

Functional action of Keggin-type mono-vanadium(V)-substituted heteropolymolybdate as a single species on catalytic hydroxylation of benzene in the presence of hydrogen peroxide

Kenji Nomiya^{*}, Kazunori Yagishita, Yukihiro Nemoto, Tada-aki Kamataki

Department of Materials Science, Kanagawa University, Hiratsuka, Kanagawa 259-12, Japan

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Abstract

Benzene hydroxylation in the presence of hydrogen peroxide has been studied using tetrabutylammonium salts of three types of mono-vanadium(V)-substituted heteropolyanions (HPA) as catalyst precursors: (i) $[\text{PMo}_{11}\text{VO}_{40}]^{4-}$ (PMo_{11}V , **1**), which has been first prepared herein and identified as a single species, (ii) $[\text{PMo}_{11}\text{VO}_{40}]^{4-}$ (PMo_{11}V , **4**), which has been obtained traditionally by the so-called ether-extraction method and known as a mixed species only with an averaged composition $\text{P}:\text{Mo}:\text{V} = 1:11:1$ and (iii) $[\text{PW}_{11}\text{VO}_{40}]^{4-}$ (PW_{11}V , **2**), which has been prepared as a single species. The PMo_{11}V , **1**, catalytically oxidized benzene to phenol under the conditions: 0.1 mmol catalyst, 10 ml (113 mmol) benzene, 5 or 10 ml of CH_3CN and 2 ml of 30% aqueous H_2O_2 . The catalytic turnover by **1** for phenol production was dependent on the amount of CH_3CN : it was 1.3 after 120 h reaction with 10 ml CH_3CN and 1.7 after 192 h reaction with 5 ml CH_3CN . On the other hand, the PW_{11}V , **2**, did not show catalytic activity even after 240 h reaction under the same conditions. In comparison, it was also confirmed there was no catalytic effect by $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ (PMo_{12} , **3**) without a vanadium(V) center. The PMo_{11}V , **4**, has apparently shown a more enhanced effect, e.g. with catalytic turnover of 7.5 after 144 h reaction with 10 ml CH_3CN . These observations significantly suggest that the catalysis by **1** for benzene hydroxylation is due to cooperative action of the molybdenum framework with one vanadium(V) center. Such action of the polyoxoanion framework has not been observed in the selectively site-substituted vanadium(V) heteropolytungstates such as $[\alpha\text{-}1,2\text{-PW}_{10}\text{V}_2\text{O}_{40}]^{5-}$ and $[\alpha\text{-}1,2,3\text{-PW}_9\text{V}_3\text{O}_{40}]^{6-}$, the catalyses by which were due to the dinuclear vanadium centers with corner-shared octahedra. Furthermore, the marked stability of the mono-vanadium(V)-substituted species **1** of several vanadium(V)-substituted heteropolymolybdates as catalyst precursors was clarified in the benzene hydroxylation. © 1997 Elsevier Science B.V.

Keywords: Hydroxylation; Benzene; Mono-vanadium(V)-substituted heteropolymolybdate; Single species; Catalyst precursor; Keggin-type

^{*} Corresponding author. Fax: +81-463-589684; e-mail: nomiya@info.kanagawa-u.ac.jp

1. Introduction

Catalytic hydroxylation of benzene is a very intriguing reaction and many catalysts have so far been reported [1–17]¹[18–20]. We have shown recently that the di-vanadium(V) substituted Keggin-type heteropolytungstate, $K_5[\alpha\text{-}1,2\text{-PW}_{10}\text{V}_2\text{O}_{40}] \cdot 4\text{H}_2\text{O}$, is the most noteworthy catalyst precursor tested in terms of its stability and catalytic activity for benzene hydroxylation [21]. An active species for this catalytic reaction has been found to be constructed on the A-site of the Keggin heteropolytungstate, specifically a bimetallic species with corner-shared vanadium(V) octahedra. A reaction mechanism in which two-vanadium(V) centers participate has been proposed.

In the synthetic viewpoint, although several species of the selectively site-substituted vanadium(V) heteropolytungstates have been established both in Keggin and Dawson types [22–26], the corresponding vanadium(V)-substituted heteropolymolybdates have not been reported. The traditional method to obtain vanadium-substituted heteropolymolybdates has been performed with the so-called ether-extraction method using altered molar ratios of the starting materials, which has been reported by Tsigdinos and Hallada [27]. The products obtained by this method have been recognized to be a mixture containing several vanadium-substituted species and their positional isomers. Nevertheless, they have been usually represented by general formulas such as $[\text{PMo}_{11}\text{VO}_{40}]^{4-}$, $[\text{PMo}_{10}\text{V}_2\text{O}_{40}]^{5-}$ and $[\text{PMo}_9\text{V}_3\text{O}_{40}]^{6-}$ and also used in several catalytic reactions as exemplified in the recent papers [28–30]. These materials have also been commercially produced. However, such materials have suggested only their averaged compositions. In fact, their ³¹P NMR spectra have shown similar distribution of spectral lines consisting of a number of ³¹P signals [29] and the ⁵¹V

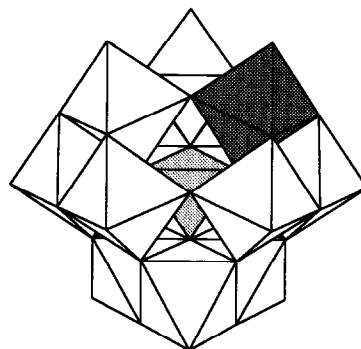


Fig. 1. Polyhedral model of $[\alpha\text{-PMo}_{11}\text{VO}_{40}]^{4-}$, **1**.

NMR spectra as well. Thus, we distinguish herein such compounds from the single species and represent their formulas with quotation marks such as ‘ $[\text{PMo}_{11}\text{VO}_{40}]^{4-}$ ’, ‘ $[\text{PMo}_{10}\text{V}_2\text{O}_{40}]^{5-}$ ’ and ‘ $[\text{PMo}_9\text{V}_3\text{O}_{40}]^{6-}$ ’.

We have aimed at preparing the selectively site-substituted vanadium(V) heteropolymolybdates. As important initial goals of this work, we isolated a single species of the $[\text{PMo}_{11}\text{VO}_{40}]^{4-}$ (PMo_{11}V , **1**) (Fig. 1) as Bu_4N salt from a reaction of a lacunary species $[\text{PMo}_{11}\text{O}_{39}]^{7-}$ with the NaVO_3 aqueous solution and examined its catalytic activity and stability for benzene hydroxylation. Also, in order to elucidate (i) the effect of the polyoxoanion framework with tungsten(VI) atoms or molybdenum(VI) atoms on the benzene hydroxylation and (ii) the relation of the vanadium(V) center with the polyoxoanion framework, we examined the catalytic properties of two types of monovanadium(V) substituted Keggin HPAs, i.e. PMo_{11}V , **1**, and $[\text{PW}_{11}\text{VO}_{40}]^{4-}$ (PW_{11}V , **2**) and also of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ (PMo_{12} , **3**) with no vanadium(V) center for comparison, all of which have been prepared here as single species of tetrabutylammonium salts.

Furthermore, we compared the catalysis by **1** for benzene hydroxylation with those by ‘ $[\text{PMo}_{11}\text{VO}_{40}]^{4-}$ ’ (‘ PMo_{11}V ’, **4**), ‘ $[\text{PMo}_{10}\text{V}_2\text{O}_{40}]^{5-}$ ’ (‘ $\text{PMo}_{10}\text{V}_2$ ’, **5**) and ‘ $[\text{PMo}_9\text{V}_3\text{O}_{40}]^{6-}$ ’ (‘ PMo_9V_3 ’, **6**) as compounds only with averaged compositions and also by their free acid forms, ‘ $\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$ ’ (‘ $\text{H}_4\text{PMo}_{11}\text{V}$ ’, **4a**),

¹ This reference and many references cited therein on Milas hydroxylation of olefins.

'H₅[PMo₁₀V₂O₄₀]' ('H₅PMo₁₀V₂', **5a**) and 'H₆[PMo₉V₃O₄₀]' ('H₆PMo₉V₃', **6a**).

Herein we report the full details of synthesis and characterization of the mono-vanadium(V)-substituted Keggin-type heteropolymolybdate, PMo₁₁V, **1**, as a single species and also its catalysis for benzene hydroxylation, in comparison with PW₁₁V, **2**, and PMo₁₂, **3**. It is particularly noteworthy that the catalysis by **1** is due to one vanadium(V) center acting in cooperation with the molybdenum-polyoxoanion framework. Also reported is the marked stability of **1** as catalyst precursor in comparison with those of several other vanadium(V)-substituted heteropolymolybdates which should be contained in the materials such as 'PMo₁₁V', **4**, 'PMo₁₀V₂', **5** and 'PMo₉V₃', **6**.

2. Experimental

2.1. Materials

The following were used as received: Na₂MoO₄ · 2H₂O, Na₂WO₄ · 2H₂O, Na₂HPO₄, 85% H₃PO₄, 6 M aqueous HCl, Et₂O, Li₂CO₃, Bu₄NBr, EtOH, CH₃CN, benzene, phenol, KBr, KCl, 30% aqueous H₂O₂, H₂SO₄, VOCl₃, commercially available H₃[PMo₁₂O₄₀] · xH₂O (all from Wako); NaVO₃ (Nacalai Tesque); D₂O, DMSO-*d*₆ (Isotec).

2.2. Apparatus and instrumentation

Elemental analyses were carried out by Mikroanalytisches Labor Pascher (Remagen, Germany). 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 per min between 20 and 500°C. ³¹P NMR (161.70 MHz) and ⁵¹V NMR (104.95 MHz) were recorded at 22°C in 5 mm o.d. tubes

on a JEOL JNM-EX 400 FT-NMR spectrometer and JEOL EX-400 NMR data-processing system. ³¹P NMR spectra were referenced to an external standard of 25% H₃PO₄ in H₂O in sealed capillary and the ⁵¹V NMR spectra referenced to an external standard of VOCl₃ by a substitution method. The chemical shifts were reported on the δ scale with resonances upfield of H₃PO₄ (δ 0) as negative and with resonances upfield of VOCl₃ (δ 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 of (Bu₄N)₄[PMo₁₁VO₄₀] (PMo₁₁V,1)

To a solution of H₃[PMo₁₂O₄₀] · xH₂O (11.8 g) dissolved in 50 ml water was slowly added solid Li₂CO₃ until the pH of the clear, yellow solution reached 4.3. At this stage, it was confirmed by only one ³¹P resonance at δ -1.39 ppm observed in the ³¹P NMR measurements that a pure form of the mono-lacunary species was produced in the solution [31]. To this solution was added a pale yellow–orange solution of NaVO₃ (0.65 g, 5.3 mmol), dissolved at 90°C and cooled to room temperature, in 50 ml water. The obtained, clear orange solution was adjusted to pH 0.5 with 6 M aqueous HCl and then the stirring was continued for 48 h. To the solution was added solid Bu₄NBr (9.67 g, 30 mmol). The immediately produced yellow powder was then stirred with additional 100 ml water for 5 h, filtered off, washed thoroughly with 500 ml water, then with EtOH (100 ml × 2) and, finally, with ether (100 ml × 2) and dried in vacuo. The yield at this stage was 13.8 g. From double recrystallization from hot CH₃CN, yellow hexagonal crystals, which were very soluble in DMSO, soluble in CH₃CN and acetone, but insoluble in water, were obtained in 4.29 g yield (31%).

Analysis: found: H, 5.28; C, 28.08; N, 2.10; P, 0.98; Mo, 38.2; V, 2.44; O, 22.8%; total, 99.88%. Calc. for $H_{144}C_{64}N_4PVMo_{11}O_{40}$, or $[(C_4H_9)_4N]_4[PMo_{11}VO_{40}]$: H, 5.29; C, 27.98; N, 2.04; P, 1.13; Mo, 38.4; V, 1.85; O, 23.3%. TG/DTA data: no weight loss was observed below 286°C. An exothermic peak due to decomposition was observed at 302°C. Prominent IR bands (KBr disk): 1482m, 1381w, 1077m, 1055m, 953s, 872s, 802s cm^{-1} ; ^{31}P NMR (DMSO- d_6 , at room temperature): δ -3.77 ppm; ^{51}V NMR (DMSO- d_6 , at room temperature): δ -526.7 ppm.

2.4. Preparation of $PW_{11}V$, **2**, PMo_{12} , **3**, ' $PMo_{11}V$ ', **4**, ' $PMo_{10}V_2$ ', **5** and ' PMo_9V_3 ', **6**

$(Bu_4N)_4[PW_{11}VO_{40}]$ ($PW_{11}V$, **2**) was prepared by adding Bu_4NBr (0.8 g, 2.5 mmol) into an aqueous solution of the $K_4[PW_{11}VO_{40}] \cdot 2H_2O$ (1.47 g, 0.5 mmol) which has been obtained as a single species according to the literature [21,24], filtered off, washed three times with 100 ml water and then dried in vacuo. Yellow powder was recrystallized from acetonitrile. The yield was 1.57 g. ^{31}P NMR in D_2O of $K_4[PW_{11}VO_{40}] \cdot 2H_2O$: δ -14.64 ppm; ^{51}V NMR in D_2O : δ -557.8 ppm; Prominent IR bands (KBr disk) were: 1099m, 1077m, 983m, 883m, 790s, 596m, 521m cm^{-1} . This data was completely coincident with those of the previously obtained, analytically pure compound [21]. For $(Bu_4N)_4[PW_{11}VO_{40}]$, **2**; ^{31}P NMR in DMSO- d_6 : δ -14.60 ppm; ^{51}V NMR in DMSO- d_6 : δ -548.0 ppm; Prominent IR bands (KBr disk): 1096m, 1070m, 962m, 889m, 809s cm^{-1} .

$(Bu_4N)_3[PMo_{12}O_{40}]$ (PMo_{12} , **3**) was prepared by adding Bu_4NBr (3.2 g, 10 mmol) into an aqueous solution of $H_3[PMo_{12}O_{40}] \cdot xH_2O$ (1.8 g, 1.0 mmol calculated on a basis of $x = 12$ determined by TG/DTA analysis), filtered off and washed three times with 100 ml water. Yellow precipitates were dried and then recrystallized from acetonitrile. Yield was 3.2 g. TG/DTA data for $H_3[PMo_{12}O_{40}] \cdot xH_2O$:

11.1% weight loss observed below 407°C: calc for $H_3[PMo_{12}O_{40}] \cdot xH_2O$, 10.6–11.4% ($x = 12$ –13). ^{31}P NMR in D_2O : δ -3.43 ppm; Prominent IR bands (KBr disk): 1637 m (hydrated waters), 1062s, 955s, 880s, 807s cm^{-1} . For $(Bu_4N)_3[PMo_{12}O_{40}]$, **3**; ^{31}P NMR in DMSO- d_6 : δ -3.32 ppm; Prominent IR bands (KBr disk): 1063s, 956s, 880s, 806s cm^{-1} .

The ' $(Bu_4N)_4[PMo_{11}VO_{40}]$ ' (' $PMo_{11}V$ ', **4**) was prepared by adding Bu_4NBr (1.0 g, 3.0 mmol) into an aqueous solution of the ' $H_4[PMo_{11}VO_{40}] \cdot 16H_2O$ ' (' $H_4PMo_{11}V$ ', **4a**) (1.38 g, 0.67 mmol, the contents of hydrated water determined by TG/DTA analysis) which has been obtained by the ether-extraction method using Na_2HPO_4 (3.55 g, 25 mmol), $NaVO_3$ (3.05 g, 25 mmol) and $Na_2MoO_4 \cdot 2H_2O$ (65.5 g, 270 mmol) according to the literature [27], filtered off, washed three times with 50 ml water and recrystallized twice from hot acetonitrile. The yield was 0.62 g. TG/DTA data for ' $H_4[PMo_{11}VO_{40}] \cdot 16H_2O$ ', **4a**: 13.99% weight loss observed below 150°C: calc. for $H_4[PMo_{11}VO_{40}] \cdot xH_2O$, 13.96% ($x = 16$). ^{31}P NMR in D_2O : δ (major peak) -3.92, δ (minor peak) -3.69, -3.59, -3.40 ppm; ^{51}V NMR in D_2O : δ (major peak) -533.9, δ (minor peak) -541.6 ppm; Prominent IR bands (KBr disk): 1062s, 958s, 866m, 778s cm^{-1} . For ' $(Bu_4N)_4[PMo_{11}VO_{40}]$ ', **4**, ^{31}P NMR in DMSO- d_6 : δ (major peak) -3.79, δ (minor peak) -3.65, -3.52 ppm; ^{51}V NMR in DMSO- d_6 : δ -526.4 ppm; Prominent IR bands (KBr disk): 1482m, 1077m, 1056m, 942s, 873m, 802s cm^{-1} .

The ' $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$ ' (' $PMo_{10}V_2$ ', **5**) or the ' $(Bu_4N)_4H_2[PMo_9V_3O_{40}]$ ' (' PMo_9V_3 ', **6**) were similarly prepared by adding excess Bu_4NBr into the aqueous solution containing ' $H_5[PMo_{10}V_2O_{40}] \cdot 14H_2O$ ' (' $H_5PMo_{10}V_2$ ', **5a**) or ' $H_6[PMo_9V_3O_{40}] \cdot 14H_2O$ ' (' $H_6PMo_9V_3$ ', **6a**), respectively, both of which have been obtained by the ether-extraction [27]. TG/DTA data for ' $H_5[PMo_{10}V_2O_{40}] \cdot 14H_2O$ ', **5a**: 12.8% weight loss observed below 150°C: calc. for $H_5[PMo_{10}V_2O_{40}] \cdot xH_2O$, 12.7% ($x = 14$). ^{31}P NMR in D_2O : δ (major peak) -3.95, -3.74,

–3.64 ppm, (minor peak) –3.46 ppm; ^{51}V NMR in D_2O : δ (major peak) –533.9, (minor peak) –541.5 ppm; Prominent IR bands (KBr disk): 1060s, 959s, 863m, 774s cm^{-1} . For $(\text{Bu}_4\text{N})_4\text{H}[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$, **5**, ^{31}P NMR in $\text{DMSO}-d_6$: δ (major peak) –3.79, –3.64, –3.51 ppm, (minor peak) –3.38, –3.22 ppm; ^{51}V NMR in $\text{DMSO}-d_6$: δ (major peak) –526.8 ppm, (minor peak) –536.8 ppm; Prominent IR bands (KBr disk): 1056m, 941s, 874m, 800s cm^{-1} .

TG/DTA data for $\text{H}_6[\text{PMo}_9\text{V}_3\text{O}_{40}] \cdot 14\text{H}_2\text{O}$, **6a**: 13.1% weight loss observed below 150°C : calc. for $\text{H}_6[\text{PMo}_9\text{V}_3\text{O}_{40}] \cdot x\text{H}_2\text{O}$, 13.0% ($x = 14$). ^{31}P NMR in D_2O : δ (major peak) –3.70, –3.61 ppm, (minor peak) –3.42, –3.01, –2.96, –2.78 ppm; ^{51}V NMR in D_2O : δ (major peak) –549.9, –541.2, –533.9 ppm; Prominent IR bands (KBr disk): 1057s, 956s, 880s, 780s cm^{-1} . For $(\text{Bu}_4\text{N})_4\text{H}_2[\text{PMo}_9\text{V}_3\text{O}_{40}]$, **6**, ^{31}P NMR in $\text{DMSO}-d_6$: δ (major peak) –3.84, –3.70, –3.56 ppm, (minor peak) –3.45, –3.37, –3.27, –3.23 ppm; ^{51}V NMR in $\text{DMSO}-d_6$: δ (major peak) –526.7 ppm, (minor peak) –536.5 ppm; Prominent IR bands (KBr disk): 1063m, 940s, 876m, 799s cm^{-1} .

2.5. Typical oxidation procedures and product analysis

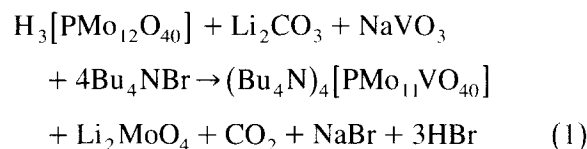
The reaction was carried out at 25°C in a 50 ml round-bottom flask. The reaction system consisted of two liquid phases: an organic layer containing benzene and acetonitrile, and an aqueous layer containing acetonitrile and 30% H_2O_2 . The colored catalysts were initially contained only in the upper, organic layer. 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 varied amounts (2, 5 and 10 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 were sampled using a microsyringe and analyzed. The reaction products were 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 more 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. Characterization of $(\text{Bu}_4\text{N})_4[\text{PMo}_{11}\text{VO}_{40}](\text{PMo}_{11}\text{V}, \mathbf{1})$

The tetrabutylammonium salt of the Keggin-type mono-vanadium(V)-substituted heteropoly-molybdate $[\text{PMo}_{11}\text{VO}_{40}]^{4-}$, **1**, was prepared from the reaction of the NaVO_3 aqueous solution with a mono-lacunary anion $[\text{PMo}_{11}\text{O}_{39}]^{7-}$, which was formed in an aqueous solution of pH 4.3 adjusted by a reaction of $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ with solid Li_2CO_3 and confirmed as a pure compound with a ^{31}P NMR single peak observed at –1.39 ppm, as shown in Eq. (1).



It is isolated as its DMSO, CH_3CN , acetone-soluble, analytically pure yellow–orange crystals in 4.29 g (31.2%) yield. The molecular formula of **1** is established by an elemental analysis, carried out for the sample dried overnight at room temperature under 10^{-3} – 10^{-4} Torr (all elements, including oxygen, 99.88% total observed; see Section 2). TG/DTA analysis with a temperature ramp of $4^\circ\text{C}/\text{min}$ showed no weight loss below 285°C and an exothermic

peak at 302°C due to decomposition, suggesting the presence of no solvated molecule, in accord with the findings of the elemental analysis. The solid FT-IR spectra, measured as KBr disks, of **1** obtained here (Fig. 2(c)) and of '(Bu₄N)₄[PMo₁₁VO₄₀]' ('PMo₁₁V', **4**) (Fig. 2(d)) separately prepared by the ether-extraction method according to Ref. [27], did not show marked differences and only confirmed that the Keggin-type 'PMo₁₂O₄₀ⁿ⁻' heteropolymolybdate framework remained [32].

Further solution characterization of **1** relied on ³¹P and ⁵¹V NMR measurements (Fig. 3(a) and Fig. 4(a)). The ³¹P NMR observed at -3.77 ppm as a single peak and the ⁵¹V NMR at -526.7 ppm as a single peak require the presence of a single species in solution and, therefore, preclude the existence of even minor impurities. In contrast to them, the ³¹P NMR of **4** shows a major peak at -3.79 ppm and minor

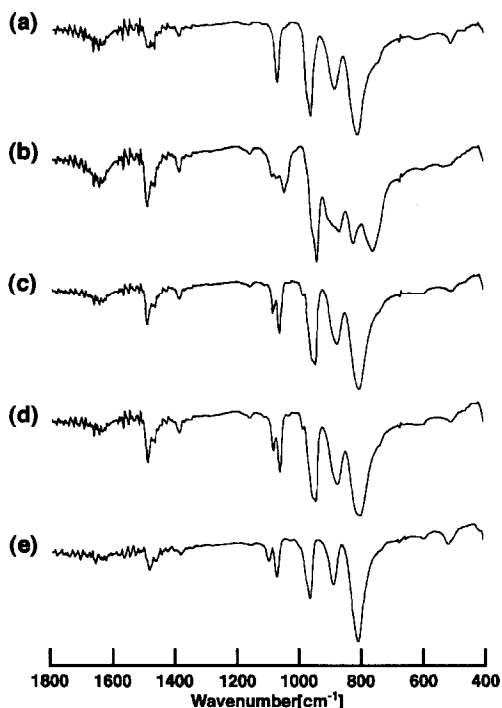


Fig. 2. IR spectra measured as KBr disks of (a) (Bu₄N)₃[PMo₁₂O₄₀], **3**, (b) (Bu₄N)₄H₃[PMo₁₁O₃₉], (c) (Bu₄N)₄[PMo₁₁VO₄₀], **1**, (d) '(Bu₄N)₄[PMo₁₁VO₄₀]', **4** and (e) (Bu₄N)₄[PW₁₁VO₄₀], **2**.

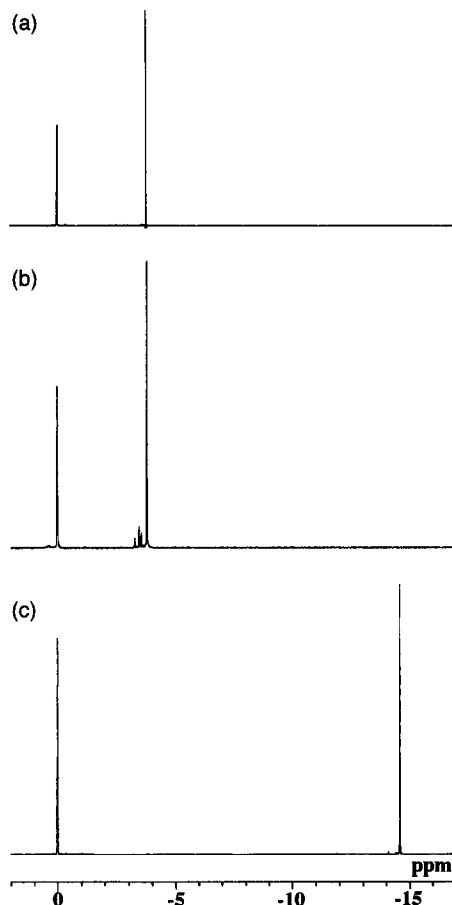


Fig. 3. ³¹P NMR spectra measured at room temperature of (a) (Bu₄N)₄[PMo₁₁VO₄₀], **1**, in DMSO-*d*₆, (b) '(Bu₄N)₄[PMo₁₁VO₄₀]', **4a**, in D₂O and (c) (Bu₄N)₄[PW₁₁VO₄₀], **2**, in DMSO-*d*₆.

peaks at -3.65 and -3.52 ppm, and its ⁵¹V NMR shows the major peak at -526.4 ppm. These spectra show that (i) the structure of compound **4** obtained by the ether-extraction method is very close to that of compound **1** obtained by the present method, (ii) compound **4** is contaminated with several minor impurities and (iii) such impurities in **4** arise from its free acid precursor and thus from the preparation method itself.

On the other hand, the tungsten analog (Bu₄N)₄[PW₁₁VO₄₀] (PW₁₁V, **2**) was prepared using K₄[PW₁₁VO₄₀], which was identified as a water-soluble single species with a single peak at -14.64 ppm in the ³¹P NMR and a single

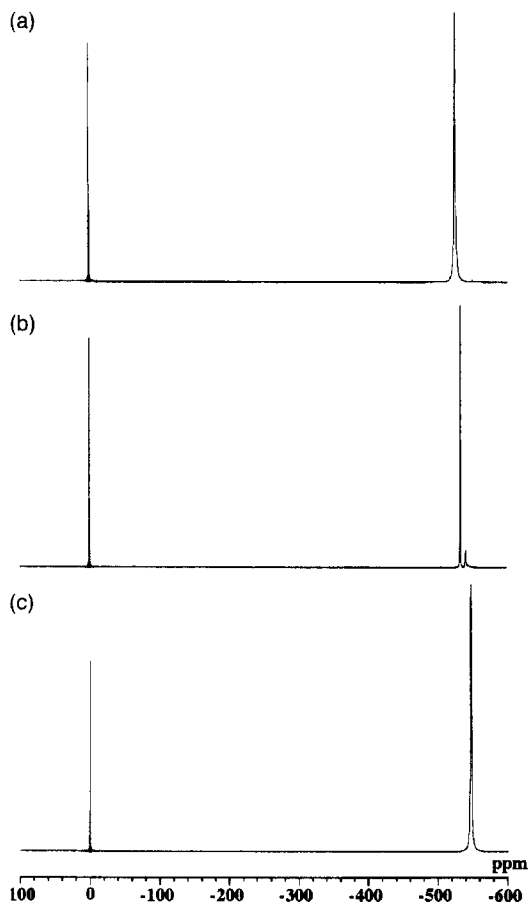
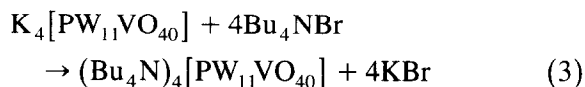
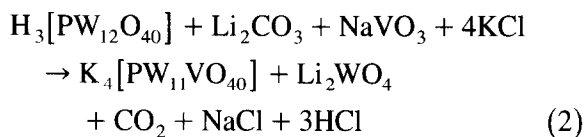


Fig. 4. ^{51}V NMR spectra at room temperature of (a) $(\text{Bu}_4\text{N})_4[\text{PMo}_{11}\text{VO}_{40}]$, **1**, in $\text{DMSO}-d_6$, (b) $[\text{H}_4\text{PMo}_{11}\text{VO}_{40}]$, **4a**, in D_2O and (c) $(\text{Bu}_4\text{N})_4[\text{PW}_{11}\text{VO}_{40}]$, **2**, in $\text{DMSO}-d_6$.

peak at -557.8 ppm in the ^{51}V NMR [21,24] and all cations were exchanged with tetrabutylammonium, as shown in Eqs. (2) and (3)



3.2. Hydroxylation catalyses by PMo_{11}V , **1**, PW_{11}V , **2**, and PMo_{12} , **3**

The benzene hydroxylation was carried out at room temperature under atmospheric pressure in a two-liquid phase, aqueous and organic pro-

cess, up to 240 h reaction under the conditions: 0.1 mmol catalyst precursors (**1**, **2** and **3**), 10 ml (113 mmol) benzene, 2 ml of 30% aqueous H_2O_2 and varied amounts (2, 5 and 10 ml) of CH_3CN , the results of which are summarized in Table 1.

The mono-substituted heteropolytungstate, PW_{11}V , **2**, did not show catalytic activity, although a trace (< 0.01 mmol yield) of phenol was detected: the catalytic turnovers were much less than 1 up to the 240 h reaction in the presence of 5 or 10 ml CH_3CN (entries 4 and 5 in Table 1). These data were reproducible and consistent with the results previously obtained using the water-soluble, potassium salt $\text{K}_4[\alpha\text{-PW}_{11}\text{VO}_{40}] \cdot 2\text{H}_2\text{O}$ [21]. Actually, the initial, clear yellow color of the organic phase in the reaction system was almost unchanged up to 240 h and the color of the aqueous phase as well was unchanged.

On the other hand, the mono-substituted heteropolymolybdate, PMo_{11}V , **1**, showed catalytic activities which increased with the increased amounts of CH_3CN (entries 1–3 in Table 1). The catalytic turnover was 1.7 after 192 h reaction with 5 ml CH_3CN and 1.3 after 120 h reaction with 10 ml CH_3CN . Only a phenol was detected in these low conversions of benzene. During the course of the 240 h reaction, both organic and aqueous phases were homogeneous. In the presence of 10 ml CH_3CN , the initial, clear yellow color of the organic phase changed to yellow–orange after 96 h, to orange after 120 h and to red–orange after 240 h. On the contrary, in the presence of 2 ml CH_3CN (entry 1 in Table 1), the catalytic turnover was only 0.7 after 240 h reaction. During the course of the 240 h reaction, the organic phase was almost colorless and a greenish undissolved powder remained at the bottom in the aqueous phase. Thus, the apparent low activity under 2 ml CH_3CN is attributed to low solubility of this HPA in both phases. As to the effect due to the amounts of CH_3CN , the tetrabutylammonium salts are soluble in CH_3CN , but insoluble in water. Since CH_3CN is soluble in benzene and

water, the two-phase reactions by the present catalyst precursors should be significantly affected by the amounts of CH_3CN . As a matter of fact, the organic phase is initially colored due to the dissolved catalyst. Thus, the present reactions should proceed in the organic phase. Such an observation is contrasted with the reactions by only water-soluble, potassium salts of PW_{10}V_2 and PW_9V_3 as previously found [21], in which the reactions proceed in the aqueous phase containing the catalyst precursors, but not the organic phase, viz., the increased amounts of CH_3CN do not result in increased catalytic activity.

FT-IR as KBr disk and ^{31}P NMR in $\text{DMSO}-d_6$ of the heteropolymolybdate recovered from the organic phase in the 240 h-reaction by **1** revealed that the original structure of **1** was kept after the reaction.

In the reaction started from the conditions: 0.1 mmol PMo_{11}V , **1**, 10 ml (113 mmol) benzene, 2 ml of 30% H_2O_2 and 10 ml CH_3CN , when the additional 2 ml of 30% H_2O_2 were added after 120 h reaction, the subsequent turnovers increased two fold, i.e. 7.7 after 192 h, 13.8 after 216 h and 21.4 after 240 h. By the addition of H_2O_2 , color changes were subsequently observed: yellow–orange of the organic phase and clear yellow of the aqueous phase to clear, red–orange in both phases after 240 h reaction.

The unsubstituted heteropolymolybdate, PMo_{12} , **3**, used for comparison, did not show catalytic activity (entries 6 and 7 in Table 1):

the turnover was ca. 0.2 during the course of the 120 h to the 240 h reaction, which was almost the same as observed in the PW_{11}V , **2**, system. With 10 ml CH_3CN , the clear yellow colors both in the organic and aqueous phases were unchanged up to the 240 h reaction.

These results provide some significant insight into the reaction mechanism, specifically: (1) hydroxylation of benzene requires at least one vanadium center in the Keggin heteropolymolybdate, whereas it requires at least two vanadium centers with the corner-shared octahedra in the Keggin heteropolytungstates as found earlier [21]; (2) the molybdenum (VI) atoms in the Keggin polyoxoanion framework significantly act in cooperation with the one vanadium center, but the tungsten (VI) atoms do not and therefore (3) the reaction mechanism, with regard to the hydroxylation proceeding on the A-site of the α -Keggin structure, should be considered with the participation of one vanadium(V) and at least one molybdenum(VI) center with the corner-shared octahedra in the heteropolymolybdate, while, on the other hand, the reaction mechanism involved the participation of two vanadium(V) centers with the corner-shared octahedra in the heteropolytungstate.

3.3. Hydroxylation catalyses by ' PMo_{11}V ', **4** and related compounds **5**, **6** and **4a–6a**

Some data obtained with the tetrabutylammonium salts of ' PMo_{11}V ', **4**, ' $\text{PMo}_{10}\text{V}_2$ ', **5**, and ' PMo_9V_3 ', **6** and the corresponding free

Table 1
Catalytic turnovers in benzene hydroxylation catalyzed by **1–3** under varied amounts of CH_3CN

Entry	Catalysts	CH_3CN (ml)	Reaction time (h)							
			1	3	24	120	144	168	192	240
1	$(\text{Bu}_4\text{N})_4[\text{PMo}_{11}\text{VO}_{40}]$, 1	2	0	0	0.1	0.2	0.2	0.2	0.3	0.7
2	1	5	0.1	0.1	0.3	0.5	0.7	0.9	1.7	4.7
3	1	10	0.2	0.3	0.3	1.3	1.6	2.3	4.0	10.1
4	$(\text{Bu}_4\text{N})_4[\text{PW}_{11}\text{VO}_{40}]$, 2	5	0	0	0	0	0	0	0	0.2
5	2	10	0	0	0	0	0	0	0	0.2
6	$(\text{Bu}_4\text{N})_4[\text{PMo}_{12}\text{O}_{40}]$, 3	5	0.1	—	0	0.2	0.2	0.3	0.3	0.3
7	3	10	0	—	0.2	0.1	0.2	0.2	0	0.1

Conditions: catalyst 0.10 mmol, benzene 10 ml, 30% H_2O_2 2 ml, temperature 25°C.

Table 2

Catalytic turnovers in benzene hydroxylation catalyzed by **4–6** and **4a–6a** with 10 ml CH₃CN

Entry	Catalysts	Reaction time (h)						
		1	5	24	120	144	170	240
8	'(Bu ₄ N) ₄ [PMo ₁₁ VO ₄₀]'	0	0	0	—	7.5	10.1	15.3
9	'(Bu ₄ N) ₄ H[PMo ₁₀ V ₂ O ₄₀]'	0	1.3	9.7	15.5	—	—	17.5
10	'(Bu ₄ N) ₄ H ₃ [PMo ₉ V ₃ O ₄₀]'	0.4	2.2	10.5	13.2	—	—	22.2
11	'H ₄ [PMo ₁₁ VO ₄₀]'	0.4	4.3	18.6	26.4	—	—	29.3
12	'H ₅ [PMo ₁₀ V ₂ O ₄₀]'	0.8	12.0	24.6	27.1	—	—	31.0
13	'H ₆ [PMo ₉ V ₃ O ₄₀]'	2.4	14.0	20.5	26.9	—	—	39.3

Conditions: catalysts 0.10 mmol, benzene 10 ml, 30% H₂O₂ 2 ml, temperature 25°C.

acids forms, 'H₄PMo₁₁V', **4a**, 'H₅PMo₁₀V₂', **5a**, and 'H₆PMo₉V₃', **6a**, all of which have been prepared as mixed species only with averaged compositions by the traditional ether-extraction method [27], are presented in Table 2. All reactions were performed at room temperature under the conditions: 0.1 mmol catalyst precursors (**4–6** and **4a–6a**), 10 ml (113 mmol) benzene, 2 ml of 30% H₂O₂ and 10 ml CH₃CN.

In the comparison of catalyses by three HPAs as the tetrabutylammonium salts, 'PMo₁₁V', **4**, 'PMo₁₀V₂', **5**, and 'PMo₉V₃', **6** (entries 8–10 in Table 2), the increased species of the vanadium(V) contents show enhanced activity. These are the cases for the catalyses by the free acid forms, 'H₄PMo₁₁V', **4a**, 'H₅PMo₁₀V₂', **5a**, and 'H₆PMo₉V₃', **6a** (entries 11–13 in Table 2). In every case, the free acid form shows much higher activity than the tetrabutylammo-

nium salt. Thus, the effect enhanced by the Brønsted acidity should be also taken into account in the reaction mechanism. The effect of the acidity has not been observed in the catalyses by the vanadium(V)-substituted heteropolytungstates [21].

In the comparison (entry 8 in Table 2 and entry 3 in Table 1), the apparent activity observed by 'PMo₁₁V', **4**, was much higher than that by the PMo₁₁V, **1**, as a single species, reflecting the additional effects by the species such as di- and/or tri-vanadium(V) species present in **4** as already shown by ³¹P and ⁵¹V NMR spectra.

3.4. Stability as catalyst

The ³¹P NMR spectra were measured in DMSO-*d*₆ of the compounds, which were re-

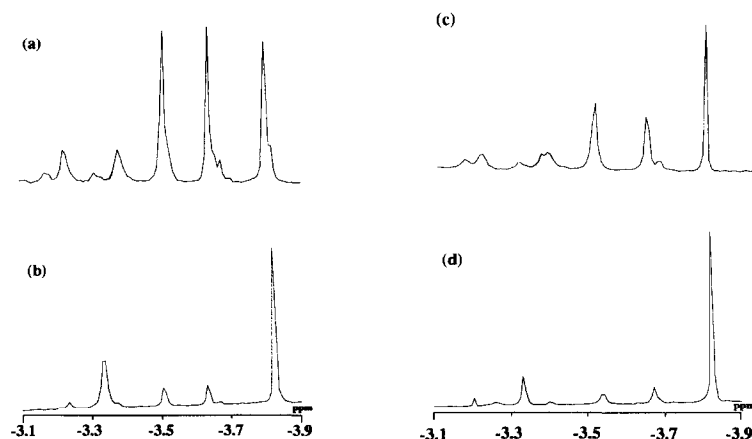


Fig. 5. ³¹P NMR spectra in DMSO-*d*₆ of **5**: (a) before the reaction and (b) after the 240 h reaction and of **6**: (c) before the reaction and (d) after the 240 h reaction.

covered from the organic phases after 240 h reactions using tetrabutylammonium salts of 'PMo₁₀V₂', **5**, and 'PMo₉V₃', **6**, and recrystallized twice from CH₃CN. Of particular note are the spectral changes observed in the 'PMo₁₀V₂', **5**, and 'PMo₉V₃', **6**, systems (Fig. 5): the multiple-line ³¹P spectra of **5** and **6** observed before the reactions were converted to the spectra with almost one peak at $\delta -3.83$ ppm in **5** and at $\delta -3.82$ ppm in **6**, respectively, after 240 h reactions, the chemical shifts of which were very close to that of the PMo₁₁V, **1**, i.e. $\delta -3.77$ ppm. These changes were also confirmed by the ⁵¹V NMR spectra before and after the reactions: the major peaks at $\delta -526.8$ ppm in **5** and at $\delta -526.7$ ppm in **6**, respectively, after 240 h reactions were very close to that of **1**, i.e. $\delta -526.7$ ppm.

At present, we can not conclude whether or not all of the di-, tri and other vanadium substituted species contaminated in **5** and **6** were changed to the mono-substituted species during the course of reaction, or whether or not only the contaminated mono-substituted species survived and the other species decomposed. In any event, these facts strongly suggest that (i) the mono-substituted species is markedly stable as a catalyst, although its activity may be not high and (ii) the di- and tri-substituted species are not stable as catalysts, although their activity should be high. At present, we can not prepare some of the selectively site-substituted vanadium(V) heteropolymolybdates which correspond to the vanadium(V)-substituted heteropolytungstates [21]. However, even if such heteropolymolybdates are obtained, these results suggest that their catalytic stability should be low.

4. Summary

Using the mono-vanadium(V) substituted heteropolymolybdate **1** as a single-species, the catalytic hydroxylation of benzene exhibits a requirement for one vanadium center acting in cooperation with the molybdenum(VI) atom

constructed on the A-site of the α -Keggin polyoxoanion structure. This is in contrast with the reaction by the previously found bimetallic vanadium species with the corner-shared octahedra. Several effects of the amounts of CH₃CN and the Brønsted acidity on the hydroxylation catalyzed by the vanadium(V)-substituted heteropolymolybdates were found. Of particular note is the marked stability as a catalyst of the mono-vanadium(V) substituted heteropolymolybdate, in comparison with the di- and tri-substituted heteropolymolybdates, even if their site-selectively pure species have been prepared.

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References

- [1] J.R. Lindsay-Smith, R.O.C. Norman, *J. Chem. Soc.* (1963) 2897.
- [2] C.R.E. Jefcoate, J.R. Lindsay-Smith, R.O.C. Norman, *J. Chem. Soc. B* (1969) 1015.
- [3] C. Walling, G.M. El-Taliawi, R.A. Johnson, *J. Am. Chem. Soc.* 96 (1974) 133.
- [4] C. Walling, R.A. Johnson, *J. Am. Chem. Soc.* 97 (1975) 363.
- [5] C. Walling, *Acc. Chem. Res.* 8 (1975) 125.
- [6] E. Steckhan, J. Wellmann, *Angew. Chem. Int. Ed. Engl.* 15 (1976) 294.
- [7] S. Tamagaki, K. Hotta, W. Tagaki, *Chem. Lett.* (1982) 651.
- [8] T. Tagawa, Y.-J. Seo, S. Goto, *J. Mol. Catal.* 78 (1993) 201.
- [9] E.P. Talsi, K.V. Shalyaev, *J. Mol. Catal.* 92 (1994) 245.
- [10] H. Mimoun, L. Saussine, E. Daire, M. Postel, J. Fischer, R. Weiss, *J. Am. Chem. Soc.* 105 (1983) 3101.
- [11] M. Bianchi, M. Bonchio, V. Conte, F. Coppa, F. Di Furia, G. Modena, S. Moro, S. Standen, *J. Mol. Catal.* 83 (1993) 107.
- [12] M. Bonchio, V. Conte, F. Di Furia, G. Modena, *J. Org. Chem.* 54 (1989) 4368.
- [13] F.P. Ballistreri, G.A. Tomaselli, R.M. Toscano, V. Conte, F. Di Furia, *J. Am. Chem. Soc.* 113 (1991) 6209.
- [14] F.P. Ballistreri, G.A. Tomaselli, R.M. Toscano, V. Conte, F. Di Furia, *J. Mol. Catal.* 89 (1994) 295.
- [15] V. Conte, F. Di Furia, S. Moro, *J. Mol. Catal.* 94 (1994) 323.
- [16] N.A. Milas, *J. Am. Chem. Soc.* 59 (1937) 2342.
- [17] Merck Index, 9th ed., 1976, ONR-61.
- [18] A. Butler, M.J. Clague, G.E. Meister, *Chem. Rev.* 94 (1994) 625.
- [19] M.J. Clague, A. Butler, *J. Am. Chem. Soc.* 117 (1995) 3475.

- [20] B.M. Choudary, P.N. Reddy, *J. Mol. Catal.* 103 (1995) L1.
- [21] K. Nomiya, H. Yanagibayashi, C. Nozaki, K. Kondoh, E. Hiramatsu, Y. Shimizu, *J. Mol. Catal. A* 114 (1996) 181.
- [22] P.J. Domaille, *J. Am. Chem. Soc.* 106 (1984) 7677.
- [23] P.J. Domaille, *Inorg. Synth.* 27 (1990) 96.
- [24] R. Massart, R. Contant, J.-M. Fruchart, J.-P. Ciabrini, M. Fournier, *Inorg. Chem.* 16 (1977) 2916.
- [25] S.P. Harmalker, M.A. Leparulo, M.T. Pope, *J. Am. Chem. Soc.* 105 (1983) 4286.
- [26] R.G. Finke, B. Rapko, R.J. Saxton, P.J. Domaille, *J. Am. Chem. Soc.* 108 (1986) 2947.
- [27] G.A. Tsigdinos, C.J. Hallada, *Inorg. Chem.* 7 (1968) 437.
- [28] C.L. Hill, C.M. Prosser-McCartha, *Coord. Chem. Rev.* 143 (1995) 407.
- [29] R. Neumann, M. Levin, *J. Am. Chem. Soc.* 114 (1992) 7278.
- [30] R. Neumann, M. de la Vega, *J. Mol. Catal.* 84 (1993) 93.
- [31] L.A. Combs-Walker, C.L. Hill, *Inorg. Chem.* 30 (1991) 4016.
- [32] C. Rocchiccioli-Deltcheff, R. Thouvenot, M. Dabbabi, *Spectrochim. Acta A* 33 (1977) 143.