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Four Alkoxohexavanadate-Based Pd-Polyoxovanadates as Robust Heterogeneous Catalysts for Oxidation of Benzyl-Alkanes

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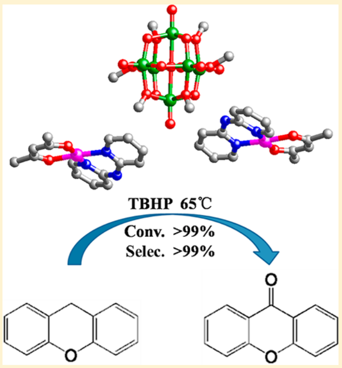
S *Supporting Information*

ABSTRACT: Four alkoxohexavanadate-based Pd-POVs $[\mathrm{Pd(dpa)(acac)}]_2[\mathrm{V_6O_{13}(OMe)_6}]$ (**1**), $[\mathrm{Pd(dpa)(acac)}]_2[\mathrm{V_6O_{11}(OMe)_8}]$ (**2**), $[\mathrm{Pd(dpa)(acac)}]_2[\mathrm{V_6O_{11}(OMe)_8}]\cdot\mathrm{H_2O}$ (**3**), and $[\mathrm{Pd(DMAP)_2(acac)}]_2[\mathrm{V_6O_{11}(OMe)_8}]\cdot\mathrm{H_2O}$ (**4**) (POV = polyoxovanadate; dpa = 2,2′-dipyridine amine; DMAP = 4-dimethylaminopyridine; acac = acetylacetone anion) have been synthesized and fully characterized by single crystal X-ray diffraction and powder X-ray diffraction analyses, Fourier transform infrared spectroscopy, element analyses, and X-ray photoelectron spectroscopy. In **1**−**4**, Pd complexes and hexavanadate anions are assembled through electrostatic interactions. Interestingly, the $[\mathrm{V_6O_{11}(OMe)_8}]^{2-}$ cores in **2** and **3** are a pair of isomers that can be isolated by controlling crystallization temperature. Moreover, to the best of our knowledge, the {V6} core in **3** represents a new octamethoxyhexavanadates cluster. It is notable that compounds **1**−**4** exhibit excellent heterogeneous catalytic performance in the oxidation of benzyl-alkanes with *t*-butylhydroperoxide as oxidant. Among them, the catalytic activity of **1** (conv. and selec. up to 99%, respectively) outperforms others and can be reused without losing its activity.



INTRODUCTION

Polyoxometalates (POMs) are an outstanding class of nanosized metal-oxo clusters with wide structural diversity and O-enriched surfaces.[1] The Lindqvist $[\mathrm{M_6O_{19}}]^{n-}$ anion is one of the classical POM structures formed by Mo, W, Nb, and Ta, but until now the theoretical $[\mathrm{V_6O_{19}}]^{8-}$ has never been observed in aqueous solution. The instability of $[\mathrm{V_6O_{19}}]^{8-}$ probably arises from the small ionic radius of $\mathrm{V^V}$ in combination with the high charge of cluster.[2] Besides using organometallic groups,[3] substitution of bridging oxygen atoms in the Lindqvist $[\mathrm{V_6O_{19}}]^{8-}$ with oxygen donor-ligands is proved to be another effective method to compensate the negative charge and stabilize the cluster.[4] Monodentate or multidentate alkoxo ligands are promising candidates as they can serve as μ_2-alkoxo bridging moieties in the $[\mathrm{V_6O_{19}}]^{8-}$. After the first case $[(n\text{-}\mathrm{C_4H_9})_4\mathrm{N}]_2[\mathrm{V_6O_{13}\{O_2NC(CH_2O)_3\}_2}]$ contributed by Zubieta,[5] quite a few alkoxohexavanadate clusters stabilized by multidentate trisalkoxo ligands are reported.[6] Through selecting proper trisalkoxo ligands, the obtained alkoxohexavanadate clusters can be further functionalized and have satisfactory properties.[7]

Compared with multidentate alkoxo ligands, the examples of alkoxohexavanadate stabilized by monodentate alkoxo ligands are limited. Methoxo as well as ethoxo are the most commonly used monodentate ligands and up to now, $[\mathrm{V^V_6O_{13}(OMe)_6}]^{2-}$,[8] $[\mathrm{V^V_6O_{12}(OMe)_7}]^{-}$,[9] $[\mathrm{V^{IV}_2V^V_4O_{11}(OMe)_8}]^{2-}$,[10] $[\mathrm{V^{IV}_3V^V_3O_8(OMe)_{11}}]$,[11] $[\mathrm{V^{IV}_2V^V_4O_8(OMe)_{11}}]^{+}$,[11] $[\mathrm{V^{IV}_4V^V_2O_7(OEt)_{12}}]$,[12] $[\mathrm{V^{IV}}_n\mathrm{V^V}_{6-n}\mathrm{O_7(OMe)_{12}}]^{(4-n)}$ (n = 3, 4, 5, 6)[13] and $[\mathrm{V^{IV}}_{(4-n)}\mathrm{V^V}_{(2+n)}\mathrm{O_7(OR)_{12}}]^{n+}$ (R = -Me, n = 0, 1; R = -Et, n = 0, 1, 2)[2] have been synthesized and structurally characterized.

The increasing interest toward alkoxohexavanadate clusters originates from their fascinating electronic, magnetic, photochemical properties and potential catalytic application.[14,15] However, it is worth mentioning that although alkoxohexavanadates are expected to have excellent performance as oxidation catalysts, to the best of our knowledge very few examples about their catalytic property have been reported.[16] Actually, alkoxohexavanadates, especially the monodentate alkoxo ligands substituted hexavanadates, are commonly highly reactive and extremely susceptible to hydrolysis by trace amount of water,[9,14] but the introduction of water is inevitable in most oxidation reactions. Therefore, exploring synthetic methods for stable and highly active catalysts based on alkoxohexavanadates is essential.

Generally, both the structure and magnetic and electronic properties of alkoxohexavanadate-based compounds can be controlled by the following three approaches (i) varying the number or the type of the substituted alkoxo ligands;[2,6a] (ii) changing the $\mathrm{V^{IV}/V^V}$ ratio in the Lindqvist cluster;[13] (iii) using different organic ammonium, alkali metal, or metal−organic complexes as counterions.[10,13] Our previous work displayed that the combination of Pd-complex cation and Keggin-type polyanions could lead to excellent catalytic activity.[17]

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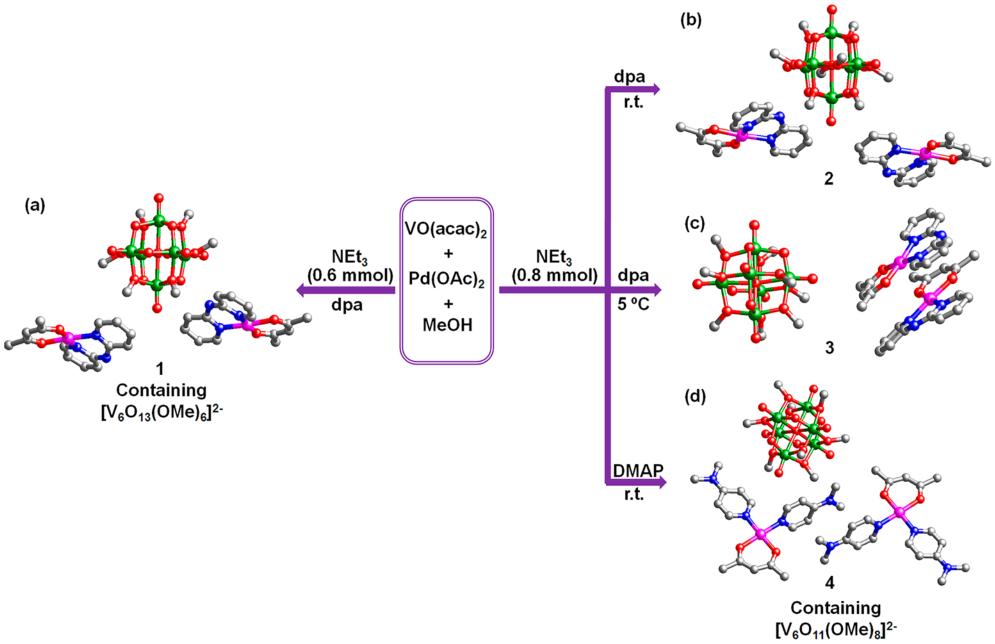
Scheme 1. Simplified Representation of the Controlling Synthesis of **1**−**4**[a]



[a]Color code: Pd, pink; V, green; N, blue; O, red; C, gray.

With this in mind, the Pd-complex was selected as countercation to couple with alkoxohexavanadate cluster through electrostatic interaction and as a result four novel Pd-POVs $[Pd(dpa)(acac)]_2[V^V_6O_{13}(OMe)_6]$ (**1**), $[Pd(dpa)(acac)]_2[V^{IV}_2V^V_4O_{11}(OMe)_8]$ (**2**), $[Pd(dpa)(acac)]_2[V^{IV}_2V^V_4O_{11}(OMe)_8]\cdot H_2O$ (**3**), and $[Pd(DMAP)_2(acac)]_2[V^{IV}_2V^V_4O_{11}(OMe)_8]\cdot H_2O$ (**4**) (POV = polyoxovanadate; dpa = 2,2′-dipyridine amine; DMAP = 4-dimethylaminopyridine; acac = acetylacetone anion) were synthesized in a simple and straightforward method. The four compounds are not only stable in air and aqueous solution but also show unexpected catalytic activities in the oxidation of benzyl-alkanes.

■ RESULTS AND DISCUSSION

Synthesis. Compounds **1**−**4** were synthesized by the reaction of VO(acac)$_2$, Pd(OAc)$_2$, and N-donor ligands in the presence of Et$_3$N and methanol. As shown in Scheme 1, all compounds contain two $[PdL_n(acac)]^+$ cations (L = dpa, n = **1**; L = DMAP, n = 2) and one so-called Lindqvist type alkoxohexavanadate anion. Because Et$_3$N might facilitate the deprotonation of MeOH, six methoxo substituted $[V_6O_{13}(OMe)_6]^{2-}$ cluster (in **1**) and eight methoxo substituted $[V_6O_{11}(OMe)_8]^{2-}$ cluster (in **2**, **3**, and **4**) can be prepared by tuning the amounts of Et$_3$N. Although the structures of compounds **2** and **3** appear to be similar, the locations of the eight substituted methoxo ligands on the hexavanadate core are different. A detailed investigation displays that the crystallization temperature plays a key role in the formations of **2** and **3**. Specially, compound **2** was obtained when the crystallization temperature remained at room temperature, and if the crystallization process was performed at 5 °C, compound **3** was isolated. To further investigate the influence of ligand on the structures of Pd-POVs, DMAP was adopted in the reaction of VO(acac)$_2$ and Pd(OAc)$_2$ and compound **4** was obtained. The experimental result suggests that the N-donor ligand has no obvious influence on the structures of Pd-POVs, especially the hexavanadate core.

Fourier Transform Infrared (FT-IR) Spectra. IR spectroscopy is a useful tool for the analysis of alkoxopolyoxovanadium clusters. In particular, the 500−1100 cm^{-1} region is of interest, containing absorption bands due to metal−oxygen stretching vibrations which are characteristic of POMs spectra in general. As shown in Figure S1, Supporting Information, the IR spectra of **1**−**4** exhibit absorption bands in the range of the 950−1100 cm^{-1} region corresponding to the O−CH$_3$ (1000−1100 cm^{-1}) and V═O (950−1000 cm^{-1}) stretching modes.[11] Further absorption bands located in the 550−650 cm^{-1} region are attributed to V−O−V bending.[10] The bands in the 940−950 cm^{-1} region are assigned to V═O vibration, 750−785 cm^{-1} region to V−O−V bridging fragments, and 650−690 cm^{-1} region to V-OCH$_3$ fragments, respectively.[10,18] In addition, the infrared spectra in the range 1100−1650 cm^{-1} are associated with the C═C and C═N ring stretches of the N-donor ligands.

Crystal Structure of 1. Single crystal X-ray diffraction (SXRD) shows that **1** consists of two $[Pd(dpa)(acac)]^+$ cations and one $[V_6O_{13}(OMe)_6]^{2-}$ polyanion (Scheme 1a). In the cation part, the four-coordinate Pd^{2+} center is ligated by two N atoms from one dpa and two O atoms from one acac$^-$ anion and adopts a nearly square-planar geometry. The structure of $[V_6O_{13}(OMe)_6]^{2-}$ is very similar to the six methoxo substituted hexavanadate in $[\{VO(bmimpm)(acac)_2\}\{V_6O_{13}(OMe)_6\}]$ (bmimpm = bis(1-methylimidazol-2-yl)-4-methoxyphen-1-yl-methanol),[8a] in which six VO$_6$ octahedra build up an {V$_6$} octahedron of Lindqvist type. In the reported case, the $[V_6O_{13}(OMe)_6]^{2-}$ core and vanadyl complexes are connected by coordination bonds forming a [V$_6$ + V$_2$] skeleton which is different from the cationic−anionic mode in compound **1** through electrostatic interaction. The bond valence sum (BVS) calculations show that the oxidation states of all the vanadium atoms are +V, which are in good agreement with the charge balance of compound **1** (Table S1, Supporting Information) and XPS analysis.[19] (Figure S2, Supporting Information)

Besides electrostatic interaction, Pd-complex and polyanion are further linked by a strong hydrogen bonding interaction between the μ_2-oxo of $[V_6O_{13}(OMe)_6]^{2-}$ and the amino group with the O···N distance of ca. 2.7 Å (Figure 1). Interestingly, a 3D supramolecular structure of **1** is constructed by another relatively weak hydrogen bonding and $\pi \cdots \pi$ interactions (Figure S3).

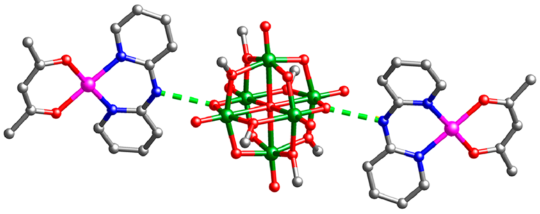


Figure 1. Strong hydrogen bonds interactions in **1**. Hydrogen atoms are omitted for clarity.

Crystal Structure of 2. By increasing the amount of base, compound **2** instead of **1** was obtained under the same conditions. The SXRD analysis shows that **2** contains two $[Pd(dpa)(acac)]^+$ cations and one $[V_6O_{11}(OMe)_8]^{2-}$ polyanion (Scheme 1b). Although the cationic part is identical with that of **1**, the number of the substituted alkoxo ligands on the hexavanadate core is changed from six to eight. The eight μ_2-methoxo groups are symmetrically arranged around central oxygen atom of $[V_6O_{11}(OMe)_8]^{2-}$ core (Figure 2 left). To balance the charge of the anion in **2**, a mixed-valence state of vanadate anion containing two V^{IV} and four V^{V} are needed, which is also identified by both BVS calculations (Table S1, Supporting Information) and X-ray photoelectron spectroscopy (XPS) analysis (Figure S2, Supporting Information). As far as we know, only one eight-methoxo substituted $[V_6O_{11}(OMe)_8]^{2-}$ has been obtained with $[Co(NCS)L]^+$ (L = tris(1-(3,5-dimethylpyrazolylmethyl)amine) as the counter-cation.[10]

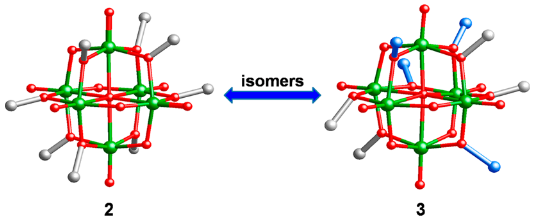


Figure 2. Locations of the eight substituted methoxo bridging ligands on the hexavanadate cores: (left) α-$[V_6O_{11}(OMe)_8]^{2-}$ in **2** and (right) β-$[V_6O_{11}(OMe)_8]^{2-}$ in **3**. Gray balls represent the symmetric methoxo bridging ligands, and blue balls represent the unsymmetric methoxo bridging ligands.

Crystal Structure of 3. Interestingly, by lowering the crystallization temperature, compound **3** was isolated, which contains two $[Pd(dpa)(acac)]^+$ cations, one $[V_6O_{11}(OMe)_8]^{2-}$ polyanion, and one lattice water molecule. Although anion parts in **2** and **3** have the same chemical formula, the locations of the methoxo groups are very different. As shown in Figure 2, in **3** four substituted methoxo groups are symmetrical by taking the central O of Lindqvist cluster as the center, while the other four are asymmetrical, but in **2** all the methoxo groups are distributed in a symmetrical mode. In order to distinguish them, hereafter the $[V_6O_{11}(OMe)_8]^{2-}$ in **2** and **3** are labeled as α-$[V_6O_{11}(OMe)_8]^{2-}$ and β-$[V_6O_{11}(OMe)_8]^{2-}$, respectively. The two polyanions represent a pair of rare isomers in the family of organic-functionalized POMs. Furthermore, to the best of our knowledge, the β-$[V_6O_{11}(OMe)_8]^{2-}$ in **3** is a new alkoxohexavanadate framework. It is worth mentioning that the formation of the two isomers could be controlled by crystallization temperature. As in **2**, there are also two V^{IV} and four V^{V} in the V_6 core of **3**, which has been confirmed by BVS calculations (Table S1) and XPS analysis (Figure S2).

In addition, the different positions of substituted methoxo ligands result in the different hydrogen bonding assembly. In **2**, two μ_2-oxo atoms in opposite positions connect with −NH groups of $[Pd(dpa)(acac)]^+$ by hydrogen bonding with the O···N distance of ca. 2.7 Å (Figure 3a). However, in **3**, the angle between two hydrogen bonds formed by μ_2-oxo atoms and −NH groups is about 120° with the O···N distance of ca. 2.9 Å (Figure 3b). The 3D supramolecular structures formed by weak hydrogen bonds and $\pi \cdots \pi$ interactions of compounds **2** and **3** are shown in Figure S3, Supporting Information.

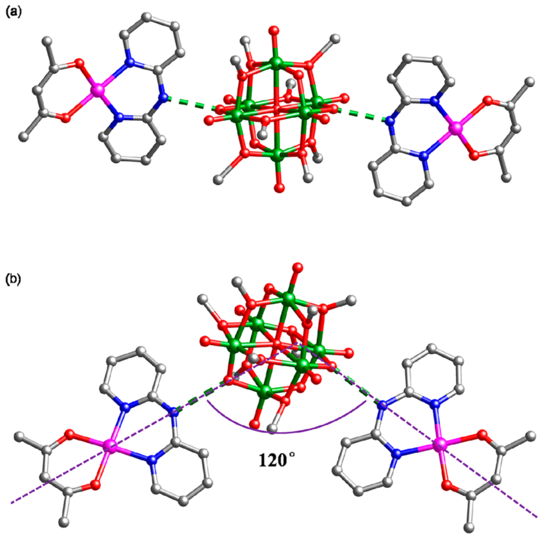


Figure 3. Hydrogen bonds interactions in **2** (a) and **3** (b). Hydrogen atoms and lattice water molecule are omitted for clarity.

Crystal Structure of 4. In order to understand the influence of the N-donor ligand on the structures of alkoxohexavanadates core, DMAP was selected instead of dpa in the synthesis Pd-POVs. Under the same reaction conditions, compound **4** can be isolated from methanol. As shown in Scheme 1d, **4** contains two $[Pd(DMAP)_2(acac)]^+$ cations and one α-$[V_6O_{11}(OMe)_8]^{2-}$ which is similar to the polyanion structure in **2** with only slight differences in the bond lengths and bond angles. The results show that when using different N-donor ligands, there is no obvious influence on the structure of hexavanadate core. But due to the absence of the −NH group, no obvious hydrogen bonding interaction is observed in **4**. The results of BVS calculations (Table S1) and XPS spectra showed that there were also two V^{IV} and four V^{V} in the α-$[V_6O_{11}(OMe)_8]^{2-}$ as in compounds **2** and **3** (Figure S2).

Catalytic Activities of Pd-POVs. Oxidation is an important pathway to large-scale production of chemicals. Selective oxidation of benzyl-alkanes is a powerful tool to generate high value chemical feedstock from less expensive raw materials. In this regard, the means to convert benzyl-alkanes into valuable compounds have received considerable attention in recent years.[20] Given the fact that both Pd complexes and alkoxohexavanadate clusters in compounds **1**−**4** have the potential to oxidize C−H bonds, we anticipated that compounds **1**−**4** could exhibit catalytic activity in the oxidation of benzyl-alkanes.

The oxidation of diphenylmethane to benzophenone was selected as a model reaction to evaluate the catalytic activities of Pd-POVs (Scheme 2). The diphenylmethane oxidation catalyzed by compounds **1**−**4** was performed in chlorobenzene at 65 °C for 16 h using *t*-butylhydroperoxide (TBHP) as the oxidant. As shown in Table 1, compounds **1**−**4** all can efficiently catalyze the oxidation of diphenylmethane with the conversion of 95.8−94.5% and selectivity of 99.8−92.5%.

Scheme 2. Oxidation of Diphenylmethane using Pd-POVs as Catalysts under the Preliminary Optimization Conditions

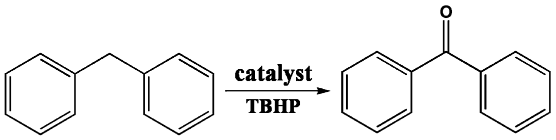


Table 1. Conversion of Diphenylmethane to Benzophenone with Different Catalysts[a]

catalyst	conv (%)	selec (%)[b]	reaction system
1	95.8	99.8	heterogeneous
2	94.8	93.5	heterogeneous
3	94.7	93.2	heterogeneous
4	94.5	92.5	heterogeneous
5	70.3	61.4	homogeneous
Pd(dpa)(OAc)$_2$ + Hacac (1:1)	45.5	78.4	homogeneous

[a] Reaction conditions: diphenylmethane (0.25 mmol, 1 equiv), catalyst (3.75 μmol, 1.5 mol %), TBHP (2.5 equiv), chlorobenzene (1 mL), 65 °C, 16 h. [b] Selectivity to ketones. The byproduct was benzhydrol.

To probe the role of Pd-complex in the diphenylmethane oxidation, Pd(dpa)(OAc)$_2$[17] and acetylacetone in a molar ratio of 1:1 was used as catalyst, and the low conversion (45.5%) and satisfactory selectivity (78.4%) were achieved under the same conditions (Table 1). To further explore the role of alkoxohexavanadate cluster in the reaction, a new compound $[HNEt_3]_2[V_6O_{13}(OMe)_6]$ (**5**) was synthesized and characterized by SXRD. The structure of $[V_6O_{13}(OMe)_6]^{2-}$ in **5** is identical with anion of **1**, in which six methoxo ligands substitute six bridging oxygen atoms in Lindqvist $\{V_6O_{19}\}$ (Figure S5, Supporting Information). The conversion of diphenylmethane catalyzed by compound **5** reached 70.3% with 61.4% selectivity (Table 1). Although Pd(pda)(AcO)$_2$ and compound **5** were used as homogeneous catalysis, their conversions and selectivities are obviously lower than those of heterogeneous catalysts **1**−**4**. The combination of Pd complex and alkoxohexavanadate cluster can dramatically enhance catalytic activities. According to the above results, we speculate that the cation part in catalysts **1**−**4** possibly contributes to enhance the selectivity, and the anion part is to increase the conversion of substrate. Generally speaking, the intramolecular cooperation between cation and anion in **1**−**4** plays some role in the catalytic oxidation process.

Then, we note that the catalytic selectivity of **1** is a little higher than **2**−**4**. For example, using **1**, without any further optimization, the conversion of diphenylmethane reaches to 95.8% with benzophenone as the only product. By comparing the oxidation state of V atoms in compounds **1**−**4**, we speculate that the existence of vanadium(IV) in **2**−**4** might be responsible for the slightly decline of conversion and selectivity in the reaction. Previous studies indicate vanadium(V) is the active site in many catalytic oxidation reactions.[21]

Because of excellent performance, compound **1** was selected to examine the long-term stability in a heterogeneous system. After completion of the oxidation reaction, the catalyst can easily be separated from the reaction mixture by filtration. The recovered catalyst was reactivated by washing with methanol and further reused directly in the subsequent oxidation reactions. The experiment results display that after four runs no obvious loss of activity [conv. 95.8% (first), 95.5% (second), 94.7% (third), 94.6% (fourth)] was observed (Figure 4). The IR spectra (Figure S6) and X-ray powder diffraction patterns (Figure S7) of **1** collected before and after the catalytic reactions indicate that the structure is maintained under turnover conditions. To check the heterogeneity of **1** in liquid phase oxidation of diphenylmethane, hot filtering experiments (separation of catalyst at the reaction temperature) was carried out. When **1** was filtered off after 2 h, the reaction still proceeded for 14 h under the same conditions but with a obviously lower final conversion than in the presence of **1** (Figure S8). Atomic absorption analysis shows that there were no palladium and vanadium ions in the filtrate of catalyst (Supporting Information S9).

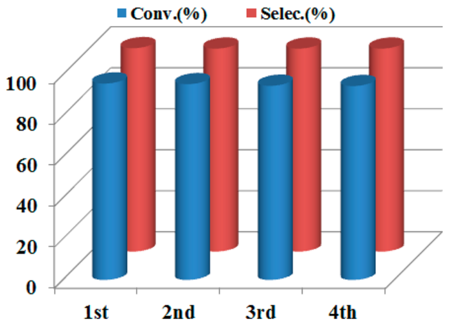
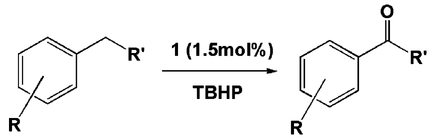
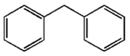
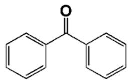
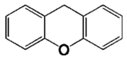
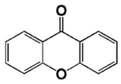
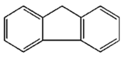
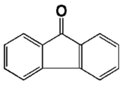
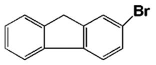
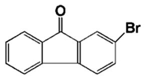
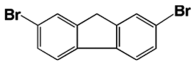
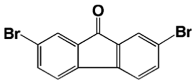
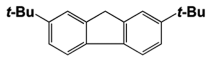
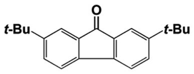
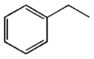
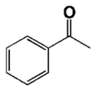
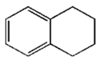
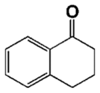


Figure 4. Recycling of **1** for oxidation of diphenylmethane.

The mild reaction conditions, excellent stability, and high yield for the transformation of diphenylmethane to benzophenone prompted us to extend the scope of **1** as heterogeneous catalyst for other benzylic hydrocarbons. As shown in Table 2, the oxidation of several substrates to the corresponding ketones using compound **1** proceeded smoothly with moderate to high yields. It is noteworthy that **1** exhibits excellent catalytic activity for oxidation of diphenylmethane, 9H-xanthenes, fluorene, and derivates of fluorene to the corresponding aryl ketones with up to 99% yield (Table 2, entries 1−6). Moderate catalytic activities for the oxidation of ethylbenzene (conv. 79.4%, selec. 92.2%) (Table 2, entry 7) and tertralin (conv. 87.5%, selec. 75.5%) (Table 2, entry 8) were observed under the same reaction conditions. For the oxidation of tertralin, the byproducts are 2,3-dihydronaphthalene-1,4-dione and α-tetralol, and for the oxidation of ethylbenzene the byproduct is 1-phenylethanol. The different activities observed for the substrates are mainly attributed to the different C−H bond energies (Table S3, Supporting Information). By comparison with previous reports, we found that compound **1** outperformed some heterogeneous catalysts such as polyoxome-

Table 2. Results of Selective Oxidation of Benylic Compounds Catalyzed by **1** Using TBHP Oxidant[a]



Entry	Substrates	Products	Conv. (%)	Selec. (%).[b]
1			95.8	>99
2			>99	>99
3			>99	>99
4			>99	>99
5			>99	>99
6			>99	>99
7			79.4	92.2
8			87.5	75.5

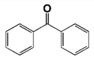
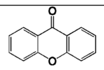
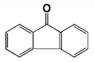
[a]Reaction conditions: substrates (0.25 mmol, 1 equiv), compound **1** (3.75 μmol, 1.5 mol %), TBHP (2.5 equiv), chlorobenzene (1 mL), 65 °C, 16 h. [b]Selectivity to ketones. The byproducts are corresponding alcohols for entries 1–7 and 2,3-dihydronaphthalene-1,4-dione and α-tetralol for entry 8.

talates,[22] MOFs,[23] cage compounds,[24] solid porous materials,[25] and even homogeneous catalysts[26] in the oxidation of diphenylmethane, fluorene, and 9*H*-xanthene (Table 3).

An interesting question is emerging: that is, how does compound **1** promote the oxidation of benzyl-alkanes. First, we assume that compound **1** plays a vital role in the activation of C–H bond on its exterior surface. If that is true, very low yield will be obtained in the oxidation of 2,7-di-*tert*-butyl-9*H*-fluorene because the huge steric hindrance from two *tert*-butyl groups might prevent methene group to approach the surface of catalyst. However, in fact the oxidation of 2,7-di-*tert*-butyl-9*H*-fluorene (entry 6 in Table 2) proceeded smoothly with quite a high yield. This indicated that the catalyst in our case might not facilitate the reaction through activating the C–H bond.

Then, according to previous investigations,[23b,24,27] we consider that a radical process might be involved in the reaction. To prove our speculation, some free-radical scavengers, such as Ph_2NH as oxygen-radical scavenger and (2,2,6,6-tetramethyl-piperidin-1-yl)oxyl (TEMPO) as carbon-radical scavenger,[24] were chosen and added in the oxidation of diphenylmethane catalyzed by compound **1** at 65 °C for16 h (see Table S4). The results (Table S4, entries 2 and 3) show that Ph_2NH could effectively retard the oxidation reaction under standard reaction conditions, and when 0.25 mmol Ph_2NH was added into the reactor, the conversion of diphenylmethane drops almost to zero (Table S4, entry 3), instead of 95.8% in the absence of radical scavengers. However, the inhibitory effect induced by TEMPO was not as obvious as Ph_2NH (Table S4, entries 4–6). The conversion of diphenylmethane only decreases to 56.5%, even if 1.00 mmol of TEMPO was used. Although both oxygen and carbon radical scavengers could retard the oxidation at different degrees, we conclude that oxygen-radical process may play a vital role, and the function of catalyst is to activate and decompose TBHP into *t*-BuOO• radical species which oxidize the substrates to generate ketones and other byproducts.[28] Our speculation was further supported by electron paramagnetic resonance (EPR) spectra of control experiments (Figure 5). When catalyst **1** was added into the reaction system in the presence of DMPO (5, 5-dimethyl-1-pyrroline-*N*-oxide) as spin trap, radicals arising from DMPO trapping were observed. The g value of DMPO/•OOBu-*t* spin adduct was measured to be 2.002, which was in good agreement with the reported data (Figure S10).[29] In contrast, the experiment under same conditions without catalyst **1** gave a negligible EPR spectrum (Figure 5 red).

Table 3. Comparison of 1 and Several Reported Catalysts

Catalyst	type	Yield (%)			Ref.
					
1	hetero-	95.8	>99	>99	this work
$[Cd(DMF)_2Mn(DMF)_2TPyP](PW_{12}O_{40})\cdot 2DMF\cdot 5H_2O$ (TPyP = tetrapyridylporphyrin)	hetero-	37	-	-	[22a]
$[V_{12}B_{18}Zn_3O_{63}H_{12}]\cdot 3(C_4N_3H_{16})\cdot 10NH_4\cdot 5H_2O$	hetero-	94	-	91	[22b]
$Cu(bped)_2(H_2O)SiF_6\cdot 4H_2O$ (bped = *meso*-1,2-bis(4-pyridyl)-1,2-ethanediol)	hetero-	28	-	84	[23a]
Fe(BTC) (BTC = 1,3,5-benzenetricarboxylate)	hetero-	-	99	73	[23b]
$[Cu_4L_4]\cdot 4NO_3$ (L = 1,3,5-tris(1-benzylbenzimidazol-2-yl)benzene)	homo-	25.2	-	61.6	[24]
$[Mn_5Cl_2(MnCl\text{-}OCPP)(DMF)_4(H_2O)_4]\cdot 2DMF\cdot 8CH_3COOH\cdot 14H_2O$ (H_8OCPP = 5,10,15,20-tetrakis(3,5-biscarboxylphenyl)porphyrin)	hetero-	18	-	42	[25]
$ReOCl_3(OPPH_3)(SMe_2)$	homo-	-	-	96	[26]

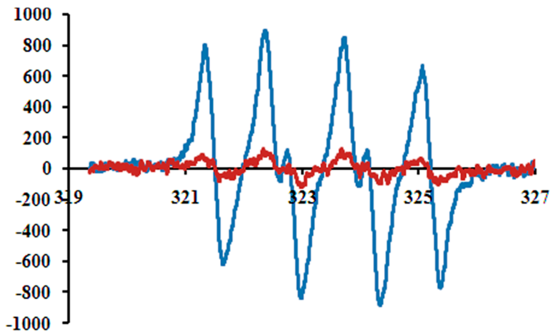


Figure 5. EPR spectrum (blue) with catalyst **1** (3.75 μmol, 1.5 mol %) and the EPR spectrum (red) without catalyst **1** were recorded at room temperature in the presence of DMPO. Reaction conditions: diphenylmethane: (0.25 mmol, 1 equiv), TBHP (2.5 equiv), chlorobenzene (1 mL), 65 °C, 10 min.

The role of cationic and anionic parts in the selective oxidation of benzyl-alkanes is under study.

■ CONCLUSIONS

In summary, through using Pd-complexes as countercations, we have successfully synthesized four novel methoxohexavanadate compounds **1**−**4** in a facile and straightforward method. The hexa- and octa-substituted methoxohexavanadate clusters could be isolated through adjusting the amount of base and a pair of rare organic-functionalized $[V_6O_{11}(OMe)_8]^{2-}$ isomers are formed by controlling crystallization temperature. As the introduction of Pd-complexes, compounds **1**−**4** are not only stable, but also can be used as heterogeneous catalyst in the selective oxidation of benzyl-alkanes with moderate to high catalytic activities. Specifically, under unoptimized conditions, compound **1** exhibits extraordinary efficiency in converting 9*H*-xanthene, fluorine, and its derivatives to corresponding ketones with high conversion and selectivity (conv. up to 99%, selec. up to 99%) and can be reused by filtration. The EPR analysis indicates that catalyst **1** can facilitate the generation of oxygen free radicals which oxidize the benzylic hydrocarbons. Investigations on the use of these Pd-POVs catalysts for other potential catalytic reactions are in progress.

■ EXPERIMENTAL SECTION

General Methods and Materials. All reagents and solvents for synthesis were purchased from commercial suppliers and used as received unless otherwise noted. The metal content of the compounds **1**−**5** was measured by inductively coupled plasma (ICP) on a JY-ULTIMA2 analyzer. Mass spectra were recorded on an Agilent 6520 Q-TOF LC/MS. The FT-IR spectra were recorded from KBr pellets in the range 4000−400 cm^{-1} on Nicolet 170 SXFT/IR spectrometer. The powder X-ray diffraction pattern was collected by using a Rigaku D/max-2550 diffractometer with $Cu_{k\alpha}$ radiation. The XPS spectra were recorded on an ESAY ESCA spectrometer with an Mg−K_a achromatic X-ray source. After the catalytic reaction was completed, the resulting mixture was analyzed by GC-MS and GC using naphthalene as internal standard substrate. The GC analyses were performed on Shimadzu GC-2014C with a FID detector equipped with an Rtx-1701 Sil capillary column. The GC-MS spectra were recorded on Agilent 7890A-5975C at an ionization voltage of 1200 V. The C, H, and N elemental analyses were conducted on PerkinElmer 240C elemental analyzer. Atomic absorption analysis was measured by inductively coupled plasma (ICP) on an ICP-6000 analyzer.

Synthesis of $[Pd(dpa)(acac)]_2[V_6O_{13}(OMe)_6]$ *(1).* $VO(acac)_2$ (0.6 mmol, 159.1 mg) and triethylamine (0.6 mmol) were added to 6 mL of methanol. The resulting solution was stirred at room temperature for 20 min, and then 2,2′-dipyridine amine (34.3 mg, 0.2 mmol) and $Pd(OAc)_2$ (44.9 mg, 0.2 mmol) were successively added. The reaction mixture was stirred for 12 h. From the resulting solution, yellow crystals suitable for X-ray diffraction grew after leaving the solution to stand for a week. Yield: 64.3%. Anal. Calcd (found) for $C_{36}H_{50}N_6O_{23}V_6Pd_2$: C, 29.75 (29.58); H, 3.47 (3.69); N, 5.78 (5.56); V, 21.03 (19.87); Pd, 14.65 (14.42). IR spectrum, ν (cm^{-1}): 3185 (N−H, m), 3065 (Ar−H, w), 1639 (s), 1579 (C═N, s), 1534 (s), 1466 (C═C, s), 1247 (s), 1164 (s), 1025 (s), 953 (s), 946 (s), 906 (s), 782 (s), 668 (s), 468 (Pd−N, m).

Table 4. Crystallographic Data for Compounds 1−5

compounds	1	2	3	4	5
formula	$C_{36}H_{50}N_6O_{23}Pd_2V_6$	$C_{38}H_{56}N_6O_{23}Pd_2V_6$	$C_{38}H_{58}N_6O_{24}Pd_2V_6$	$C_{46}H_{82}N_8O_{25}Pd_2V_6$	$C_{18}H_{50}N_2O_{19}V_6$
M_r	1453.26	1483.32	1501.34	1665.63	904.24
crystal system	triclinic	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$	$P\bar{1}$	$P2(1)/c$
temperature (K)	296(2)	296(2)	296(2)	296(2)	296(2)
a (Å)	10.594(2)	10.686(4)	15.949(4)	10.7283(8)	17.2607(3)
b (Å)	10.709(2)	10.790(4)	24.934(6)	11.9106(6)	10.4781(2)
c (Å)	12.472(3)	12.571(5)	13.822(3)	13.1328(9)	19.6314(4)
α (deg)	89.615(7)	89.876(7)	90	86.490(5)	90.00
β (deg)	75.262(7)	75.108(6)	98.513(4)	73.385(6)	95.1640(10)
γ (deg)	84.946(7)	85.398(7)	90	78.023(5)	90.00
V (Å^3)	1363.0(5)	1396.0(1)	5436(2)	1573.04(19)	3536.11(12)
Z	1	1	4	1	4
D_{calc} (g cm^{-3})	1.77	1.764	1.834	1.758	1.699
$F(000)$	722	740	3000	844	1848
R_1 [$I > 2\sigma(I)$]	0.0615	0.0805	0.0842	0.0502	0.0344
wR_2 [$I > 2\sigma(I)$]	0.1474	0.2246	0.2286	0.1380	0.0848
R_1 (all data)	0.1172	0.1171	0.1552	0.064	0.0491
wR_2 (all data)	0.1783	0.2679	0.2849	0.1503	0.0927
GOF	1.008	1.053	1.044	1.057	1.067
CCDC No.	942425	935841	935840	1008976	973741

*Synthesis of [Pd(dpa)(acac)]$_2$[V$_6$O$_{11}$(OMe)$_8$] (**2**).* VO(acac)$_2$ (0.6 mmol, 159.1 mg) and triethylamine (0.8 mmol) were added to 6 mL of methanol. The resulting solution was stirred at room temperature for 20 min, and then 2,2′-dipyridine amine (34.3 mg, 0.2 mmol) and Pd(OAc)$_2$ (44.9 mg, 0.2 mmol) were successively added. The reaction mixture was stirred for 12 h. From the resulting solution, yellow crystals suitable for X-ray diffraction grew after leaving the solution to stand for a week. Yield: 62.5%. Anal. Calcd (found) for $C_{38}H_{56}N_6O_{23}V_6Pd_2$: C, 30.77 (30.52); H, 3.81 (3.98); N, 5.67 (5.41); V, 20.61 (20.38); Pd, 14.35 (14.12). IR spectrum, ν (cm^{-1}): 3177 (N−H, m), 3076 (Ar−H, w), 1649 (s), 1582 (C═N, s), 1531 (s), 1464 (C═C, s), 1344 (m), 1244 (s), 1166 (s), 1024 (s), 951 (s), 945 (s), 760 (s), 651 (s), 465 (Pd−N, m).

*Synthesis of [Pd(dpa)(acac)]$_2$[V$_6$O$_{11}$(OMe)$_8$]·H$_2$O (**3**).* The synthetic procedure was the same as for compound **2**. After the reaction was finished, yellow crystals suitable for X-ray diffraction were obtained when the resulting solution was maintained at 5 °C for 10 days. Yield: 60.2%. Anal. Calcd (found) for $C_{38}H_{58}N_6O_{24}V_6Pd_2$: C, 30.4 (30.17); H, 3.89 (4.12); N, 5.6 (5.36); V, 20.36 (20.12); Pd, 14.18 (13.91). IR spectrum, ν (cm^{-1}): 3610 (O−H, m), 3280 (N−H, m), 3067 (Ar−H, w), 1645 (s), 1582 (C═N, s), 1534 (s), 1478 (C═C, s), 1365 (m), 1251 (s), 1152 (s), 1032 (s), 952 (s), 940 (s), 763 (s), 684 (s), 466 (Pd−N, m).

*Synthesis of [Pd(DMAP)$_2$(acac)]$_2$[V$_6$O$_{11}$(OMe)$_8$]·H$_2$O (**4**).* The synthetic procedure was same as for compound **2** except that DMAP was used instead of dpa. From the resulting solution, yellow crystals suitable for X-ray diffraction grew after leaving the solution to stand for a week. Yield: 65.6%. Anal. Calcd (found) for $C_{46}H_{82}N_8O_{25}V_6Pd_2$: C, 33.17 (33.02); H, 4.96 (5.12); N, 6.73 (6.41); V, 18.35 (18.13); Pd, 12.78 (12.65). IR spectrum, ν (cm^{-1}): 3629 (O−H, m), 3079 (Ar−H, w), 1639 (s), 1586 (C═N, s), 1534 (s), 1466 (C═C, s), 1353 (m), 1247 (s), 1164 (s), 1021 (s), 953 (s), 943 (s), 760 (s), 651 (s), 466 (Pd−N, m).

*Synthesis of [NHEt$_3$]$_2$[V$_6$O$_{13}$(OMe)$_6$] (**5**).* VO(acac)$_2$ (0.6 mmol, 159.1 mg) and triethylamine (0.6 mmol) were added to 6 mL of methanol (methanol was dried over 4 Å molecular sieves for a week and distilled before use). The reaction mixture was stirred for 12 h. From the resulting solution, light yellow crystals suitable for X-ray diffraction grew after leaving the solution to stand for a week. Yield: 41.5%. Anal. Calcd (found) for $C_{18}H_{50}N_2O_{19}V_6$: C, 23.91 (23.79); H, 5.57 (5.68); N, 3.1 (2.97); V, 33.8 (32.4). IR spectrum, ν (cm^{-1}): 2921 (m), 2815 (m), 1576 (m), 1531 (m), 1453 (m), 1033 (s), 956 (s), 755 (s), 660(m).

X-ray Crystallography. Single-crystal X-ray diffraction data for compounds **1**−**5** were conducted on a Bruker-AXS CCD diffractometer equipped with a graphite-monochromated Mo-K$_a$ radiation (λ = 0.71073 Å) at 296 K. All absorption corrections were applied using multiscan technique. The structures were solved by the direct method and refined through full-matrix least-squares techniques method on F^2 using the SHELXTL 97 crystallographic software package.[30,31] The hydrogen atoms of the organic ligands were refined as rigid groups. Crystallographic data for compounds **1**−**5** are summarized in Table 4. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as entries 942425 (**1**), 935841 (**2**), 935840 (**3**), 1008976 (**4**), 973741 (**5**). The selected bond lengths and bond angles of compounds **1**−**5** please see Table S2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic files in CIF format, some structural figures, X-ray powder diffraction patterns, IR spectra, XPS spectra, EPR spectra and ICP analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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