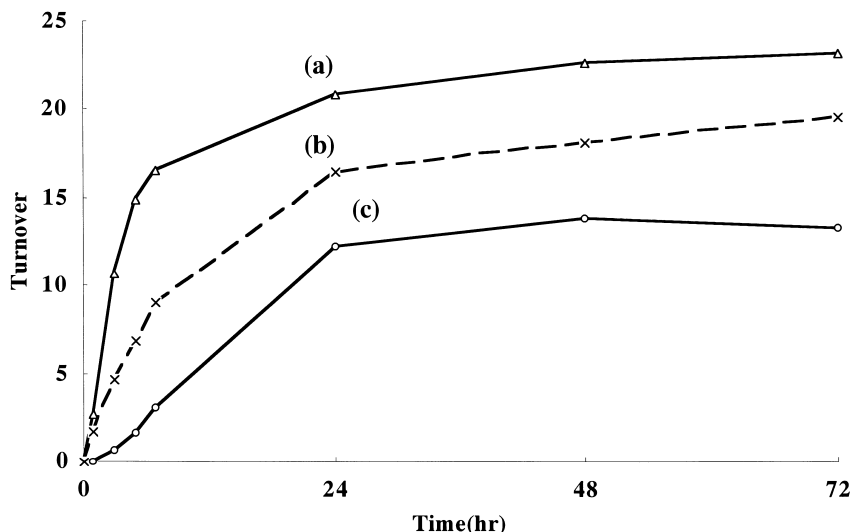Fig. 4. Turnover vs. time curve of (a) the first benzene hydroxylation catalyzed by ''$H_5[PMo_{10}V_2O_{40}]$'' **3**, (b) the second reaction using the solid sample recovered by passing the aqueous layer after the first 72-h reaction by **3** through an Amberlyst® 15(wet) cation-exchange resin column, removing the cationic species such as VO_2^+ and $VO(O_2)^+$, and evaporating to dryness, and (c) the first reaction by freshly prepared $Na_4[PMo_{11}VO_{40}]$ as single species. The conditions in (a) and (c) were 0.1 mmol catalyst precursors, 2 ml (25.4 mmol) of 30% H_2O_2, 10 ml (111.6 mmol) benzene and 5 ml of CH_3CN at room temperature.

3.4. Synthesis of selectively site-substituted vanadium(V) polyoxomolybdates

In the synthetic viewpoint, selectively site-substituted vanadium(V) polyoxomolybdates have been very difficult to prepare. The reactions of tri-lacunary species of Keggin polyoxomolybdates with vanadates and those of Keggin and Dawson polyoxomolybdates under varied pH with vanadates always produced monovanadium(V)-substituted Keggin species $[PMo_{11}VO_{40}]^{4-}$. The compound **1** shows existence of all of the five positional isomers of divanadium(V)-substituted α-Keggin polyoxomolybdates, only as a mixture. Further, the crystal structure of $Na_3H_6[PMo_6V_6O_{40}] \cdot 16H_2O$ with normal Keggin structure, previously reported by Russian workers [21], has been well-refined and interpreted to be valid [12]. Nevertheless, our attempts at isolation of the single species of selectively site-substituted Keggin polyoxomolybdates and even monovanadium(V)-substituted Dawson species $[P_2Mo_{17}VO_{62}]^{7-}$ have been unsuccessful.

4. Conclusion

In this work, benzene hydroxylation with hydrogen peroxide was examined using several vanadium(V)-substituted polyoxomolybdates as catalyst precursors: (1) $Na_5[PMo_{10}V_2O_{40}]$ **1**, recently reported and well-characterized with ^{31}P and ^{51}V NMR spectra by Pettersson's group to be a mixture of five α-Keggin and two β-Keggin type divanadium(V)-substituted polyoxomolybdates; and (2) the three vanadium-substituted polyoxomolybdates obtained by the so-called ether-extraction method, ''$H_4[PMo_{11}VO_{40}]$'' **2**, ''$H_5[PMo_{10}V_2O_{40}]$'' **3** and ''$H_6[PMo_9V_3O_{40}]$'' **4**. The composition of **1** as reported was confirmed, while those of **2–4** consisted of Keggin-type $H_4[PMo_{11}VO_{40}]$ and many non-Keggin-type unstable polyoxo species. In **2–4**, divanadium(V)-substituted Keggin species like **1** were not contained. The

^{31}P and ^{51}V NMR characterization of the samples recovered after the first reaction, and the second reaction using them showed that the reaction by **1** was catalyzed by the vanadium(V) species within the Keggin-type polyoxomolybdates, whereas those by **2–4** were promoted by the cationic oxovanadium species $VO(O_2)^+$, directly derived from the unstable non-Keggin-type polyoxo species and also indirectly from the Keggin-type $H_4[PMo_{11}VO_{40}]$. In the synthetic viewpoint, in contrast to the well-known, selectively site-substituted vanadium(V) polyoxotungstates, the corresponding polyoxomolybdates are difficult to prepare.

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