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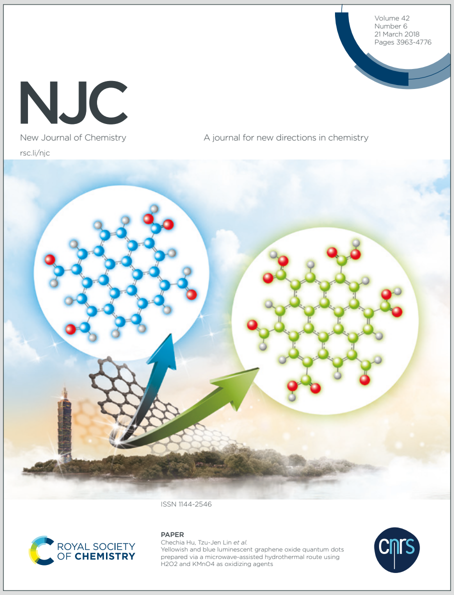

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ARTICLE

The ruthenium(II)-supported phosphovanadomolybdates $[Ru(dmso)_3PMo_6V_3O_{32}]^{6-}$ and $[Ru(PMo_6V_3O_{32})_2]^{14-}$, and their use as heterogeneous catalysts for oxidation of alcohols

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Self-assembly of *cis*-$[RuCl_2(dmso)_4]$, $NaVO_3$, Na_2MoO_4 and NaH_2PO_4 in a molar ratio of 1:3:6:1 in HOAc-NaOAc buffer (pH = 4~5) in the presence of CsCl gave a ruthenium(II)-supported phosphovanadomolybdate $[Ru^{II}(dmso)_3PMo^{VI}_6V^{V}_3O_{32}]^{6-}$ (**1**). While the similar reaction with the reactants in a molar ratio of 1:6:12:2 afforded a ruthenium substituted "sandwich" type polyoxometalate $[Ru^{II}(PMo^{VI}_6V^{V}_3O_{32})_2]^{14-}$ (**2**). Clusters **1** and **2** were well characterized by single-crystal X-ray diffraction. Their use as heterogeneous catalysts for oxidation of alcohols in the presence of molecular oxygen was also investigated.

Introduction

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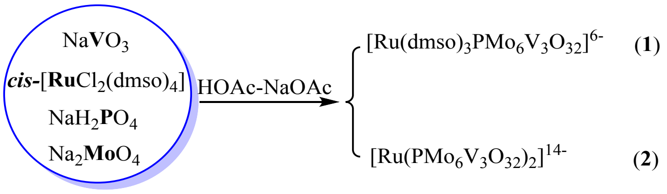
In the past two decades, polyoxometalate cluster compounds have attracted great attention due to their intriguing structures and potential applications in catalysis, gas storage, selective adsorption, magnetism, and medicine.[1-4] The research of polyoxometalate chemistry mainly focuses on the coordination of polyoxometalate with organometallic fragment or organic ligand to prepare a catalyst with high selectivity and catalytic activity.[5,6] Up to date, many polyoxometalates supported by various transition metals have been reported, such as gold,[7,8] palladium,[9-16] platinum,[17,18] osmium, [19-21] copper,[22] zinc,[23] and cobalt.[24,25] Since 1995, Neumann and coworkers have reported that the ruthenium-substituted polyoxometalate $\{[WZnRu_2(OH)(H_2O)](ZnW_9O_{34})_2\}^{11-}$ could activate molecular oxygen and thus catalyzed the selective hydroxylation of adamantine at the tertiary carbon position and catalyzed epoxidation of alkenes.[26-28] Afterwards, much effort has been devoted to the design and synthesis of new ruthenium-supported polyoxometalates in order to improve their catalytic activity and catalytic selectivity. [29-35] For examples, Nomiya and coworkers reported two water-soluble organometallic ruthenium(II) species, $[\{(benzene)Ru^{II}(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})]^{8-}$ and $[\{(p\text{-}cymene)Ru^{II}(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})]$, which showed effective catalytic activities during the oxidation of a wide range of alcohols with 1 atm molecular oxygen in water.[36] Mizuno and Yamaguchi stated that the Ru^{3+}-substituted silicotungstate $[n\text{-}C_4H_9)_4N]H[SiW_{11}Ru(H_2O)O_{39}]$ could act as a heterogeneous catalyst for the oxidation of alkanes and alcohols using 1 atm of molecular oxygen.[37] Moreover, a series of ruthenium substituted polyoxotungstates were used to catalyze the cleavage oxidation of styrene to produce benzaldehyde with quantitative conversion and high selectivity (83%~96%).[38]

In 2003, Neumann reported the synthesis of a ruthenium(II)-supported polyoxometalate $[Ru(dmso)_3Mo_7O_{24}]^{4-}$, and its good catalytic oxidation performance on the aerobic oxidation of alcohols to ketones/aldehydes.[29] Afterwards, several $Ru(dmso)_3$ group supported heteropolytungstates, such as $[HW_9O_{33}Ru^{II}_2(dmso)_6]^{7-}$,[39] $[HVW_7O_{28}Ru(dmso)_3]^{6-}$,[40] $[Ru(dmso)_3(H_2O)XW_{11}O_{39}]^{6-}$ (X = Ge, Si),[41] and $[\alpha\text{-}PW_{11}O_{39}\{Ru(dmso)_3(H_2O)\}]^{5-}$,[42] were synthesized by employment of the ruthenium(II) precursor *cis*-$[RuCl_2(dmso)_4]$. These studies suggested that the $Ru(dmso)_3$ group could stabilize polyoxometalates. On the other hand, the phosphovanadomolybdates could link with both transition metal fragments (copper, cobalt)[24,25] and lanthanide–organic framework, the latter could catalyze alkene epoxidation with H_2O_2.[43] Guided by these results, we tried the self-assembly of *cis*-$[RuCl_2(dmso)_4]$, $NaVO_3$, Na_2MoO_4 and NaH_2PO_4 under controlled conditions and obtained two new ruthenium(II)-supported phosphovanadomolybdates $[Ru^{II}(dmso)_3PMo^{VI}_6V^{V}_3O_{32}]^{6-}$ (**1**) and $[Ru^{II}(PMo^{VI}_6V^{V}_3O_{32})_2]^{14-}$ (**2**) (Scheme 1). The two heterometallic clusters were characterized by X-Ray crystallography and the catalytic oxidation behaviors of the two clusters on several alcohols were investigated.



Scheme 1 Synthesis of ruthenium-supported heterometallic polyoxometalates **1** and **2**.

Experimental

General considerations

All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were purified, distilled and degassed prior to use. *Cis*-$[RuCl_2(dmso)_4]$,[44] sodium dihydrogen phosphate, sodium vanadate, sodium molybdate, and cesium chloride were purchased from Alfa Aesar Ltd. and used as received. Infrared spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrophotometer. Elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer. Gas chromatography analyses were performed with an FID detector on a Shimadzu GC-2010 Plus spectrometer using the RTX-5 column.

Synthesis of $Cs_3Na_3[Ru(dmso)_3PMo_6V_3O_{32}]\cdot 8H_2O$ (1)

A solution of *cis*-$[RuCl_2(dmso)_4]$ (0.10 g, 0.21 mmol), $NaVO_3$ (0.12 g, 0.63 mmol), Na_2MoO_4 (0.31 g, 1.3 mmol) and NaH_2PO_4 (0.025 g, 0.21 mmol) in 0.5 M HOAc-NaOAc (20 mL) buffer was stirred at 80 ºC for 1 h, during which the color of solution changed from light yellow to brown-black. After cooling, 1 M CsCl aqueous solution (2 mL) was added and the mixture was filtered. The filtrate was allowed to stand at room temperature, giving 0.23 g (51% yield) red-brown crystals of $Cs_3Na_3[Ru(dmso)_3PMo_6V_3O_{32}]\cdot 8H_2O$ (**1**) in two weeks. IR (KBr): ν = 3418 (br), 2926 (m), 1630 (s), 1411 (m), 1108 (s), 1069 (m), 1018 (m), 916 (s), 865 (s), 827 (s), 643 (s) cm^{-1}. Anal. calcd for $Cs_3Na_3[Ru(dmso)_3PMo_6V_3O_{32}]\cdot 8H_2O$: C, 3.32; H, 1.58; Found: C, 3.16; H, 1.51%.

Synthesis of the $Cs_8Na_6[Ru(PMo_6V_3O_{32})_2]\cdot 3H_2O$ (2)

A solution of *cis*-$[RuCl_2(dmso)_4]$ (0.10 g, 0.21 mmol), $NaVO_3$ (0.24 g, 1.3 mmol), Na_2MoO_4 (0.62 g, 2.5 mmol) and NaH_2PO_4 (0.051 g, 0.42 mmol) in 0.5 M HOAc-NaOAc (20 mL) buffer was stirred at 80 ºC for 4 h, during which the color of solution changed from light yellow to brown-black. After cooling, 1 M CsCl aqueous solution (2 mL) was added and the mixture was filtered. The filtrate was allowed to stand at room temperature, affording 0.38 g (46% yield) black crystals of $Cs_8Na_6[Ru(PMo_6V_3O_{32})_2]\cdot 3H_2O$ (**2**) in ten days. IR (KBr): ν = 3447 (br), 1614 (s), 1414 (m), 1122 (s), 1076 (m), 961 (s), 911 (s), 872 (s), 827 (s), 630 (s) cm^{-1}. Anal. calcd for $Cs_3Na_3[Ru(dmso)_3PMo_6V_3O_{32}]\cdot 8H_2O$: H, 0.15; Found: H, 0.18%.

X-Ray crystallography

A summary of crystallographic data and experimental details for clusters **1** and **2** are summarized in Table S1 (CCDC 2041200/2041201). Selected bond lengths and angles for clusters **1** and **2** are listed in Tables S2 and S3, respectively. Intensity data were collected on a Bruker SMART APEX 2000

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CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 296(2) K. The collected frames were processed with the software SAINT.[45] The data was corrected for absorption using the program SADABS.[46] Structures were solved by the direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package.[47,48] All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms of dmso ligands were generated geometrically (C_{sp3}–H = 0.96 Å) and included in the structure factor calculations with assigned isotropic thermal parameters but were not refined. The hydrogens of surrounding hydrate molecules were not added due to disorder. The large residual peak in cluster **2** may be due to the effect of heavy cesium atom.

General procedure for oxidation of alcohols.

The reaction was carried out in a glass vial containing a magnetic stir bar. A typical procedure was as follows. Into a glass vial were successively added **1** or **2** (5 μmol), and alcohol substrate (2 mmol). The reaction mixture was stirred at 120 °C under 1 atm of molecular oxygen. After the reaction was completed, the precatalyst **1** or **2** was separated by filtration and the conversion and product selectivity were determined by GC analysis.

Results and discussion

Reactions of *cis*-[$RuCl_2(dmso)_4$], $NaVO_3$, NaH_2PO_4 and Na_2MoO_4 in HOAc-NaOAc buffer at 80 °C afforded two stable ruthenium-supported heteropolyoxometalates $[Ru^{II}(dmso)_3PMo^{VI}_6V^{V}_3O_{32}]^{6-}$ (**1**) and $[Ru^{II}(PMo^{VI}_6V^{V}_3O_{32})_2]^{14-}$ (**2**). When the molar ratio of the reactants was 1:3:1:6 (*cis*-[$RuCl_2(dmso)_4$]:$NaVO_3$:NaH_2PO_4:Na_2MoO_4) and the reaction time was 1 h, cluster **1** was isolated. However, when the molar ratio was changed to be 1:6:2:12 (*cis*-[$RuCl_2(dmso)_4$]:$NaVO_3$:NaH_2PO_4:Na_2MoO_4) and the reaction time was extended to be 4 h, cluster **2** was obtained. The formation of **2** may possibly be due to the leave of three weakly coordinated dmso ligands on the ruthenium atom in cluster **1** under controlled conditions, forming a ruthenium substituted "sandwich" type polyoxometalate $[Ru^{II}(PMo^{VI}_6V^{V}_3O_{32})_2]^{14-}$ (**2**).

As shown in Figures 1 and 2, the infrared spectra of clusters **1** and **2** showed the typical band around 737 cm^{-1} attributed to *v*(Mo–O, V–O), band at 2926 cm^{-1} for cluster **1** was assigned to characteristic of methyl groups and bands at 1108 and 1069 cm^{-1} for cluster **1** and 1122 and 1076 cm^{-1} for cluster **2** attributed to v(P–O) of PO_4^{3-} group.[49] The S-O stretching vibrations of the coordinated dmso ligands in cluster **1** may overlap with the P–O vibrations at ~1108 cm^{-1}. The stretching vibrations of the Mo=O bonds were observed at 997, 947, 916, and 865 cm^{-1} for cluster **1**, and 999, 961, 911, and 872 cm^{-1} for cluster **2**, similar to those for analogous polyoxomolybdate clusters.[29]

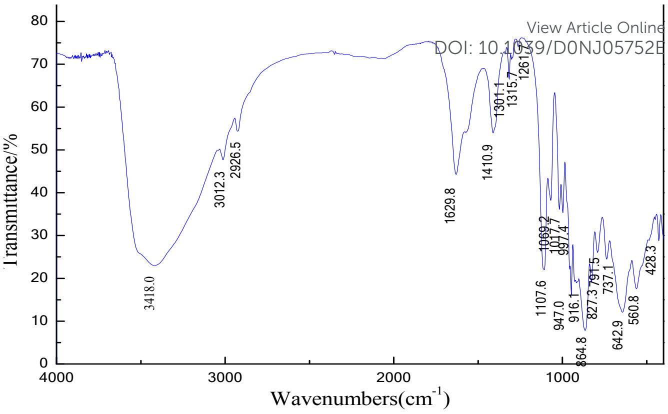

Fig. 1 IR spectrum of cluster **1**.

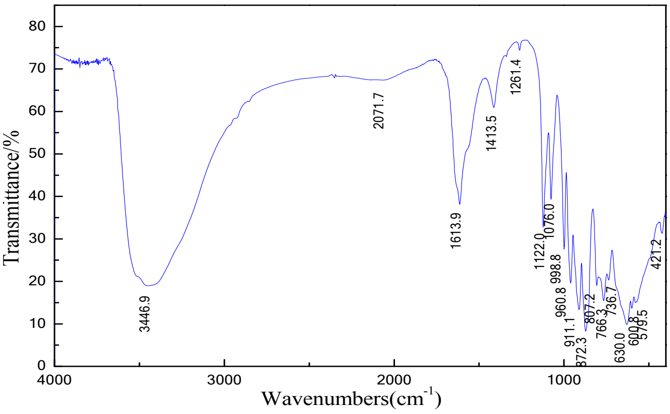

Fig. 2 IR spectrum of cluster **2**

Molecular structures of clusters **1** and **2** are shown in Figures 3 and 4. For cluster **1**, the ruthenium center is six-coordinated to three sulfur atoms from three dmso ligands and three oxygen atoms from the phosphovanadomolybdate $[PMo_6V_3O_{32}]^{8-}$. For sandwich-type cluster **2**, the ruthenium center is coordinated to six oxygen atoms from two phosphovanadomolybdates of $[PMo_6V_3O_{32}]^{8-}$. The polyanion $[PMo_6V_3O_{32}]^{8-}$ contains six MoO_6 octahedrons linked by the tetrahedral PO_4 unit, two VO_5 square pyramids sharing square edges with the MoO_6 octahedrons, and one VO_4 tetrahedron sharing corners of two MoO_6 octahedrons, as exhibited in Figures 3b and 4b. According to the bond valence sum calculations (Tables S4 and S5),[50,51] the oxidation states of ruthenium(II), vanadium(V) and molybdenum(VI) in clusters **1** and **2** are not changed compared to the corresponding starting materials of *cis*-[$RuCl_2(dmso)_4$], $NaVO_3$ and Na_2MoO_4. The Ru–S and Ru–O bond distances in cluster **1** are 2.24–2.26 and 2.04–2.08 Å, respectively, similar to those in the related complex $[Ru(DMSO)_3Mo_7O_{24}]^{4-}$ (Ru–S~2.25, Ru–O 2.06–2.08 Å).[29] While in cluster **2**, the Ru–O bond distances range from 1.96–2.04 Å, slightly shorter than those in cluster **1**. The Mo–O and V–O bond lengths in clusters **1** and **2** [Mo–O_t 1.69–1.74 Å, Mo–O_b 1.88–2.41 Å, V–O_t 1.60–1.64 Å and V–O_b 1.68–2.02 Å] are a little different from those in $[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]^{6-}$ (Mo–O_b 1.85–1.98 Å, 1.92–1.99 Å),[24]

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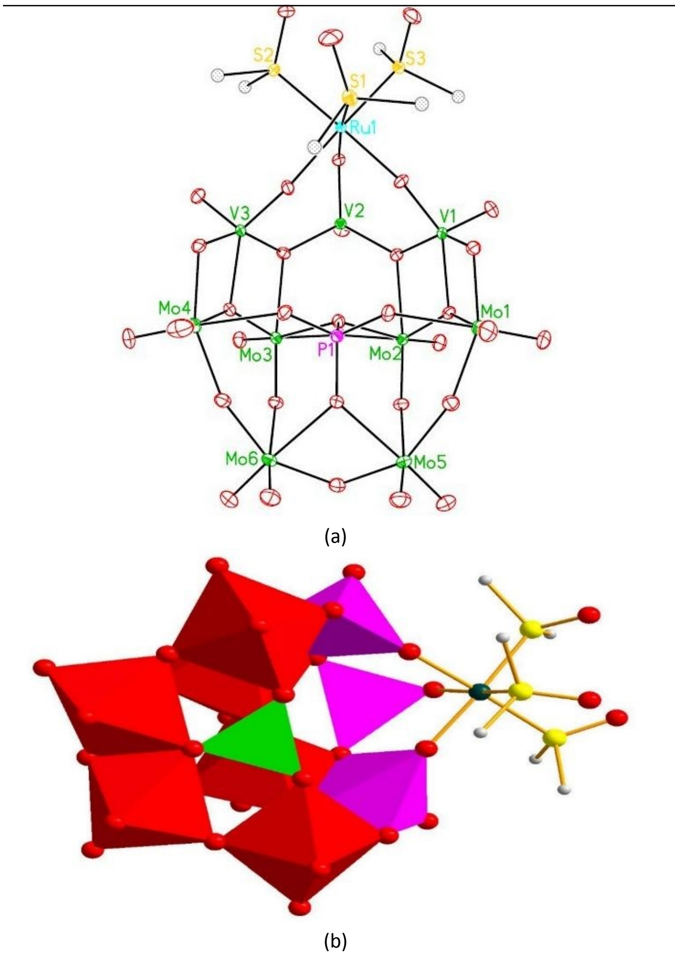
possibly due to the different oxidation states of molybdenum and vanadium metal centers. The Ru–O–V bond angles in cluster **1** are in the range of 122°~160°, compared to those in the symmetrical cluster **2** (121°~152°).

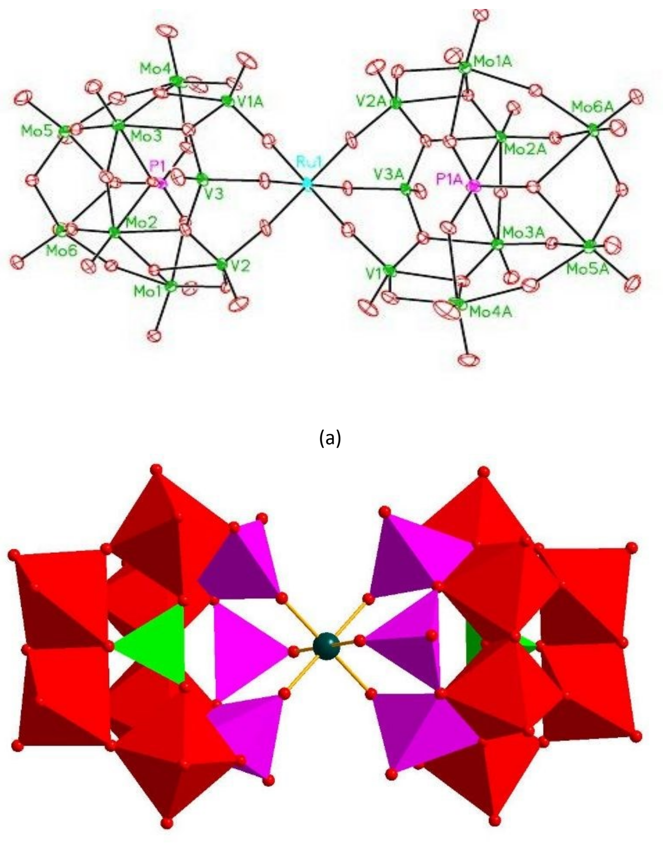
Entry	Alcohol	Catalyst	TON[b]	Product (selectivity (%))	Conversion (%)
1	$C_6H_5CH_2OH$	**1**	320	C_6H_5CHO (92) C_6H_5COOH (8)	80
2	$C_6H_5CH_2OH$	**2**	336	C_6H_5CHO (94) C_6H_5COOH (6)	84
3	*p*-$CH_3C_6H_4CH_2OH$	**1**	312	*p*-$CH_3C_6H_4CHO$ (89) *p*-$CH_3C_6H_4COOH$ (11)	78
4	*p*-$CH_3C_6H_4CH_2OH$	**2**	320	*p*-$CH_3C_6H_4CHO$ (92) *p*-$CH_3C_6H_4COOH$ (8)	80
5	$C_6H_{11}OH$	**1**	140	$C_6H_{10}O$ (81)	80
6	$C_6H_{11}OH$	**2**	176	$C_6H_{10}O$ (84)	78
7	*n*-$C_8H_{17}OH$	**1**	32[c]	*n*-$C_7H_{15}CHO$ (73) *n*-$C_7H_{15}COOH$ (27)	8
8	*n*-$C_8H_{17}OH$	**2**	28[d]	*n*-$C_7H_{15}CHO$ (78) *n*-$C_7H_{15}COOH$ (22)	7



(a)

(b)

Fig. 3 (a) Molecular structure of cluster **1**, counter cations and hydrate solvent molecules are omitted for clarity. (b) Stick/polyhedral representation of $[Ru(dmso)_3PV_3Mo_6O_{32}]^{6-}$ in cluster **1**. The red octahedra represent MoO_6 and the green tetrahedron represents PO_4. Two VO_5 square pyramids and one VO_4 tetrahedron are purple.



(a)

(b)

Fig. 4 (a) Molecular structure of cluster **2**, counter cations and hydrate solvent molecules are omitted for clarity. (b) Stick/polyhedral representation of $[Ru^{II}(PMo^{VI}_6V^{V}_3O_{32})_2]^{14-}$ in cluster **2**. The red octahedra represent MoO_6 and the green tetrahedron represents PO_4. Two VO_5 square pyramids and one VO_4 tetrahedron are purple.

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9	n-$C_6H_{13}CH(OH)CH_3$	**1**	100	n-$C_6H_{13}COCH_3$ (80)	25
10	n-$C_6H_{13}CH(OH)CH_3$	**2**	84	n-$C_6H_{13}COCH_3$ (78)	21

[a]Reaction conditions: cluster **1** or **2** (5 μmol), benzyl alcohol, *p*-methylbenzyl alchol, cyclohexanol, 1-octanol, and 2-octanol (2 mmol), reaction temperature 120 °C. [b]Turnover number (TON) after 72 h. [c]Determined by GC using naphthalene as an internal standard. Yield = sum of oxidation products (mol)/initial substrate (mol)×100. [d]After 96 h.

Table 1 Catalytic activities for oxidation of alcohols with 1 atm molecular oxygen catalyzed by Ru-containing phosphovanadomolybdates **1** and **2**[a].

Catalytic activities of clusters **1** and **2** were examined for the oxidation of several alcohols, including benzyl alcohol, *p*-methylbenzyl alcohol, cyclohexanol, 1-octanol and 2-octanol, with 1 atm oxygen molecule at 120 °C, as summarized in Table 1. The oxidation of benzyl alcohol gave benzaldehyde as the main product (selectivity: 92% catalyzed by cluster **1**, 94% catalyzed by cluster **2**), and a little benzoic acid was also detected (selectivity: 8% for **1**, 6% for **2**) (Entries 1, 2). The conversion of benzyl alcohol using cluster **1** is 80% (TON = 320), a little lower than that of 84% by employment of cluster **2** (TON = 336). Similar results were observed for oxidation of *p*-methylbenzyl alcohol (Entries 3, 4). The conversion and selectivity of oxidation of benzyl alcocol/*p*-methylbenzyl alcohol catalyzed by heteropolyoxometalates **1** and **2** could not reach the catalytic behavior of the ruthenium-supported homopolyoxometalate $[Ru(dmso)_3Mo_7O_{24}]^{4-}$ (> 99% conversion and > 99% selectivity).[29] The catalytic behavior of clusters **1** and **2** towards oxidation of 1-octanol and 2-octanol was poor compared to the relatively good catalytic result of cyclohexanol. However, the selectivity for the conversion of 2-octanol to 2-octanone catalyzed by heteropolyoxometalates **1** (80%) and **2** (78%) was much higher than that of homopolyoxometalate $[Ru(dmso)_3Mo_7O_{24}]^{4-}$ (32% selectivity).[29] Control reactions with *cis*-$[RuCl_2(dmso)_4]$ as catalyst showed no oxidation for benzyl alcohol.[29] Additionally, $[PMo_{12}O_{40}]^{3-}$, $[Mo_6O_{19}]^{2-}$, $[MoO_4]^{2-}$, and $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ species could not catalyze aerobic oxidation of benzyl alcohol either.[29,36] Combination of the ruthenium fragment and polyoxometalte unit in clusters **1** and **2** may lead to the formation of the key metal-alcoholate intermediate easily in the catalytic aerobic oxidation system.[29,36]

Conclusions

Two stable ruthenium(II)-substituted phosphovanadomolybdates $[Ru^{II}(dmso)_3PMo^{VI}_6V^{V}_3O_{32}]^{6-}$ (**1**) and $[Ru^{II}(PMo^{VI}_6V^{V}_3O_{32})_2]^{14-}$ (**2**) are synthesized by self-assembly of *cis*-$[RuCl_2(dmso)_4]$, $NaVO_3$, Na_2MoO_4 and NaH_2PO_4 in HOAc-NaOAc solution. The oxidation states of ruthenium(II), vanadium(V) and molybdenum(VI) in clusters **1** and **2** are not changed compared to the corresponding reactants, which are confirmed by bond valence sum calculations.[50,51] While in other hydrothermally synthesized phosphovanadomolybdates, mixed valences of molybdenum(VI/V) and vanadium(IV) were usually observed, such as $[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]^{6-}$ [24] and $[PMo^{VI}_8Mo^{V}_2V^{IV}_4O_{32}]^{5-}$.[25] The new ruthenium-supported polyoxometalates are found to be effective heterogeneous catalysts for the oxidation of alcohols using 1 atm of molecular oxygen. The selectivity for oxidation of 2-octanol to 2-octanone improved from 32% to 80%.[29] Design and synthesis of other ruthenium-supported polyoxometaltes as effective catalysts for oxidation of organic substrate are undergoing in our laboratory.

Acknowledgements

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The ruthenium(II)-supported phosphovanadomolybdates $[Ru(dmso)_3PMo_6V_3O_{32}]^{6-}$ and $[Ru(PMo_6V_3O_{32})_2]^{14-}$, and their use as heterogeneous catalysts for oxidation of alcohols

Hao-Yu Shi, Wen-Yan Zhou, Xiao-Ming Song, Ai-Quan Jia,* Hua-Tian Shi, and Qian-Feng Zhang*

Two stable ruthenium(II)-substituted phosphovanadomolybdates $[Ru^{II}(dmso)_3PMo^{VI}_6V^V_3O_{32}]^{6–}$ and $[Ru^{II}(PMo^{VI}_6V^V_3O_{32})_2]^{14–}$ are synthesized by self-assembly of *cis*-$[RuCl_2(dmso)_4]$, $NaVO_3$, Na_2MoO_4 and NaH_2PO_4. They could catalyze oxidation of alcohols with good conversion and selectivity.