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Room-Temperature Catalytic Oxidation of Alcohols with the Polyoxovanadate Salt $Cs_5(V_{14}As_8O_{42}Cl)$

McKenzie L. Campbell, Dino Sulejmanovic, Jacqueline B. Schiller, Emily M. Turner, Shiou-Jyh Hwu*, Daniel C. Whitehead*

Department of Chemistry, Clemson University, Clemson, SC, 29634 USA

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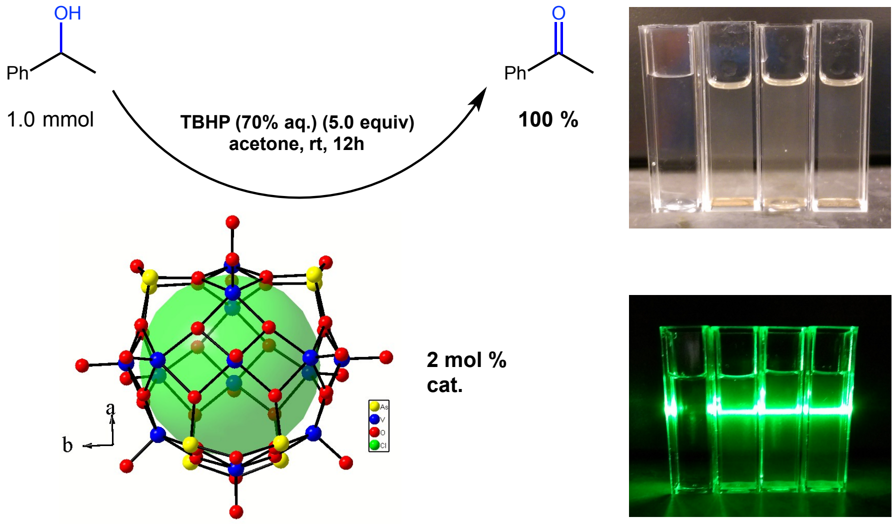
Abstract. While many known methods for oxidation mediated by polyoxometalates (POMs) employ environmentally friendly co-oxidants, they tend to employ large catalyst loadings (*e.g.* 40 mol %) and costly high reaction temperatures (~90-135 ˚C) that potentially contribute to the degradation of the catalyst and reduce their effectiveness. Herein, we present some initial results demonstrating a room temperature catalytic oxidation using the reduced salt-inclusion polyoxometalate, $Cs_5(V_{14}As_8O_{42}Cl)$, that contains polyoxovanadate (POV) clusters as an efficient catalyst (*e.g.*, 2 mol%) in the transformation of secondary alcohols to their corresponding ketones in very good to quantitative yields. Further, the catalyst can be suspended on celite and recycled.



INTRODUCTION:

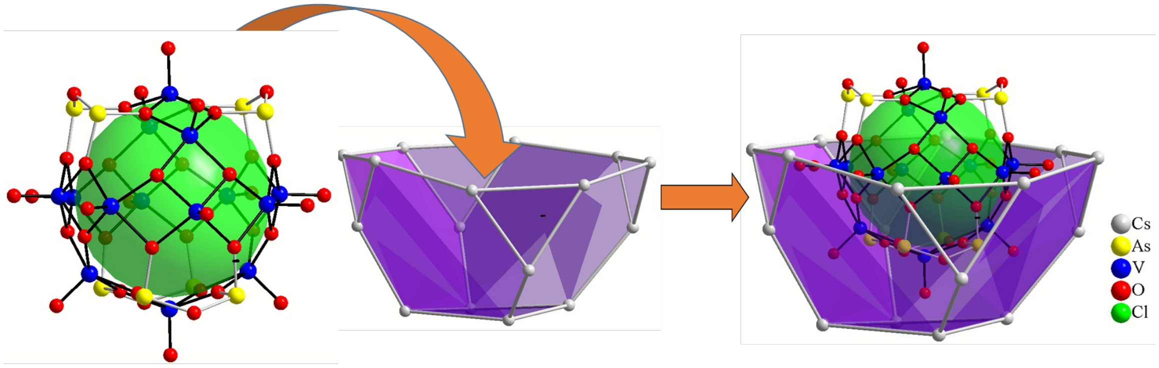
Polyoxometalates (POMs) have been used rather extensively in the past few decades as catalysts in alcohol oxidations to aldehydes and ketones.[1–5] Of the catalysts used in these transformations, reports employing Keggin type POMs are more prevalent, while Wells-Dawson scaffolds are employed to a lesser extent.[6, 7] Our work is focused on a complementary approach that exploits the use of relatively unexplored reduced polyoxovanadates (POVs) in catalytic oxidation transformations.

Currently, heteropolyoxotungstates and heteropolyoxomolybdates are among the most frequently utilized POM catalysts due to their strong Lewis acidic properties and rich redox capabilities.[8, 9] For example, Zhou and co-workers describe the dilacunary silicotungstate, $K_8[\gamma\text{-}SiW_8O_{36}]\cdot 13H_2O$, as a precatalyst with 5.0 equiv of 30% aq. H_2O_2 as the co-oxidant for the selective oxidation of activated benzylic alcohols as well as nonactivated aliphatic alcohols in greater than 90% yields. An elevated reaction temperature of 90 ˚C using an economically feasible 0.67 mol% catalyst loading converted most substrates investigated with the more hydrophobic aliphatic alcohols requiring the use of a phase-transfer catalyst.[10] A related Keggin type polyoxomolybdate, $H_xPMo_{12}O_{40} \subset H_4Mo_{72}Fe_{30}(CH_3COO)_{15}O_{245}$ behaves as a water soluble nanocapsule in the selective oxidation of alcohols to their corresponding aldehydes and ketones using 0.1 mol% of the POM catalyst at 45 ˚C.[11] Again this transformation employed 5.0 equiv of 30% aq. H_2O_2 as the co-oxidant. Benzylic alcohols containing *para*-, *meta*-, and *ortho*- substituted electron withdrawing and donating groups, testing for both electronic and steric effects, returned quantitative yields after varied reaction times determined by GC analysis. Nonactivated cyclic and aliphatic primary alcohols also gave quantitative yields under assorted reaction times.

Work showing increased catalytic efficiency and oxidative selectivity with tailored incorporation of vanadium-metal ions (n= 0, 1, 2, 3) into the molybdophosphoric acid (MPA) Keggin structure Cs_2MPAV_n/TiO_2 shifted catalytic activation from acid-controlled to redox-dominated oxidative processes displayed in the selective formation of benzaldehyde with increased vanadium substitution.[12] A major limitation of the catalyst system investigated is the decreased conversion of benzyl alcohol starting material with increasing vanadium incorporation.[12] Extending the idea of enhanced redox-capable POM catalysts through increased vanadium substitution, a recent literature review cites vanadium-substituted POMs, *i.e. hetero-transition-metal POMs*,[13,14] as the most extensively explored transition metal POM in the oxidation of alcohols to aldehydes and ketones[.15] Unlike the commonly explored Keggin and Dawson POMs, including vanadium-substituted POMs, POVs featuring exclusively vanadium as the transition-metal cations in the POM framework, as in our catalyst structure, are largely unexplored for catalytic reactions.[16]

A few notable examples of vanadium-substiututed POM catalysts do promote selective aerobic oxidations; such as $H_5PV_2Mo_{10}O_{40}$ in the oxidation of benzyl alcohol to benzaldehyde studied in a reaction medium comprised of either polyethylene glycol[17] or supercritical carbon dioxide.[18] While many of these reactions feature high selectivity, acceptable yields, and utilize environmentally benign co-oxidants, some reports of POVs requiring co-catalysts may reduce the practical utility of these methods.[9c,19] POVs were reported to participate in the catalytic oxidation of alcohols through oxygen transfer from sulfoxides, but only in the presence of DMSO as the solvent.[20, 21] The most striking limitations of current oxidation methods promoted by POVs include high catalyst loadings (*e.g.* 40 mol % in some cases)[12,22] and reaction temperatures ranging from 90 to 135 ˚C.[20, 23, 24] Such high temperatures may lead to the catalyst overheating, termed cooking, which results in concomitant catalyst deactivation.[15, 24, 25]

Our interest in exploring the catalytic properties of the reduced POVs described herein was sparked by the significantly different features of these materials compared to the commonly used POM catalysts. Given their unique electronic state (*i.e.* V^{4+}) and high negative charge, these POVs are more basic than their fully oxidized counterparts and as such would likely be efficient at proton abstraction from organic alcohol substrates, which could for instance accelerate association of the substrate with the catalyst. Specifically, the composition of the reduced POV that is the subject of the present study, $Cs_5(V_{14}As_8O_{42}Cl)$, features $(V_{14}As_8O_{42}Cl)^{5-}$ clusters in which fourteen square pyramidal vanadium sites are reduced, *i.e.* V^{4+}. The crystal structure of $Cs_5(V_{14}As_8O_{42}Cl)$ is manifested through the artwork shown in Fig. 1, where the mixed



$(V_{14}As_8O_{42}Cl)^{5-}$ cluster

Cs^+-based half SOD β-cage

$(V_{14}As_8O_{42}Cl)^{5-}$ inside a Cs half-cage in $Cs_5(V_{14}As_8O_{42}Cl)$ compound

Figure 1 Representation of the $(V_{14}As_8O_{42}Cl)^{5-}$ cluster (left) residing in the Cs^+-based half SOD β-cage (midle) to form a partial structure of the composite lattice (right) of the water-soluble $Cs_5(V_{14}As_8O_{42}Cl)$.

arsenic(III)-POV cluster $[V^{4+}{}_{14}As^{3+}{}_{8}O_{42}Cl]^{5-}$ is residing in the Cs^+-based half sodalite (SOD) β-cage. The compound is soluble in water, due to the ionic interaction at the interface of this composite framework, and it forms micron-size $(V_{14}As_8O_{42}Cl)^{5-}$ aggregates in aqueous solution (*vide infra*). Each of the catalytically active vanadium atomic sites features apical vanadyl (V^{4+}=O) short oxygen bonds pointing away from the center of the cluster.

With regards to the synthesis of these POV catalysts, we have been employing the newly emerged salt-inclusion chemistry (*SIC*), which has been developed in our laboratories to yield a collection of novel composite materials featuring an integrated composite lattice of ionic salts and covalent metal oxide frameworks. Numerous studies have shown *SIC* to be an alternative method for the creation of new porous materials *via* salt-inclusion, solid-state methods. The salt, like the organic cation in their zeolite and zeolite-like counterparts, serves as a template and due to the weak interactions at the interface between these two chemically dissimilar lattices, the incorporated salt can be removed by washing with water.[26, 27] While the utility of *SIC* has been demonstrated in the synthesis of unusually large porous frameworks (~2 nm in pore dimension) using molten-salt synthesis, it has been reiterated recently in the synthesis of reduced water-soluble salt-inclusion solids containing polyoxometalate clusters.[28-30] These polyoxometalate salts are soluble in water to generate finely dispersed nanoclusters featuring a covalent metal oxide framework with counter cations surrounding the cluster.

The study presented herein details the exploration of several water-soluble, reduced POV salts synthesized by means of *SIC* as catalysts for the selective oxidation of 2° alcohols. Ultimately, we discovered that catalytic loadings of the polyoxovanadate

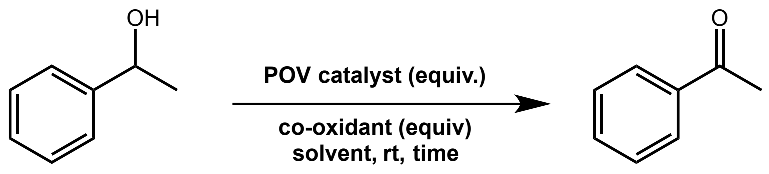
$Cs_5(V_{14}As_8O_{42}Cl)$ efficiently promotes the oxidation of 2° alcohols in the presence of *tert*-butyl hydrogen peroxide (*t*BuOOH) as the terminal co-oxidant. Our optimal conditions proceed at room temperature thus obviating possible thermal degradation of the POV catalyst. The transformation proceeds with good to excellent yields over the course of 12 to 48 h depending upon the particular substrate.

RESULTS & DISCUSSION:

We elected to evaluate the catalytic potential of three POV catalysts that were prepared by the salt-inclusion method: $Cs_{3.5}Na_{1.47}(V_5O_9)(AsO_4)_2Cl_{2.33}$ (**1**),[28] $Cs_5(V_{14}As_8O_{42}Cl)$ (**2**),[29] and $Cs_{11}Na_3Cl_5(V_{15}O_{36}Cl)$ (**3**).[30] These catalysts were prepared analogous to the method described below for $Cs_5(V_{14}As_8O_{42}Cl)$. POV **2** was synthesized by employing a slightly modified stoichiometric reaction compared to previously reported conditions.[29] Briefly, CsCl, Cs_3VO_4, As_2O_3, V_2O_3 and VO_2 were loaded in a 3:4:12:2:34 molar ratio (0.75 g total mass), respectively, and employing procedures described in literature returned a dark brown polycrystalline powder that was ground and was subjected to powder X-ray diffraction to confirm the phase formation (Figure S1).

For our initial investigation, we probed the ability of catalysts **1-3** (0.05 equiv) to promote the oxidation of 1-phenylethanol (**4**) to acetophenone (**5**) in water in the presence of 1.5 equiv of aqueous *t*BuOOH as a terminal co-oxidant. The reactions were conducted at room temperature for 24 h and monitored by GC in triplicate (Table 1, entries 1-3). Product GC peak areas were correlated to yield by means of standard curves (see SI). The yields appearing in Table 1 are averages of triplicate runs. Among

Table 1 Optimization of catalytic oxidation of 1-phenylethanol using 2 mol % catalytic $Cs_5(V_{14}As_8O_{42}Cl)$



4, 0.1 mmol

5

Entry	Catalyst (equiv)	Solvent [M]^{a}	Co-oxidant (equiv)	Time	Yield (%)
1	$Cs_{3.5}Na_{1.47}(V_5O_9)(AsO_4)_2Cl_{2.33}$ (0.05) (**1**)	H_2O [0.3]	TBHP (aq.)^{b} (1.5)	24h	28% +/- 4
2	$Cs_5(V_{14}As_8O_{42}Cl)$ (0.05) (**2**)	H_2O [0.3]	TBHP (aq.) (1.5)	24h	36% +/- 8
3	$Cs_{11}Na_3Cl_5(V_{15}O_{36}Cl)$ (0.05) (**3**)	H_2O [0.3]	TBHP (aq.) (1.5)	24h	22% +/- 2
4	none	H_2O [0.3]	TBHP (aq.) (1.5)	24h	15% +/- 3
5	$Cs_5(V_{14}As_8O_{42}Cl)$ (0.05)	H_2O [0.3]	TBHP (aq.) (5.0)	24h	62% +/- 13
6	$Cs_5(V_{14}As_8O_{42}Cl)$ (0.05)	H_2O [0.3]	H_2O_2 (aq.)^{c} (5.0)	24h	7% +/- 3
7	$Cs_5(V_{14}As_8O_{42}Cl)$ (0.05)	H_2O [0.3]	oxone (5.0)	24h	13% +/- 0
8	$Cs_5(V_{14}As_8O_{42}Cl)$ (0.05)	H_2O [0.3]	UHP (5.0)	24h	5% +/- 1
9	$Cs_5(V_{14}As_8O_{42}Cl)$ (0.05)	---	TBHP (aq.) (5.0)	24h	60% +/- 8
10	**$Cs_5(V_{14}As_8O_{42}Cl)$ (0.02)**	**acetone [0.25]**	**TBHP (aq.) (5.0)**	**12h**	**100% +/- 3**
11	$Cs_5(V_{14}As_8O_{42}Cl)$ (0.02)	acetone [0.25]	TBHP (aq.) (1.5)	12h	87% +/- 5
12	$Cs_5(V_{14}As_8O_{42}Cl)$ (0.02)	acetone [0.25]	TBHP (aq.) (3.0)	12h	95% +/- 2
13	$Cs_5(V_{14}As_8O_{42}Cl)$ (0.01)	acetone [0.25]	TBHP (aq.) (5.0)	12h	62% +/- 4
14	$Cs_5(V_{14}As_8O_{42}Cl)$ (0.005)	acetone [0.25]	TBHP (aq.) (5.0)	12h	47% +/- 2
15	$Cs_5(V_{14}As_8O_{42}Cl)$ (0.02)	acetone [0.25]	H_2O^{d}	12h	7% +/- 0
16	$Cs_5(V_{14}As_8O_{42}Cl)$ (0.02)	acetone [0.25]	none	12h	7% +/- 0
17^{e}	$Cs_5(V_{14}As_8O_{42}Cl)$ (0.02)	acetone [0.25]	TBHP (aq.) (5.0)	12h	100% +/- 1
18^{f}	$Cs_5(V_{14}As_8O_{42}Cl)$ (0.02)	acetone [0.25]	none	12h	6% +/- 2

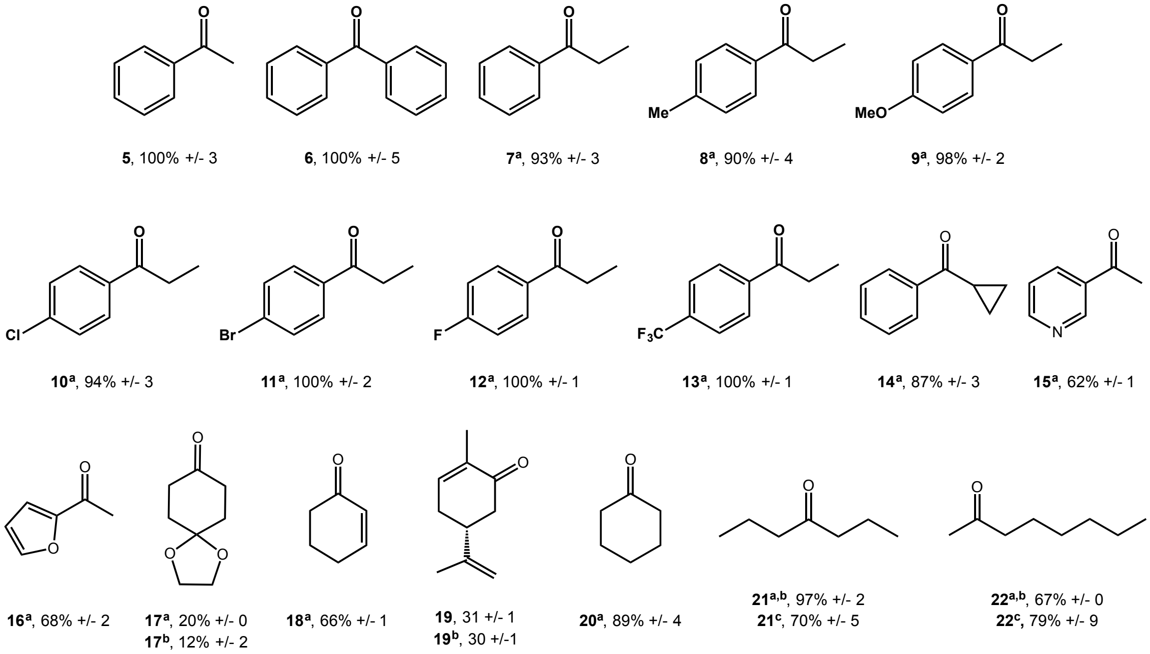
[a] [M]=(0.1 mmol starting material / x mL solvent). [b] TBHP (aq.) denotes a 70% aq solution of TBHP empolyed as a co-oxidant. [c] H_2O_2 (aq.) denotes a 30% aq solution of H_2O_2 empolyed as a co-oxidant. [d] Equal volume to TBHP. [e] Ran under N_2. [f] Ran under O_2 balloon.

the three POV catalysts, $Cs_5(V_{14}As_8O_{42}Cl)$ (**2**, entry 2) returned the desired product in 36% yield. In all cases, the POV catalysts outperformed the uncatalyzed background reaction mediated by aqueous *t*BuOOH alone (15% yield, entry 4). Based on these initial results, we elected to pursue the optimization of the reaction catalyzed by $Cs_5(V_{14}As_8O_{42}Cl)$ (**2**).

Increasing the loading of the co-oxidant to 5 equiv led to an increase in yield to 62% of **5** (entry 5). Other common terminal co-oxidants, including aqueous hydrogen peroxide, Oxone®, and urea-hydrogen peroxide complex (UHP) were inferior, returning

5 in 7%, 15%, and 5% yields, respectively (entries 6-8). Omitting the inclusion of additional water, the ketone was recovered in 60% yield (entry 9). Conducting the reaction in acetone (entry 10) led to a significant breakthrough culminating in an optimized protocol that returned quantitative yields of acetophenone (**5**). Thus, optimized conditions of 2 mol % catalyst loading with 5 equiv of aqueous *t*BuOOH in acetone [0.25 M] for 12 hours at room temperature allowed for 100% conversion of the starting material to product. Lowering the equivalents of co-oxidant as low as 1.5 equiv did not drastically affect the yield of the reaction (entries 11 and 12). Nonetheless, when the loading of $Cs_5(V_{14}As_8O_{42}Cl)$ was reduced below 2 mol %, a large reduction in yield was observed (entries 13 and 14). Given that the reaction proceeded at significantly improved yield in acetone, we wondered whether the POV might merely serve as a coordination site to facilitate the well-known Oppenauer oxidation.[31,32] To rule out a possible Oppenauer-like transformation, we investigated the transformation of **4** to **5** in the presence of catalyst **2** without the addition of co-oxidant (entries 15 and 16). In both acetone and aqueous acetone solvent systems, acetophenone **5** was isolated in 7% yield in the absence of *t*BuOOH. These results clearly indicated that the oxidation of 2-phenylethanol by means of acetone is not favorable in the presence of POV **2** catalyst. Next, we wished to rule out the notion that the observed oxidation might be mediated by atmospheric oxygen. Conducting the reaction under anoxic conditions (*i.e.* under dry N_2) did not reduce the yield of acetophenone product (entry 17). Further, conducting the reaction under an oxygen atmosphere (*i.e.* 1 atm, O_2 balloon) in the absence of *t*BuOOH failed to return acetophenone product (entry 18). Taken together these two results clearly indicate that POV **2** is not catalytically competent under aerobic conditions without the addition of a suitable co-oxidant.

Next, we turned to an investigation of the substrate scope for the transformation of secondary alcohols to their corresponding ketones (Figure 2). Similar to the quantitative conversion of 1-phenylethanol (**4**) to acetophenone (**5**), a number of other substituted benzylic alcohols were readily oxidized to their corresponding ketone products (*i.e.* **6-13**), in excellent yields ranging from 90% to quantitative, regardless of the electronic nature of the arene substituent. The cyclopropyl substituted ketone **14** was recovered in a good yield of 87% while both the heterocyclic pyridine and furyl-activated alcohols gave modest yields of **15** in 62% and **16** in 68%. The successful preparation of ketone **14** from the corresponding cyclopropyl substituted benzyl alcohol is particularly noteworthy. Specifically, the survival of the cyclopropyl moiety in **14** strongly suggests that the process is governed by a two electron oxidation in lieu of a radical mediated process that would likely result in the rupture of the strained cycloalkane to give an allyl radical. The spirocyclic ketone **17** was regrettably recovered in only a 20% yield, and significant decomposition of the substrate was noted with either 2 or 10 mol % catalyst. Oxidation 2-cyclohexenol returned the α,β-unsaturated ketone **18** in a moderate 66% yield, while oxidation of the more sterically encumbered (-)-carveol lead to a disappointing ~30% of carvone **19** with both 2 and 10 mol % catalyst. Unfortunately, the yield could not be further improved with prolonged reaction time. Gratifyingly, the non-activated 2° alcohol cyclohexanol returned cyclohexanone (**20**) in 89% yield. Disappointingly, however, the oxidation of 4-heptanol returned the corresponding ketone **21** in a 70% yield after an impractical 5 day reaction time. Nevertheless, this



5, 100% +/- 3 **6**, 100% +/- 5 **7**[a], 93% +/- 3 **8**[a], 90% +/- 4 **9**[a], 98% +/- 2

10[a], 94% +/- 3 **11**[a], 100% +/- 2 **12**[a], 100% +/- 1 **13**[a], 100% +/- 1 **14**[a], 87% +/- 3 **15**[a], 62% +/- 1

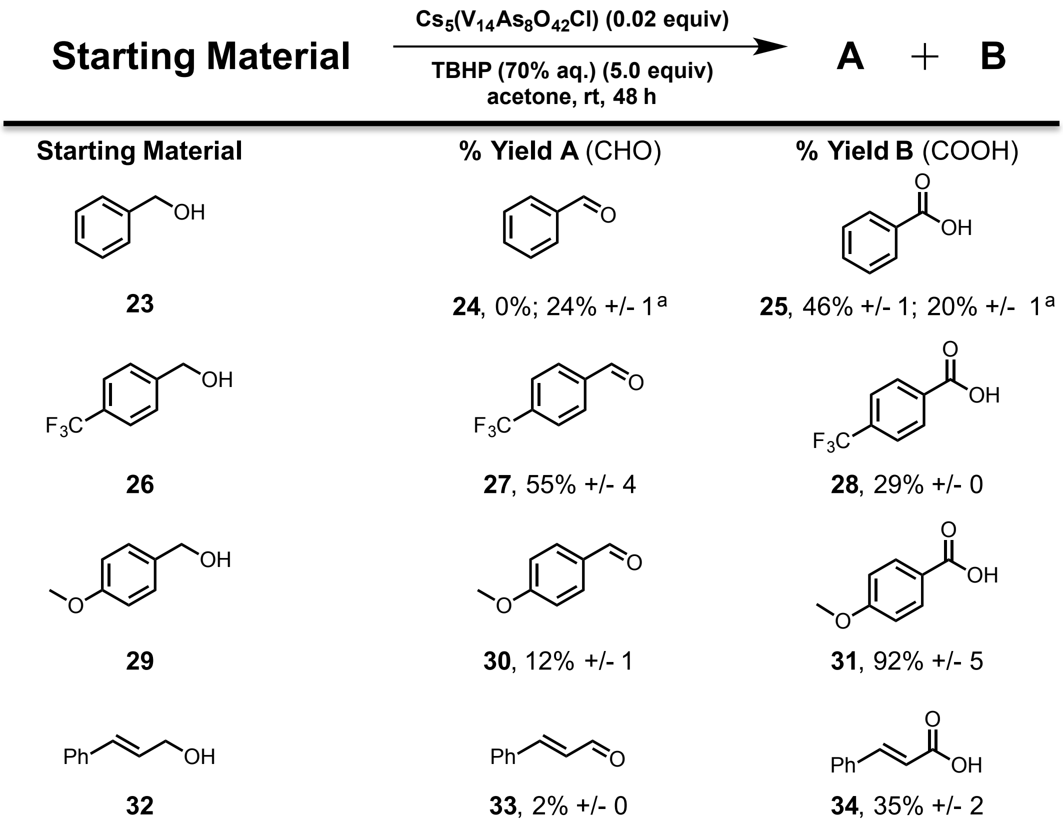
16[a], 68% +/- 2 **17**[a], 20% +/- 0 **17**[b], 12% +/- 2 **18**[a], 66% +/- 1 **19**, 31 +/- 1 **19**[b], 30 +/-1 **20**[a], 89% +/- 4 **21**[a,b], 97% +/- 2 **21**[c], 70% +/- 5 **22**[a,b], 67% +/- 0 **22**[c], 79% +/- 9

[a] 48h reaction time. [b] 10 mol% of POV catalyst used. [c] 5d reaction time.

Figure 2 Substrate Scope for Secondary Alcohols

limitation could be easily overcome by increasing the catalyst loading to 10 mol % for 48 h. Using these optimized conditions for aliphatic ketones, the yield of **20** was raised to 97%. Similarly, 2-octanol returned 67% of the product **22** when using 10 mol % of the POV catalyst. A higher 79% yield of **22** was realized at 2 mol % catalyst loading, albeit after 5 d.

Next, we investigated the oxidation of benzyl alcohol (**23**) (Figure 3), which returned a mixture of 24% benzaldehyde (**24**) and 20% benzoic acid (**25**) after 24 h, along with unreacted starting material. After 72 h, however, no benzaldehyde (**24**) was present via GC analysis and a 46% yield of the benzoic acid (**25**) was recovered. Using benzaldehyde as the starting material under the optimized conditions returned roughly 40% of **25** as well. Substituting the electron withdrawing trifluromethyl group at the *para*-position of the aryl ring (Figure 3, **26**) did enhance conversion of the starting



[a] 24 h reaction time.

Figure 3 Catalytic oxidation of benzyl alcohol and derivatives using 2 mol % $Cs_5(V_{14}As_8O_{42}Cl)$

material. However, substitution of an electron donating *para*-methoxy (*p*-OMe) allowed for a full conversion of the starting alcohol with selectivity for the acid product **31** in a 92% yield while the aldehyde product **30** was recovered in a 12% yield. Cinnamyl alcohol gave 35% conversion to cinnamic acid **34**. Nevertheless, this reaction was accompanied by significant degradation of the starting alcohol. While 1° benzylic systems are subject to oxidation (albeit rather unselectively) under our optimized conditions, attempted conversion of unactivated 1-octanol resulted in complete recovery of starting material. Further, treatment of cyclohexane under the optimized conditions for 72 h returned only 2% cyclohexanone (**20**), and no detectable cyclohexanol, indicating that our standard conditions are not amenable for alkane C-H activation.

Finally, we sought to evaluate whether the catalyst was recyclable. In order to facilitate catalyst recovery, $Cs_5(V_{14}As_8O_{42}Cl)$ was impregnated on celite (see SI for details). In doing so, the catalyst could be readily recovered after a simple filtration step. Figure 4A clearly indicates that the impregnated catalyst can be recycled up to three times in the oxidation of 1-phenylethanol (**4**) without any detectable reduction in isolated yield of acetophenone product on a 1 mmol scale. Nevertheless, further attempts at recycling lead to reduced yields of **5**. Figure 4B illustrates a qualitative light-scattering experiment (using a green laser) that suggests that the $Cs_5(V_{14}As_8O_{42}Cl)$ molecules readily form micron size aggregates in solution. Further, these aggregates are maintained throughout the entire course of the oxidative transformation. This experiment may be taken as qualitative evidence that the POV maintains its structural integrity throughout the catalytic cycle. We are currently pursuing more quantitative

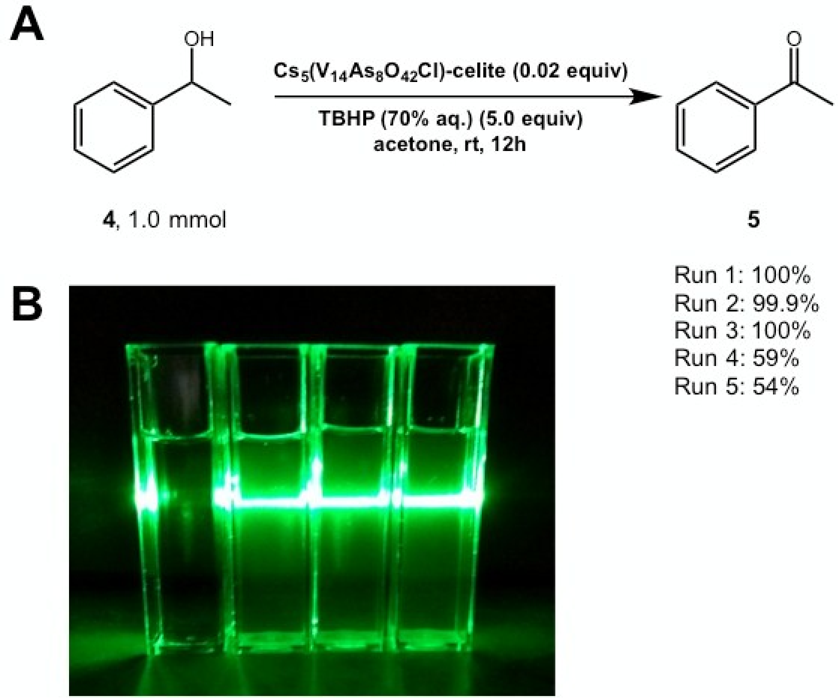


Figure 4 (*a*) Scalable regeneration of $Cs_5(V_{14}As_8O_{42}Cl)$ catalyst isolated and reused consecutively over three reactions. (*b*) Light Scattering experiment showing the aggregation of the $Cs_5V_{14}As_8O_{42}Cl$ clusters in solution from left to right; 1. acetone 2. acetone + POV 3. acetone + POV + substrate + TBHP 4. acetone +POV +substrate + TBHP after 15 minute stir.

means to verify this supposition, and the results of these studies will be reported in due course.

CONCLUSION:

In conclusion, we demonstrated the use of the polyoxovanadate, $Cs_5(V_{14}As_8O_{42}Cl)$ (**2**), as a catalyst for the selective oxidation of secondary alcohols to ketones at room temperature with as little as 2 mol % of the catalyst. The use of finely dispersed POV clusters avoids current limitations with oxidation methods promoted by POVs including high catalyst loadings (*e.g.* 40 mol %)[12, 22] and reaction temperatures ranging from 90 to 135 ˚C.[20, 23, 24] The conversion of 1-phenylethanol (**4**) to acetophenone (**5**) proceeded at quantitative conversions at both a 0.1 and 1.0 mmol scale. Other substituted 2˚ benzylic alcohols were oxidized in good to excellent yields. The catalyst also effectively oxidizes 2˚ alkyl alcohols, albeit at higher (i.e. 10 mol %) catalyst loadings. Further efforts to understand the mechanism of the transformation as well as to expand the synthetic utility of these novel POV catalysts are underway.

Associated Content-

Author Information:
Corresponding Author
*Email: dwhiteh@clemson.edu

Acknowledgements-

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References:

1. I. V. Kozhevnikov, V. E. Taraban'ko and K. I. Matveev, *Doklady Akademii Nauk SSSR*, 1977, **235**, 1347-1349.

2. K. Nomiya, Y. Sugie, T. Miyazaki and M. Miwa, *Polyhedron*, 1986, **5**, 1267-1271.
3. R. Neumann, A. M. Khenkin, D. Juwiler, H. Miller and M. Gara, M., *J. Mol. Catal. A: Chem.*, 1997, **117**, 169-183.
4. H. Firouzabadi, N. Iranpoor and K. Amani, *Synthesis*, 2003, **3**, 408-412.
5. Y. Leng, P. Zhao, M. Zhang and J. Wang, *J. Mol. Catal. A: Chem.*, 2012, **358**, 67-72.
6. (*a*) Y, Kikukawa, K. Yamaguchi and N. Mizuno, *Angew. Chem. Int. Ed.*, 2010, **49**, 6096-6100. (*b*) J. Wang, L. Yan, G. Li, X. Wang, Y. Ding and J. Suo, *Tetrahedron Lett.*, 2005, **46**, 7023-7027. (*c*) P. Tundo, G. P. Romanelli, P. G. Vazquez and F. Arico, *Catal. Commun.*, 2010, **11**, 1181-1184. (*d*) W. Zhao, Y. Zhang, B. Ma, Y. Ding and W. Qiu, *Catal. Commun.*, 2010, **11**, 527-531. (*e*) Y. Ding and W. Zhao, *J. Mol. Catal. A: Chem.*, 2011, **337**, 45-51. (*f*) C. N. Kato, A. Tanabe, S. Negishi, K. Goto and K. Nomiya, *Chem. Lett.*, 2005, **34**, 238-239. (*g*) A. Yokoyama, K. Ohkubo, T. Ishizuka, T. Kojima and S. Fukuzumi, *Dalton Trans.*, 2012, **41**, 10006-10013. (*h*) J. Wang, L. Yan, G. Qian, G. Lv, G. Li, J. Suo and X. Wang, *React. Kinet. Catal. Lett.*, 2007, **91**, 111-118. (*i*) S. Hasannia and B. Yadollahi, *Polyhedron*, 2015, **99**, 260-265. (*j*) S. Pathan and A. Patel, *Catal. Sci. Technol.*, 2014, **4**, 648-656.
7. (*a*) M. R. Farsani, F. Jalilian, B. Yadollahi and H. A. Rudbari, *Polyhedron*, 2014, **76**, 102-107. (*b*) J. H. Choi, J. K. Kim, S. Park, J. H. Song and I. K. Song, *Appl. Catal., A: Gen.*, 2012, **427-428**, 79-84. (*c*) D. R. Park, H. Kim, J. C. Jung, S. H. Lee and I. K. Song, *Res. Chem. Intermed.*, 2008, **34**, 845-851. (*d*) J. H. Choi, T. H. Kang, Y. Bang, J. H. Song and I. K. Song, *Catal. Commun.*, 2014, **55**, 29-33.

(*e*) M. Masteri-Farahani, Gh. R. Najafi, M. Modarres and M. Taghvai-Nakhjiri, *J. Porous Mater.*, 2015, Ahead of Print.

8. (*a*) I. V. Kozhevnikov, *Chem. Rev.*, 1998, **98**, 171-198. (*b*) Y. Ding, W. Zhao, Y. Zhang, B. Ma and W. Qiu, *Reac. Kinet. Mech. Cat.*, 2011, **102**, 85-92. (*c*) M. R. Farsani, E. Assady, F. Jalilian, B. Yadollahi and H. A. Rudbari, *J. Iran Chem. Soc.*, 2015, **12**, 1207-1212. (*d*) M. R. Farsani and B. Yadollahi, *J. Mol. Catal. A: Gen.*, 2014, **392**, 8-15. (*e*) Y. Chen, R. Tan, W. Zheng, Y. Zhang, G. Zhao and D. Yin, *Catal. Sci. Technol.*, 2014, **4**, 4048-4092.
9. (*a*) M. Misono, *Chem. Commun.*, 2001, **13**, 1141-1152. (*b*) R. Ben-Daniel and R. Neumann, *Angew. Chem. Int. Ed.*, 2013, **42**, 92-95. (*c*) R. Ben-Daniel, P. Alsters and R. Neumann, *J. Org. Chem.*, 2001, **66**, 8650-8653. (*d*) L. M. Dornan and M. J. Muldoon, *Catal. Sci. Technol.*, 2015, **5**, 1428-1432. (*e*) X. Huang, X. Zhang, D. Zhang, S. Yang, X. Feng, J. Li, Z. Lin, J. Cao, R. Pan, Y. Chi, B. Wang and C. Hu, *Chem. Eur. J.*, 2014, **20**, 2557-2564.
10. B. Ma, Y. Zhang, Y. Ding and W. Zhao, *Catal. Commun.*, 2010, **11,** 853-857.
11. E. Nikbakht, B. Yadollahi and M. R. Farsani, *Inorg. Chem. Commun.*, 2015, **55**, 135-138.
12. P. S. N. Rao, G. Parameswaram, A. V. P. Rao and N. Lingaiah, *J. Mol. Catal. A: Chem.*, 2015, **399**, 62-70.
13. V. Palermo, P. I. Villabrille, P. G. Vazquez, C. V. Caceres, P. Tundo and G. P Romanelli, *J. Chem. Sci.*, 2013, **125**, 1375-1383.
14. P. S. N. Rao, K. T. Venkateswara Rao, P. S. Sai Prasad and N. Lingaiah, *Catal. Commun.*, 2010, **11**, 547-550.

15. S. Wang and G. Yang, *Chem. Rev.*, 2015, **115**, 4893-4962.
16. K. Y. Monakhov, W. Bensch and P. Kogerler, *Chem. Soc. Rev.*, 2015,
17. A. Haimov and R. Neumann, *Chem. Commun.*, 2002, 876-878.
18. G. Maayan, B. Ganchegui, W. Leitner and R. Neumann, *Chem. Commun.*, 2006, 2230-2232.
19. R. Neumann, A. M. Khenkin and I. Vigdergauz, *Chem. Eur. J.*, 2000, **6**, 875-882.
20. A. M. Khenkin, G. Leitus and R. Neumann, *J. Am. Chem. Soc.*, 2010, **132**, 11446-11448.
21. A. M. Khenkin and R. Neumann, *J. Org. Chem.*, 2002, **67**, 7075-7079.
22. A. Bordoloi, S. Sahoo, F. Lefebvre and S. B. Halligudi, *J. Catal.*, 2008, **259**, 232-239.
23. T. Okuhara, *Chem. Rev.*, 2002, **102**, 3641-3666.
24. L. Jing, J. Shi, F. Zhang, Y. Zhong and W. Zhu, *Ind. Eng. Chem. Res.*, 2013, **52**, 10095-10104.
25. I. V. Kozhevnikov, *J. Mol. Catal. A: Chem.*, 2007, **262**, 86.
26. J. P. West and S. –J. Hwu, *J. Solid State Chem.*, 2012, **195**, 101-107.
27. Q. Huang, M. Ulutagay, P. A. Michener and S. –J. Hwu, *J. Am. Chem. Soc.*, 1999, **121**, 10323-10326.
28. W. L. Queen, S. –J. Hwu and S. Reighard, *Inorg. Chem.*, 2010, **49**, 1316-1318.
29. W. Queen, J. P. West, S. –J. Hwu, T. T. Tran, P. S. Halasyamani and D. VanDerveer, *Chem. Commun.*, 2012, **48**, 1665-1667.
30. W. L. Queen, J. P. West, J. Hudson and S. –J. Hwu, *Inorg. Chem.*, 2011, **50**, 11064-11068.

31. R. V. Oppenauer, *Recl. Trav. Chim. Pays-Bas*, 1937, **56**, 137-144.

32. E. J. Creyghton and J. C. Van Der Waal, *Stud. Surf. Sci. Catal.*, 2001, 438-448.