Letter

Heterogeneously catalyzed liquid-phase oxidation of alkanes and alcohols with molecular oxygen

Kazuya Yamaguchi and Noritaka Mizuno*

Department of Applied Chemistry, School of Engineering, The University of Tokyo
Bunkyo-ku, Tokyo 113-8656,, Japan. E-mail: tmizuno@mail.ecc.u-tokyo.ac.jp;
Fax: +81-3-5841-7220; Tel: +81-3-5841-7272

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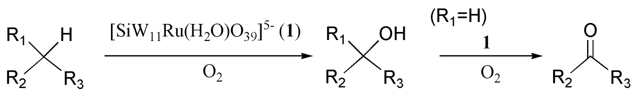
RuCl$_3$ successfully reacts with the lacunary silicotungustate in organic medium, giving a Ru^{3+}-substituted silicotungstate that can act as a heterogeneous catalyst for the oxidation of a wide range of alkanes and alcohols using 1 atm of molecular oxygen as the sole oxidant.

The development of catalytic oxidations of organic molecules with molecular oxygen or air alone is technologically and environmentally important and has attracted much attention.[1] There are only a few examples for these oxidations in the liquid phase because of catalyst deactivation, difficulty of C–H bond/O$_2$ activation, *etc.*,[2–4] while numerous catalytic systems using molecular oxygen in combination with additives such as reducing agents and radical initiators have been reported. For example, for the oxidation (tertiary C–H bond activation) of adamantane, whose derivatives have been used for pharmaceuticals and microelectronics, stoichiometric oxidation methods have been used. For alcohol oxidation, stoichiometric oxidants such as permanganate and dichromate are still being used. Thus, there are only a few examples reported for the reductant- and additive-free, O$_2$-based oxidation of alkanes[5,6] and alcohols[7–10] catalyzed by ruthenium. However, turnover numbers are less than 120 and 20 for the oxidation of alkanes and alcohols, respectively, and still low. Therefore, it is clearly desirable to carry out oxidation reactions with higher turnover numbers under environmentally friendly (green) conditions. Additionally, it is often more desirable to use solid catalysts because of their easy isolation from the products (by filtration) and recycling.[11]

Catalysis by polyoxometalates has attracted much attention because of their strong acidity and redox properties.[12] An additional attractive aspect of polyoxometalates in catalysis is their inherent stability toward oxygen doners.[12] We report here that a mono-ruthenium-substituted silicotungstate, [(n-C$_4$H$_9$)$_4$N]$_4$H[SiW$_{11}$Ru$^{\rm III}$(H$_2$O)O$_{39}$]·2H$_2$O (**1**), synthesized by the reaction of the lacunary polyoxometalate [SiW$_{11}$O$_{39}$]$^{8-}$ with Ru^{3+} in an *organic solvent*, is an efficient heterogeneous catalyst with high turnover numbers for the oxidation of various alkanes and alcohols using 1 atm molecular oxygen, eqn. (1):



(1)

Transition-metal-substituted polyoxometalates have usually been synthesized from a salt of the lacunary polyoxometalate and the corresponding transition metal ion in aqueous medium. In the case of Ru, the insertion reaction was unsuccessful when the reaction was carried out in aqueous solution, analogous to recent reports on other polyoxometalate complexes.[13] Therefore, we attempted to use an organic medium, acetone and acetonitrile, for the insertion reaction of Ru^{3+} into [(n-C$_4$H$_9$)$_4$N]$_4$H$_4$[SiW$_{11}$O$_{39}$]·2H$_2$O (**2**) to form **1** by modification of the procedure reported for the synthesis of [(n-C$_4$H$_9$)$_4$N]$_4$[PMo$_{11}$M(H$_2$O) O$_{39}$] (M = Ru or Sb).[14]

The yields of oxygenated products for the oxidation of adamantane at 356 K after 96 h were 42, 34, 29 and 28% in isobutyl acetate, *tert*-butyl acetate, trifluorotoluene and 1,2-dichloroethane, respectively, while the oxidation was much slower in acetonitrile and DMF. Among the solvents used, isobutyl acetate was the most effective for the oxygenation. The control experiment without adamantane showed that no oxidation of isobutyl acetate proceeded under the present conditions.

It is notable that **1** is insoluble in isobutyl acetate, *tert*-butyl acetate and trifluorotoluene and can be used as a heterogeneous catalyst. After the conversion of adamantane reached 12%, **1** was removed by filtration. No Ru and W ($<$24 ppb) were detected in the filtrate by ICP. No further oxidation proceeded with the filtrate. It was confirmed by IR and UV-vis spectroscopy that the structure of the spent **1** was retained. When the oxygenation of adamantane was repeated with the recovered **1** under the same conditions, the reaction proceeded at almost the same rate and selectivity as those for the first run. These results indicate that any Ru species that leached into the

Table 1 Oxidation of adamantane using various catalysts[a]

Entry	Catalyst	Yield[b] /%	Selectivity[b] /% 1-ol	2-ol	2-one	1,3-diol
1	**1**	42	65	2	12	21
2	RuCl$_3$	$<$1	n.d.	n.d.	n.d.	n.d.
3	**2**	$<$1	n.d.	n.d.	n.d.	n.d.
4[c]	RuCl$_3$ + **2**	4	75	10	5	n.d.
5[d]	Na$_2$WO$_4$	$<$1	n.d.	n.d.	n.d.	n.d.
6[e]	RuCl$_3$ + Na$_2$WO$_4$	$<$1	n.d.	n.d.	n.d.	n.d.
7[f]	[(n-C$_4$H$_9$)$_4$N]Cl	$<$1	n.d.	n.d.	n.d.	n.d.
8[g]	NaCl	$<$1	n.d.	n.d.	n.d.	n.d.
9	None	$<$1	n.d.	n.d.	n.d.	n.d.

[a] Reaction conditions: substrate (1 mmol), **1** (1.4 μmol), isobutyl acetate (3 mL), 356 K, 96 h, O$_2$ atmosphere. [b] Determined by GC using naphthalene as an internal standard. Yield = sum of oxidation products (mol)/initial substrate (mol) × 100. [c] RuCl$_3$ (1.4 μmol) + **2** (1.4 μmol). [d] Na$_2$WO$_4$ (15.4 μmol). [e] RuCl$_3$ (1.4 μmol) + Na$_2$WO$_4$ (15.4 μmol). [f] [(n-C$_4$H$_9$)$_4$N]Cl (5.6 μmol). [g] NaCl (30.8 μmol).

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Table 2 Oxidation of alkanes and alcohols with molecular oxygen catalyzed by Ru-substituted silicotungstate **1**[a]

Entry	Substrate	Time/h	Yield[b]/%	TON[c]	Products	Selectivity[b]/%
1[d]	Adamantane	72	64	1282	1-Adamantanol	59
					2-Adamantanol	2
					2-Adamantanone	14
					1,3-Adamantanediol	25
2[d e]	Cyclohexane	48	3	1110	Cyclohexanol	33
					Cyclohexanone	67
3	Cyclooctane	96	12	242	Cyclooctanol	13
					Cyclooctanone	87
4	*n*-Octane	96	3	64	Octanols[f]	14
					Octanones[g]	86
5	Ethylbenzene	96	11	222	1-Phenylethanol	22
					Acetophenone	78
6	Fluorene	96	10	198	9-Fluorenone	99
7	2-Octanol	120	90	1584	2-Octanone	88
8[d]	Cyclohexanol	48	67	1085	Cyclohexanone	81
9	Cyclooctanol	96	98	1900	Cyclooctanone	97
10[d]	2-Adamantanol	96	99	1960	2-Adamantanone	99
11	Benzhydrol	120	92	1821	Benzophenone	99
12	Benzyl alcohol	120	36	540	Benzaldehyde	65
					Benzoic acid	10
13	1-Octanol	48	14	207	*n*-Octanal	44
					n-Octanoic acid	30

[a] Reaction conditions: substrate (1 mmol), **1** (0.5 μmol), isobutyl acetate (3 mL), 383 K, O_2 atmosphere. [b] Determined by GC using naphthalene as an internal standard. Yield = sum of oxidation products (mol)/ initial substrate (mol) × 100. [c] TON = sum of oxidation products (mol)/**1** (mol). [d] 373 K. [e] Cyclohexane (18.5 mmol) was used. Prolonging the reaction time over 48 h results in decreasing selectivity to the desired products because of the successive oxidative cleavage of cyclohexanone to various C_5 or C_6 acids. [f] 2-ol:3-ol:4-ol = 42:33:25. [g] 2-one:3-one:4-one = 51:27:22.

reaction solution is not an active homogeneous catalyst and that the observed catalysis is truly heterogeneous.[15]

As shown in Table 1, the reaction did not proceed in the absence of $[(n\text{-}C_4H_9)_4N]_4H[SiW_{11}Ru^{III}(H_2O)\ O_{39}]\cdot 2H_2O$ or in the presence of $RuCl_3$ (soluble), the polyoxometalate precursor $[(n\text{-}C_4H_9)_4N]_4H_4[SiW_{11}O_{39}]\cdot 2H_2O$ (insoluble), or $[(n\text{-}C_4H_9)_4N]Cl$ (soluble). A mixture of the catalyst precursors, $[(n\text{-}C_4H_9)_4N]_4H_4[SiW_{11}O_{39}]\cdot 2H_2O$ and $RuCl_3$, gave a 4% yield for the oxidation of adamantane, that is, a much lower activity than that of **1**. These facts show that there is a synergistic effect between the $[SiW_{11}O_{39}]^{8-}$ polyoxometalate and the active Ru^{3+} center in **1**.

The present system could be applied to the oxidation of various kinds of alkanes. Representative results are summarized in Table 2. The oxidation of adamantane proceeded with high conversion. The oxidation of the tertiary C–H bonds to yield 1-adamantanol and 1,3-adamantanediol was much faster than that of secondary C–H bonds (entry 1). The oxidation of cyclohexane and cyclooctane with only secondary C–H bonds mainly yields the corresponding ketones (entries 2 and 3). *n*-Octane was also oxidized at the only secondary C–H bonds to afford mainly the corresponding ketones (entry 4). Primary C–H bonds could not be oxidized. Ethylbenzene and fluorene were oxidized at the benzylic C–H bonds to the corresponding ketones (entries 5 and 6). More significantly, the turnover numbers of **1**† were more than 10 times higher than those reported for the selective oxidation of alkanes with molecular oxygen alone catalyzed by the Ru compounds $\{[WZnRu^{III}_2(\text{-}OH)\ (H_2O)\ ](ZnW_9O_{34})_2\}^{11-}$ (turnover number = 120 for adamantane)[5] and Ru-hydrotalcite (10 for fluorene).[6] These facts show that the present system can oxidize tertiary, secondary and benzylic C–H bonds of alkanes and that the main products are ketones for secondary C–H bond oxidation.

By lowering the reaction temperature, 1-adamantanol and cyclohexanol were produced as the primary products in the oxygenation of adamantane and cyclohexane, respectively, and the successive oxidation of cyclohexanol to cyclohexanone was observed. In contrast, both cyclohexanol and cyclohexanone were the primary products for the auto-oxidation of cyclohexane catalyzed by cobalt.

The present catalytic system could efficiently oxidize various alcohols into the corresponding carbonyl compounds in high to quantitative yields. For the oxidation of 2-octanol, the corresponding ketone was produced in excellent yield (entry 7). Similarly, cyclic alcohols such as cyclohexanol, cyclooctanol and 2-adamantanol were selectively oxidized to the corresponding ketones without any formation of cleaved products (entries 8–10). The oxidation of primary alcohols, such as benzyl alcohol and 1-octanol, was slower and gave a mixture of the corresponding aldehydes and acids (entries 12 and 13). In the case of allylic alcohols such as cinnamyl alcohol, the oxidation hardly proceeded.

There are only a few reports on Ru-catalyzed alcohol oxidations using molecular oxygen or air alone. For example, $RuCl_2(PPh_3)_3$ (turnover number = 20 for geraniol),[7] RuO_2 (10 for cinnamyl alcohol),[8] and Ru-hydrotalcite (10 for benzyl alcohol)[6] have been shown to catalyze the aerobic alcohol oxidation, but even in these cases the scope was limited to activated alcohols such as benzylic and allylic ones. On the other hand, Ru-hydroxyapatite (TON = 6 for 2-octanol)[9] and tetrapropylammonium perruthenate (18 for cyclohexanol)[10] catalyze the oxidation of nonactivated alcohols in the presence of molecular oxygen alone. In comparison with these systems, the turnover numbers of **1** were at least a factor of 100 higher although the rates and turnover frequencies should be increased. Thus, it is clearly shown that the present system can oxidize not only alkanes but also alcohols with high turnover numbers. Further detailed mechanistic studies are in progress.

In conclusion, the Ru^{3+}-substituted silicotungstate **1** is found to be an effective heterogeneous catalyst for the oxidation of alkanes and alcohols using 1 atm of molecular oxygen.

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† The BET surface area of **1** is 2.5 $m^2\ g^{-1}$. It is noted that the turnover numbers increase by a factor of 54 when they are estimated with the calculated surface areas of the polyoxometalates (*ca.* 10 Å in diameter).

Experimental

Synthesis

The lacunary polyoxometalate **2** was synthesized according to ref. 15 and characterized by IR and UV-vis spectroscopy and elemental analysis.[16] Next, 0.5 mmol (1.8 g) of **2** was added to 20 mL of acetone to afford a white slurry, and then 10 mL of $RuCl_3$ (0.06 M in acetone) was slowly added. After stirring for 24 h under Ar at room temperature, unreacted **2** was filtered off. The solution was evaporated to dryness and a dark brown solid was obtained. The solid was dissolved in acetonitrile (25 mL) followed by addition of a small amount of water. Molecular oxygen was then passed through the solution for 2 h and the solvent was evaporated. The dark brown powder obtained was recrystallized from acetonitrile, giving 0.97 g (51% yield) of the purified compound **1**. The characterization results for ruthenium-substituted silicotungstate **1** are as follows. Anal. calcd for $\{[(n\text{-}C_4H_9)_4N]_4H[SiW_{11}Ru(H_2O)\,O_{39}]\cdot 2H_2O\}_n$: C, 20.23; H, 4.00; N, 1.47; O, 17.68; Ru, 2.66; Si, 0.74; W, 53.21%. Found: C, 20.24; H, 3.91; N, 1.55; Ru, 2.52; Si, 0.75; W, 53.7%. TG/DTA: weight loss between 300 and 473 K was 1.3% (1.4% calcd for $3H_2O$ in **1**). IR (400–4000 cm^{-1}: KBr disk; below 600 cm^{-1}: polyethylene disk): ν/cm^{-1} 1007 (w, W=O), 966 (s, Si–O), 913, 801 (s, W–O–W), 533 (m), 381 (m), 337 (w), 287 (w). The IR spectrum of **1** is apparently identical with those of other transition-metal-substituted silicotungstates.[13,17] UV-vis (CH_3CN): λ_{max}/nm (ε/$M^{-1}cm^{-1}$) 260 (40 900), 414 (1780), 511 (890). Both IR and UV-vis spectra are characteristic of an α-Keggin structure.[18] The ESR spectrum in CH_2ClCH_2Cl at 100 K shows a peak at $g = 2.10$, which is assigned to Ru^{3+} with a low-spin d^5 electron configuration.[19] ^{29}Si and ^{183}W NMR spectra were recorded after Ru^{3+} in **1** was reduced to Ru^{2+} with ascorbic acid. ^{29}Si NMR (53.5 MHz, CD_3CN, TMS): δ −79.9. ^{183}W NMR (11.2 MHz, CD_3CN, Na_2WO_4): δ −88.7, −92.4, −102.6, −114.2, −118.0, −154.8. The respective relative intensities were 2:2:2:2:2:1. These spectral data shows that **1** is a mono-substituted Keggin-type polyoxometalate.

Procedure for the oxidation reaction

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 placed **1** (5.6 mg, 1.4 μmol), adamantane (0.14 g, 1 mmol), and *tert*-butyl acetate (3 mL). The reaction mixture was stirred at 356 K under 1 atm of molecular oxygen. After the reaction was finished, **1** was separated by filtration and the conversion and product selectivity were determined by GC analysis.

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