Polyoxometalates

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Diamond-Shaped $[Ag_4]^{4+}$ Cluster Encapsulated by Silicotungstate Ligands: Synthesis and Catalysis of Hydrolytic Oxidation of Silanes**

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The design and synthesis of well-defined polynuclear metal or metal–oxygen clusters have attracted much attention in many fields of science such as catalysis, magnetism, electrochemistry, and photochemistry.[1] Generally, well-defined polynuclear clusters have been synthesized by using structure-directing agents such as oxygen- and/or nitrogen-donor organic ligands.[1] Polyoxometalates (POMs) are a large family of anionic metal–oxygen clusters consisting of the group V and VI metals in their highest oxidation states and are thermally and oxidatively stable in comparison with commonly utilized organic ligands.[2] In addition to high durability, their chemical properties, for example, redox potentials, (multi)electron-transfer properties, acidities, and solubilities, can be finely tuned by choice of constituent elements and countercations, and diverse structures can be synthesized.[2] These properties make POMs a class of potential materials for catalysis.[2] In particular, lacunary POMs are very attractive and can act as efficient homogeneous catalysts for H_2O_2-based oxidation.[3] Moreover, they can be regarded as "inorganic multidentate oxygen-donor ligands". Diverse lacunary POMs ranging from mono- to trilacunary have readily been synthesized. By employing these lacunary POMs as inorganic ligands (structural motifs), various kinds of metal–oxygen clusters (substituted into the lacunary pockets[4] or encapsulated by two or more lacunary POMs[5]) with unique structures and interesting catalytic properties have been designed.

Herein we focus on the development of efficient catalysts (or precatalysts) for hydrolytic oxidation of silanes. Selective oxidation of silanes to silanols is of paramount importance in organic synthesis in academia and chemical industry because of the versatile use of silanols as synthons for silicon-based functional (polymeric) materials and cross-coupling reactions.[6] In addition, hydrolytic oxidation using water and/or dioxygen theoretically produces only hydrogen or water as coproduct. To date, several efficient catalysts based on precious metals such as gold,[7] ruthenium,[8] rhenium,[9] platinum,[10] iridium,[11] and silver[12] have been reported for hydrolytic oxidation of silanes. In particular, we paid attention to catalysis by silver, because silver has a high potential to catalyze various functional-group transformations[12,13] and is cheaper and more abundant than other precious metals for hydrolytic oxidation of silanes.

Hydrolytic oxidation of dimethylphenylsilane (**1a**) to dimethylphenylsilanol (**2a**) was initially carried out with AgOAc under the conditions described in Table 1. In this case, formation of glossy precipitates (i.e., silver metal), was clearly observed just after addition of **1a** to the reaction solution containing AgOAc, and a low yield of **2a** resulted (Table 1, entry 1). Formation of silver metal could not be avoided in the presence of commonly utilized nitrogen-donor ligands such as pyridine and 2,2′-bipyridyl (Table 1, entries 6 and 7), as well as fully occupied silicotungstate $TBA_4[\alpha\text{-}SiW_{12}O_{40}]$ (SiW12, TBA = tetra-*n*-butylammonium; Table 1, entry 2). Hydrolytic oxidation of **1a** efficiently proceeded in the presence of lacunary POMs such as $TBA_4H_4[\alpha\text{-}SiW_{11}O_{39}]$ (SiW11) and $TBA_4H_4[\gamma\text{-}SiW_{10}O_{36}]$ (SiW10; Table 1, entries 3 and 4). In particular, the effect of SiW10 was very significant; **1a** was selectively transformed into the desired silanol **2a** in 88 % yield without formation of the corresponding disiloxane, and the stoichiometric amount of gaseous hydrogen with respect to **2a** was formed (92 % H_2 yield at complete conversion of **1a**; Supporting Information Figure S1a).[14] The yellow color of the reaction solution did not change, and no formation of silver metal was observed on allowing the solution to stand at 50 °C for 24 h (Supporting Information Figure S1b). Even when **1a** (0.5 mmol) and water (5.6 equiv with respect to **1a**) were newly added to this solution,

Table 1: Hydrolytic oxidation of **1a** to **2a** (effects of POM ligands).[a]

Entry	Catalyst (mol %)	*t* [min]	Yield [%]
1	AgOAc (0.2)	4	4
2	AgOAc (0.2) + SiW12 (0.1)	4	7
3	AgOAc (0.2) + SiW11 (0.1)	4	34
4	AgOAc (0.2) + SiW10 (0.1)	4	88
5[b]	AgOAc (0.2) + SiW10 (0.1)	12	79
6	AgOAc (0.2) + pyridine (0.2)	4	17
7	AgOAc (0.2) + 2,2′-bipyridyl (0.2)	4	9
8	SiW10 (0.1)	60	< 1
9	None	60	< 1

[a] Standard conditions: **1a** (0.5 mmol), water (5.6 equiv with respect to **1a**), acetonitrile (2 mL), 50 °C, under 1 atm of air. Yields were determined by GC with naphthalene as internal standard. [b] Acetone (2 mL) was used instead of acetonitrile.

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formation of **2a** and gaseous hydrogen was observed with almost the same rate as for the first run (86 % yield of **2a** over 4 min based on newly added **1a**; cf. Table 1, entry 4). Therefore, it is likely that SiW10 can act as an efficient oxygen-donor ligand to stabilize (active) silver species,[15] resulting in promotion of the hydrolytic oxidation and prevention of the aggregation of silver species as is observed for the reaction without the SiW10 ligand. These results stimulated us to synthesize a silver-containing POM by employing SiW10 as an inorganic ligand, which would be expected to be active for hydrolytic oxidation of silanes and other functional-group transformations.[13]

Usually, transition metal containing POMs have been synthesized by reaction of alkali metal salts of lacunary POMs and the corresponding transition metal salts in aqueous media, but isomerization and decomposition of lacunary POMs often proceed in aqueous (acidic) media. Synthesis in organic media from appropriate lacunary precursors (e.g., TBA salts) can avoid isomerization and decomposition of the original lacunary frameworks. For example, we synthesized zinc-containing sandwich-type silicotungstate $TBA_8[\{Zn(OH_2)(\mu_3\text{-}OH)\}_2\{Zn(OH_2)_2\}_2(\gamma\text{-}HSiW_{10}O_{36})_2]\cdot 9\,H_2O$, which is not possible to synthesize in aqueous media, by the reaction of SiW10 with $Zn(acac)_2$ (acac = acetylacetonato) in acetone.[5a] Likewise, we attempted to synthesize a silver-containing POM in organic media, while taking the results in Table 1 into account. Silver-containing POM **Ag4** could be synthesized by reaction of SiW10 and AgOAc in acetone (70 % yield based on SiW10), and single crystals suitable for X-ray crystallographic analysis were obtained by recrystallization from acetone/dimethyl sulfoxide (DMSO; see Supporting Information).[16] The molecular structure of the anion part of **Ag4** is shown in Figure 1.

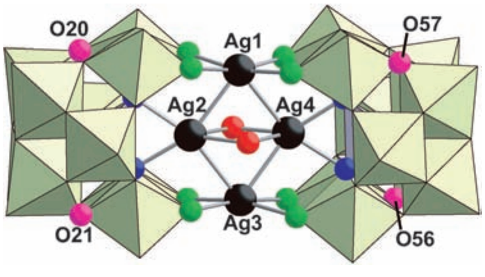


Figure 1. Polyhedral and ball-and-stick representation of the anion part of **Ag4** (see Figure S2 of the Supporting Information for ORTEP). The $\{WO_6\}$ units and a $\{SiO_4\}$ unit are shown as green octahedra and a gray tetrahedron, respectively. Black, red, green, blue, and pink spheres indicate silver atoms, oxygen atoms of DMSO (O_{DMSO}), oxygen atoms of the $\{WO_6\}$ units (O_W), oxygen atoms of the $\{SiO_4\}$ units (O_{Si}), and monoprotonated oxygen atoms, respectively. DMSO molecules, except for the oxygen atoms, are omitted for clarity.

Eight TBA cations per **Ag4** anion could be crystallographically assigned, in accord with the result of the elemental analysis. The bond valence sum (BVS) values of silicon (3.98 and 4.02), tungsten (5.83–6.26), and silver atoms (0.91–1.07) in **Ag4** indicate that the respective valences are +4, +6, and +1. In addition, the four oxygen atoms with lower BVS values (1.12–1.25 for O20, O21, O56, and O57) found in **Ag4** suggest that protons are likely located on these oxygen atoms. The X-ray, elemental analysis, and thermogravimetric data show that the formula of **Ag4** is $TBA_8[Ag_4(DMSO)_2(\gamma\text{-}H_2SiW_{10}O_{36})_2]\cdot 2\,DMSO\cdot 2\,H_2O$. Compound **Ag4** can form according to Equation (1).

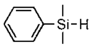
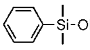
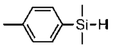
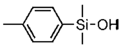
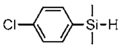
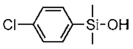
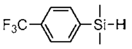
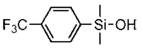
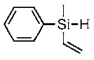
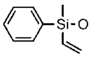
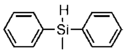
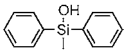
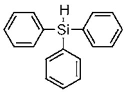
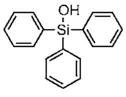
$$\begin{aligned} &2\,TBA_4H_4[\gamma\text{-}SiW_{10}O_{36}] + 4\,AgOAc \rightarrow \\ &\qquad TBA_8[Ag_4(\gamma\text{-}H_2SiW_{10}O_{36})_2] + 4\,AcOH \end{aligned} \tag{1}$$

As shown in Figure 1, **Ag4** has a diamond-shaped tetrasilver $[Ag_4]^{4+}$ cluster cation encapsulated by two SiW10 subunits. Two DMSO molecules are coordinated to Ag2 and Ag4. The Ag1 and Ag3 atoms are bridged by two SiW10 subunits in a slightly distorted square-planer environment, and the average $Ag{-}O_W$ distance is 2.38 Å. The Ag2 and Ag4 atoms are coordinated to two oxygen atoms of the central $\{SiO_4\}$ tetrahedrons with an average $Ag{-}O_{Si}$ distance of 2.46 Å. Thus, the $[Ag_4]^{4+}$ cluster is stabilized in the lacunary pocket of SiW10. The Ag1−Ag2, Ag2−Ag3, Ag3−Ag4, and Ag4−Ag1 distances are 2.962(2), 3.070(2), 3.016(2), and 3.074(2) Å, respectively. Since they are shorter than twice the van der Waals radius of the silver atom (3.44 Å), they suggest the existence of argentophilic interaction between silver atoms in **Ag4**. It is well known that d^{10} metals tend to show closed-shell interactions,[17] and such argentophilic interactions were often observed in previously reported organometallic complexes with similar $[Ag_4]^{4+}$ cores.[18] The Ag1⋯Ag3 and Ag2⋯Ag4 separations are 4.868(2) and 3.683(2) Å, respectively. The Ag1-Ag2-Ag3 and Ag2-Ag3-Ag4 angles are 105.66(6)° and 74.47(5)°, respectively. The above-mentioned Ag−Ag distances, Ag⋯Ag separations, and angles in **Ag4** are within the ranges of reported complexes with $[Ag_4]^{4+}$ cores.[18]

Although various kinds of POMs substituting or encapsulating metal–oxygen clusters have been synthesized until now,[2,4,5] we note that POMs containing multimetallic cores with metal–metal interactions are very rare.[19–22] Polyoxometalate assemblies with dimeric[19] or infinite[20] structures connected by metal–metal interactions (Ag−Ag[19a,b,20] or Rh−Rh[19c]) have been reported. The dirhodium-containing POMs were synthesized by attaching dicarboxylatodirhodium complexes to monolacunary POMs.[21] The γ-Keggin silicotungstates $[\gamma\text{-}SiW_{10}M_2S_2O_{38}]^{6-}$ (M = W or Mo) with $[M(O)(\mu\text{-}S)_2M(O)]^{2+}$ oxothio core show M−M interactions.[22] All reported POMs with metal–metal interaction have dimetallic cores, and multimetallic cores consisting of more than two metals, as observed in **Ag4**, have not been reported so far, to the best of our knowledge.[23]

Finally, we investigated catalysis of hydrolytic oxidation of silanes by **Ag4**. As we expected, various structurally diverse silanes including aromatic, double bond containing, and aliphatic ones, could selectively be converted to the corresponding silanols in high yields in the presence of **Ag4** (Table 2). Selectivities to the desired silanols were greater than 99 % (except for **1d**). The hydrolytic oxidation of commonly examined **1a** efficiently proceeded with **Ag4** (0.05 mol %), giving **2a** in 96 % yield under the conditions described in Table 2.[14,15] In this case, the stoichiometric

Table 2: Hydrolytic oxidation of various silanes.[a]

Entry	Substrate		*t*	Product		Yield [%]
1[b]		**1a**	4 min		**2a**	96 (88)
2		**1b**	2 min		**2b**	83 (88)
3		**1c**	1 h		**2c**	90 (94)
4[c]		**1d**	3 h		**2d**	92 (92)[d]
5		**1e**	7 min		**2e**	96 (98)
6		**1f**	5 min		**2f**	91 (96)
7[c]		**1g**	3 h		**2g**	88 (77)
8[c,e]	Bn_3SiH	**1h**	3 h	Bn_3SiOH	**2h**	94 (90)
9	Et_2MeSiH	**1i**	10 h	$Et_2MeSiOH$	**2i**	78 (88)
10[c]	Et_3SiH	**1j**	8 h	Et_3SiOH	**2j**	78 (93)
11[c]	*n*Pr_3SiH	**1k**	24 h	*n*Pr_3SiOH	**2k**	92 (90)
12[c,f]	*i*Pr_3SiH	**1l**	24 h	*i*Pr_3SiOH	**2l**	72 (71)

[a] Standard conditions: **Ag4** (0.5 mol%), silane (0.25 mmol), water (5.6 equiv with respect to silanes), acetonitrile (1 mL), 50°C, under 1 atm of air. Yields were determined by GC with naphthalene as internal standard. The values in parentheses are yields with the catalyst prepared in situ by mixing SiW10 and AgOAc. [b] **Ag4** (0.05 mol%), **1a** (0.5 mmol), water (5.6 equiv with respect to **1a**), acetonitrile (2 mL), 50°C, under 1 atm of air. [c] 70°C. [d] The corresponding disiloxane was formed as a byproduct (2% yield for **Ag4**; 3% yield for the catalyst prepared in situ). [e] Acetonitrile (2 mL). [f] **Ag4** (1 mol%).

amount of gaseous hydrogen with respect to **2a** was also formed (98% H_2 yield at complete conversion of **1a**). Notably, the amount of **Ag4** could be much reduced. When the hydrolytic oxidation of **1a** was carried out with 0.004 mol% of **Ag4** at 70°C, **2a** was obtained in 72% yield over 10 min (Supporting Information Figure S3). In this case, the turnover frequency (TOF) based on silver was 27000 h^{-1} and the highest among previously reported catalysts including AgHAP catalyst (silver nanoclusters supported on hydroxyapatite, TOF = 178 h^{-1} at 80°C[12], Supporting Information Table S1).[7–12] The second highest turnover number (TON) of 15625 (based on silver) was obtained when using 0.0008 mol% of **Ag4** (Supporting Information Figure S3 and Table S1).[7–12]

The electronic effect of substrates is very significant. Hydrolytic oxidation of **1b** smoothly proceeded to afford the corresponding silanol **2b** in 83% yield over only 2 min. In contrast, dimethylphenylsilane derivatives with electron-withdrawing substituents such as chloro (**1c**) and trifluoromethyl (**1d**) groups required longer reaction times and/or a higher reaction temperature (70°C) to attain high yields (90–92%) of the corresponding silanols. These results suggest that formation of a positively charged intermediate, such as a silyl cation, is likely involved in the present transformation. The present system could be applied to sterically bulky silanes such as **1f** (diphenylmethyl), **1g** (triphenyl), and **1h** (tribenzyl), and gave the corresponding silanols in high yields (88–94% yields), though the steric effect was also significant. In the case of double bond containing silane **1e**, the desired unsaturated silanol **2e** was selectively obtained in 96% yield without formation of over-reduced products. It has been reported that hydrolytic oxidation of aliphatic silanes hardly proceeds in the presence of AgHAP catalyst.[12] In contrast, **Ag4** could promote hydrolytic oxidation of various aliphatic silanes, such as **1i**, **1j**, **1k**, and **1l** (72–92% yields).

As mentioned in Table 1, a simple mixture of SiW10 and AgOAc ("in-situ-prepared catalyst") efficiently promoted hydrolytic oxidation of **1a**, whereby SiW10 could act as an oxygen-donor ligand to stabilize active silver species.[15] It would be advantageous for practical applications if the hydrolytic oxidation could be carried out with such an in-situ-prepared catalyst, because the reaction can readily be performed even without isolation of truly active species.[24] The catalyst prepared in situ by simply mixing the required components of SiW10 and AgOAc showed very similar performance to **Ag4** (see values in parentheses in Table 2).

In summary, we have demonstrated that it is possible to synthesize a novel POM containing the diamond-shaped $[Ag_4]^{4+}$ core (**Ag4**) by reaction of SiW10 with AgOAc in an organic medium. This POM is a rare compound which contains a multimetallic core with metal–metal interaction. In the presence of **Ag4**, hydrolytic oxidation of various structurally diverse silanes selectively proceeded to give the corresponding silanols in high yields (72–96%). Moreover, the catalyst prepared in situ by simply mixing the required components of precursors (SiW10 and AgOAc) showed similar performance (71–98% yields) to **Ag4**.

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[14] When the hydrolytic oxidation of **1a** with **Ag4** was carried out under 1 atm of Ar, the reaction rate was almost the same as under 1 atm of air, and **2a** was obtained in 88 % yield after 4 min (cf. Table 2, entry 1). In this case, formation of gaseous hydrogen was also observed. In addition, hydrolytic oxidation of **1a** with ^{18}O-labeled water (^{18}O content: ≥98 %) under the conditions described in Table 2 led to formation of ^{18}O-labeled **2a** as major product (77 % yield, ^{18}O content in **2a**: 94 % by GC-MS analysis). These results show that the silanol oxygen atom originates from water and are in agreement with the formation of a stoichiometric amount of gaseous hydrogen.

[15] The positive-ion cold-spray ionization mass spectrum of a solution of **Ag4** in acetonitrile just after addition of **1a** exhibited several sets of signals centered around *m*/*z* 3623 (**A**), 3682 (**B**), 3818 (**C**), 3925 (**D**), and 4034 (**E**) possibly due to $[SiW_{10}O_{36}]^{8-}$, $[SiW_{10}O_{36}]^{8-}$, $[SiW_{10}O_{36}Ag^{I}_{2}]^{6-}$, $[SiW_{10}O_{36}Ag^{I}_{2}Ag^{0}]^{6-}$, and $[SiW_{10}O_{36}Ag^{I}_{2}Ag^{0}_{2}]^{6-}$, respectively (Supporting Information Figure S4a). After the reaction was completed (complete consumption of **1a** or water), signal sets **A**, **B**, **D**, and **E** almost disappeared, while signal set **C** was still observed (Supporting Information Figure S4b). A similar phenomenon was also observed for use of the catalyst prepared in situ from SiW10 and AgOAc (Supporting Information Figure S4c and d). Therefore, the Ag^{0} species generated in situ and stabilized by SiW10 are possible active species in the present hydrolytic oxidation of silanes. Once the reaction is complete, Ag^{0} species are likely reoxidized and stabilized in the lacunary pocket of SiW10, which prevents their aggregation for long times (see Supporting Information Figure S1).

[16] CCDC 854101 (**Ag4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The structural and crystallographic data are summarized in Tables S2 and S3 of the Supporting Information, respectively.

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