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Calcium tungstate: a convenient recoverable catalyst for hydrogen peroxide oxidation[†]

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Calcium tungstate was found to be an excellent catalyst for large scale "green" oxidations of organic substrates (amines, alkenes, alcohols, sulfides) with hydrogen peroxide. It displays the unusual dual characteristics of producing a soluble pertungstate species, allowing for homogeneous reaction conditions, but then precipitating, unchanged, at the end of the oxidation. These qualities allow for easy catalyst recovery and minimal waste stream generation for large scale application.

Introduction

Oxidations using hydrogen peroxide/tungsten catalyst combinations have attracted considerable attention because they offer environmentally clean methods of oxidizing various organic substrates.¹ For large industrial scale application, catalyst recovery and catalyst reuse become significant issues. These issues have prompted a few reports of heterogeneous tungsten catalysts such as mesoporous solid supported WO₃-nanoparticles,² insoluble polyoxytungstates,³ basic phosphotungstates,⁴ and immobilized peroxotungstate.⁵ A drawback to their use is related to mass transfer problems and mechanical mixing due to the heterogeneous nature of the catalyst. This problem would be exacerbated as the scale of such oxidations increases.

Ideally, for large scale batch reactions, the catalyst would be homogeneous during the early stage of the reaction, then become heterogeneous only at the end of the oxidation. We now report herein that $CaWO_4$ offers this dual behavior of generating a homogeneous catalyst system at high hydrogen peroxide levels, but re-precipitating at very low levels allowing for easy recovery. We demonstrate the application of this oxidation catalyst to a variety of substrates including, amines,

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alcohols, alkenes and sulfides. Furthermore, the $CaWO_4$ is unchanged under even in the presence of stabilizing cofactors⁶ and can be recovered by simple filtration.

Results and discussion

When CaWO₄ is suspended in 30% H₂O₂ at >45 °C, the colorless solid slowly dissolves resulting in a homogeneous solution whose yellow color is indicative of the formation of an active pertungstate⁷ species. Also, this solution of CaWO₄/H₂O₂ has an identical UV-Visible spectrum (1 mM, λ_{max} = 335 nm) to that of Na₂WO₄/H₂O₂. The CaWO₄/H₂O₂ combination remains homogeneous at high peroxide concentrations (1-35%), but the CaWO₄ readily precipitates when the peroxide level drops below this level. In the absence of an oxidizable substrate, these solutions exhibit slow, and mildly, exothermic decomposition of hydrogen peroxide. Maintaining the temperature \leq 65 °C leads to a loss of only 2.3% peroxide content after 8 h. Above this temperature, the nonproductive decomposition significantly increases, but can be minimized by the addition of stabilizing agents such as 9,10-phenanthroline. The stabilizer allows for oxidations to be carried out for periods of 24 h or more. The phenanthroline also precipitates at room temperature along with the CaWO₄ when the peroxide has been exhausted to below 1%.

Table 1 shows that various substrates, including amines,⁸ alcohols,⁹ alkenes,¹⁰ and sulfides,¹¹ are readily oxidized using only 0.5–1.0 mol% of catalyst. Oxidations using the more conventional Na₂WO₄ (Table 1; entries 2, 3, 5–7) gave no significant improvement over CaWO₄ with respect to time, temperature and yield. Where appropriate, the catalyst may be used with cosolvents such as *t*-butyl alcohol or methanol to facilitate solubility of the substrate. At the end of each reaction, the excess hydrogen peroxide was decomposed by increasing the temperature to approximately 95–100 °C. When the peroxide level drops below 1%, CaWO₄ precipitates unchanged from the mixture.

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Table 1 Oxidation of compounds with 30% H_2O_2 and $CaWO_4$ ¹²

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	Substrate ^a	Product	30% H ₂ O ₂ (mole equiv.)	CaWO (mole equiv.)	Na ₂ WO ₄ (mole equiv.)	Temp (°C)	Time (h)	Yield ^f (%)
1	NH ₂	NO ₂	4.0	0.005		50°	0.5	95
2	NH ₂	NO ₂	4.0^{b}		0.01	50°	0.5	93
				0.01		50°	0.5	92
	CH3	CH ₃				50°	0.5	92
						50°	0.5	92
						50°	0.5	92
						50°	0.5	92
		0 1	4.0	0.01		50°	0.5	82
3	NHa	NO ₂			0.01	50°	0.5	85
4	a a	\sim '	4.0^{c}	0.01		70°	6	98^b
	b	$\int \sum_{n}$	4.0	0.01		70°	6	98
	L L		4.0	0.01		70°	6	99
	4 ~ •	\sim	4.0	0.01		70°	6	98
	u		4.0	0.01		70°	6	99
5	٨	٨	$2 0^d$	0.01		500	4	0.0
5	Λ	Λο	3.0	0.01	0.01	500	4	90
	A	A P			0.01	50	4	30
6	ОН	0	$4.0^{c,e}$		0.01	75°	16	91
0		Ĩ		0.01	0101	75°	20	92
	\wedge			0.01		75°	20	92
		$\left(\right)$		0.01		75°	20	92
				0.01		75°	20	91
	\sim			0.01		75°	20	91
7	ОН	0				75°	20	92
	Ī	Ĩ	5.0	0.01		65°	8	76
	\searrow	\backslash			0.01	65°	8	78
0	~ / ~	\sim	5.0	0.01		650	4	70
0	ОН	Оон	5.0	0.01		05-	4	78
9	s	O ₂ S	2.0	0.01		25°	0.5	97
10	s	O ₂ S	2.0	0.01		25°	0.5	96

^{*a*} All reactions were run on a 0.1 mole scale unless otherwise indicated. ^{*b*} Run on 2.3 mol scale. ^{*c*} An equal volume of methanol cosolvent was used. ^{*d*} An equal volume *t*-butanol cosolvent was used. ^{*e*} 9,10-Phenanthroline (1 mol%) stabilizer was added. ^{*f*} Isolated yields.

The catalyst is easily recovered by filtration, and we have demonstrated that the recovered catalyst shows no loss in activity after five cycles of oxidation (*e.g.* Table 1; 2, 4, 6). Additionally, no difference in appearance or IR spectrum of the catalyst was noted after these repeated cycles.

By contrast to the CaWO₄/H₂O₂ system, MgWO₄ displayed substantially higher water solubility making it unattractive for efficient recovery. We also observed that BaWO₄, ZnWO₄ and Zr(WO₄)₂ catalyzed various oxidations, but these were comple-

tely heterogeneous throughout the reaction, and their tendency to rapidly, nonproductively decompose hydrogen peroxide solutions makes them synthetically useless.

The oxidation of amines¹² proceeded rapidly at ambient temperature to afford high yields of the corresponding nitro products. The nitro product could be separated as an insoluble organic phase, and the catalyst recovered from the aqueous residue by filtration. As an example of the benefit of CaWO₄ for large scale batch oxidations, we applied this method to the oxidation of ~2 lbs (1 kg) of *p*-toluidine (entry 2) and obtained a 92% yield of *p*-nitro-toluene and with a >99% recovery of the catalyst. The course of the amine oxidations proceeds *via* both the hydroxylamino and nitroso intermediates which could be easily detected by thin-layer chromatography. Therefore, slow addition of the amine to the homogeneous $H_2O_2/CaWO_4$ mixture was important in suppressing the formation of azoand/or azoxy by-products which often accompany these oxidations. By carefully monitoring the reaction progress, we could consistently obtain high yields of the desired nitro compounds.

In the case of alkene oxidations¹³ (entries 4 & 5), methanol or *t*-butanol was employed as a cosolvent to facilitate solubilization of the substrate. The epoxidation of norbornene (entry 5) gave >99% of the expected *exo*-epoxide, as was determined by ¹H & ¹³C spectra.¹⁴ Additionally, we did not observe the formation of norborneol, or norbornanone which has been observed with other hydrogen peroxide/catalyst systems.^{10c,15}

As previously mentioned, temperature plays a significant role in determining the final yield of product due to the competing nonproductive decomposition of H₂O₂ by this catalyst. This is particularly important for substrates, such as alcohols, that are oxidized slowly by hydrogen peroxide systems. Alcohol oxidations were conducted between 65-70 °C to avoid increasing the rate of nonproductive decomposition of hydrogen peroxide which occurs at higher temperatures. However, it is possible to employ reaction temperatures as high as 85-90 °C by adding stabilizing agents such as 9,10-phen-anthroline. The stabilizing 9,10-phenanthroline, being water insoluble at room temperature, was recovered along with the catalyst. We did not observe any change in the recovered CaWO4 when used in combination with this stabilizer. We used this combination for the oxidation of cyclohexanol due to the sluggish rate of conversion to cyclohexanone when compared with other types of substrates.

The oxidation of 3-pentanol (entry 7) proceeded as expected to afford 3-pentanone in good yield. The oxidation of geraniol (entry 8) gave mostly the 2,3-epoxide in 78% yield, but was complicated by approximately 20% hydrolysis of the epoxide to afford the corresponding 1,2,3-triol.¹⁶ Notwithstanding, oxidation of the allylic alcohol double bound occurred preferentially with the formation of only trace amounts of the 2,3/6,7-bis-epoxide.

The oxidation of sulfides (entries 9 & 10) with 2.0 equivalents of 30% H_2O_2 at 25 °C for 0.5 h gave, as expected, high yields of the corresponding sulfones. Interestingly, the use of only 1.0 equiv. of 30% H_2O_2 did not give high yields of sulfoxides.¹⁶ Under these conditions, we obtained ~45–50% yields of sulfones and only small amounts (<5%) of sulfoxides, the remaining being unreacted sulfide. Attempts to suppress the over-oxidation to obtain only sulfoxide by employing slow addition of peroxide, reducing the amount of catalyst, or decreasing the temperature to 0 °C, were not successful. The reasons for these results remain unclear and may have implications regarding the nature of the peroxotungstate species in solution. We are examining this particular reaction in more detail.

Conclusion

As "green" oxidation methods gain popularity for commercial production, the need for homogeneous, but easily recovered, catalysts becomes paramount. Our current work demonstrates the value of using $CaWO_4$ as the catalyst of choice for large scale, batch mode oxidations. It is sufficiently broad in scope to oxidize various classes of organic substrates. This material is readily available, inexpensive and provides technical simplicity for recovery thus minimizing waste stream generation and handling. We are presently using this catalytic system for oxidizing multi-pound quantities of heterocyclic amines toward commercial production of heterocyclic nitro analogues.

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- 12 General procedure for the oxidation of amines. To 2.2 L of 30% H₂O₂ (12.4 mol) was added 3.4 g (0.12 mol) of CaWO₄. The mixture was warmed to 45 °C and the solid dissolved to produce a yellow solution. Then was added dropwise over a 30 min period, 1 kg (2.3 mol) of *p*-toluidine while maintaining the temperature below 50 °C. After complete addition, the mixture was warmed to 95 °C for about 1 h at which point the yellow color of the aqueous phase disappeared and the colorless CaWO₄ precipitated. The mixture was separated and distilled to afford, 1.1 kg (92%) of *p*-nitrotoluene, bp 100–101 °C, whose ¹H-NMR and IR

spectra were consistent with reported data. The aqueous phase was filtered and the $CaWO_4$ (3.4 g, >99%+) was recovered.

- 13 General procedure for the oxidation of alkenes. To 9.0 mL of 30% H₂O₂ (80 mmol) and 9 mL of t-butanol was added 0.057 g (0.2 mmol) of CaWO₄. The mixture was warmed to 45 °C and the solid dissolved to produce a yellow solution. Then was added 1.88 g (20 mmol) of norbornene and the mixture was stirred vigorously for 4 h at 65 °C. The mixture was then warmed to 95 °C for approximately 10 min at which point the yellow color of the aqueous phase disappeared and the colorless CaWO₄ precipitated. The mixture was cooled to room temperature, and organic product was extracted with ethyl acetate. The organic phase was dried over anhydrous MgSO₄, and evaporated to afford 2.15 g (98%) of exo-2,3epoxynorbornane. ¹H-NMR (CDCl₃) δ 0.92 (2H, d), 1.32 (4H, d), 2.20 (2H, br s) and 3.18 (2H, br s). Decoupled ¹³C-NMR (CDCl₃) δ 24.4, 25.5, 34.2, 51.0. The aqueous phase was filtered and the CaWO4 (3.4 g, 99%+) was recovered.
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