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Selective oxidations of allylic alcohols using vanadyl and cobalt(II) alkyl phosphonate modified silicas

Magdalena Jurado-Gonzalez, Alice C. Sullivan* and John R. H. Wilson

Centre for Materials Research, Department of Chemistry, Queen Mary, University of London, Mile End Road, London, E1 4NS UK

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Abstract—A range of allylic alcohols can be selectively oxidised to either the corresponding epoxide or the enone in good yields using catalytic quantities of vanadyl or cobalt(II) alkyl phosphonate modified silicas, CoEPS3 and VOEPS3 and *tert*-butyl hydroperoxide.

The identification and implementation of effective catalytic systems for liquid phase oxidation, particularly in the manufacture of fine chemicals, is considered[1] to be one of the chemical industry's major targets. The need for such systems is widely accepted, specifically to replace inorganic oxidants that are used in greater than stoichiometric quantities and which also possess significant handling and environmental issues. Several different approaches are being investigated and include homogeneous catalysis, microencapsulation and heterogeneous catalysis. In homogeneous catalysis significant progress has been made utilising soluble metal salts and oxidants such as hydrogen peroxide and organic peroxides. Microencapsulation[2] has also shown promise for oxidation reactions involving a metal complex immobilised within a polymer, such as polystyrene. Heterogeneous catalysis has many inherent advantages such as ease of recovery and recycling of the catalyst as well as being suitable for continuous processing. A number of different strategies for the heterogenisation of redox active elements are being explored and include framework-substituted molecular sieves and encapsulation and ion exchange in layered double hydroxides. These approaches have been recently reviewed.[3]

Allylic alcohols are very important intermediates for the preparation of a wide range of organic compounds either via epoxidation of the olefin or oxidation of the alcohol. Thus effective chemoselective heterogeneous catalytic systems would be of particular interest to conduct these transformations. Titanium containing silicates with hydroperoxides have been extensively explored[4,5] leading to a number of commercial epoxidation processes. Materials obtained via the isomorphous substitution of vanadium in the framework of APOs and silicalites have been investigated[6,7] as heterogeneous epoxidation catalysts. Under liquid phase reaction conditions some of the vanadium is leached from the lattice leading to significant homogeneous catalysed oxidation. Similar problems were encountered with vanadium supported on silica[8] and vanadomolybdophosphate polyoxometalate[9] supported on mesoporous MCM-41. [VO(acac)$_2$] and [VO$_3$]$^-$ have been immobilised onto a variety of derivatised polystyrene resins as well as ion-exchange resins. Although epoxidation proceeds well, difficulties in recycling and metal leaching were encountered (see Ref. 2 and references cited therein).

A variety of heterogeneous catalytic systems have been reported for the selective oxidation of allylic alcohols to the corresponding carbonyl compounds. These include a number of supported ruthenium based catalysts and recent notable examples are ruthenium incorporated hydroxy apatites[10] and hydrotalcites,[11] perruthenate catalysts based on cross-linked polymer[12] and mesoporous MCM-41[13] and ruthenium(III) complexes of

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Keywords: Allylic alcohols; Epoxidation; Oxidation; Vanadyl; Cobalt; Phosphonate; Silica; Immobilised reagents.

* Corresponding author. Tel.: +44-20-7882-3274; fax: +44-20-7882-7794; e-mail: a.c.sullivan@qmul.ac.uk

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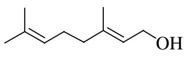
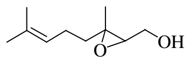
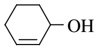
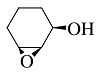
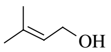
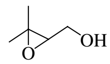
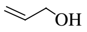
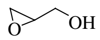
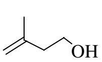
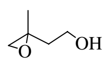
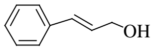
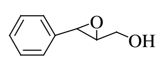
1,4,7-trimethyl-1,4,7-triazacyclononane on silica gel.[14] Palladium(II) hydrotalcites[15] have also been reported to catalyse this selective oxidation. Immobilised substituted TEMPO on polystyrene[16] can also selectively oxidise allylic alcohols to the unsaturated carbonyl compounds.

We recently reported[17,18] on the synthesis and characterisation of the first examples of phosphonate and phosphonic acid modified silicas, $[O_2Si]_x[O_{3/2}Si(CH_2)_nPO(OR)_2]_y$ $R = H$, alkyl; $n = 2, 3$; $x : y = 1 : 1–10 : 1$. The silica ethyl and propyl phosphonate materials (EPS) and (PPS) prepared to date have Q:T ratios in the range 1:1–10:1. In all cases we found the T components to have around 66% condensation and Q components around 90%. We have reported on a range of metal EPS derivatives including cobalt(II),[19] cerium(IV)[20] and vanadyl[21] materials and some of their catalytic oxidation chemistry. In this paper we wish to report our initial work on the chemoselective catalytic oxidation of a variety of allylic alcohols utilising VOEPS3 and CoEPS3 (see Scheme 1). The EPS3, VOEPS3 and CoEPS3, see Figure 1, used in this study were prepared as we have previously described.[19,21] We chose first to investigate the effectiveness and selectivity of the VOEPS3 material to catalyse the *tert*-butyl hydroperoxide (TBHP) mediated epoxidation of allylic alcohols.

The initial series of reactions was conducted on geraniol and we found, as illustrated in Table 1, that epoxidation proceeds quickly and in good yield. The VOEPS3-TBHP catalyst system selectively epoxidises the 2,3 double bond of geraniol and no traces of other epoxides or carbonyl compounds were detected in the reaction mixture. At the end of the reaction the VOEPS3 catalyst was removed by filtration. The VOEPS3 catalyst can be reused without any apparent loss of activity as illustrated by the recycle experiments involving geraniol as the substrate. In the absence of the VOEPS3 catalyst only the starting material, geraniol, was obtained. To investigate whether the silica surface or the attached phosphonate groups were possibly playing a role in the epoxidation we conducted the reaction in the presence of the precursor of the VOEPS3 catalyst, Na_2EPS3. No reaction was observed and only starting material was recovered. To check for leaching the catalyst was removed by filtration, at the reaction temperature, after half an hour and the filtrate was kept at this temperature for a further 2 h. No further epoxidation occurred. This suggests that epoxidation is occurring at the immobilised vanadyl site. A typical procedure[22] involves stirring a gently refluxing mixture containing the substrate and catalyst (0.96 mmol V g^{-1} catalyst, 5.7 mol% V relative to substrate) and excess *tert*-butyl hydroperoxide, as the reoxidant, in acetonitrile. The VOEPS3 catalyst system can be used to epoxidise selectively a range of other allylic alcohols in good yield (Table 1). Epoxidation of cyclohex-2-enol proceeds with complete *cis* stereoselectivity. Although the reaction is noticeably slower, homoallylic alcohols can also be selectively epoxidised in good yield.

Table 1. Allylic alcohol oxidation activated by VOEPS3

Substrate[a]	Product	Time (h)	Isolated yield (%)
		2.5	80
		2.5	81[b]
		2.5	0[c]
		2.5	0[d]
		0.5	60[e]
		6	79
		7	71
		7	73
		24	79
		16	83

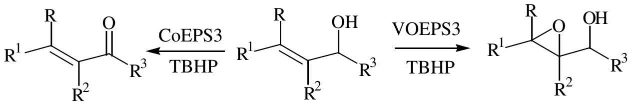
[a] All reactions were conducted using 1 mmol organic substrate in acetonitrile at 80 °C, 5.7 mol% vanadium (0.96 mmol V g^{-1} catalyst) and 6 mmol *tert*-butyl hydroperoxide.

[b] Average yield from three runs using recycled catalyst. After each run the catalyst was filtered off, washed well with water and with diethyl ether and then dried at 100 °C at 0.01 Torr.

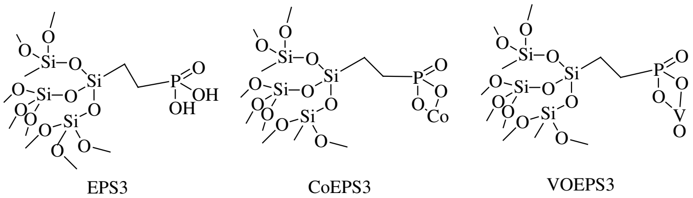
[c] No catalyst was used.

[d] Na_2EPS3 (60 mg) was used in place of the catalyst.

[e] The standard test for catalyst leaching was applied and no further conversion was observed in hot filtrates of the reaction mixture after a further 2 h.



Scheme 1.



EPS3 CoEPS3 VOEPS3

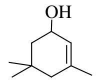
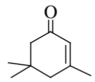
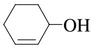
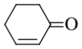
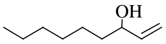
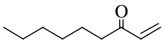
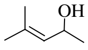
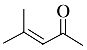
Figure 1.

Apart from our own investigations on CoEPS3 we are unaware of any other reports on the use of either homogeneous or heterogeneous Co(II) phosphonates as catalysts for liquid phase oxidation reactions. Thus we decided to investigate the effectiveness and selectivity of CoEPS3 to catalyse the TBHP mediated oxidation of allylic alcohols. We recently reported[19] the effective allylic and benzylic oxidation of a wide range of substrates using TBHP and CoEPS3, as catalyst. In the examples we explored, there was no evidence to suggest that any epoxidation had occurred. In addition no traces of allylic alcohols were observed in any of the reaction mixtures.

Utilising identical reaction conditions for the allylic and benzylic oxidation, treatment of 3,5,5-trimethylcyclohex-2-en-1-ol with CoEPS3 and TBHP, at 50 °C, afforded only trace amounts of the enone product and starting material. The reaction proceeds at a higher temperature, 80 °C, to give 3,5,5-trimethylcyclohex-2-en-1-one, selectively. No trace of any epoxide could be detected from spectral analysis of the reaction product. No reaction occurred in the absence of the catalyst or in the presence of Na_2EPS3 in place of the catalyst. CoEPS3 can be reused as catalyst without any apparent loss of activity as illustrated by the recycle experiments. To check for leaching the catalyst was filtered off, at the reaction temperature after an hour and the filtrate was kept for a further 2 h. No further oxidation occurred. Table 2 provides some further examples of the selective oxidation of allylic alcohols to the corresponding enones using the CoEPS3-TBHP system.

Before we rationalise the difference between the cobalt and vanadyl catalysts, it is pertinent to make comparative points about the previously reported CoEPS3 catalysed allylic oxidation[19] and the current results with the corresponding allylic alcohols. The outcome is the same in both cases since both reactions proceed selectively to the enones. However since the oxidation of the alkene compounds proceeds at a lower temperature than is required for the allylic alcohol oxidation, and given that we do not observe the formation of any intermediate allylic alcohol in that case, it is clear that different mechanisms pertain. A tentative proposal, based in part on the Chong and Sharpless mechanisms for the homogeneous cases,[23] is suggested (see Scheme 2).

Table 2. Allylic alcohol oxidation activated by CoEPS3

Substrate[a]	Product	Time (h)	Isolated yield (%)
		14	89
		14	88[b]
		14	0[c]
		14	0[d]
		1	80[e]
		12	87
		10	82
		10	76

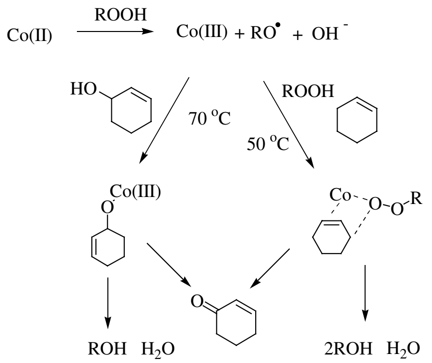
[a] All reactions were conducted using 1 mmol organic substrate in acetonitrile at 80 °C, 5.8 mol% Co (0.97 mmol Co(II) g^{-1} catalyst) and 6 mmol *tert*-butyl hydroperoxide.

[b] Average yield from three runs using recycled catalyst. After each run the catalyst was filtered off, washed well with water and with diethyl ether and then dried at 100 °C at 0.01 Torr.

[c] Reaction was run without catalyst.

[d] Na_2EPS3 (60 mg) was used in place of the catalyst.

[e] The standard test for catalyst leaching was applied and no further conversion was observed in hot filtrates of the reaction mixture after a further 2 h.



Scheme 2.

The allylic alcohol oxidation is likely to involve an alkoxide intermediate while the cyclic alkene is more likely to involve a transition state where both alkene and peroxide are simultaneously coordinated to the metal. The alkoxide intermediate can proceed to the enone product with reduction of cobalt. In the analogous vanadyl case a transition state involving both coordinated alkoxide and peroxide is believed to pertain from which the *syn*-epoxide evolves. In conclusion we have demonstrated that new catalytic systems based on vanadyl or cobalt(II) alkyl phosphonate modified silica can selectively oxidise allylic alcohols to the epoxide or enone, respectively, in good yields utilising *tert*-butyl hydroperoxide as the reoxidant.

Acknowledgements

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22. Typical procedure. A mixture containing the substrate (1 mmol) dissolved in acetonitrile (6 mL) either the cobalt(II) or vanadyl alkyl phosphonate silica catalyst (60 mg) and *tert*-butyl hydroperoxide (6 mmol in decane) was heated and stirred under an atmosphere of nitrogen at the temperature and for the period of time indicated in the tables. On completion the catalyst was filtered off and washed well with dichloromethane. The combined filtrate was washed well with an aqueous sodium sulfite solution (10%) and then with water dried and concentrated under reduced pressure. Purification where necessary to remove traces of starting material was via recrystallisation or by column chromatography.
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