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Two ionic organic-inorganic hybrid compounds, $[Cu^{II}(C_2N_2H_8)_2]_4[Cu^{II}(C_2N_2H_8)_2]_4[Cu^{II}(C_2N_2H_8)_2]_2[PNb_{12}O_{40}V^{V}V^{IV}O_2] (OH)_2 \cdot 11H_2O$ (1) and $[Co^{III}(C_2N_2H_8)_3]_2[Co^{III}(C_2N_2H_8)_2]_{4.5}PNb_{12}O_{40}V^{V}V^{IV}O_2] \cdot 20H_2O$ (2), based on P-centered dicapped polyoxoniobates and organometallic cations were isolated and structrually characterized by routine techniques. The trivalent cobalt complexes-containing compound exhibits a looser arrangement compared with the divalent copper complexes-containing counterpart, with a space volume of 34.9% for the former and 17.0% for the latter. The two compounds were proved to be effective in facilitating the oxidation of benzyl-alkanes to ketone products in a heterogeneous manner, evidencing the feasible strategy of self-immobilization of catalytically active, readily soluble PNb₁₂O₄₀(VO)₂ species in crystalline solids.

Introduction

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The exploration of green catalysts working in a heterogeneous manner is of considerable interest in industrial application due to their ready recovery and recyclability from the reaction environments.¹ Polyoxometalates (POMs) are discrete anionic clusters of transition metals primarily from Group VI (V, Nb, and Ta) and Group V (Mo, W),² and continue to gain attention as a kind of promising heterogeneous catalysts in such reactions as oxidation, hydrolysis, photocatalysis, and electrocatalysis.³⁻⁶ Effective matrixes like silica/carbon-based compounds^{4,5} and layered double hydroxides⁶ have been ever studied to immobilize those soluble POMs. However, lacking of finely-tunable disperisty as well as leaching of the catalytically active POM species during the reaction and the subsequent recycling remains the issues to be solved.

Another feasible strategy to the heterogenization of molecular polyoxometalates is construction of POM-based organic-inorganic crystalline hybrids with high tunability intrinsic to molecular materials.⁷ In the POM-based ionic solids, the two components are simply combined via H-bonding and/or electrostatic interactions, with retention of the catalytically active POMs at the molecular level. To this point, one remarkable system is POM-based metal-organic

frameworks (MOFs), in which the polyanions are alternately arranged as non-coordinating guests and exhibit charming substrate size selective properties induced by confined channel sizes.⁸ Another promising way to access to POM-based ionic organic-inorganic catalysts is introducing organometallic cations ionically interacting with the polyanions in the crystalline lattices, leading to insoluble solids and hence realizing the self-immobilization of catalytic POM species.⁹ For example, Mizuno proposed that complexation of {SiW₁₀O₃₈V₂} with $Ni(tacn)_2$ (where tacn = 1,4,7-triazacyclononane) gave rise to an ionic compound that was effective towards epoxidation cyclooctene.^{9a} 1-octeneand In the POM-based of heterogeneous catalysts mentioned-above, the POM species are much restricted to Group V consisting of tungstates, molybdates as the addenda atoms. Group V POMs, bearing high negative charges, have proved to be much more suitable building components for supramolucular crystalline solids, 10,11 however, their potentials as catalysts are much less explored.

Polyoxoniobate, XNb₁₂O₄₀(VO)₂, where X is heteroatom and it can be Si/Ge^{11a} or P/V,¹² is one of the well-studied polyoxoniobates (PONbs). In particular, TMA₉PNb₁₂O₄₀(VO)₂ (where TMA = tetramethylammonium) can be readily synthezed in high yield as soluble organic salts, promising an homogenously catalystic system in oxidative transformation, as we have tested that it was effective towards catalytic decontamination of chemical warfare agent simulants.¹³ We envisage the combination of $XNb_{12}O_{40}(VO)_2$ with organometallic cations may lead to insoluble materials as heterogeneous catalysts with ready recovery and separation, which is of great significance with respect to the practical utilization. Herein we successfully isolated two ionic organicinorganic hybrid compounds based on PNb₁₂O₄₀(VO)₂ and copper/cobalt complexes,

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[Cu^{II}(C₂N₂H₈)₂]₄[Cu^{II}(C₂N₂H₈)₂(H₂O)₂]₂[PNb₁₂O₄₀V^VV^{IV}O₂]·(OH)₂·1 $1H_{2}O$ (1) and $[Co^{III}(C_2N_2H_8)_3]_2[Co^{III}(C_2N_2H_8)_2(H_2O)_2]_{0.5}[H_{2.5}PNb_{12}O_{40}]$ $V^{V}V^{V}O_{2}$]·20H₂O (2). The catalytically active polyanion, $PNb_{12}O_{40}(VO)_2$, is solidified in the ionic crystalline solids, and thus a PONb-based heterogeneous system is established. With selective oxidation of benzyl-alkanes to ketone products as the model reaction, the two compounds were investigated as heterogeneous contaning effecient catalysts. The copper/cobalt-diamine complexes as the cation components shall also contribute to the catalytic activity. Moreover, a radical mechanism involving OOBu-t formed from TBHP decomposition is proposed.

Experimental section

Materials

All common laboratory chemicals were reagent grade, purchased from commercial sources and used without further purification. Hexaniobate precursors $K_7HNb_6O_{19}\cdot 8H_2O$ and $VOPO_4\cdot 2H_2O$ were prepared according to the literature method.^{14,15}

Synthesis of 1

To a solution of K₇HNb₆O₁₉·8H₂O (0.15 g, 0.11 mmol) in 8 mL of H₂O, VOPO₄·2H₂O (0.1 g, 0.51 mmol), Cu₂(OH)₂CO₃ (0.22g, 1.00 mmol) were added successively, followed by the addition of 0.5 mL 1,2-diaminoethane. The mixture was stirred for 30 min at room temperature. The resulting solution was transferred to a Teflon-lined stainless steel autoclave (23 mL), kept in an oven at 160 °C for 24 h, and then cooled to room temperature at a rate of 5 °C/h. Block-shaped dark purple crystals of 1 were isolated and washed with deionized water. Yield: 0.10 g, ~ 55.87 % based on Nb. Anal. Calc. for $C_{24}H_{128}Cu_6N_{24}Nb_{12}O_{59}PV_2$: C, 8.67%; H, 3.88%; N, 10.11%, P, 0.93%, Cu, 11.46%, V, 3.06%, Nb, 33.52%; Found: C, 8.78%; H, 3.61%; N, 10.32%, P, 0.89%, Cu, 11.62%, V, 3.02%, Nb, 33.43%. IR (KBr, cm⁻¹): 3308(s), 3214(s), 3138(m), 2965(w), 2947(w), 2886(w), 1638(m), 1586(s), 1453(w), 1386(m), 1324(w), 1280(w), 1168(m), 1104(m), 1047(s), 1028(s), 988(w), 975(w), 953(m), 872(s), 810(w), 679(s), 625(w), 526(m), 474(m).

Synthesis of 2

To a solution of $K_7HNb_6O_{19}\cdot 8H_2O$ (0.15 g, 0.11 mmol) in 8 mL of H_2O , $VOPO_4\cdot 2H_2O$ (0.1 g, 0.51 mmol), $Co(CH_3COO)_2\cdot 4H_2O$ (0.14g, 0.55 mmol) were added successively, followed by the addition of 0.5 ml 1,2-ethylenediamine. The mixture was stirred for 30 min at room temperature. And the resulting solution was transferred to a Teflon-lined stainless steel autoclave (23 mL) and was kept in an oven at 160 °C for 72 h, and then cooled to room temperature at a rate of 5 °C/h. The reaction mixture was left undisturbed for ten days at room temperature, and block-shaped light yellow crystals of **2** were isolated and washed with deionized water. Yield: 0.005 g, ~ 3.48 % based on Nb. Anal. Calc. for $C_{14}H_{100.5}Co_{2.5}N_{14}Nb_{12}O_{63}PV_2$: C, 5.86%; H, 3.53%; N, 6.84%, P, 1.08%, Co, 5.14%, V, 3.55%, Nb, 38.87%; Found: C, 5.73%; H, 3.71%; N, 6.59, P, 1.13%, Co,

5.02%, V, 3.62%, Nb, 38.94%; IR (KBr, cm⁻¹): 3424(s), 3101(m), 2970(w), 2900(w), 1619(m), 01579(3), 01462(m), 1384(w), 1366(w), 1325(w), 1300(w), 1250(w), 1156(m), 1122(w), 1057(s), 1027(s), 973(w), 944(w), 876(m), 703(s), 632 (w), 580(m), 488(m).

Catalytic experiments

Benzyl-alkanes (0.125mmol, 1 equiv), catalysts (0.004 mmol, 0.03 mol %), tert-butyl hydroperoxide (TBHP, 70% in water, 2.5 equiv), naphthalene (internal standard, 0.125mmol, 1 equiv), and benzonitrile(0.5 mL) were added in a Schlenk Tube under ambient atmosphere and stirred at 60 °C. After refluxing for 24 hours, the resulting reaction mixture was diluted with acetonitrile and quantitatively analyzed by gas chromatography (GC).

Characterization

Elemental analyses (C, H and N) were measured on a ELEMENTAR vario EL cube Elmer CHN elemental analyzer; Nb, V and Cu/Co were determined with a Thermo iCAP 6000 atomic emission spectrometer. IR spectrum was collected in the range 40000-400 cm⁻¹ with KBr pellets dispersed with sample on a Nicolet 170SXFT-IR spectrophotometer. Powder Xray diffraction (PXRD) data on samples were recorded on a Bruker instrument equipped with graphite-monochromatized Cu-K α radiation (λ = 0.154060 nm, scan speed of 8 °/min, 2 θ = 5-50°) at room temperature. The EPR analysis was conducted on a Bruker ECS 300 spectrometer. Experimental parameters: microwave frequency 9.068 GHz, microwave power 0.998 mW, modulation frequency 100 kHz, and modulation width 0.2 mT. The GC analyses were performed on Shimadzu GC-2014C with a FID detector equipped with a HP-5ms capillary column. Complete crystallographic data for 1 and 2 were collected at 296(2) K on Bruker APEX-II CCD detector with graphite monochromatic Mo K α radiation (λ = 0.71073 Å). The structure were solved and refined using the OLEX2 program suite,¹⁶ equipped with SheIXT and SheIXL program.¹⁷ All non-hydrogen atoms were located from Fourier map directly by ShelXT and refined anisotropically. Hydrogen atoms on all non-hydrogen atoms were placed in calculated positions, and their coordinates and displacement parameters were constrained to ride on the carrier atoms. In addition, some restrains, like RIGU and DFIX, were performed to get better structure models. In both compounds, the structures contain large voids, and the exact amount of solvent molecules located in the voids couldn't be identified due to their high disorder and small residual peaks. Therefore, SQUEEZE in PLATON program was performed remove those solvent molecules. to Crystallographic data and selected bond lengths are summarized in Table S1 and Table S2-S5, respectively.

Results and discussion

Synthesis and Structures

Following our previous work on vanadium-containing PONbs, herein we explored the potential combination of P-centered polyanion $PNb_{12}O_{40}(VO)_2$ with organometallic cations to

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construct ionic organic-inorganic hybrids, with hope to "fix" the catalytically active polyanion in crystalline lattices. Different organometallic cations were introduced to enrich the three-dimensional structures. Specifically, the reaction of potassium hexaniobates, vanadyl phosphate, and copper carbonate in the presence of 1,2-diaminoethane under hydrothermal conditions at 140 °C gave rise to **1**. Following a procedure similar to that of **1**, where the copper carbonate was replaced with cobalt carbonate hydroxide, **2** was isolated. The 1,2-diaminoethane molecule serves as both protective ligand and reagent for the pH value adjustment. The digital photographs of the two compounds are shown in Fig. S1.

The phase purity of the crystalline products is veried by powder X-raydiffraction (PXRD) (Fig. S2). The oxidation states of V ions are evidenced by IR and XPS analysis. In the IR spectra (Fig. S3), both compounds share peaks at 952 cm⁻¹ (for 1) and 944 cm⁻¹ (for **2**), 975cm⁻¹ (for **1**) and 973 cm⁻¹ (for **2**), characteristic of vibration mode of of $V^{IV}\!\!=\!\!O^{18}$ and $V^V\!\!=\!\!O^{,12}$ respectively. We can further determine the oxidation states of vanadium species in both compounds by XPS. In the XPS of the core level region of V2p, two well-resolved peaks at 515.81 and 517.26 eV for 1, 515.84 and 517.28 eV for 2 can be found (Fig. S6), where the former is attributable to V^{4+} , and the later can be assignable to V^{5+} .¹⁹ The V^{5+} in the starting materials can be partially reduced by organoamine to V⁴⁺ under hydrothermal conditions.^{11b,20,21} In the XPS of the core level region of Cu2p, Peaks at 934.96 and 954.36 eV with satellites (Fig. S7, left) support the presence of Cu^{2+} in **1**.²² It's worth noting that peaks at 933.32 and 953.19 eV are originated from $Cu^{0,22a}$ the fully reduced form of Cu^{2+} in the presence of organoamine. Accordingly, we assign the peak at 781.84 eV being arose from Co2p_{3/2} (Fig. S7, right) to Co ions in +3 oxidation state in 2 in the XPS of the core level region of Co2p.²³ It's reasonable for the assignment of Co^{3+} species in **2**, which is isolated after leaving the baker undisturbed, while exposure to air for 1 month, facilitating the oxidation of Co²⁺ ions to Co^{3+} .

Single crystal X-ray diffraction reveals that **1** crystallizes in the tetragonal *P4/mnc* space group and possesses a discrete PONb cluster $PNb_{12}O_{40}(VO)_2$ (Fig. 1), with copper complexes compensating for the charge of the polyanion. The polyanion $PNb_{12}O_{40}(VO)_2$ is a surface-modified Keggin PONb, i.e., the α - $PNb_{12}O_{40}$ captures two vanadyl groups in two opposite sites. Under hydrothermal conditions, the Nb precursor Nb_6O_{19} is likely to be broken up into fragments Nb_3O_{13} , which is then to



Fig. 1 (a) Representation of polyanion $PNb_{12}O_{40}(VO)_2$: (a) Ball and stick mode and (b) polyhedron mode. Color codes: Nb (cyan V (pink), Cu (light green), O (red).

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be directed by PO_4^{3-} from the vanadyl phosphate nite reassemble a Keggin type polyanion $PNB_{12}^{-1}O_{40}^{-1}O_{30}^{-1}O$

There are two crystallographically distinct copper centers in 1. One(Cu1) is tetra-coordinated with square geometry (Fig. 2a) and the other(Cu2) is hexa-coordinated with octahedral geometry. Both copper centers coordinate with four nitrogen atoms from two 1,2-diaminoethane ligands, and additionally two aqua ligands can be located for Cu2 to complete the geometrical sphere. The bond lengths are 1.963-2.035 Å for Cu-N. The introducing coordinated unsaturated metal sites(Cu1) provide potential Lewis acid sites, and are very attractive in catalysis. In 1, the polyanion $PNb_{12}O_{40}(VO)_2$ is ionically interacted with twelve copper complexes cations, with each copper center located approximately 7.239-7.711 Å from the central phosphorus atoms of the polyanion. The copper complexes cations form a ten-membered ring (red broken circle in Fig. 3a), where the polyanion resides inside. The specific arrangement as well as the relative small size of these copper complexes leads to discrete polyanion in the crystalline lattices in 1, in line with the previous reports.^{11a,11c} As a result, a three-dimensional (3D) supramolecular framework is assembled. Lattice water molecules are filled in the voids of the 3D network, as supported by TG analysis (Fig S4, right).

When introducing cobalt ions, a cobalt-based $PNb_{12}O_{40}(VO)_2$ ionic hybrid is isolated as **2**, and crystallizes in



Fig. 2 (a) Copper(Cu1) complexes in 1 and cobalt complexes in 2. Color codes: Cu (light green), Co (olive green), O (red), C (gray), N (blue).



Fig. 3 Stacking view of $PNb_{12}O_{40}(VO)_2$ and copper complexes in **1**: (a) supramolecular layer along the b axis and (b) supramolecular arrangement in the three-dimensional lattices. Color codes: Nb (cyan), V (pink), Cu (light green), O (red), C (gray), N (blue).

Catalysis Investigations

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the triclinic P-1 space group. Similar to 1, the central P atom resides on an inversion centre, and is surrounded by eight O atoms with each site of them half-occupied. The two crystallographically distinct cobalt centers are both hexacoordinated with octahedral geometries; each cobalt center located approximately 7.264 - 7.367 Å from the central phosphorus atoms of the polyanion. For Co1 ion, the coordination mode is defined by six nitrogen atoms from three 1,2-diaminoethane ligands. The Co-N bond lengths are 1.936-1.981 Å. Differently, Co2 center is equatorially coordinated by four nitrogen atoms from two 1,2-diaminoethane ligands and axially coordinated by two aqua ligands, resulting in a 4+2 mode with a slight Jahn-Teller-distortion (Fig. 2b,2c). The bond lengths are 1.947-1.980 Å for Co-N and 1.988 Å for Co-O_w, respectively. It's worth nothing that the coordinated water molecules can be removable and thus are potential Lewis acid sites. In $\boldsymbol{2},$ the polyanion $\mathsf{PNb}_{12}\mathsf{O}_{40}(\mathsf{VO})_2$ is surrounded by eight cobalt complexes cations via electronic interactions and hydrogen bonding interactions. The cobalt complexes cations form a six-membered ring (red broken circle in Fig. 4a), as observed in the supramolecular layer (Fig. 4a). The twodimensional layer then stacks into the 3D network in 2 (Fig. 4). The resulting voids of the 3D network are filled with lattice water molecules, in accordance with the TG analysis (Fig S4, left). Among the reported few Co-based PONb hybrids in hetero-PONb chemistry,²⁴ 2 present another new organicinorganic hybrid based on hetero-PONb and cobalt complexes, illustrating the generality of cobalt complexes to access to a diverse set of new structures based on PONbs.

There are several capped PONb-based organic-inorganic hybrids where the polyanion usually integrates with TM complexes via covalent bonds or weak interactions, and the introduced TM ions are copper,^{12,25} zinc,²² nickel,²³ and very recently cobalt.²³ It's worth nothing that all these transition-metal ions share oxidation state of +2. In **2**, the complexation of a PONb polyanion with trivalent cobalt complexes is realized, which shall make a difference in the three-dimensional arrangement. Using SQUEEZE treatment and with PLATON calculations, the space volume of **2** is determined to be 34.9% of the crystal lattice, larger than that (17.0%) of **1**. This is expected in that cation-anion interaction decreases with an increase in the charges of the cationic counterpart, leading to the looser packing of the ions in **2**.²⁶



Fig. 4 Stacking view of $PNb_{12}O_{40}(VO)_2$ and cobalt complexes in **2**: (a) supramolecular layer along the c axis and (b) supramolecular arrangement in the three-dimensional lattices . Color codes: Nb (cyan) V (pink), Co (olive green), O (red), C (gray), N (blue).

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Given the fact that vanadium-containing compounds have the potential to catalytically oxidize C–H bonds,²⁷ we anticipated that **1–2** could show catalytic activity in the oxidative transformation of benzyl-alkanes. The oxidation of diphenylmethane to benzophenone was selected as a model reaction. In a typical reaction process, **1/2** with 0.03 mol % catalyst loading was dispersed in benzonitrile (0.5 mL), followed by addition of *tert*-butyl hydroperoxide (TBHP) as an oxidant. The reaction was conducted under stirring at 60 °C for 24 hours, and was quantitatively analyzed by GC. As shown in Table 1, the conversions of diphenylmethane are 95.8% and 93.4% after 24h in the presence of **1** and **2**, respectively. The corresponding selectivity for benzophenone is 92.7% (for **1**), and 91.3% (for **2**). Blank test without catalyst give a poor conversion of 37.2%.

To gain insight into the heterogeneity of the oxidative system, a hot leaching test was carried out with 1 as the catalyst. After the reaction has performed for 6 hours, 1 was filtrated off and the filtrate was subsequently stirred at 60 $^\circ$ C for another 18 hours. Result shows that the conversion of diphenylmethanewas slightly increased by 6.1% (Fig. S12). No V/Cu ions were detected in the filtrate solution as confirmed by atomic absorption analysis. These results collectively confirm that the catalytic system is heterogeneous in nature. The catalyst can be easily separated by centrifugation or filtration after the reaction, and subsequently used in the successive runs for at least 3 times without obvious loss in catalytic activity. The PXRD patterns and IR spectrum before and after the catalysis process demonstrated that 1 maintained its structural integrity during the reaction process (Fig. S13 and S14).

When $TMA_9[PNb_{12}O_{40}(VO)_2]^{13b}$ is utilized under otherwise

Table 1 Conversion and selectivity of diphenylmethane to benzophenone with catalysts.^a

	\bigcirc	$\bigcup \frac{1}{\text{TBHP 60°C}} \bigcup \bigcup \bigcup \bigcup$			
	Catalyst	Conv. (%)	Sele. (%) ^b	Reaction system	
_	1	95.8	93.7	Heterogeneous	
	2	93.4	91.3	Heterogeneous	
	$TMA_9PNb_{12}V_2$	87.7	93.7	Homogeneous	
	$Na_{16}SiNb_{12}O_{40}$	39.7	68.3	Homogeneous	
	$Cu(en)_2SO_4$	68.3	92.6	Heterogeneous	
	No catalyst	37.2	67.6	-	
	1	93.52	95.74	2 nd run	
	1	92.71	93.28	3 rd run	

^aReaction conditions: diphenylmethane (0.125 mmol, 1 equiv), catalyst (0.004 mmol, 0.03 mol %), solvent benzonitrile (0.5mL), TBHP (70% in water, 2.5equiv), 60°C, 24 h. ^bSelectivity to ketones.

identical conditions, a moderate conversion of 87.7% is achieved. In this case, however, the reaction proceeds in a homogenous manner, being largely restricted in industrial _ application where recovery and separation is a prerequisite. In contrast, when the catalytically active species $PNb_{12}O_{40}(VO)_2$ is "immobilized" as insoluble solids, 1 or 2 works in a heterogeneous way, and can be separated from the reaction mixture by simply filtration or centrifugation. Hence, the heterogenization of catalytically active $PNb_{12}O_{40}(VO)_2$ is realized. We believe the counter-ions of organometallic cations, where transition metal ions hold either unsaturated coordinated sites (in 1) or the removable agua ligands (in 1/2), can also contribute to the reaction to some extent, given the certain conversion by copper complexes Cu(en)₂SO₄. The PONb component shall make no contributions to the reaction, as indicated by the poor conversion as to that of blank test in the control experiment using Na₁₆SiNb₁₂ as a catalyst. Hence, a synergetic effect between the two components, the vanadyl groups in $PNb_{12}O_{40}(VO)_2$ and $[Cu(en)_2]^{2+}/[Co(en)_2(H_2O)_2]^{3+}$ in 1/2 should be better illustrated for the enhanced activity.

To study the general applicability of 1, a wide range of benzyl-alkanes were subjected to this catalytic oxidation reaction under the same conditions. Table 2 summarizes the results of the oxidative transformation. Compound 1 catalyzed transformation of diphenylmethane, 9H-xanthenes, fluorene, 2-bromofluorene, 2,7-dibromofluorene and 2,7-di-tertbutylfluorene to the corresponding ketones with excellent conversions (95.8-99%) and selectivity (93.7-99%) (Table 2, entries 1-6). That is, comparable performance is observed towards substrates with different molecule sizes. Hence 1 was not substrate size-selective, and might promote the oxidation of benzyl-alkanes on its exterior surface. The alkyl-substituted benzylichydrocarbons (ethylbenzene, 4-ethylnitrobenzene and 4-ethylanisole) were oxidized to the corresponding carbonyl compounds in a more moderate conversion (63.3-78.3%) (Table 2, entries 7-9). The different conversions for these substrates are most likely due to the activation energy of the phenyl groups.

A radical process might be involved in the catalytic reaction, as 1 can also smoothly promote the oxidative transformation of 2,7-di-tert-butyl-9H-fulorene (Table 2, entry 6) bearing methane group with high steric hindrance and hence should be not accessible to the surface of catalyst.²⁸ A radical probe reaction was thus designed and carried out to understand the catalytic mechanism of the oxidation reaction. Diphenylamine was used as an oxygen-radical scavenger.^{28b} The catalytic oxidation of diphenylmethane was totally inhibited when diphenylamine was added in the reaction system at 60 $^{\circ}$ C for 24 h in the presence of 1. Using 5,5dimethyl-1-pyrroline-N-oxide (DMPO) as spin trap, the generated DMPO/·OOBu-t spin adduct were well detectable by EPR spectra as indicated by g value of 2.0017 (Fig. 5), 29 suggesting the formation of ·OOBu-t during the reaction. Thus we propose that 1 promoted the oxidation reaction by decomposing the oxidant into OOBu-t radical, which then oxidized the benzylic substrates. As a result, the synergistic effect between the cation and vanadyl groups in the polyanion

View Article Online Table 2 Results of Selective Oxidation of Benylic Compounds Catalyzed by 1.

_			Conv.	Sele.				
Entry	Substrates	Products	(%)	(%) ^b				
1		0°0	95.8	93.7				
2			>99	>99				
3			>99	>99				
4	Br	Br	>99	>99				
5	Br. Br	Br Br	>99	>99				
6	(H ₃ C) ₃ C	(H ₃ C) ₃ C	>99	>99				
7	\bigcirc		78.3	98.5				
8	0 ₂ N	O ₂ N	63.3	95.1				
9	H ₃ CO	H ₃ CO	92.1	90.3				
^a Reaction conditions: substrates (0.125 mmol, 1 equiv), catalyst (0.004 mmol, 0.03 mol %), solvent benzonitrile (0.5mL), TBHP (70% in water, 2.5equiv), 60°C, 24 h. ^b Selectivity to ketones.								
_		A		alton T				



Fig. 5 EPR spectra with (line in blue) and without (line in black) 1, using DMPO as spin trap. Reaction conditions: diphenylmethane (0.125 mmol), solvent benzonitrile (0.5mL). TBHP (70% in water. 2.5equiv). 60 °C. 10min.

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components in **1** shall be responsible for the radical formation. The insight into the role of cationic and anionic parts in the oxidative transformation of benzyl-alkanes

corresponding ketone products is under study.

Conclusions

In summary, using organometallic cations with different charge, two polyoxoniobate-based ionic organic-inorganic compounds with diverse three-dimensional arrangements were assembled, and assessed as efficient heterogeneous catalysts towards the selective oxidation of benzyl-alkanes. A heterogeneous system based on PONbs was established for the first time. This work takes a step toward polyoxoniobatebased materials for catalytic applications.

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Notes and references

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Immobilization of Keggin Polyoxovanadoniobate in Crystalline Solids as Effective Heterogeneous Catalysts towards Selective Oxidation of Benzyl-Alkanes

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The catalytically active $PNb_{12}O_{40}(VO)_2$ was immobilized in crystalline solids and worked as effective robust catalysts towards selective oxidation of benzyl-alkanes.