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Three Pd-decavanadates with a controllable molar ratio of Pd to decavanadate and their heterogeneous aerobic oxidation of benzylic C–H bonds†

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By the combination of Pd-complexes and $[V_{10}O_{28}]^{6-}$, three Pd-decavanadate compounds [Pd $(NH_3)_4]_3[V_{10}O_{28}]\cdot 8H_2O$ (**1**), [Pd(deta)(H₂O)]₂(NH₄)₂[V₁₀O₂₈]·2H₂O (**2**) (deta = diethylenetriamine) and [Pd $(dpa)_2](Hdpa)_2(Et_3NH)_2[V_{10}O_{28}]\cdot 2H_2O$ (**3**) (dpa = 2,2'-dipyridylamine) have been successfully synthesized and thoroughly characterized using single X-ray diffraction (SXRD), powder X-ray diffraction (PXRD), infrared spectroscopy (FT-IR) and elemental analyses (EA). Interestingly, in the three compounds, the molar ratios of Pd to decavanadate vary from 3:1 to 1:1 by changing N-ligands. The three Pd-decavanadates as heterogeneous catalysts are active in the aerobic oxidation of benzylic hydrocarbons under solvent-free conditions without adding any additives and co-catalysts. Moreover, compound **1** can be reused three times without losing its activity.

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Introduction

Polyoxometalates (POMs), as a remarkable class of discrete anionic clusters, are mainly composed of early transition metals (Mo, W, V, Nb and Ta) and oxo ligands.¹ As vanadium has excellent reversible redox properties, polyoxovanadates (POVs) have been explored as oxidation catalysts in recent years.² In addition, the counter-cations play an important role in the self-assembly of POMs, which influence not only the solubility of POMs, but also their catalytic activities.³ Pd-complexes have been proved to be active in some oxidation reactions.⁴ In our previous investigations Pd-complexes have been selected as counter-cations to combine with V-containing phosphomolybdates or alkoxohexavanadates by electrostatic attraction and the formed Pd-POMs are highly active for the

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selective oxidations.⁵ Importantly, by virtue of the strong electrostatic interaction between POM and Pd-complexes, the solidification of POMs is easily realized and this provides a new approach for the reuse of POMs. Because the assembly process of Pd-POMs is affected by several factors including ligands, the type of POM, pH value and reaction temperature, until now, only a handful of Pd-POMs with determined structures have been reported⁶ and the construction of Pd-POMs still remains a challenge.

The selective oxidation of C-H bonds is a primary and essential transformation in the synthesis of high value chemicals.⁷ Due to the extensive use of aryl ketones as building blocks in the manufacture of pharmaceuticals and agrochemicals, the selective oxidation of benzylic hydrocarbons has attracted much attention recently.8 To date, although a rather high yield was achieved in the benzylic C-H bond oxidation, in most cases, hydrogen peroxide,9 tert-butylhydroperoxide,10 and PhI(OAc)₂ or oxone¹¹ were used as oxidants. Molecular oxygen is regarded as an ideal oxidant as it is cheap and green. However, because O2 is difficult to activate, the aerobic oxidation of benzylic hydrocarbons is still a challenge. Some Pd complexes¹² molecules¹³ and organic (such as N-hydroxyphthalimine) have been reported to be active in the aerobic transformation of benzylic hydrocarbons, but they have been used in a homogeneous system and in the presence of additives (organic bases). From an economic and environmental viewpoint, heterogeneous catalytic systems without using any additives are more desirable. Several metal organic

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frameworks (MOFs) were found to activate molecular oxygen in the catalytic oxidation of benzylic C–H bonds, but some cases face a leaching problem.¹⁴ Recently, the investigation of Y. Wang *et al.* showed that Pd nanoparticles supported on N-doped carbon not only exhibited good catalytic performance (conv. 8.4% of diphenylmethane) under solvent-free conditions but also that this catalyst can be reused without leaching.¹⁵

Herein, two components, Pd-organic amine complexes and decavanadates, both of which have the potential ability to catalyze the aerobic oxidation of benzylic hydrocarbons, were coupled by self-assembly and as a result, $[Pd(NH_3)_4]_3$ $[V_{10}O_{28}]\cdot 8H_2O$ (1), $[Pd(deta)(H_2O)]_2(NH_4)_2[V_{10}O_{28}]\cdot 2H_2O$ (2) (deta = diethylenetriamine) and $[Pd(dpa)_2](Hdpa)_2(Et_3NH)_2$ $[V_{10}O_{28}]\cdot 2H_2O$ (3) (dpa = 2,2'-dipyridylamine) have been synthesized and thoroughly characterized using SXRD, PXRD, FT-IR and EA. The three Pd-decavanadate compounds as heterogeneous catalysts show catalytic activity in the aerobic oxidation of benzylic hydrocarbons under solvent-free conditions without using any additives or co-catalysts.

Experimental

Materials and methods

All reagents and solvents for synthesis were purchased from commercial suppliers and used as received, except for V6O15(1mIM)₈ (1-mIM = 1-methylimidazole) which was synthesized according to the related literature.^{2c} The metal content of the compounds 1-4 was measured by inductively coupled plasma (ICP) on an ICP-6000 analyzer. The FT-IR spectra were recorded as KBr pellets in the range of 4000–400 cm⁻¹ on a Nicolet 170 SXFT/IR spectrometer. The powder X-ray diffraction pattern was collected by using a Rigaku D/max-2550 diffractometer with CuK_{α} radiation. After the catalytic reaction was completed, the resulting mixture was analyzed using GC-MS and GC using naphthalene as an internal standard substrate. The GC analyses were performed on a Shimadzu GC-2014C system with an FID detector equipped with an Rtx-1701 Sil capillary column. The GC-MS spectra were recorded on an Agilent 7890A-5975C at an ionization voltage of 1200 V. The C, H, and N elemental analyses were conducted on a PerkinElmer 240C elemental analyzer. The XPS spectrum was recorded on an ESAY ESCA spectrometer with an Mg-Ka achromatic X-ray source.

Synthetic procedures

Synthesis of $[Pd(NH_3)_4]_3[V_{10}O_{28}]\cdot 8H_2O$ (1). V_2O_5 (0.5 g, 2.75 mmol) and 25% Et₄NOH (1.62 g, 2.75 mmol) were added to 20 mL water. The resulting solution was stirred at room temperature for 60 min, and then $Pd(OAc)_2$ (0.05 g, 0.223 mmol) and NH₄Cl (0.065 g, 1.2 mmol) were successively added. The resulting mixture was stirred for 12 h and heated at 50 °C for 30 min, and then the precipitate was removed by filtration. After leaving the resulting solution to stand under ambient conditions for three days, red crystals suitable for

X-ray diffraction were obtained. Yield: *ca.* 0.042 g, 34.7% (based on Pd(OAc)₂). Anal. calcd (%) (found) for $H_{52}N_{12}O_{36}V_{10}Pd_3$: H, 3.23 (3.45); N, 10.34 (10.46); V, 31.35 (31.27); Pd, 19.65 (19.51). IR (KBr, cm⁻¹): 3280 (N–H, m), 1616 (s), 1243 (s), 942 (s), 819 (s), 734 (s), 586 (s), 522 (w), 455 (Pd–N, m).

Synthesis of $[Pd(deta)(H_2O)]_2(NH_4)_2[V_{10}O_{28}]\cdot 2H_2O$ (2). The synthesis procedure of compound 2 is similar to that of compound 1 except that NH₄Cl (0.065 g, 1.2 mmol) was replaced by deta (0.062 g, 0.6 mmol). Yield: *ca.* 0.038 g, 22.9% (based on Pd(OAc)_2). Anal. calcd (%) (found) for C₈H₄₂N₈O₃₂V₁₀Pd₂: C, 6.47 (6.52); H, 2.85 (2.94); N, 7.55 (7.43); V, 34.31 (34.38); Pd, 14.34(14.25). IR (KBr, cm⁻¹): 3138 (N-H, m), 1623 (w), 1581 (w), 1438 (w), 1265 (s), 1027(m), 942 (s), 821 (s), 747 (s), 557 (s), 462 (Pd–N, m).

Synthesis of $[Pd(dpa)_2](Hdpa)_2(Et_3NH)_2[V_{10}O_{28}]\cdot 2H_2O$ (3). V₆O₁₅(1-mIM)₈ (0.42 g, 0.35 mmol), dpa (0.14 g, 0.8 mmol) and triethylamine (0.041 g, 0.4 mmol) were successively added to 20 mL HAc-NAAc buffer (pH = 4.5) and the solution was stirred at room temperature for 60 min. To this, Pd(OAc)₂ (0.045 g, 0.2 mmol) was added. The resulting mixture was further stirred for 12 h under 50 °C, and then the precipitate was removed by filtration. Red crystals suitable for X-ray diffraction were collected after evaporation for two weeks. Yield: *ca*. 0.068 g, 17.3% (based on Pd(OAc)₂). Anal. calcd (%) (found) for C₅₂H₇₂N₁₄O₃₀V₁₀Pd: C, 31.40 (31.26); H, 3.65 (3.53); N, 9.86 (9.74); V, 25.61 (25.71); Pd, 5.35 (5.31). IR (KBr, cm⁻¹): 3232 (N–H, m), 3023 (w), 1609(s), 1573 (s), 1484(s), 1406 (m), 1327 (s), 1218 (s), 956 (s), 821 (s), 748 (s), 591 (s), 455 (Pd–N, m).

Synthesis of [N(CH_3)_4]_4[H_2V_{10}O_{28}]\cdot 5H_2O (4). V_2O_5 (0.16 g, 0.88 mmol) and 25% Me₄NOH (0.32 g, 0.88 mmol) were added to 6 mL H₂O. The reaction mixture was stirred for 12 h. From the resulting solution, light red crystals suitable for X-ray diffraction grew upon allowing them to stand under ambient conditions for a week. Yield: *ca.* 0.083 g, 35.07% (based on V_2O_5). Anal. calcd (%) (found) for $C_{16}H_{60}N_4O_{33}V_{10}$: C, 14.27 (14.39); H, 4.46 (4.35); N, 4.16 (4.35); V, 37.89 (37.67). IR (KBr, cm⁻¹): 3434 (m), 1629 (m), 1481 (m), 1403 (m), 958 (s), 834 (s), 748 (s), 568 (m).

Crystallography

Single-crystal X-ray diffraction data of compounds 1-4 were collected on a Bruker-AXS CCD diffractometer equipped with graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). All absorption corrections were applied using a multi-scan technique. The structure solution and refinement were carried out with SHELXS-2014 and SHELXL-2014 program packages.^{16,17} The solvent molecules could not be refined satisfactorily; hence, they were removed by applying the SQUEEZE option of PLATON.18 The void volumes were estimated using the PLATON SQUEEZE program¹⁹ in which the solvated molecules in the compounds 3-4 were excluded. The hydrogen atoms of organic ligands were refined as rigid groups. the Crystallographic data of compounds 1-4 are summarized in Table 1. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as entries

Table 1 Crystallographic data of compounds 1-4

	1	2	3	4
Formula	N ₁₂ H ₅₂ Pd ₃ V ₁₀ O ₃₆	$C_8H_{42}N_8Pd_2V_{10}O_{32}$	C ₅₂ H ₇₀ N ₁₄ PdV ₁₀ O ₂₈	C ₁₆ H ₅₀ N ₄ V ₁₀ O ₂₈
$M_{\rm r}$	1625.13	1484.69	1955.02	1256.00
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$Par{1}$	P2(1)/c	$P\bar{1}$	$P\bar{1}$
$T(\mathbf{K})$	298(2) K	296(2) K	293(2) K	296(2) K
a (Å)	9.5424(8)	9.715(7)	11.353(6)	12.6170(12)
$b(\mathbf{A})$	11.2379(9)	10.642(7)	13.219(7)	12.6550(12)
c (Å)	11.8608(11)	19.195(13)	13.408(7)	15.6028(15)
$\alpha(\circ)$	115.251(2)	90	89.754(8)	68.3170(10)
$\beta(\circ)$	108.0690(10)	93.083(12)	77.245(8)	83.535(2)
γ (°)	98.8730(10)	90	64.976(7)	78.824(2)
$V(Å^3)$	1031.12(15)	1982(2)	1769.2(15)	2268.8(4)
Z	1	2	1	2
$D_{\rm calc}$ (g cm ⁻³)	2.617	2.488	1.867	1.839
F(000)	792	1448	998	1256
$R_1 \left[I > 2\sigma(I) \right]$	0.0298	0.0737	0.0347	0.0607
$wR_2 [I > 2\sigma(I)]$	0.0702	0.2254	0.0711	0.2033
R_1 (all data)	0.0373	0.0879	0.0442	0.0834
wR_2 (all data)	0.0733	0.2518	0.0759	0.2797
GOOF	0.988	1.063	0.978	1.126
CCDC no.	975175	975174	1495357	974935

975175 (1), 975174 (2), 1495357 (3) and 974935 (4).† For the selected bond lengths and bond angles of compounds 1–4, please see Table S2.†

Aerobic oxidation of benzylic hydrocarbons

In a 50 mL stainless-steel autoclave with a magnetic stirring bar, catalyst (8 mol%) and benzylic hydrocarbons (10 mmol) were added. The reaction was carried out under 8 atm O_2 in the absence of solvents, additives and co-catalysts. The reaction was conducted with magnetic stirring for the appropriate time upon heating at 90 °C. After the reaction was completed, the solution was analyzed using GC-MS and GC.

Reuse experiments

The reuse experiment was carried out under the conditions listed in Table 3. After the reaction was conducted for 36 h, compound **1** was filtered, washed with 10 mL methanol three times, dried under ambient conditions, and used for the next cycle.

Results and discussion

Synthesis and crystal structures

Compounds 1–3 were synthesized by the reaction of V_2O_5 or $V_6O_{15}(1\text{-mIM})_8$, $Pd(OAc)_2$ and the N-containing compounds (NH₄Cl, deta, or dpa) in Et₄NOH or Et₃N aqueous solution (Scheme 1). Although different vanadate sources were used in the synthesis of 1–3 (V_2O_5 was used for compounds 1 and 2, and $V_6O_{15}(1\text{-mIM})_8$ was used for compound 3), only the [$V_{10}O_{28}$] cluster is observed as a polyanion. The decavanadate cluster is built from ten highly condensed distorted { VO_6 } octahedra with a cage-like structure where six vanadiums are arranged in a plane with four vanadiums above and below the

plane. The bond lengths and angles of $[V_{10}O_{28}]$ are comparable to the reported ones.²⁰ BVS calculations show that all the vanadium atoms are in the +v state (Table S1[†]).²¹ Interestingly, we found that the ratio of the Pd-complex to $[V_{10}O_{28}]$ varies from 3 : 1 in 1, 2 : 1 in 2, to 1 : 1 in 3.

Compound 1 was isolated when using V_2O_5 , $Pd(OAc)_2$, NH_4Cl and Et_4NOH as starting materials. Crystal structure analysis reveals that 1 crystallizes in the triclinic $P\overline{1}$ space group and consists of three $[Pd(NH_3)_4]^{2+}$ cations, one $[V_{10}O_{28}]^{6-}$ polyanion and eight crystallographic water molecules (Scheme 1). In this case, the ligand NH_3 is formed *in situ* by the acid-base reaction between NH_4Cl and Et_4NOH . In three $[Pd(NH_3)_4]^{2+}$ cations, each palladium center exhibits square-planar geometry with the Pd–N bond distance in the range of 2.034(4)–2.046 (4) Å, which is very close to the Pd– NH_3 bond length of 2.039 (3) Å in the *trans*- $[Pd(NH_3)_2(1-MeC)_2]^{2+}$ complex.²²

When the organic ligand, deta, was added, compound 2 instead of compound 1 was obtained. Structural analysis shows that 2 is composed of two $[Pd(deta)(H_2O)]^{2+}$ cations, two NH_4^+ cations, one $[V_{10}O_{28}]^{6-}$ polyanion, and two lattice water molecules (Scheme 1). As deta has a chelating coordination mode, Pd is apt to bond with deta rather than the NH_3 ligand. Pd cations exhibit a planar PdN3O model, where three coordination sites are occupied by the nitrogen atoms of the deta ligand, and the fourth site is occupied by one water molecule. The Pd–N and Pd–O bond distances are comparable with those found in the previous PdN3O model complexes.²³

Compound 3 was synthesized by the reaction of $V_6O_{15}(1-mIM)_8$, trimethylamine, dpa and Pd(OAc)₂ in a HAc-NaAc buffer. As shown in Scheme 1, compound 3 contains one $[Pd(dpa)_2]^{2+}$ cation, one $[V_{10}O_{28}]^{6-}$ polyanion, two protonated Et₃NH⁺ ions and two protonated Hdpa⁺ ions. When compound 3 was synthesized in HAc-NaAc buffer, the pH value in this case was dramatically decreased. Although the formation of



Scheme 1 The controlling synthesis of compounds 1–3. Color codes: Pd, orange; V, lavender; C, gray-40%; O, red; N, blue. All lattice solvent molecules and hydrogen atoms are omitted for clarity.

the $[V_{10}O_{28}]^{6-}$ cluster is not affected, the coordination ability of the dpa ligand decreases. Some dpa ligands coordinate with the Pd cation, but the others are protonated and act as counter-cations. The Pd cations showed a planar PdN4 coordinate model where four coordination sites are occupied by the nitrogen atoms of two dpa ligands. The bond angles of N–Pd–N are all 180°, which are identical to those found in **1**.

FT-IR spectra and PRXD

The IR spectra of the compounds 1–3 are shown in Fig. S1–S3.† The absorptions in the region 455–465 cm⁻¹ (455 cm⁻¹ for 1, 462 cm⁻¹ for 2, and 455 cm⁻¹ for 3) are characteristic peaks of Pd–N bonds, which are in agreement with the reports.²⁴ The stretching vibrations of V=O in the decavanadate cluster are observed around 950 cm⁻¹.²⁵ The asymmetric vibrations of V–O-V groups are observed at 734 cm⁻¹ (compound 1), 747 cm⁻¹ (compound 2), and 748 cm⁻¹ (compound 3), respectively, and the corresponding symmetric vibrations are observed at 586 cm⁻¹ (compound 1), 557 cm⁻¹ (compound 2), and 581 cm⁻¹ (compound 3), respectively.²⁶ The experimental and simulated PXRD patterns of three Pd-POV compounds 1–3 are shown in Fig. S5–S7.† Their peak positions were in good agreement with each other, indicating the phase purity of the three compounds.

Catalytic activities of Pd-POVs

Given the fact that both the cations, the Pd-complexes, and the anion, $[V_{10}O_{28}]^{6-}$, of compounds 1–3 are active in aerobic oxidation, the transformation of diphenylmethane to benzophenone was used as a model reaction to evaluate the catalytic activities of three Pd-POVs (Scheme 2). The reactions were per-



Scheme 2 Transformation of diphenylmethane to benzophenone using Pd-POVs as catalysts.

Table 2 Aerobic oxidation of diphenylmethane to benzophenone^a

Entry	Catalysts	Conv. (%)	Sele. (%)	Reaction system
1	No	_	_	
2	$Pd(OAc)_2^b$	10.3	87.5	Homogeneous
3	$Pd(OAc)_2$ and NH_4Cl^c	12.8	98.8	Heterogeneous
4	$Pd(OAc)_2$ and $EDTA^d$	10.6	98.4	Heterogeneous
5	$Pd(OAc)_2$ and dpa^e	9.2	97.9	Heterogeneous
6	$[NMe_4]_4[H_2V_{10}O_{28}]$	4.9	97.2	Heterogeneous
7	$Pd(OAc)_2$ and	14.7	94.3	Heterogeneous
	$[NMe_4]_4[H_2V_{10}O_{28}]$			
8	1	22.5	98.6	Heterogeneous
9	2	18.7	96.5	Heterogeneous
10	3	15.4	94.8	Heterogeneous
11	1^{f}	22.5	98.5	Heterogeneous

^{*a*} Reaction conditions: Diphenylmethane (10 mmol), catalyst (0.8 mmol), 90 °C, O_2 (8 atm), 36 h. ^{*b*} Pd(OAc)₂ (2.4 mmol). ^{*c*} Pd(OAc)₂ (2.4 mmol) and NH₄Cl (9.6 mmol). ^{*d*} Pd(OAc)₂ (2.4 mmol) and EDTA (2.4 mmol). ^{*e*} Pd(OAc)₂ (2.4 mmol) and dpa (4.8 mmol). ^{*f*} Reaction time 40 h.

formed in a 50 mL stainless steel autoclave containing diphenylmethane (10 mmol) and the Pd-POV catalyst (0.8 mmol) under 8 atm O₂ pressure at 90 °C. The results indicate that compounds **1–3** (Table 2, entries 8–10) can successfully catalyze the aerobic oxidation of diphenylmethane under solvent-free conditions and that **1** (conv. 22.5%, sele. 98.6%) is more active than **2** (conv. 18.7%, sele. 96.5%) and **3** (conv. 15.4%, sele. 94.8%).

The blank experiment indicates that no substrate is consumed in the absence of catalysts (Table 2, entry 1). To assess the influence of the cation and the anion of Pd-POVs on aerobic transformation, a series of control experiments were performed. Although $Pd(OAc)_2$ as a homogeneous catalyst can produce benzophenone (Table 2, entry 2), the conversion (10.3%) is obviously lower than those of compounds 1-3 and palladium black is observed after the reaction (Fig. S9[†]). When Pd(OAc)₂ and N-containing ligands such as NH₄Cl, deta and dpa were used together, the conversion of diphenylmethane was slightly increased (Table 2, entries 3-5) but no palladium black was found (Fig. S9[†]). To further explore the role of the decavanadate cluster in the reaction, compound 4 $[NMe_4]_4[H_2V_{10}O_{28}]$ (Fig. 1) was prepared, which converts 4.9% diphenylmethane into benzophenone with the selectivity of 97.2% (Table 2, entry 6). In addition, the mechanical mixture of Pd(OAc)₂ and compound 4 leads to a yield comparable to that of compound 3. The above results show that both the Pdcomplex and the decavanadate polyanion in 1-3 play some roles in the aerobic oxidation of diphenylmethane and, compared to each single component, their electrostatic combination significantly enhances the catalytic activity.

The heterogeneity of compound **1** was confirmed by a hot leaching experiment. The solid catalyst of **1** was filtered from the reaction after 12 h under the optimum conditions and the filtrate was subsequently reacted at 90 °C for an additional 24 h. GC analysis showed a negligible conversion after filtration (Fig. 2). In addition, mercury was added to the reaction to check the heterogeneity of Pd. Under otherwise identical conditions, the conversion of diphenylmethane is basically unchanged, revealing that no active Pd nanoparticles are formed in the aerobic transformation. In addition, atomic absorption analysis shows that there were no palladium and vanadium ions in the filtrate of the reaction system, which further proves that the catalytic system using **1** is heterogeneous. Moreover, the recycle experimental results display that after three runs no obvious loss of activity was observed (Fig. 3)

The oxygen atom of benzylic ketone has two possible sources from decavanadate or molecular oxygen. When catalyst 1 (10 mmol) and diphenylmethane (10 mmol) were mixed to



Fig. 1 The crystal structure of compound 4. V, lavender; C, gray-40%; O, red; N, blue, H, white.



Fig. 2 Kinetics of the aerobic oxidation of diphenylmethane with compound 1 (black); compound 1 was filtered from the reaction mixture after 12 h (red). Reaction conditions: diphenylmethane (10 mmol), catalyst (8 mol%), 90 °C, O₂ (8 atm), 36 h.



Fig. 3 Recycle experiments of compound 1 in the aerobic oxidation of diphenylmethane. Reaction conditions: diphenylmethane (10 mmol), catalyst (8 mol%), 90 °C, O_2 (8 atm), 36 h.

react under an argon atmosphere (8 atm), the detected product is in trace amount, indicating that the oxygen atom of benzylic ketone does not directly come from POM. By comparison, the conversion of diphenylmethane reaches 22.5% under oxygen atmosphere (8 atm, Table 2, entry 8). According to the results, we speculate that molecular oxygen is first activated by Pd-POVs and then diphenylmethane is oxidized to benzophenone. In addition, we found that the catalytic activity of Pd-POVs increases with the ratio of the Pd complex to $[V_{10}O_{28}]$ (Fig. S11†). For example, the turnover number (TON) of 1 containing three Pd centers is higher than that of 2 and 3. The yield of benzophenone (22.2%) using 1 outperforms many reported heterogeneous catalysts, such as ZJU-18²⁷ and Pd@Ndoped carbon.¹⁵

Next, according to the previous investigations,²⁸ we consider that a radical process might be involved in the reaction. To prove our speculation, Ph_2NH as an oxygen-radical scavenger was chosen and added in the oxidation of diphenylmethane catalyzed by compound **1**. The results show that Ph_2NH could effectively retard the oxidation reaction under standard reaction conditions and when 15 mmol Ph_2NH was

Scheme 3 The possible mechanism for the aerobic oxidation of diphenylmethane to benzophenone using Pd-POVs as catalysts.

added into the reactor, the conversion of diphenylmethane almost drops to zero, instead of 22.5% in the absence of radical scavengers. Based on the above results and the reported literature,²⁹ a possible mechanism for the aerobic oxidation of diphenylmethane to benzophenone is proposed. As shown in Scheme 3, first molecular oxygen could be activated by Pd and POMs to form an active species ($^{\circ}O_2^{-}$).^{30–32} Subsequently, the formed $^{\circ}O_2^{-}$ oxidizes diphenylmethane **a** to produce the intermediate diphenylmethyl hydroperoxide **b**, which transforms to diphenylmethanol **c** or benzophenone **d**. Moreover, the formed diphenylmethanol **c** could be further oxidized to benzophenone **d** by O_2^{-} .

After the preliminary optimization (Table 2, Fig. S12 and S13†), the solvent-free aerobic oxidation of other benzylic substrates using the Pd-POV catalyst **1** was examined. As shown in Table 3, the oxidations of different benzylic substrates to the corresponding products were performed with high selectivity.

 Table 3
 The aerobic oxidation of benzylic compounds catalyzed by 1^a

Products



In preliminary experiments, tertralin oxidation proceeds with 19.5% conversion (Table 3, entry 2) with 2,3-dihydronaphthalene-1,4-dione and α -tetralol as by-products. Moderate catalytic activities for the oxidation of ethylbenzene (conv. 16.5%, sele. 89.2%) (Table 3, entry 3) and substituted ethylbenzene (conv. 13.7–17.6%, sele. 85.5–88.6%) (Table 3, entries 4–5) were observed under the same reaction conditions. The different activities observed for the substrates are mainly attributed to the different C–H bond reaction activities.^{33–35}

Conclusions

In conclusion, compounds **1–3** with Pd-complexes as the cation and $[V_{10}O_{28}]^{6-}$ as the anion were synthesized and interestingly the molar ratio of Pd to decavanadate in the three compounds is controlled by using different N-containing ligands. The three Pd-POVs are active in the aerobic oxidation of diphenylmethane to benzophenone under solvent-free conditions and we found that compound **1** with the highest ratio of Pd to $[V_{10}O_{28}]^{6-}$ can effectively catalyze the oxidation of a series of benzylic hydrocarbons in a heterogeneous system and its activity is basically maintained after three cycles. Investigations on using these Pd-POV catalysts for other catalytic reactions are in progress.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Sele.^b (%)

98.6

80.1

17.5

89.2

85.5

88.6

Conv. (%)

22.5

19.5

16.5

13.7

17.6

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Notes and references

- (a) C. L. Hill, Chem. Rev., 1998, 98, 1; (b) M. Sadakane and E. Steckhan, Chem. Rev., 1998, 98, 219; (c) N. Mizuno, K. Yamaguchi and K. Kamata, Coord. Chem. Rev., 2005, 249, 1944; (d) D.-L. Long, E. Burkholder and L. Cronin, Chem. Soc. Rev., 2007, 36, 105; (e) F. Y. Song, Y. Ding, B. C. Ma, C. M. Wang, Q. Wang, X. Q. Du, S. Fu and J. Song, Energy Environ. Sci., 2013, 6, 1170.
- 2 (a) J. Li, X. Huang, S. Yang, Y. Xu and C. Hu, Cryst. Growth Des., 2015, 15, 1907; (b) Y. Chen, H.-Y. Song, Y.-Z. Lu, H. Meng, C.-X. Li, Z.-G. Lei and B.-H. Chen, Ind. Eng. Chem. Res., 2016, 55, 10394; (c) B. Chen, X. Huang, B. Wang, Z. Lin, J. Hu, Y. Chi and C. Hu, Chem. - Eur. J., 2013, 19, 4408; (d) J. Dong, J. Hu, Y. Chi, Z. Lin, B. Zou, S. Yang,

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Substrates

C. L. Hill and C. Hu, Angew. Chem., Int. Ed., 2017, **56**, 4473; (e) A. Bayaguud, J. Zhang, R. N. Khan, J. Hao and Y. Wei, *Chem. Commun.*, 2014, **50**, 13150; (f) P. Yin, J. Wang, Z. Xiao, P. Wu, Y. Wei and T. Liu, *Chem. – Eur. J.*, 2012, **18**, 9174.

- 3 (a) C. Y. Sun, S. X. Liu, D. D. Liang, K. Z. Shao, Y. H. Ren and Z. M. Su, J. Am. Chem. Soc., 2009, 131, 1883;
 (b) F. J. Ma, S. X. Liu, C. Y. Sun, D. D. Liang, G. J. Ren, F. Wei, Y.-G. Chen and Z.-M. Su, J. Am. Chem. Soc., 2011, 133, 4178; (c) X. Wang, D. Zhao, A. Tian and J. Ying, Dalton Trans., 2014, 43, 5211; (d) M. Araghi, V. Mirkhani, M. Moghadam, S. Tangestaninejad and I. Mohammdpoor-Baltork, Dalton Trans., 2012, 41, 3087.
- 4 (a) R. Dun, X. Wang, M. Tan, Z. Huang, X. Huang and W. Ding, ACS Catal., 2013, 3, 3063; (b) B. A. Steinhoff, S. R. Fix and S. S. Stah, J. Am. Chem. Soc., 2002, 124, 766; (c) S. Xie, Y. Liu, J. Deng, X. Zhao, J. Yang, K. Zhang, Z. Han, H. Dai and X. Lu, J. Catal., 2016, 342, 17.
- 5 (a) X. Huang, X. Zhang, D. Zhang, S. Yang, X. Feng, J. Li, Z. Lin, J. Cao, R. Pan, Y. Chi, B. Wang and C. Hu, *Chem. – Eur. J.*, 2014, 20, 2557; (b) J.-K. Li, X.-Q. Huang, S. Yang, H.-W. Ma, Y.-N. Chi and C.-W. Hu, *Inorg. Chem.*, 2015, 54, 1454.
- 6 (a) T. Hirano, K. Uehara, K. Kamata and N. Mizuno, J. Am. Chem. Soc., 2012, 134, 6425; (b) J. Ettedgui and R. Neumann, J. Am. Chem. Soc., 2009, 131, 4.
- 7 (a) C. S. Yeung and V. M. Dong, Chem. Rev., 2011, 111, 1215; (b) S. P. Argent, A. Greenaway, M. C. Gimenez-Lopez, W. Lewis, H. Nowell, A. N. Khlobystov, A. J. Blake, N. R. Champness and M. Schröder, J. Am. Chem. Soc., 2012, 134, 55; (c) H.-L. Jiang, Y. Tatsu, Z.-H. Lu and Q. Xu, J. Am. Chem. Soc., 2010, 132, 5586; (d) Q.-R. Fang, G.-S. Zhu, Z. Jin, Y.-Y. Ji, J.-W. Ye, M. Xue, H. Yang, Y. Wang and S.-L. Qiu, Angew. Chem., Int. Ed., 2007, 46, 6638; (e) M. M. Wanderley, C. Wang, C.-D. Wu and W. Lin, J. Am. Chem. Soc., 2012, 134, 9050.
- 8 (a) K. Chen, P. Zhang, Y. Wang and H. Li, Green Chem., 2014, 16, 2344; (b) Y. Liu, S.-M. N. Lam, W. Y. William, S.-M. Yiuand and T.-C. Lau, Angew. Chem., Int. Ed., 2016, 55, 288; (c) G. Pandey, R. Laha and D. Singh, J. Org. Chem., 2016, 81, 7161.
- 9 (a) S. Verma, R. B. N. Baig, M. N. Nadagouda and R. S. Varma, ACS Sustainable Chem. Eng., 2016, 4, 2333;
 (b) A. Al-hunaiti, M. Raisanen and T. Repo, Chem. Commun., 2016, 52, 2043; (c) D. Shen, C. Miao, S. Wang, C. Xia and W. Sun, Org. Lett., 2014, 16, 1108;
 (d) T. Chattopadhyay, M. Kogiso, M. Aoyagi, H. Yui, M. Asakawa and T. Shimizu, Green Chem., 2011, 13, 1138.
- 10 (a) Z. Ma, H. Zhang, Z. Yang, G. Ji, B. Yu, X. Liu and Z. Liu, Green Chem., 2016, 18, 1976; (b) Y. Wang, Y. Kuang and Y. Wang, Chem. Commun., 2015, 51, 5852; (c) Y. Gao, G. Hu, J. Zhong, Z. Shi, Y. Zhu, D. S. Su, J. Wang, X. Bao and D. Ma, Angew. Chem., Int. Ed., 2013, 52, 2109; (d) H. Chen, Y. Deng, Z. Yu, H. Zhao, Q. Yao, X. Zou, J.-E. Baeckvall and J. Sun, Chem. Mater., 2013, 25, 5031.

- 11 (a) T.-H. Chen, K. W. Kwong, A. Carver, W. Luo and R. Zhang, *Appl. Catal., A*, 2015, **497**, 121; (b) K. Moriyama, M. Takemura and H. Togo, *Org. Lett.*, 2012, **14**, 2414; (c) P. Liu, Y. Liu, E. L.-M. Wong, S. Xiang and C.-M. Che, *Chem. Sci.*, 2011, **2**, 2187.
- 12 G. Urgoitia, R. SanMartin, M. T. Herrero and E. Domínguez, *Green Chem.*, 2011, **13**, 2161.
- 13 G. Zheng, C. Liu, Q. Wang, M. Wang and G. Yang, *Adv. Synth. Catal.*, 2009, **351**, 2638.
- 14 (a) A. Santiago-Portillo, S. Navalón, F. G. Cirujano, F. X. L. Xamena, M. Alvaro and H. Garcia, ACS Catal., 2015, 5, 3216; (b) J. Long, L. Wang, X. Gao, C. Bai, H. Jiang and Y. Li, Chem. Commun., 2012, 48, 12109.
- 15 P. Zhang, Y. Gong, H. Li, Z. Chen and Y. Wang, *Nat. Commun.*, 2013, 4, 1593, DOI: 10.1038/ncomms2586.
- 16 G. M. Sheldrick, Phase Annealing in SHELX-90: Direct Methods for Larger Structures, Acta Crystallogr., Sect. A: Found. Crystallogr., 1990, 46, 46.
- 17 G. M. Sheldrick, A Short History of SHELX, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112.
- 18 (a) A. L. Spek, J. Appl. Crystallogr., 2003, 36, 7;
 (b) A. L. Spek, Acta Crystallogr., Sect. C: Struct. Chem., 2015, 71, 9.
- 19 Crystal Structure 4.0: Crystal Structure Analysis Package, Rigaku Corporation (2000–2010), Tokyo 196–8666.
- 20 G.-G. Gao, P.-S. Cheng and T. C. W. Mak, J. Am. Chem. Soc., 2009, 131, 18257.
- 21 N. E. Brese and M. O'Keeffe, Acta Crystallogr., Sect. B: Struct. Sci., 1991, 47, 192.
- 22 M. Krumm, I. Mutikainen and B. Lippert, *Inorg. Chem.*, 1991, **30**, 884.
- 23 Z. D. Bugarcic, S. T. Nandibewoor, M. S. A. Hamza, F. W. Heinemann and R. V. Eldik, *Dalton Trans.*, 2006, 24, 2984.
- 24 (a) M. Krumm, B. Lippert, L. Randaccio and E. Zangrando, J. Am. Chem. Soc., 1991, 113, 5129; (b) M. Krumm, E. Zangrando, L. Randaccio, S. Menzer and B. Lippert, Inorg. Chem., 1993, 32, 700.
- 25 P. Roman, A. Aranzabe, A. Luque, J. M. Gutierrez-Zorrilla and M. Martinez-Ripoll, *J. Chem. Soc., Dalton Trans.*, 1995, 13, 2225.
- 26 A. Udomvech, P. Kongrat, C. Pakawatchai and H. Phetmung, *Inorg. Chem. Commun.*, 2012, **17**, 132.
- 27 X. L. Yang, M. H. Xie, C. Zou, Y. He, B. Chen, M. O'Keeffe and C. D. Wu, *J. Am. Chem. Soc.*, 2012, **134**, 10638.
- 28 J. Long, L. Wang, X. Gao, C. Bai, H. Jiang and Y. Li, *Chem. Commun.*, 2012, **48**, 12109.
- 29 A. Santiago-Portillo, S. Navalón, F. G. Cirujano, F. X. L. Xamena, M. Alvaro and H. Garcia, *ACS Catal.*, 2015, 5, 3216.
- 30 (a) S. S. Stahl, Science, 2005, 309, 1824; (b) G.-J. Brink,
 I. W. C. E. Arends and R. A. Sheldon, Science, 2000, 287,
 1636; (c) Y.-H. Zhang, B.-F. Shi and J.-Q. Yu, J. Am. Chem. Soc., 2009, 131, 5072.
- 31 (a) G. Yan, X. Feng, L. Xiao, W. Xi, H. Tan, H. Shi, Y. Wang and Y. Li, *Dalton Trans.*, 2017, 46, 16019; (b) T. Yokota,

M. Tani, S. Sakaguchi and Y. Ishii, *J. Am. Chem. Soc.*, 2003, **125**, 1476; (c) J. Song, Z. Luo, D. K. Britt, H. Furukawa, O. M. Yaghi, K. I. Hardcastle and C. L. Hill, *J. Am. Chem. Soc.*, 2011, **133**, 16839; (d) A. Rubinstein, P. Jiménez-Lozanao, J. J. Carbó, J. M. Poblet and R. Neumann, *J. Am. Chem. Soc.*, 2014, **136**, 10941.

32 (a) H. L. Liu, Y. L. Liu, Y. W. Li, Z. Y. Tang and H. F. Jiang, J. Phys. Chem. C, 2010, 114, 13362; (b) B. Chowdhury, J. J. Bravo-Suárez, N. Mimura, J. Lu, K. K. Bando, S. Tsubota and M. Haruta, *J. Phys. Chem. B*, 2006, **110**, 22995; (c) J. D. Stiehl, T. S. Kim, S. M. McClure and C. B. Mullins, *J. Am. Chem. Soc.*, 2004, **126**, 1606.

- 33 G. Bordwell, J. P. Cheng, G. Z. Ji, A. V. Satish and X. Zhang, J. Am. Chem. Soc., 1991, 113, 9790.
- 34 I. W. C. E. Arends, P. Mulder, K. B. Clark and D. D. M. Wayner, J. Phys. Chem., 1995, 99, 8182.
- 35 D. F. McMillen and D. M. Golden, *Annu. Rev. Phys. Chem.*, 1982, **33**, 493.