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Hydroxylation of benzene catalyzed by selectively site-substituted vanadium(V) heteropolytungstates in the presence of hydrogen peroxide

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Abstract

Using selectively site-substituted vanadium(V) Keggin and Dawson heteropolytungstates (HPA), the catalytic activities for hydroxylation of benzene in the presence of 30% aqueous H_2O_2 were examined at room temperature under atmospheric pressure in a two liquid phase, aqueous and organic process. In particular, potassium salts of di- and tri-vanadium(V) substituted Keggin HPAs, α -1,2- $PW_{10}V_2$ and α -1,2,3- PW_9V_3 , showed catalytic turnovers 0.81 and 8.69 for phenol production with excellent selectivity, respectively, for 48 h reaction under the conditions: 0.1 mmol catalyst, 1 ml (11.3 mmol) benzene, 2 ml of acetonitrile and 2 ml of 30% H_2O_2 . The activity of tri-substituted, PW_9V_3 HPA was initially high, but it maximized after 48 h and its structure completely decomposed, whereas that of di-substituted, $PW_{10}V_2$ HPA gradually increased and exceeded that of the PW_9V_3 after 120 h. The polyoxoanion structure of the $PW_{10}V_2$ was maintained even after 576 h. Their activities and stabilities as catalysts were compared with those of vanadium(V)-substituted Dawson HPAs (α - $P_2W_{17}V$ and α -1,2,3- $P_2W_{15}V_3$), vanadium(V)-containing isopolyanions (IPA; VW_5 and V_{10}), the Milas reagent (V_2O_5 and aqueous H_2O_2), and the picolinate-vanadium(V) oxo peroxo complex.

Keywords: Hydroxylation; Benzene; Vanadium(V)-substituted polyoxoanions; Keggin-type; Dawson-type; Heteropolytungstate; Catalyst precursor

1. Introduction

Catalytic hydroxylation of benzene is a very intriguing reaction and many catalysts have so far been reported [1–16] (for many references on Milas hydroxylation of olefins, see, for example, [17]). One of them, the Milas reagent which consists of V_2O_5 and aqueous H_2O_2

[16,17], is indeed a very effective catalyst for hydroxylation of organic unsaturated substances such as benzene and many types of alkenes. In the Milas reagent, the catalytically active species has been considered to be a blood-red species, called pervanadate [16]. Recently, the reactivity of vanadium(V) peroxide complexes is receiving renewed attention [18,19]. The formation of the red oxoperoxovanadium(V) ion and a variety of net two-electron oxidation reactions containing hydroxylations of benzene and other arenes and alkanes catalyzed by the peroxo-

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Table 1
Formulae and abbreviations of the catalyst precursors used in the present work

	Molecular formula	Abbreviations	Refs.
Modified HPAs	$K_7[\alpha\text{-}1,5\text{-PW}_{10}\text{Ti}_2\text{O}_{40}] \cdot 6\text{H}_2\text{O}$	$\text{PW}_{10}\text{Ti}_2$	[26]
	$K_7[\beta\text{-}1,2,3\text{-SiW}_9\text{Nb}_3\text{O}_{40}] \cdot 3\text{H}_2\text{O}$	SiW_9Nb_3	[27,28]
	$K_9[\alpha\text{-}1,2,3\text{-P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}] \cdot 3\text{H}_2\text{O}$	$\text{P}_2\text{W}_{15}\text{Nb}_3$	[29,30]
Keggin-type HPAs	$K_4[\alpha\text{-PW}_{11}\text{VO}_{40}] \cdot 2\text{H}_2\text{O}$	PW_{11}V	[22]
	$K_5[\alpha\text{-}1,2\text{-PW}_{10}\text{V}_2\text{O}_{40}] \cdot 4\text{H}_2\text{O}$	PW_{10}V_2	[20,21]
	$K_6[\alpha\text{-}1,2,3\text{-PW}_9\text{V}_3\text{O}_{40}] \cdot 2\text{H}_2\text{O} \cdot \text{NaCl}$	PW_9V_3	[20,21]
Dawson-type HPAs	$K_7[\alpha\text{-P}_2\text{W}_{17}\text{VO}_{62}] \cdot 4\text{H}_2\text{O}$	$\text{P}_2\text{W}_{17}\text{V}$	[24]
	$K_8\text{H}[\alpha\text{-P}_2\text{W}_{15}\text{V}_3\text{O}_{62}] \cdot 4\text{H}_2\text{O}$	$\text{P}_2\text{W}_{15}\text{V}_3$	[25]
IPAs	$(n\text{-Bu}_4\text{N})_3[\text{VW}_5\text{O}_{19}]$	VW_5	[20]
	$\text{Na}_6[\text{V}_{10}\text{O}_{28}] \cdot 18\text{H}_2\text{O}$	V_{10}	[23]
Others	V_2O_5	V_2O_5	
	Picolinato-vanadium(V) oxo peroxy complex	$\text{VO}(\text{O})_2(\text{Pic})(\text{H}_2\text{O})_2$	[10]

vanadium(V) complexes have been reviewed [18]. In this work, we have asked the question of whether or not at least one of the active

species in the Milas reagent for the hydroxylation of benzene can be modeled by either of the vanadium(V)-substituted Keggin or Dawson

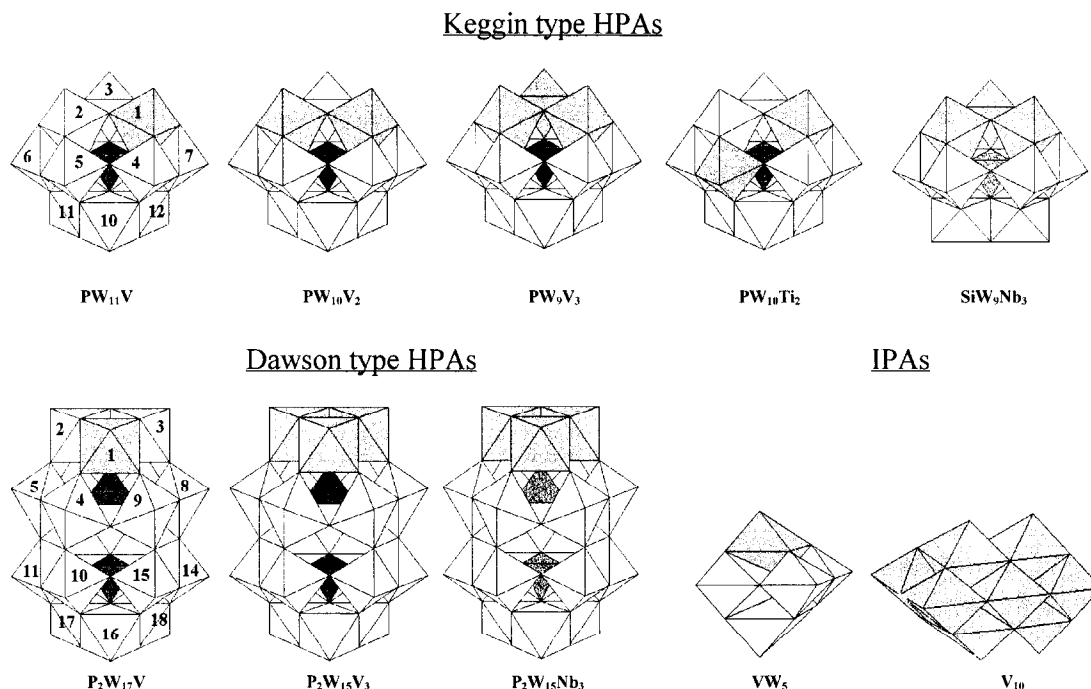


Fig. 1. Polyhedral representations of selectively site-substituted vanadium(V) α -Keggin and α -Dawson heteropolytungstates (HPA), and some other modified HPA and vanadium(V)-containing isopolyanions (IPA) used herein as catalyst precursors. Substituted sites in HPA are shown as follows. In the Keggin type PW_{11}V , PW_{10}V_2 and PW_9V_3 , and in the Dawson type $\text{P}_2\text{W}_{17}\text{V}$ and $\text{P}_2\text{W}_{15}\text{V}_3$, the vanadium(V) atoms are substituted by either or all of the hatched octahedra in the 1–3 positions in the α -Keggin (A-site) and α -Dawson (B-site) structures, respectively. In the Keggin type $\text{PW}_{10}\text{Ti}_2$, the titanium(IV) atoms are substituted in the two octahedra in the 1,5 positions in the α -Keggin structure. In the Keggin type SiW_9Nb_3 and the Dawson type $\text{P}_2\text{W}_{15}\text{Nb}_3$, the niobium(V) atoms are replaced by three hatched octahedra in the 1–3 positions in the β -Keggin (A-site) and α -Dawson (B-site) structures, respectively.

heteropolytungstates (HPA), or vanadium(V)-containing isopolyanions (IPA), in which some vanadium(V) atoms are site-selectively incorporated in the polyoxoanion structures. In particular, we have expected thermally stable catalyst systems using such vanadium(V)-substituted heteropolytungstates, since the picolinate-vanadium(V) oxo peroxy complex, reported as an effective catalyst with high selectivity for benzene hydroxylation [10–12], was not thermally stable in our preliminary experiments. Several catalyst precursors used herein and their abbreviations are shown in Table 1 and their polyhedral representations are given in Fig. 1. Herein we report that the di-vanadium(V) substituted Keggin HPA, α -1,2-PW₁₀V₂, is the most noteworthy catalyst precursor tested in its stability and catalytic activity for benzene hydroxylation.

2. Experimental

2.1. Materials

The selectively site-substituted vanadium(V) Keggin HPAs, PW₁₁V [22] and PW₁₀V₂ [20,21], were prepared as potassium salts according to the literature methods. Another vanadium(V)-substituted Keggin HPA, the potassium salt of PW₉V₃ [20,21], was obtained by three times recrystallizations from water acidified with hydrochloric acid to pH 1.5 for the powder sample prepared according to the literature, and its formation was checked and confirmed by ⁵¹V NMR measurement. The vanadium(V)-substituted Dawson HPA, the yellow potassium salt of P₂W₁₇V(V), was obtained by oxidation with bromine of the potassium salt of deep blue P₂W₁₇V(IV) prepared according to the literature [24]. The tri-vanadium(V)-substituted Dawson HPA, the orange–red potassium salt of P₂W₁₅V₃, was prepared according to the literature [25] and recrystallized three times from water acidified with hydrochloric acid to pH 1.5. Two IPAs, the Bu₄N salt of VW₅ [20] and the sodium salt of

V₁₀ [23], were also prepared according to the literature. For control experiments, the potassium salts of other modified HPA such as PW₁₀Ti₂ [26], SiW₉Nb₃ [27,28] and P₂W₁₅Nb₃ [29,30], and the picolinate-vanadium(V) oxo peroxy complex VO(O₂)(pic)(H₂O)₂ [10] were also prepared based on the literature. All of these compounds were identified before use as single species with some hydrated water except the Bu₄N salt of VW₅ by full elemental analyses, TG/DTA, ⁵¹V and ³¹P NMR and solid FT-IR. In Table 1, their molecular formulas or compositions determined here are listed. The PW₁₀V₂ and PW₉V₃ HPA catalyst precursors were also characterized after the reaction by ⁵¹V and ³¹P NMR and FT-IR. These results are summarized in Table 8, listed later.

2.2. Apparatus and instrumentation

Elemental analyses were carried out by Mikroanalytisches Labor Pascher (Remagen, Germany). Infrared spectra were recorded on a Nicolet 510 FT-IR spectrometer in KBr disks at room temperature. Thermogravimetric (TG) and differential thermal analyses (DTA) were acquired using a Seiko SSC 5000 TG/DTA 300. TG/DTA were run under air with a temperature ramp of 10°C per min between 20 and 600°C. ¹H NMR (399.65 MHz), ¹³C NMR (100.40 MHz), 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 EX-400 NMR data processing system. ¹H NMR and ¹³C NMR spectra were referenced to an internal standard of TMS. ³¹P NMR spectra were referenced to an external standard of 25% H₃PO₄ in H₂O in a sealed capillary and the ⁵¹V NMR spectra were referenced to an external standard of VOCl₃ by a substitution method. 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. Catalytic testing and product identification

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% H₂O₂. The colored catalysts, except the Bu₄N salt of VW₅, were initially contained only in the bottom, aqueous layer. In a typical experiment, 0.10 mmol of catalyst precursor, 1 ml (11.3 mmol) of benzene, 2 ml (25.4 mmol) of aqueous 30% H₂O₂, and 2 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. For the aqueous phase, the pre-treatment including extraction with ether, evaporation to dryness, and then addition of 1 ml of acetonitrile was performed before the GC analysis. The reaction products were quantitatively analyzed using the calibration curve based on the relative area of each of the authentic samples relative to acetonitrile. For the organic phase without acetonitrile, 0.03 ml of cyclooctane was used as an internal standard. The reaction products were also identified by GC-MS and ¹H and ¹³C NMR. 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. Survey experiments

The results shown in Table 2 were obtained from 48 h reactions using 0.1 mmol each of the

HPAs, PW₁₀Ti₂, SiW₉Nb₃ and P₂W₁₅Nb₃, 1 ml (11.3 mmol) of benzene, 2 ml of acetonitrile and 2 ml of 30% H₂O₂. Only a trace (< 0.001 mmol yield) of phenol was produced. Hence, these HPAs have poor activities for benzene hydroxylation.

Under the same conditions, two types of Keggin HPAs, PW₁₀V₂ and PW₉V₃ (Table 2) showed catalytic activities giving phenol as the major product and benzoquinone as the minor. However, the mono-substituted Keggin HPA, PW₁₁V showed no activity, nor did the two types of Dawson HPAs, P₂W₁₇V and P₂W₁₅V₃.

However, the mono-substituted IPA VW₅ showed effective activity with high selectivity. The only product was phenol (0.22 mmol yield and 1.93% conversion over 48 h) under the same conditions. The other IPA, V₁₀, showed activity, but only stoichiometric, not catalytic activity. After 2 h of reaction, the original orange color changed to blood-red, then to deep green, which persisted. In fact, the hydroxylation stopped within 2 h.

The V₂O₅/H₂O₂ catalyst system, i.e., the Milas reagent, gave phenol and benzoquinone even in a 2 h reaction. The well-described picolinate-vanadium(V) oxo peroxo complex [10], used as a control experiment, showed excellent activity for phenol production (1.34 mmol yield and < 11.9% conversion over 48 h), but several minor products were also observed.

The selectivities, estimated from the phenol (PL)/(phenol (PL) + benzoquinone (BQ)) ratio and shown in the last column of Table 2, of two types of Keggin HPA, PW₁₀V₂ and PW₉V₃, were superior to that of the V₂O₅/H₂O₂ catalyst. In these reactions (Table 2), the main product was phenol and the minor ones were based on further oxidation of phenol. Thus, the selectivity relates to phenol oxidation and it appears to be high at lower conversion of benzene. However, these reactions by vanadium(V)-based catalysis are in contrast to other hydroxylations, e.g. catalyzed by the Fenton reagent, in which biphenyl as one of well-known byproducts is produced [8]. The excel-

Table 2

Hydroxylation of benzene by some vanadium(V)-substituted Keggin and Dawson HPAs, and some IPAs and other related compounds

Catalyst precursors	Products					
	phenol		benzoquinone (mmol)	catechol (mmol)	biphenyl (mmol)	selectivity ^a
	mmol	turnover				
Keggin-type HPAs						
PW ₁₁ V	0	0	—	—	—	—
PW ₁₀ V ₂	0.08	0.81	0.007	—	—	0.92
PW ₉ V ₃	0.86	8.69	0.02	—	—	0.98
PW ₁₀ Ti ₂	trace ^b	—	—	—	—	—
SiW ₉ Nb ₃	trace ^b	—	—	—	—	—
Dawson-type HPAs						
P ₂ W ₁₇ V	0	0	—	—	—	—
P ₂ W ₁₅ V ₃	0	0	—	—	—	—
P ₂ W ₁₅ Nb ₃	trace ^b	—	—	—	—	—
IPAs						
VW ₅	0.22	2.18	0	—	—	1.00
V ₁₀ ^c	0.095	0.95	0.019	—	—	0.83
others						
V ₂ O ₅ ^d	0.24	1.19	0.034	—	—	0.88
VO(O ₂)(Pic)(H ₂ O) ₂	1.34	13.4	trace ^b	trace ^b	trace ^b	—

Conditions: catalyst precursors (SiW₉Nb₃ 0.11 mmol; P₂W₁₅Nb₃ 0.082 mmol; others 0.10 mmol), benzene 1 ml (11.3 mmol), 2 ml CH₃CN, 30% H₂O₂ 2 ml (25.4 mmol), temperature 25°C, reaction time 48 h.

^a Selectivity as the PL/(PL + BQ) ratio.

^b Trace: < 0.001 (mmol).

^c This reaction proceeds stoichiometrically, not catalytically.

^d Catalyst precursor 0.20 mmol, reaction time 2 h.

lent selectivity was kept even for a 240 h reaction by the PW₁₀V₂ system and for a 26 h reaction by the PW₉V₃ system for the hydroxylation of 10 ml benzene under varying amounts (1–10 ml) of acetonitrile.

These results give some significant insights, specifically: (1) the hydroxylation of benzene exhibits an apparent requirement for vanadium centers; (2) the mono-vanadium(V) substituted HPAs in both the Keggin and the Dawson structures showed no activity, while the mono-substituted IPA exhibited effective activity; (3) the Keggin type PW₁₀V₂ and PW₉V₃ are much more active than the Dawson type P₂W₁₅V₃; (4) the selectivity for phenol is, when compared with the V₂O₅/H₂O₂ catalyst, improved by vanadium-incorporation into the A-site of the α -Keggin structure; therefore, (5) the active form of the vanadium is suggested to be *at least a*

bimetallic species constructed from two corner-shared octahedra, as suggested in the drawing of PW₁₀V₂ (Fig. 1).

3.2. Further studies of PW₁₀V₂ and PW₉V₃ based catalysis

The catalytic properties of two types of Keggin HPAs containing corner-sharing vanadium(V) octahedra, PW₁₀V₂ and PW₉V₃, have been further investigated for the hydroxylation of benzene under various conditions, the results of which are summarized in Tables 3–7.

Tables 3 and 5 show the effect of the amounts of added acetonitrile for the hydroxylation of 10 ml benzene. Since acetonitrile is soluble in both benzene and water, the reaction should be affected by the amounts of acetonitrile. The optimal amount of acetonitrile which was added

Table 3
Effect of the amounts of added acetonitrile on benzene hydroxylation catalyzed by PW_9V_3

Added acetonitrile	Turnover at various reaction times						
	1 h	2 h	3 h	4 h	5 h	24 h	26 h
0 ml	0.39	1.15	1.37	1.47	1.84	5.36	7.11
1 ml	0.60	1.29	1.49	1.85	2.36	8.00	8.84
2 ml	1.01	1.44	1.33	1.68	5.37	11.6	11.0
10 ml	1.17	2.24	4.56	7.80	8.76	11.7	10.4

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

Table 4
Effect of pH in the aqueous layer on benzene hydroxylation catalyzed by PW_9V_3

pH	Turnover at various reaction times						
	1 h	2 h	3 h	4 h	5 h	24 h	26 h
pH=1	0.53	0.74	0.81	0.70	0.88	2.39	2.45
pH=2	0.83	0.81	1.06	1.23	0.87	3.94	4.63
pH=3	0.86	0.84	1.00	1.40	1.90	5.89	6.63
pH=4	0.74	1.02	1.06	1.47	1.53	6.60	8.46

Conditions: catalyst precursor 0.10 mmol, CH_3CN 1 ml, 30% H_2O_2 2 ml, temperature 25°C, 10 ml benzene.

was 2 ml. These tables also show their stabilities as catalysts. In fact, the activity of the PW_9V_3 is initially high, but it maximizes after 48 h of reaction and its structure completely decomposes. In contrast, the activity of the $PW_{10}V_2$ is initially low, but it gradually increases and exceeds that of the PW_9V_3 after 120 h of reaction. The structure of $PW_{10}V_2$ was kept even after 576 h of reaction. These facts were confirmed by ^{51}V and ^{31}P NMR measurements, as described later.

Table 5
Effect of the amounts of added acetonitrile on benzene hydroxylation catalyzed by $PW_{10}V_2$

Added acetonitrile	Turnover at various times						
	5 h	24 h	26 h	72 h	120 h	192 h	240 h
0 ml	0	0.66	0.79	3.97	1.25	1.69	1.41
1 ml	0	0.58	0.68	7.01	8.84	13.3	21.3
2 ml	0	0.90	1.05	8.96	13.3	16.4	25.1
10 ml	0	0.80	1.03	8.59	16.7	19.5	20.3

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

Table 4 shows the effect of pH in the aqueous layer, adjusted using hydrochloric acid, on catalysis by PW_9V_3 . Since the 'natural' pH of the aqueous solution of this HPA catalyst is about 5, the results show that the higher acidity in aqueous layer results in a slightly decreased activity. This effect indicates that the active species in solution possesses an ionic character and its formation is lowered under more acidic circumstances. In contrast to this, in the benzene hydroxylation by the picolinato-vanadium(V) oxo peroxy complex, it has been recently observed that addition of strong acid resulted in an enhancement of the reaction rate and proposed that this effect might be related to the anionic nature of the active species in solution such as a radical anion [11,12].

Table 6 shows the results from catalysis by $PW_{10}V_2$ for 2 ml benzene in the presence of 2 ml acetonitrile. These results can be compared with those shown in the 3rd column of 5, 24 and 26 h reactions of Table 5, where 10 ml of benzene is used. These show the effect of the amounts of benzene as substrate and/or solvent. The fact that the varied amounts (2 ml to 10 ml) of benzene do not significantly affect the amounts of the produced phenol strongly suggests that the reaction proceeds in the aqueous phase containing the catalyst precursor, but not the organic phase. This fact will be also attributed to the low solubility of benzene as a reactant in water and the produced phenol is much more soluble in benzene than in water.

All oxidants disproportionate, i.e. 'catalase activity' is here $2H_2O_2 \rightarrow 2H_2O + O_2$. In the hydroxylation by the picolinato-vanadium(V)

Table 6
Catalysis by $PW_{10}V_2$ in the presence of 2 ml acetonitrile

Added acetonitrile	Turnover at various reaction times						
	1 h	2 h	3 h	4 h	5 h	24 h	26 h
2 ml	0	0.06	0.05	0.07	0.08	0.94	1.41

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

Table 7
Effect of the rate of addition of H_2O_2 on benzene hydroxylation catalyzed by $PW_{10}V_2$ and PW_9V_3

Catalyst precursors	Turnover at various reaction times						
	1 h	2 h	3 h	4 h	5 h	24 h	26 h
$PW_{10}V_2^a$	0	0	0	0	0	0.06	0.13
$PW_{10}V_2^b$	0	0	0	0	0	0.89	1.04
$PW_9V_3^a$	0.29	0.38	0.62	0.96	1.47	7.48	7.25
$PW_9V_3^b$	1.00	1.43	1.32	1.66	5.32	11.5	10.9

Conditions: catalyst precursors 0.10 mmol, CH_3CN 2 ml, temperature 25°C, 10 ml benzene.

^a A total of 2 ml of 30% H_2O_2 was added in 0.5 ml portions at 0, 2, 4 and 20 h.

^b 2 ml of 30% H_2O_2 was initially added (i.e. all at once).

oxo peroxy complex, the addition of H_2O_2 in small portions has been recommended [11,31], because the decomposition or the disproportionation of H_2O_2 is also promoted by the picolinate-vanadium(V) complex. Indeed, Table 7 shows that the rate of addition of H_2O_2 affects

the reaction: phenol production was more effective when all of the H_2O_2 was initially added at once, whereas the addition in small portions of the same amounts of H_2O_2 results in decreased amounts of phenol. This trend is, however, contrary to that of the picolinate-vanadium(V) complex system, suggesting that the present systems do not significantly promote the decomposition of H_2O_2 .

In the reaction for 10 ml benzene under varying amounts of acetonitrile, the $PW_{10}V_2$ catalyst system showed excellent selectivity even for a 240 h reaction.

3.3. ³¹P and ⁵¹V NMR studies: The nature of the active catalyst

As the reaction proceeded, the reaction system was significantly changed after a 26 h reaction, the organic layer of the PW_9V_3 system was intensely colored, and that of the $PW_{10}V_2$ system was also colored, but just slightly. For the organic layer of the $PW_{10}V_2$ system after a 576 h reaction, both ³¹P and ⁵¹V NMR signals were observed to be assignable to the Keggin structure in the reasonable regions (Table 8). The HPA species present in the organic layer will be probably due to phenol adducts of $PW_{10}V_2$. In addition, the aqueous layer species

Table 8
³¹P and ⁵¹V NMR characterization of the catalyst precursors, $PW_{10}V_2$ and PW_9V_3 , before and after the reaction ^a

Catalyst precursors	Before use		After the reaction			
	³¹ P NMR	⁵¹ V NMR	aqueous layer ^b		organic layer ^b	
			³¹ P NMR	⁵¹ V NMR	³¹ P NMR	⁵¹ V NMR
$PW_{10}V_2$	-14.06	-549.1	-14.05	-528.4 -548.7 -554.7 -555.9	-14.11 -14.38	-551.5 -557.1
PW_9V_3	-13.31	-533.0	— ^c	— ^c	no peak	-238.5

^a All of ³¹P and ⁵¹V NMR spectra, of the catalyst precursors before use and of the aqueous layer species from the $PW_{10}V_2$ system after a 576 h reaction, were measured in D_2O at room temperature with reference to external standards, 25% aqueous H_3PO_4 and $VOCl_3$, respectively. All of ³¹P and ⁵¹V NMR spectra of the organic layer species from the $PW_{10}V_2$ system after a 576 h reaction and from the PW_9V_3 system after a 48 h reaction, were measured in benzene at room temperature with reference to external standards, 25% aqueous H_3PO_4 and $VOCl_3$, respectively.

^b After 576 h reaction using $PW_{10}V_2$. After 48 h reaction using PW_9V_3 .

^c Solids insoluble in DMSO, $CDCl_3$ and D_2O were produced, and their IR spectra showed no P–O band.

from the PW_{10}V_2 system after a 576 h reaction also exhibits the preserved Keggin polyoxoanion structure, as shown by ^{31}P and ^{51}V NMR (Fig. 2). On the contrary, the NMR spectra of the organic layer of the PW_9V_3 system after a 48 h reaction showed, both for 2 and 10 ml of benzene, no ^{31}P signal, but only a ^{51}V signal with a quite different chemical shift (Table 8). The colored organic layer from the PW_9V_3 system is probably due to some vanadium species removed from the Keggin HPA structure. Moreover, the solids produced in the aqueous layer were insoluble in most solvents and their IR spectra showed no P–O band characteristic of the Keggin structure. Thus, the stability as catalyst of the PW_{10}V_2 system is quite different from that of the PW_9V_3 system. The noteworthy stability of the PW_{10}V_2 system, compared with the PW_9V_3 system, may be discussed based on X-ray structural data of their HPAs [32].

Fig. 2 is the ^{51}V NMR spectra measured in D_2O of the aqueous solution of V_2O_5 ¹ and of the aqueous layer species from the PW_{10}V_2 system after a 576 h reaction. Their spectral patterns are very similar, although their chemical shifts are different. This figure also suggests that the Milas reagent from V_2O_5 and aqueous H_2O_2 will consist of a mixture of several species for catalytic hydroxylation of organic unsaturated substances. The ^{51}V NMR chemical shifts are very sensitive to the nature of the coordination sphere of the metal. Recently, ^{51}V NMR chemical shifts of a series of mono- and di-peroxo vanadium complexes containing both mono- and bi-dentate ligands which bind to the metal either by oxygen or nitrogen atoms have been measured and a direct correlation between the electron donating ability of the ligand and the shielding of the metal measured by its ^{51}V NMR chemical shift has been found [33].

It should be noted that the vanadium species

¹ The ^{51}V NMR measurement of the solution containing V_2O_5 and aqueous H_2O_2 was dangerous, because of violently evolving gas due to decomposition of $2\text{H}_2\text{O}_2$ to $2\text{H}_2\text{O} + \text{O}_2$.

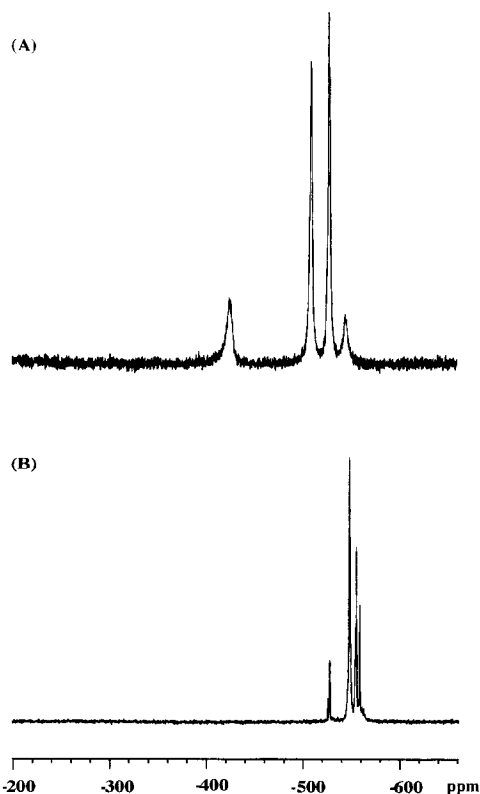


Fig. 2. ^{51}V NMR spectra measured in D_2O by a substitution method with an external reference of VOCl_3 at room temperature of (A) aqueous V_2O_5 and of (B) the aqueous layer species from the PW_{10}V_2 system after a 576 h reaction.

produced in the organic layer from the PW_9V_3 system after a 48 h reaction showed catalytic activity again upon the addition of fresh H_2O_2 . In the case of the PW_{10}V_2 system, both the organic and aqueous species after a 576 h reaction can be reused for further hydroxylation of benzene simply by the addition of fresh H_2O_2 .

3.4. A proposed catalytically active site: Bimetallic corner-sharing octahedra

The results with especially the stable PW_{10}V_2 system allow us to propose that the true active-site geometry of the vanadium centers of the Milas reagent for the hydroxylation of benzene is realized on the Keggin type PW_{10}V_2 , in which bimetallic oxo vanadium species with two corner-sharing octahedra are present. As a pro-

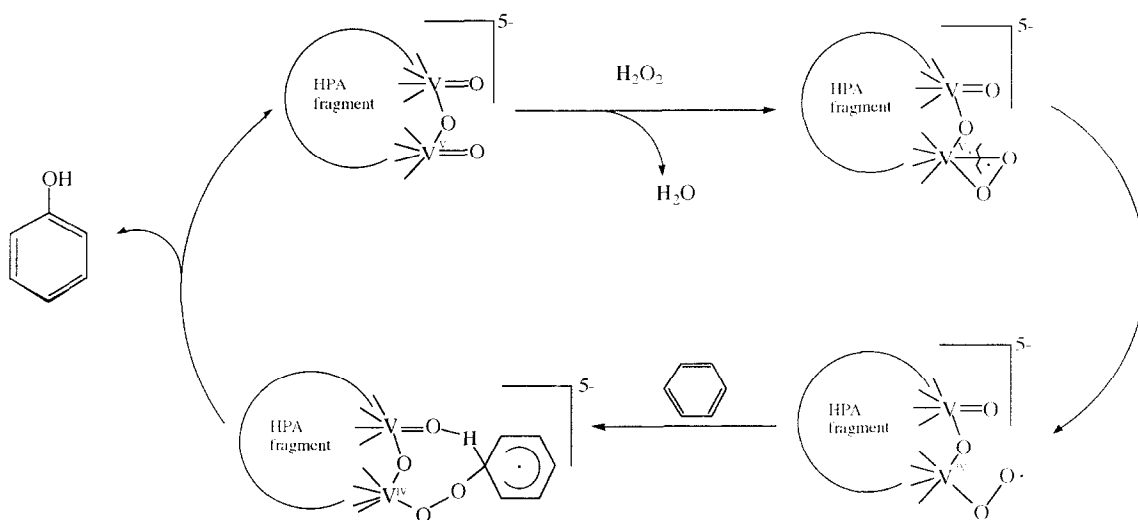
posed *working* mechanism (Scheme 1), one oxo group end of the bimetallic species in the A-site of the Keggin structure could form the previously proposed, diradical species $-V(IV)-O-O\cdot$ by interaction with H_2O_2 [9,10], and benzene then attaches to it. In the transition state of a subsequent step, the other oxo could form a bonding between oxo oxygen and hydrogen of benzene, resulting in removal of the required H^+ . This can explain the high selectivity of the $PW_{10}V_2$ catalyst system.

However, the bimetallic oxo vanadium species with *edge-sharing* octahedra as shown in the B-site of the Dawson structure cannot form such a bonding in the transition state, because an angle between two oxo groups is too large, consistent with the observed inactivity of the B-type $P_2W_{15}V_3$.

If the bimetallic oxo vanadium species with corner-sharing octahedra is requisite to the active species for hydroxylation of benzene, how then can we understand the catalytic properties of the mono-substituted HPAs and IPAs? An intermolecular association between two mono-substituted Keggin HPAs, $PW_{11}V$, or between two mono-substituted Dawson HPAs, $P_2W_{17}V$, will be difficult, because of repulsions with their large negative charges and also due to their

large steric site. However, an intermolecular association between two small mono-substituted IPAs, VW_5 , may be possible because of their small negative charges and smaller sizes. Or, they may degrade and form bimetallic units in situ. On the other hand, tri- and di-substituted Keggin HPAs, PW_9V_3 and $PW_{10}V_2$, have pre-formed bimetallic oxo vanadium species with corner-sharing octahedra in their HPA frameworks, although one extra vanadium octahedron in the PW_9V_3 remarkably lowers its stability as catalyst, if it is assumed that the PW_9V_3 structure remains intact during the reaction. Thus, the $PW_{10}V_2/H_2O_2$ catalyst system may mimic the 'pervanadate' in the Milas reagent. On the other hand, in the Dawson HPA, $P_2W_{15}V_3$, three vanadium octahedra are edge-shared on its B-site, the geometry of which is different from the true active species for hydroxylation of benzene. However, this geometry does not necessarily rule out the possibility of different geometries for other active species for the hydroxylation of unsaturated substances other than benzene.

The key role by the bimetallic oxo vanadium(V) species consisting of two corner-sharing octahedra might be related to the evidence for a reactive, binuclear vanadium(V)



Scheme 1. A proposed working mechanism for the hydroxylation of benzene catalyzed by $PW_{10}V_2$ in the presence of aqueous H_2O_2 .

peroxo complex, which has been recently found to be formed by dimerization of monomeric oxoperoxovanadium(V) species in the mechanistic studies of *cis*-dioxovanadium(V)-catalyzed oxidation of bromide by hydrogen peroxide [19].

As a caveat, we note here that of course we have performed no experiments which rule out the formation of low-level, but highly active, $[L_xV-O-VL_x]^{n-}$, bimetallic or other vanadium species as the actual true catalysts. However, we have discovered a system, namely $PW_{10}V_2$, from which we can perform kinetic studies that will address this key issue, and the needed studies will be repeated in due course.

4. Summary

Catalytic hydroxylation of benzene exhibits an apparent requirement for vanadium centers. The Milas reagent consists of a mixture of species for catalytic hydroxylation of organic unsaturated substances. A model for the active form for benzene hydroxylation can be constructed on the A-site of the Keggin polyoxoanion, specifically a bimetallic species with corner-shared vanadium(V) octahedra, as found in $PW_{10}V_2$. The excellent selectivity and stability as catalyst observed in the catalysis by the $PW_{10}V_2$ system is consisted by this model, and provides a heretofore unexcelled system for additional kinetic and mechanistic studies.

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