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Unique Catalytic Performance of the Polyoxometalate $[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]^{8-}$: The Role of 5-Coordinated Titanium in H_2O_2 Activation

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Tetra-*n*-butylammonium (TBA) salts of the dititanium sandwich-type 19-tungstodiarsenate(III) $[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]^{8-}$ (**1**) revealed a unique catalytic performance in the selective oxidation of organic compounds with aqueous hydrogen peroxide. The selectivity of alkene oxidation strongly depends on the amount of acidic protons in the cationic part of **1**, which can be controlled by pH of precipitation of the TBA salt. Selectivities of almost 100 % were achieved for cyclohexene epoxidation by using $TBA_{5.5}Na_{1.5}K_{0.5}H_{0.5}$-**1**. In the presence of $TBA_{5.5}K_{0.5}H_2$-**1**, cyclohexene epoxide readily transformed into *trans*-1,2-cyclohexanediol, 2-hydroxycyclohexanone, and C–C bond-cleavage products. No allylic oxidation products were found. Vicinal diols yielded α-hydroxyketones and (di)carboxylic acids. Ketonization of cyclohexanol proceeded with selectivity as high as 98 %, whereas 1-hexanol produced hexanal and hexanoic acid. The oxidation products are consistent with a heterolytic mechanism of H_2O_2 activation. The stability of **1** under turnover conditions was confirmed by IR spectroscopy. The presence of titanium atoms in the belt of **1** is vital for the catalytic performance. The titanium-free analogue, $[As_2W_{21}O_{67}(H_2O)]^{6-}$ (**2**), revealed lower activity and selectivity in the oxidation of alcohols and was not active in the oxidation of alkenes. The catalytic performance of **1** contrasts that of polyoxometalates containing hexacoordinate Ti atoms, for example, $TBA_7[(PTiW_{11}O_{39})_2OH]$, $TBA_8H_7[\{Ti_3PW_9O_{37}(OH)\}_3(PO_4)]$, and $TBA_{17}[(\alpha\text{-}Ti_3SiW_9O_{37}OH)_3\{TiO_3(OH_2)_3\}]$, for which a homolytic oxidation mechanism was manifested by the formation of cyclohexene allylic oxidation products. The unique ability of **1** to catalyze heterolytic oxidations with the use of hydrogen peroxide most likely originates from the specific coordination number (5) and geometry (square-pyramidal) of the Ti atoms in this polyanion.

Introduction

Titanium-containing catalysts have attracted increasing attention due to their ability to activate the green oxidant hydrogen peroxide.[1] In the early 1980s, the Enichem group developed the famous microporous titanium-silicalite TS-1, which initiated a large family of the so-called Ti single-site catalysts.[1a,2] TS-1 possesses a unique ability to activate H_2O_2 and oxidize small organic substrates (<0.6 nm) through heterolytic oxidation mechanisms.[1c,3] To meet the demands of the fine chemicals industry, many research groups have been working on the development of a mesoporous Ti single-site catalyst that would display catalytic properties of TS-1 but could be used in the oxidation of bulk organic molecules.[4] However, the majority of mesoporous Ti single-site catalysts revealed a catalytic behavior different from that of TS-1: a significant contribution of homolytic mechanisms is typical for mesoporous titanium silicates in H_2O_2-based oxidations.[1c] To date, the reasons for this are not completely understood and remain under debate.

Because homogeneous catalysts are often tractable and suitable for probing interactions at the molecular level, studies on soluble titanium compounds with different structures could shed light on the mechanisms of H_2O_2 activation by different kinds of Ti centers. However, titanium complexes with organic and organosilicon (silsesquioxane) ligands are prone to oxidative and hydrolytic degradation, polymerization, and so on; consequently, they cannot be employed for studying mechanisms of H_2O_2-based oxidations. In contrast, titanium-substituted polyoxometalates (POMs) have inorganic nature, are thermodynamically

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stable to oxidation, and possess hydrolytic stability under appropriate pH conditions, which makes them suitable molecular models for Ti centers in aqueous–organic media.[5]

The apparent structural analogy of POMs and metal oxide surfaces allows one to view POMs as discrete, soluble fragments of extended metal oxide lattices.[6] Recently, Kholdeeva et al. demonstrated that the catalytic performance of tetra-*n*-butyl ammonium (TBA) salts of titanium-monosubstituted Keggin-type heteropolytungstates, $(Bu_4N)_4$-$[PTi(L)W_{11}O_{39}]$ (Ti-POM), in the oxidation of alkenes, thioethers, and alkylphenols with H_2O_2 is very similar to that of hydrophilic mesoporous titanium silicate catalysts.[5,7] In Ti-POM, the $PW_{11}O_{39}{}^{7-}$ lacunary POM acts as a pentadentate ligand for the hexacoordinate Ti^{IV} ion. Thus, Ti is strongly bound to four neighboring tungsten atoms and one central phosphorus atom through oxygen bridges, and in fact, only the sixth coordination position, which is occupied by ligand L, is labile and can participate in interactions with reactants in the course of an oxidation process. It has been established that such hexacoordinate isolated Ti centers catalyze oxidations with H_2O_2 predominantly through homolytic oxidation routes but are not capable of a heterolytic oxygen atom transfer.[5]

Recently, the "sandwich"-type dititanium 19-tungstodiarsenate(III) $[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]^{8-}$ (**1**; Figure 1) was synthesized and characterized by single-crystal X-ray diffractometry, IR spectroscopy, TGA/DSC, electrochemistry, and elemental analysis.[8]

Polyanion **1** comprises two (B-α-$As^{III}W_9O_{33}$) Keggin moieties linked through two square-pyramidal $[Ti(OH)]^{3+}$ groups and an octahedral $[WO(H_2O)]^{4+}$ fragment. The unprecedented arrangement of the two TiOH groups in **1** allows neither intra- nor intermolecular Ti–O–Ti bond formation. It was shown that the acidic tetra-*n*-butyl ammonium salt of **1**, TBA_5H_3-**1**, is highly active in cyclohexene (CyH) oxidation with aqueous H_2O_2 and leads to products typical of a heterolytic oxidation mechanism.[8] Following our interest in Ti-containing soluble probes and keeping in mind the unusual coordination environment of Ti in polyanion **1**, we explored further the catalytic properties of **1** in the selective oxidation of a range of organic compounds with H_2O_2. To clarify the role of the five-coordinate titanium atoms in **1**, a comparison with the Ti-free analogue $[As_2W_{21}O_{67}(H_2O)]^{6-}$ (**2**), monosubstituted Keggin Ti-POM, multi-Ti-center POMs (Ti$_n$-POM), and the TBA salt of the Venturello complex $TBA_3\{PO_4[W(O)(O_2)_2]_4\}$ (TBA-PW$_4$) was made. The stability of **1** under turnover conditions of the H_2O_2-based oxidations was addressed.

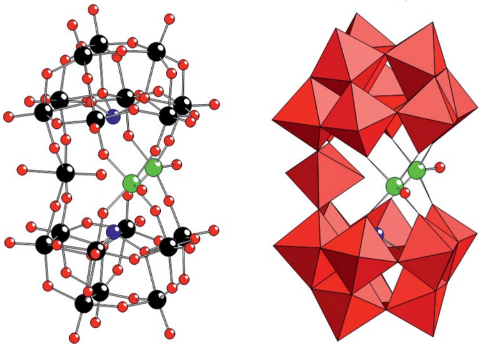


Figure 1. Ball-and-stick representation of polyanion **1**. Color code: W black, As blue, Ti green, O red.

Results and Discussion

Depending on the pH of the solution at which the precipitation of the TBA salt occurred, the resulting solids were found to contain different amounts of acidic protons in the cationic part. Potentiometric titration with methanolic TBAOH revealed that TBA salts with ca. 2 and 0.5 H^+ were obtained at pH 2.1 and 2.7, respectively. The corresponding titration curves are shown in Figure 2.

TGA has shown that the amount of TBA cations was 5.5 in both TBA salts of **1**. On the basis of the elemental analysis data (see the Experimental Section), we suggest the formula $TBA_{5.5}K_{0.5}H_2$-**1** and $TBA_{5.5}Na_{1.5}K_{0.5}H_{0.5}$-**1** for the compounds prepared at pH 2.1 and 2.7, respectively (hereafter referred as H_2-**1** and $H_{0.5}$-**1**, respectively).

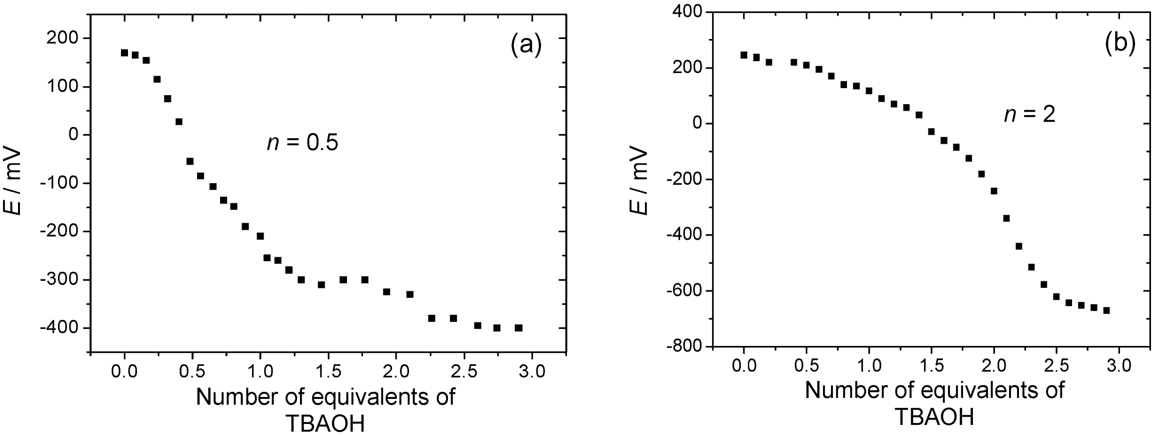


Figure 2. Potentiometric titration of $H_{0.5}$-**1** (a) and H_2-**1** (b) with methanolic 0.8 M TBAOH in MeCN.

Interestingly, the IR spectra of the two TBA salts of **1** are nearly identical and resemble the spectrum of the Ti-free analogue $TBA_6[As_2W_{21}O_{69}]$ (TBA-**2**; Figure 3). The only difference is the presence of the band at 817 cm^{-1} in the spectrum of the TBA-**1** salts, which can be, therefore, attributed to Ti–O stretching vibrations.

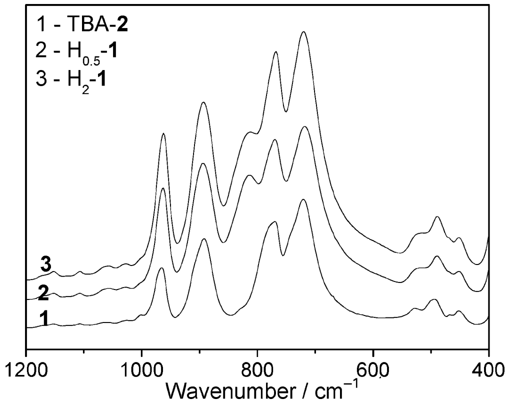


Figure 3. FTIR spectra (in KBr) of $H_{0.5}$-**1**, H_2-**1**, and TBA-**2**.

The catalytic activity of $H_{0.5}$-**1** and H_2-**1** was first assessed in the homogeneous H_2O_2-based oxidation of cyclohexene (CyH) as a model alkene substrate in MeCN medium. It was found that the amount of H^+ had no significant impact on the rate of CyH consumption (Supporting Information, Figure S1); however, it strongly affected the product composition. The results of the catalytic experiments are presented in Table 1. In the presence of $H_{0.5}$-**1**, the main oxidation product was cyclohexene epoxide. With one equivalent of 30% H_2O_2, the epoxide selectivity reached 81% at 80% substrate conversion (Table 1, Entry 1). Only minor traces of allylic oxidation products, 2-cyclohexene-1-ol and 2-cyclohexene-1-one, were found. The main byproducts were *trans*-1,2-cyclohexanediol and 2-hydroxycyclohexanone. Given that these byproducts form in consecutive processes, one would expect higher epoxide selectivity at a lower CyH conversion. Indeed, at 46% conversion, the selectivity reached 96% (Table 1, Entry 2). Moreover, it could be improved further up to 100% by decreasing the reaction temperature (Table 1, Entry 3), the amount of water introduced with H_2O_2 (Table 1, Entry 4), and initial concentration of H_2O_2 (Table 1, Entry 5). Importantly, the H_2O_2 efficiency (selectivity to epoxide on the basis of the oxidant consumed) was also high and achieved 92%. Interestingly, when *tert*-butyl hydroperoxide was used as the oxidant instead of hydrogen peroxide, very little (<5%) conversion of CyH was found after 5 h under the same reaction conditions.

With H_2-**1**, the selectivity of CyH epoxidation was significantly lower than that obtained with $H_{0.5}$-**1**, and only 21% selectivity at 70% conversion under the same reaction conditions was observed (Table 1, Entry 6). By using a fourfold excess of H_2O_2 we studied the dynamics of the formation of the products in the presence of H_2-**1**. The kinetic curves of CyH consumption and products accumulation are shown in Figure 4. Adipic acid was quantified only at the end of the reaction.

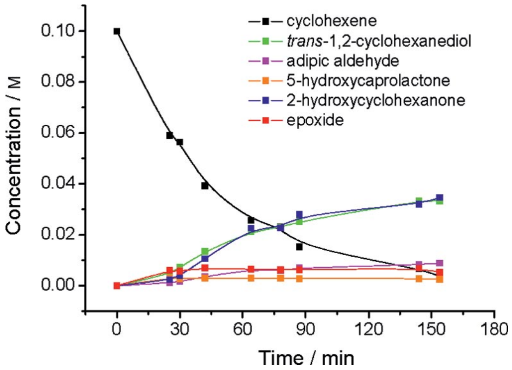


Figure 4. Kinetic curves for CyH oxidation in the presence of H_2-**1** ([CyH] = 0.1 м, $[H_2O_2]$ = 0.4 м, [H_2-**1**] = 4×10^{-3} м, 50 °C, MeCN).

After 5 h, CyH conversion achieved 100%, and the yields of epoxide, *trans*-1,2-cyclohexanediol, 2-hydroxycyclohexanone, 5-hydroxycaprolactone, adipic aldehyde, and adipic acid were 4, 26, 41, 8, 9, and 9%, respectively. Again, no 2-cyclohexene-1-ol and 2-cyclohexene-1-one were found even at the initial period of the reaction.

The kinetic curves in Figure 4 show that initially CyH epoxide predominated among the reaction products and then *trans*-1,2-cyclohexanediol, 2-hydroxycyclohexanone, 5-hydroxycaprolactone, and adipic aldehyde appeared. The character of the kinetic curves allows suggesting that the epoxide can be either first hydrolyzed to diol or directly converted into α-hydroxyketone. This was confirmed by the experiment where epoxide was taken as a reaction substrate. The kinetic curves in Figure S2 (Supporting Information) revealed simultaneous formation of diol and α-hydroxyketone. The results acquired show that oxidation of

Table 1. Cyclohexene oxidation with H_2O_2 in the presence of $H_{0.5}$-**1** and H_2-**1**.[a]

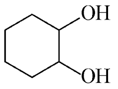
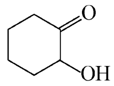
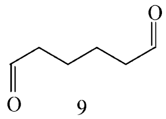
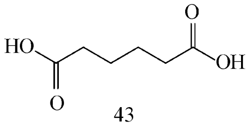
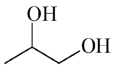
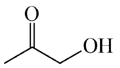
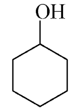
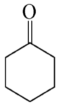
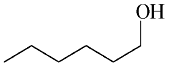
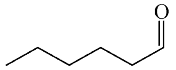
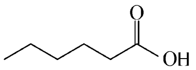
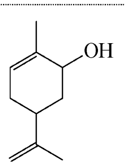
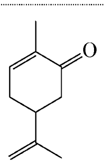
Entry	Catalyst	*T* / °C	H_2O_2 / %	$[H_2O_2]$ / м	CyH conversion / %	Epoxide selectivity[b] / %
1	$H_{0.5}$-**1**	50	30	0.2	80	81
2	$H_{0.5}$-**1**[c]	50	30	0.2	46	96
3	$H_{0.5}$-**1**	40	30	0.2	58	97
4	$H_{0.5}$-**1**	50	70	0.2	50	100
5	$H_{0.5}$-**1**	50	30	0.1	46	100
6	H_2-**1**	50	30	0.2	70	21

[a] Reaction conditions: [CyH] = 0.2 м, [**1**] = 2×10^{-3} м, MeCN, 50 °C, 5 h. [b] GC yield based on substrate consumed. [c] Reaction time was 3 h.

trans-1,2-cyclohexanediol and 2-hydroxycyclohexanone is rate-limiting in the process of CyH transformation to adipic acid, which agrees with the literature.[9]

The results on the catalytic oxidation of representative vicinal diols and alcohols with four equivalents of H_2O_2 in the presence of H_2-**1** are presented in Table 2. Cyclohexanediol produced 2-hydroxycyclohexanone and adipic acid as the main oxidation products; adipic aldehyde was also found. At a lower conversion, 2-hydroxycyclohexanone predominated among the oxidation products. The character of the kinetic curves for the α-hydroxyketone and aldehyde accumulation (Supporting Information, Figure S3) indicated that these products might be produced from diol in parallel pathways. Plausible routes of CyH transformation to adipic acid in the presence of H_2-**1** are shown in Scheme 1.

Table 2. Oxidation of alcohols and diols with H_2O_2 in the presence of H_2-**1**.[a]

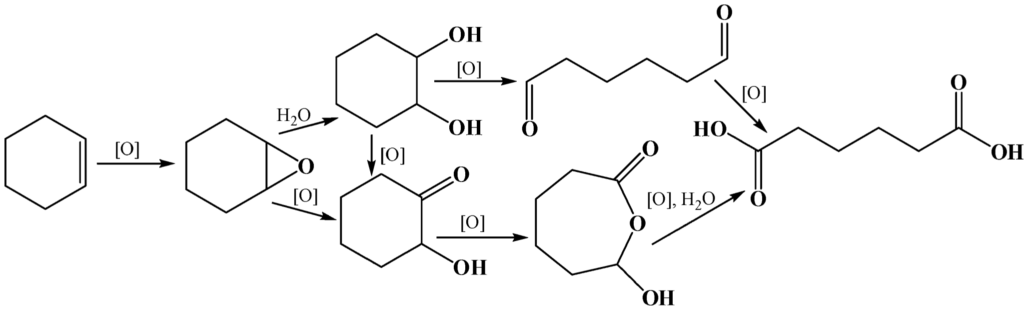
Substrate, Conversion / %	T / °C	TOF_{Ti}[b] / h^{-1}	Products, Selectivity / %[c]
 50[d]	50	1.3	 48  9  43
 35	70	0.9	 77 CH_3COOH 23
 70[e]	70	3.9	 98
 23	70	0.1	 45  55
 80[f]	50	14	 70

[a] Reaction conditions: [S] = 0.1 M, $[H_2O_2]$ = 0.4 M, $[H_2\text{-}\mathbf{1}]$ = 4×10^{-3} M, MeCN, 5 h. [b] TOF_{Ti} = (mols of substrate consumed)/[(mols of Ti) × time]; determined from initial rates. [c] GC yield based on substrate consumed. [d] Without catalyst, diol conversion was 12%. [e] Without catalyst, cyclohexanol conversion was 13%. [f] $[H_2O_2]$ = 0.1 M.

Another representative *vic*-diol, 1,2-propanediol, in the presence of H_2-**1** gave predominantly α-hydroxyacetone; acetic acid was identified as the main byproduct (Table 2). The oxidation of cyclohexanol and 1-hexanol was examined to evaluate the potential of H_2-**1** for oxidation of secondary (cyclic) and primary alcohols. The results are also presented in Table 2. In the presence of H_2-**1**, cyclohexanol was smoothly oxidized to cyclohexanone with a selectivity as high as 98%. In turn, cyclohexanone was found to be inert under the reaction conditions; after 5 h its conversion was close to zero. This ensured high selectivity towards ketonization at rather high cyclohexanol conversions. The catalytic activity and selectivity of $H_{0.5}$-**1** and H_2-**1** in cyclohexanol oxidation with H_2O_2 were very close. The primary alcohol 1-hexanol was less reactive compared to cyclohexanol and produced hexanal and hexanoic acid in the presence of H_2-**1** (Table 2). Even at low conversions (10–20%) the carboxylic acid product was found in considerable amounts. This contrasts the catalytic performance of the Ishii system ($H_3PW_{12}O_{40}/H_2O_2$; two-phase conditions), which produced aldehydes as the main products at comparable conversions of primary alcohols.[10]

The oxidation of the unsaturated alcohol carveol in the presence of H_2-**1** yielded mostly the corresponding unsaturated ketone, carvone, and the main byproduct was the *trans* isomer of carvone epoxide (Table 2). Note that in the Ishii system unsaturated alcohol 2-cyclohexene-1-ol yielded a mixture of epoxide and enone with a ratio of ca. 2:1.[10]

It has been established by several research groups that the catalytic activity of the PW_{12}/H_2O_2 system is due to in situ formation of lower nuclearity peroxotungstates, the Venturello complex $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ (PW_4) being the most active species.[11] Importantly, under the conditions employed in our work (MeCN, 50–70 °C, $[H_2O_2]$/[POM] = 100), the heteropolyacid $H_3PW_{12}O_{40}$ was stable towards solvolytic degradation with H_2O_2, as was confirmed by ^{31}P NMR spectroscopy. As a result, neither alkenes nor alcohols were oxidized by H_2O_2 in the presence of PW_{12}, which contrasts significantly with the catalytic performance of TBA-**1** (compare results in Tables 3 and 4 for the oxidation of cyclohexene and cyclohexanol, respectively). Neumann suggested that POM resistance towards H_2O_2 should increase with increasing negative charge of the polyanion.[12] This implies that sandwich-type POMs are expected to be more stable than PW_{12}. Additionally, we performed a direct comparison of the catalytic performance of TBA-**1** and TBA-PW_4. The results for cyclohexene and cyclohexanol oxidation are shown in Tables 3 and 4, respectively. A pronounced difference is observed in the catalytic properties of these two compounds. Under the same reaction conditions, the yield of epoxide is higher for PW_4. On the contrary, the yield of cyclohexanone is lower because a lower substrate conversion is achieved with PW_4, most likely, due to its rapid deactivation. If we compare the TOF values determined from the initial rates and normalized to the number of W atoms, we may conclude that PW_4 is ca. six times more active than **1** in cyclohexene epoxidation and ca. three times more active in cyclohexanol oxidation. This



Scheme 1.

Table 3. Effect of POM nature on cyclohexene oxidation with H_2O_2.[a]

POM	Cyclohexene conversion / %	TOF_{Ti}[b] / h^{-1}	TOF_W[c] / h^{-1}	Epoxide selectivity[d] / %
No catalyst	0	–	–	–
$TBA_{5.5}Na_{1.5}K_{0.5}H_{0.5}[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]$	80	13	1.4	81
$TBA_6[As_2W_{21}O_{69}(H_2O)]$	0	–	–	–
$H_3PW_{12}O_{40}$	0	–	–	–
$TBA_3\{PO_4[W(O)(O_2)_2]_4\}$	84	–	9	98
$TBA_7[(PTiW_{11}O_{39})_2OH]$	59	27	2.5	6[e]
$TBA_8H_7[\{Ti_3PW_9O_{37}(OH)\}_3(PO_4)]$	6	1.1	0.36	2[e]
$TBA_{17}[(\alpha\text{-}Ti_3SiW_9O_{37}OH)_3\{TiO_3(OH_2)_3\}]$	1	n.d.[f]	n.d.	n.d.

[a] Reaction conditions: [CyH] = 0.2 M, $[H_2O_2]$ = 0.2 M, [POM] = 2 × 10–3 M, MeCN, 50 °C, 5 h. [b] TOF_{Ti} = (mols of substrate consumed)/[(mols of Ti) × time]; determined from the initial rates. [c] TOF_W = (mols of substrate consumed)/[(mols of W) × time]; determined from the initial rates. [d] GC yield based on substrate consumed. [e] Allylic oxidation products, cyclohexene-2-ol-1 and cyclohexene-2-one-1, formed along with *trans*-1,2-cyclohexanediol. [f] Not determined.

Table 4. Effect of POM nature on cyclohexanol oxidation with H_2O_2.[a]

POM	Cyclohexanol conversion / %	TOF_{Ti}[b] / h^{-1}	TOF_W[c] / h^{-1}	Cyclohexanone selectivity[d] / %
No catalyst	13	–	–	n.d.[e]
$TBA_{5.5}K_{0.5}H_2[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]$	70	3.9	0.41	98
$TBA_6[As_2W_{21}O_{69}(H_2O)]$	30	–	0.10	90
$H_3PW_{12}O_{40}$	0	–	–	–
$TBA_3\{PO_4[W(O)(O_2)_2]_4\}$	57	–	1.23	98
$TBA_7[(PTiW_{11}O_{39})_2OH]$	20	2.25	0.2	71
$TBA_{17}[(\alpha\text{-}Ti_3SiW_9O_{37}OH)_3\{TiO_3(OH_2)_3\}]$	4	–	–	n.d.

[a] Reaction conditions: [S] = 0.1 M, $[H_2O_2]$ = 0.4 M, [POM] = 4 × 10–3 M, MeCN, 70 °C, 5 h. [b] TOF_{Ti} = (mol of substrate consumed)/[(mols of Ti) × time]; determined from the initial rates. [c] TOF_W = (mols of substrate consumed)/[(mols of W) × time]; determined from the initial rates. [d] GC yield based on substrate consumed. [e] Not determined.

implies that 15–30 % of **1** should be transformed into a Venturello-like species if the observed activity was due to the tungsten species. However, such a transformation would be observed by IR.

Previously, we demonstrated by IR and UV/Vis spectroscopy and cyclic voltammetry that **1** is stable towards transformation into low nuclearity species.[8] Given that oxidation conditions were more severe for the oxidation of alcohols, we separated H_2-**1** after the reaction of cyclohexanol oxidation and checked the catalyst stability by IR (Figure 5). One can judge from the comparison of the spectra in Figure 5 that **1** preserves its sandwich structure after the catalytic reaction. Some low-energy shifting of the 817 cm^{-1} feature in the IR spectrum is most likely due to changes in the coordination environment of Ti during the reaction. The same changes were previously found for TBA-**1** after catalytic CyH oxidation.[8] Hence, all the results collectively indicate that the catalytic properties of TBA-**1** are not related to the formation of lower nuclearity species.

The presence of titanium atoms in the belt of **1** is vital for the catalytic performance. The titanium-free analogue $TBA_6[As_2W_{21}O_{67}(H_2O)]$ (TBA-**2**), which has three tungsten atoms in the belt, revealed no catalytic activity in CyH oxidation (Table 3). It showed some activity in the oxidation of cyclohexanol (Table 4), but both activity and selectivity were significantly lower than those of TBA-**1**. The stability of TBA-**2** under turnover conditions was also confirmed by IR spectroscopy. The IR spectrum of TBA-**2** separated after the catalytic cyclohexanol oxidation was identical to the spectrum of initial TBA-**2** shown in Figure 3. Therefore, we may conclude that the belt tungsten atoms are not able to catalyze alkene epoxidation with H_2O_2, but reveal some ac-

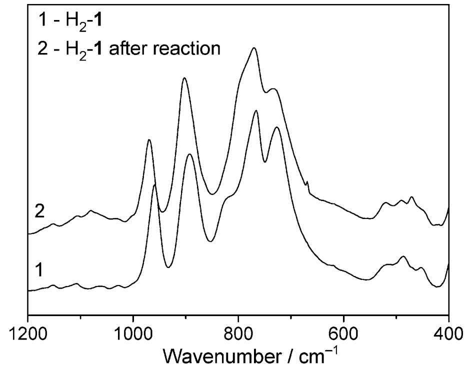


Figure 5. FTIR spectra (in KBr) of H_2-**1** before and after cyclohexanol oxidation (reaction conditions are mentioned in Table 2).

tivity in catalyzing oxidation of secondary alcohols. In turn, the inactivity of PW_{12} in both reactions (see Tables 3 and 4) implies that tungsten atoms in a Keggin structure are not the centers that can accomplish the catalytic transformations of alkenes and alcohols with H_2O_2.

Many POMs containing multiple Ti centers (Ti_n-POM) are reported in the literature.[13] We found that the catalytic performance of **TBA-1** differs markedly from the performance of both monosubstituted Ti-POM and Ti_n-POM having Ti atoms connected through Ti–O–Ti bonds, namely, $TBA_8H_7[\{Ti_3PW_9O_{37}(OH)\}_3(PO_4)]$ (Ti_9-POM) and TBA_{17}-$[(\alpha\text{-}Ti_3SiW_9O_{37}OH)_3\{TiO_3(OH_2)_3\}]$ (Ti_{10}-POM). One can judge from the data given in Table 3 that the TOF values in CyH oxidation normalized with respect to the amount of Ti atoms fall in the order: Ti-POM > **1** >> Ti_9-POM > Ti_{10}-POM. The monosubstituted Ti-POM is highly active at the initial stage of the reaction, but a lower CyH conversion can be achieved (Supporting Information, Figure S4), most likely because of a high rate of nonproductive H_2O_2 decomposition (vide infra). For all but **TBA-1**, the epoxide selectivity was very low and allylic oxidation products, 2-cyclohexene-1-ol and 2-cyclohexene-1-one, were found in considerable amounts along with *trans*-1,2-cyclohexanediol. This implies that homolytic oxidation mechanism applies in the presence of Ti_n-POM, which coincides with our previous observations on Ti-POM.[5] In the cyclohexanol oxidation, both Ti-POM and Ti_{10}-POM were significantly less active compared to **TBA-1** (Table 4).

We have studied H_2O_2 decomposition in the absence of an organic substrate and found that the rates of H_2O_2 decomposition normalized with respect to the amount of Ti atoms fall in the order Ti-POM > Ti_{10}-POM > **1** (Figure 6), which does not correlate with the order of catalytic activity of these POMs in selective oxidations. Interestingly, Ti_{10}-POM possesses a considerable activity in H_2O_2 dismutation but is practically inactive in both CyH and cyclohexanol oxidation with H_2O_2.

Since titanium atoms in both Ti-POM and Ti_n-POM are hexacoordinate, we may suppose that the unique ability of **1** to catalyze heterolytic oxidations by using hydrogen peroxide most likely originates from the specific coordination number (5) and geometry (square-pyramidal) of the Ti atoms in this polyanion.

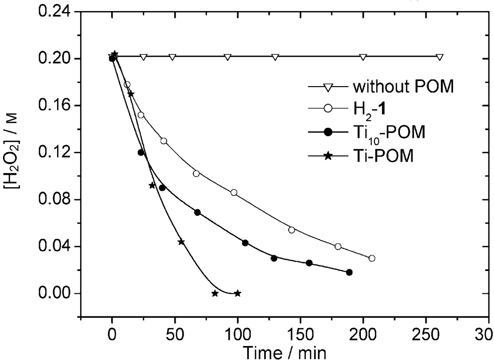


Figure 6. H_2O_2 decomposition in the presence of H_2-**1**, $TBA_7[(PTiW_{11}O_{39})_2OH]$ (Ti-POM) and $TBA_8H_7[\{Ti_3PW_9O_{37}(OH)\}_3(PO_4)]$ (Ti_{10}-POM). Reaction conditions: ([Ti] = 0.008 M, $[H_2O_2]$ = 0.2 M, MeCN, 70 °C).

Conclusions

The dititanium sandwich-type 19-tungstodiarsenate(III) $[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]^{8-}$ (**1**) was found to be highly active in the oxidation of organic substrates with aqueous hydrogen peroxide as oxidant. In the oxidation of alkenes, the reaction selectivity is strongly affected by the amount of protons in the cationic part of **1**, which can be altered by pH of precipitation of TBA-salt. Selectivities of almost 100% for alkene epoxidation can be achieved by using $H_{0.5}$-**1** under optimal reaction conditions. In the presence of H_2-**1**, epoxides readily transform into diols, α-hydroxyketones, and C–C bond-cleavage products. The allylic oxidation products do not form even at the initial stages of the reaction. Vicinal diols produce α-hydroxyketones and (di)carboxylic acids as the main oxidation products in the presence of H_2-**1**, whereas secondary alcohols yield ketones with very high selectivity. Primary alcohols produce aldehydes and the corresponding carboxylic acids. The catalytic performance of **1** contrasts significantly with that of mono- and polysubstituted POMs containing Ti atoms in an octahedral environment, for which homolytic oxidation mechanisms mostly operate. Hence, only **1** revealed an ability to activate H_2O_2 and to oxidize organic substrates by heterolytic oxidation mechanisms. We believe that this unique feature of **1** is related to the specific coordination number (5) and geometry (square-pyramidal) of the Ti atoms in this polyanion. Spectroscopic and theoretical studies are in progress to get insight into the nature of the active peroxo species responsible for the high activity and selectivity of **1** in H_2O_2-based oxidations.

Experimental Section

Materials: Acetonitrile, cyclohexene (CyH), cyclohexene oxide, *trans*-1,2-cyclohexanediol, and other organic substrates were purchased from Aldrich. Tetra-*n*-butylammonium hydroxide, TBAOH, (0.8 M in MeOH, Aldrich) was titrated with 1.0 M HCl. H_2O_2 (30 wt.-% in water) was titrated iodometrically prior to use. All the reactants were the best-available reagent grade and used without purification.

Synthesis: An aqueous solution of the K salt of **1** was prepared according to a published procedure.[8] The TBA salts of **1**, $TBA_{5.5}K_{0.5}H_2$-**1**, and $TBA_{5.5}Na_{1.5}K_{0.5}H_{0.5}$-**1** were prepared by adding an excess amount of solid TBABr to a freshly synthesized solution of **1** at pH 2.1 and 2.7, respectively. In the latter case, the pH was adjusted by using NaOH. The resulting white precipitates were isolated by filtration, washed with H_2O, and then dried in an oven at 50 °C. Potentiometric titration with 0.8 M methanolic solution of TBAOH in MeCN indicated the presence of 2 and 0.5 acid protons in $TBA_{5.5}K_{0.5}H_2$-**1** and $TBA_{5.5}Na_{1.5}K_{0.5}H_{0.5}$-**1**. Thermogravimetric analysis (TGA) supported the presence of 5.5 TBA cations per formula unit in both compounds. $TBA_{5.5}K_{0.5}H_2[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]$ (6217.6) calcd. C 16.99, H 3.31, As 2.41, K 0.31, N 1.24, Ti 1.54, W 56.2; found C 17.48, H 3.45, As 2.52, K 0.25, N 1.21, Ti 1.37, W 60.2. $TBA_{5.5}Na_{1.5}K_{0.5}H_{0.5}[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]$ (6250.6): calcd. C 16.99, H 3.31, As 2.40, K 0.31, N 1.24, Ti 1.53, W 55.9; found C 17.48, H 3.45, As 2.55, K 0.25, N 1.21, Ti 1.37, W 59.5. The IR spectra of $TBA_{5.5}K_{0.5}H_2$-**1** and $TBA_{5.5}Na_{1.5}K_{0.5}H_{0.5}$-**1** were identical (KBr, 1200–550): $\tilde{\nu}$ = 966 ($W–O_d$), 894 ($W–O_b–W$), 813 (Ti–O), 767 ($W–O_c–W$), 718 ($W_e–O$) cm^{-1}.

The Ti-free analogue $[As_2W_{21}O_{69}]^{6-}$ (**2**) was synthesized according to a published procedure.[14] The TBA salt of $[As_2W_{21}O_{69}]^{6-}$ (TBA-**2**) was obtained by precipitation with TBABr. IR (KBr, 1200–550): $\tilde{\nu}$ = 965, 891, 770, 721 cm^{-1}.

Synthesis of $TBA_7[(PTiW_{11}O_{39})_2OH]$ (Ti-POM) was performed as described earlier (^{31}P NMR in dry MeCN: –12.76 ppm).[7a] Polyoxometalates $TBA_8H_7[\{Ti_3PW_9O_{37}(OH)\}_3(PO_4)]$ (Ti_9-POM) and $TBA_{17}[(\alpha\text{-}Ti_3SiW_9O_{37}OH)_3\{TiO_3(OH_2)_3\}]$ (Ti_{10}-POM) were prepared following the procedures described earlier[13h] using TBABr to precipitate TBA salts. The amount of TBA cations was determined by TGA.

The TBA salt of the Venturello complex $TBA_3\{PO_4[W(O)(O_2)_2]_4\}$ (TBA-PW_4) was prepared by the peroxide-mediated decomposition of $H_3PW_{12}O_{40}$ following a slightly modified published procedure.[10]

Catalytic Oxidations: The catalytic oxidations were carried out in temperature-controlled glass vessels at 50–70 °C in MeCN solution. Samples were taken during the reaction course by a syringe, and the reaction products were identified by GC–MS and GC by using reference compounds. Substrate conversions and product yields were quantified by GC using biphenyl or dodecane as internal standards. Adipic acid was determined as its methyl ester after addition of α-methyl-α-nitrosourea into the aliquot.[15] The TOF (turnover frequencies) values were determined from the initial rates of substrate consumption. After the reaction, water was added to the reaction mixture, the catalyst was separated by centrifugation, washed with water, dried in air, and checked by IR. H_2O_2 concentration was determined by iodometric titration.

Instrumentation: GC analyses were performed using a gas chromatograph "Tsvet-500" equipped with a flame ionization detector and a quartz capillary column (30 m × 0.25 mm) Agilent DB-5MS. GC–MS analyses were carried out by using a gas chromatograph Agilent 6890 (quartz capillary column 30 m × 0.25 mm/HP-5 ms) equipped with a quadrupole mass-selective detector Agilent MSD 5973. FTIR spectra were recorded in KBr pellets containing 2 mg of a sample and 500 mg of KBr with a Bomem-MB-102 spectrometer or a Nicolet Avatar spectrometer. Thermogravimetric analysis was carried out with a TA Instrument SDT Q600 thermobalance with a 100 mL min^{-1} flow of nitrogen; the temperature was ramped from 20 to 800 °C at a rate of 5 °C min^{-1}. Potentiometric titration was performed using a Mettler-Toledo 320 pH meter.

Supporting Information (see footnote on the first page of this article): TGA data for TBA-**1** and kinetic profiles for oxidation reactions.

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