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The very efficient oxidation of alcohols by poly(4-vinylpyridine)-supported sodium ruthenate

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Abstract

Primary and internal alcohols are efficiently and selectively oxidised to their corresponding aldehydes or ketones at room temperature by a new poly(4-vinylpyridine)-supported sodium ruthenate catalyst. © 2000 Elsevier Science Ltd. All rights reserved.

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The selective oxidation of primary and secondary alcohols to their corresponding aldehydes and ketones, respectively, plays a pivotal role in synthetic organic chemistry.¹ Consequently, various homogeneous oxidising reagents have been developed to effect these transformations. However, a major drawback of such oxidants is their lack of selectivity such as the over-oxidation of aldehydes to carboxylic acids and the degradation of unsaturated substrates.^{1,2} Due to the poor selectivity and recoverability of these oxidants, attempts were made to anchor the homogeneous oxidant onto a support material, thereby combining the advantages of both homogeneous and heterogeneous catalysts.

The study of polymer-supported reagents and catalysts is motivated by the major advantage of the physical separation of the supported reagent from the substrates and products, thereby allowing the recycling of expensive catalysts (e.g. noble metals) or of toxic products and is of prime economic and environmental importance.^{3,4} Both poly(2-vinylpyridine) (P₂VP) and poly(4-vinylpyridine) (P₄VP) have been used previously as supports for chromium peroxide (P₂VP-CP and P₄VP-CP, respectively) and these were reported to be efficient and selective stoichiometric oxidising agents for the oxidation of various benzylic and allylic alcohols.⁵ Poly(4-vinylpyridinium dichromate) (P₄VP-DC) and poly(4-vinylpyridinium chlorochromate) (P₄VP-CC) were also reported in the literature, with the former polymeric oxidant being commercially available.⁶ However, some of the major goals of 'green chemistry' are to replace traditional stoichiometric reagents such as chromium(VI) oxidants with catalysts and to facilitate the efficient recovery of the catalyst from the reaction products thereby reducing inorganic waste.^{7,8}

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Following our observation that Os(VI) oxides bond strongly to P₄VP and that the supported oxides are excellent dihydroxylation catalysts, we concluded that the chemistry of ruthenate on P₄VP might be worth investigating.⁹ Unsupported ruthenate is a well-known, but not very selective, oxidant of alcohols. To our knowledge there has been no reported literature of any poly(4-vinylpyridine)-supported ruthenium complexes for the oxidation of alcohols. However, [RuCl₂(CO)₃]₃ supported on poly(4-vinylpyridine) for alkene hydrogenation has been reported.¹⁰ A ruthenium complex in the form of potassium perruthenate supported on Amberlyst anion exchange resin (IR27) was also prepared.¹¹ We now report on sodium ruthenate supported on poly(4-vinylpyridine) cross-linked with 2% divinylbenzene in a series of catalytic alcohol to carbonyl oxidation reactions.

A 2% metal loading (by weight) was achieved by stirring 45 mg of sodium ruthenate in 3.8 ml of a 1 M NaOH solution with 1 g of poly(4-vinylpyridine) for 2 h. The loaded polymer was then dried under vacuum and stored under nitrogen. Flame emission spectroscopy was used to determine the ruthenium loading on the polymer as well as the extent of leaching of the sodium ruthenate from the polymeric support. Negligible leaching of the sodium ruthenate from the support into the solvent was found to occur, thereby indicating coordination or an interaction between the ruthenate ion and the nitrogen atom of the pyridine ring of the polymer as observed for P₄VP-supported osmium tetroxide.⁹

The general procedure for the catalytic oxidation of alcohols is as follows: Activated 4 Å molecular sieves (180 mg), 6 ml of nitrogen saturated solvent (dichloromethane or toluene) and the alcohol (4.78×10^{-4} mol) together with 80 µl (5×10^{-4} mol) of isobutyl-methacrylate as the internal standard were added to a nitrogen filled Schlenk tube. Then 1.5 equivalents (relative to the substrate) of the appropriate co-oxidant, together with 200 mg of the supported oxidant were added and the resulting mixture was stirred at room temperature under a nitrogen atmosphere.

Using the 2% loaded polymer supported oxidising agent, benzylic and allylic alcohols were selectively oxidised to their corresponding oxidation products without any over-oxidation products being formed or attack at double bonds or heteroatoms occurring. Thus, for example, the nitro group of 4-nitrobenzyl alcohol was not subject to oxidative attack by this oxidant. The use of tetrabutylammonium periodate was found to be superior to iodosylbenzene and this effect was more pronounced during the oxidation of 4-nitrobenzyl alcohol. Geraniol was oxidised to geranial only, whereas isomerisation to citronellal can occur using perruthenate catalysts.¹³ Double bond isomerisation during the oxidation of crotyl alcohol was also not observed. The quantitative oxidation of cyclobutanol to cyclobutanone suggests that Ru-P₄VP acts as a two electron oxidant.¹² The results are shown in Table 1. Preliminary results indicate that the catalyst is also active with a wide range of other co-oxidants, e.g. trimethylamine-*N*-oxide, methylmorpholine-*N*-oxide, H₂O₂, tertiary butyl-hydroperoxide and NaOCl. The absence of any carboxylic acid formation or double bond attack also indicates that supported ruthenate is a significantly milder oxidant than unsupported ruthenate, since unsupported ruthenate oxidises crotyl alcohol, cinnamyl alcohol and 4-nitrobenzyl alcohol to carboxylic acids.¹⁴

The recycling of the polymer-supported sodium ruthenate was carried out by filtering the supported oxidant from the reaction mixture. It was then used in another oxidation reaction. A slight decrease in the yields for each subsequent recycle was observed and this was in accordance to the results obtained for the polymer-supported perruthenate. The method of recycling the polymer-supported sodium ruthenate differed to the reported techniques for the P₄VP, P₂VP-CP and P₄VP-DC oxidants as only the polymeric backbone was recycled for these oxidants and not the supported chromium peroxide and dichromate species.^{5,6}

In conclusion, the poly(4-vinylpyridine)-supported sodium ruthenate was found to be an easily synthesised, recyclable polymeric oxidant for the efficient and selective oxidation of benzylic and allylic

Table 1
Oxidation of alcohols with the 2% Ru-loaded polymer in CH₂Cl₂

| Alcohol | Product | Co-oxidant | Yield (%) | Time (hrs) |
|-----------------------|---------------------|--------------------|-----------------------|------------|
| Cinnamyl alcohol | Cinnamaldehyde | PhIO ^a | 100 (14) ^c | 3 |
| Cinnamyl alcohol | Cinnamaldehyde | T-BAP ^b | 100 (14) | 24 |
| Cinnamyl chloride | Cinnamaldehyde | PhIO | 0 (0) | 24 |
| Cinnamyl chloride | Cinnamaldehyde | T-BAP | 0 (0) | 24 |
| Crotyl alcohol | Crotonaldehyde | PhIO | 65 (6) | 24 |
| Crotyl alcohol | Crotonaldehyde | T-BAP | 93(11) | 3 |
| Cyclobutanol | Cyclobutanone | PhIO | 100 (13) | 3 |
| Cyclobutanol | Cyclobutanone | T-BAP | 84 (11) | 48 |
| Cyclohexanol | Cyclohexanone | PhIO | 84 (11) | 48 |
| Cyclohexanol | Cyclohexanone | T-BAP | 100 (13) | 24 |
| Furfuryl alcohol | Furfuraldehyde | PhIO | 84 (11) | 48 |
| Furfuryl alcohol | Furfuraldehyde | T-BAP | 96 (12) | 3 |
| Geraniol | Citral | PhIO | 88 (11) | 48 |
| Geraniol | (Geranial) | T-BAP | 93 (11) | 24 |
| 1-hexanol | Hexanal | PhIO | 93 (11) | 24 |
| 1-hexanol | Hexanal | T-BAP | 100 (13) | 24 |
| 2-hexanol | 2-hexanone | PhIO | 89 (11) | 48 |
| 2-hexanol | 2-hexanone | T-BAP | 91 (11) | 48 |
| 4-Nitrobenzyl alcohol | 4-Nitrobenzaldehyde | PhIO | 55 (6) | 24 |
| 4-Nitrobenzyl alcohol | 4-Nitrobenzaldehyde | T-BAP | 98(11) | 24 |

a- iodosylbenzene

b- tetrabutylammonium periodate

c- turnovers in parentheses

alcohols to their corresponding oxidation products at room temperature without heteroatom oxidation, double bond isomerisation or cleavage.

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