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A study of poly(4-vinylpyridine)-supported ruthenate in the oxidation of alcohols

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Sodium ruthenate was supported on 2% and 25% cross-linked poly(4-vinylpyridine). These compounds were found to be efficient and selective catalysts for the room temperature oxidation of internal and external alcohols to aldehydes and ketones, respectively. The catalysts were active with a wide range of co-oxidants and no over-oxidation products were observed.

KEY WORDS: alcohols; oxidation; polymer-supported; ruthenium.

1. Introduction

The selective oxidation of alcohols to carbonyl compounds is an important transformation in synthetic organic chemistry, as it is essential for the preparation of many key synthetic intermediates [1–4]. Traditionally such transformations have been performed with inorganic oxidants, e.g., chromium(VI) compounds in stoichiometric quantities [5,6]. However, the toxic and corrosive nature of these compounds has limited their use. Whilst a number of effective homogeneous systems are known, [1,6] issues such as product separation from the catalyst and catalyst recovery remain problematic. It is usually desirable to replace stoichiometric reagents with catalysts and to facilitate the efficient recovery of the catalyst from the reaction products thereby reducing inorganic waste [7,8].

The study of polymer-supported catalysts and reagents 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 [9,10]. Poly(4-vinylpyridine) (P4VP) and poly(2-vinylpyridine) have been used as supports for chromium peroxide and these stoichiometric oxidants have been reported to be efficient for the oxidation of various benzylic and allylic alcohols [11]. The stoichiometric oxidants poly(4-vinylpyridinium dichromate) and poly(4-vinylpyridinium chlorochromate) have also been reported, with the former being commercially available [12]. A major disadvantage of the above systems is that only the polymeric backbone can be recycled and not the supported chromium peroxide and dichromate species.

Following our observation that Os(VI) oxides can be supported on poly(4-vinylpyridine) and that these supported oxides are effective dihydroxylation catalysts [13], we concluded that the chemistry of ruthenate on P4VP may be worth investigating. Unsupported ruthenate is a well-known, but not very selective, oxidant of alcohols [14,15]. Poly(vinylpyridine) is a microporous resin which posses high flexibility and readily swells in solvents, increasing accessibility to active sites. To our knowledge, prior to our work, there has been no reported literature of any P4VP-supported ruthenium compounds for the oxidation of alcohols [16]. However, $[RuCl_2(CO)_3]_3$ supported on P4VP for olefin hydrogenation has been reported [17], as has been perruthenate supported on Amberlyst anion exchange resin [18]. We now report on a study of ruthenate supported on cross-linked P4VP in a series of catalytic alcohol to carbonyl oxidation reactions.

2. Results and discussion

2.1. Catalyst characterisation

Sodium ruthenate was prepared by the reduction of ruthenium tetroxide with NaOH. The ruthenate was loaded on the polymer, poly(4-vinylpyridine) cross-linked with 2% divinyl benzene, following an incipient wet impregnation technique. Both 1% and 2% ruthenium loaded (by weight) polymers were prepared. A ruthenate loaded P4VP compound cross-linked with 25% divinyl benzene was also prepared. Flame emission spectroscopy showed that this latter compound was 0.5% ruthenium loaded, and the expected 2% loading could thus not be achieved. X-ray photoelectron

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spectroscopy (XPS) on the 2% loaded polymer showed an electron binding energy of 282.14 eV, which is characteristic of a Ru(VI) species [19], and supports our proposal that ruthenate is the supported species.

Infra-red band assignments for P4VP and the supported ruthenium P4VP compounds are shown in table 1. The spectrum of the 2% ruthenium loaded P4VP showed characteristic Ru=O symmetric and asymmetric vibrations at 885 and 864 cm^{-1}, respectively. The weak intensities of these bands could be attributed to the low metal loading on the polymeric support. In contrast the IR spectrum for unsupported $K_2[RuO_4]$ showed an intense band at 832 cm^{-1} assigned to the trans-oxo ruthenium asymmetric stretch [20]. The co-ordination of the polymer to the ruthenium species through the nitrogen atom of the pyridine ring is strongly indicated by the presence of a peak at 1618 cm^{-1}. This could be attributed to the C=C and C=N vibrations of pyridine attached to the ruthenium. These results are in strong accordance with those reported for $[RuCl_2(CO)_3]_3$ supported on P4VP, where the shifting of the peak from 1600 cm^{-1} (in uncoordinated P4VP) to 1618 cm^{-1} indicated that the ruthenium was coordinated to the pyridine ring through the nitrogen atom [17]. A very intense band at 1456 cm^{-1} in the spectra of both the 1% and 2% loaded polymers was found to be absent in the spectra of both the unloaded 2% and 25% cross-linked P4VP spectra. Washing reduces the intensity of this peak. This peak may represent a carbonate species that could be proposed to have formed during the interaction of NaOH with atmospheric CO_2 during the synthesis of sodium ruthenate [21].

The observation of a peak at 873 cm^{-1} in the diffuse reflectance IR (DRIFT) spectrum could imply that a certain proportion of sodium ruthenate is surface-supported on the polymer. However, the absence of the peak characteristic to the coordination of ruthenium to nitrogen at 1618 cm^{-1} in the DRIFT spectrum could indicate a different mode of 'attachment' or that the metal loading on the surface is too low for this peak to be detected. Since a weak peak characteristic of the symmetric Ru=O stretch (886–889 cm^{-1})was also observed in the IR spectra captured by an IR microscope focussing on the surface supported species, it would seem that a degree of the ruthenium species is surface supported. This is in agreement with the scanning electron microscopy (SEM) images, discussed below.

The SEM images of the 1% and 2% loaded polymers show remarkably different morphologies (figures 1 and 2). A sparse distribution of fine crystals is seen for the 1% loaded polymer, whereas a much denser distribution of rod-shaped crystals was seen for the 2% loaded polymer. These observations are quite different relative to the smooth, undulating surface of the unloaded 2% (figure 3) and 25% cross-linked polymeric supports. These images thus confirm that surface deposition does occur to some extent for the 1% loaded polymer and to a greater degree for the 2% loaded polymer. The SEM image of the 0.5% ruthenate loaded 25% cross-linked polymer shows that the surface morphology is dominated by large particles of the supported ruthenium species (figure 4). A higher degree of surface deposition, compared to those of the 2% cross-linked polymers was observed. It can be hypothesised that a certain portion

Table 1
Assignment of selected infra-red bands

Complex	Infra-red spectra – selected bands (cm^{-1})
Poly(4-vinyl pyridine)	815 m (ν_{asym})(C—H)
	1412 s (C=N) – pyridine ring
	1600 vs (C=C) – pyridine ring
	2924 m (CH_2) – vinyl chain
	3030 w (C—H) – pyridine ring
2% (2% cross-linked) Ru loaded polymer	821 w (ν_{asym}) (C—H)
	864 w (ν_{asym}) (Ru=O)
	873 m (ν_{asym}) (Ru=O) (DRIFT)[a]
	885 w (ν_{sym}) (Ru=O)
	889 w (ν_{sym}) (Ru=O) (DRIFT)[a]
	1453 s (CO_3^{2-})
	1618 s (C=C) and (C < @IEq11 > N) – co-ordination of Ru to N of pyridine ring
	2927 w (CH_2) – vinyl chain
25 % cross-linked Ru loaded polymer	822 m (ν_{asym}) (C—H)
	880 w (ν_{sym}) (Ru=O)
	1457 s (CO_3^{2-})
	1599 m (C=C) – pyridine ring
	2924 m (C—H) – vinyl backbone

[a] DRIFT – Diffuse Reflectance Infra-red Fourier-Transform.

Figure 1. SEM image of the 1% RuP4VP (2% cross-linked).

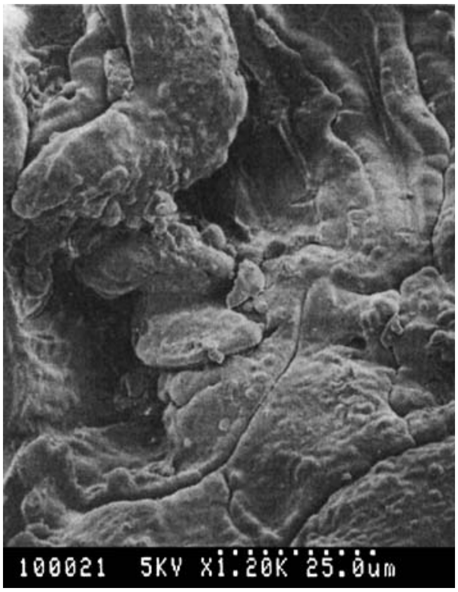

Figure 3. SEM image of P4VP.

of the ruthenate experiences steric constraints when penetrating the tightly enmeshed polymeric chains. Therefore, there can be a saturation point, where the ruthenium species can no longer penetrate the entangled polymeric chain, thereby causing surface deposition to occur and also limiting the percentage ruthenium loading possible.

2.2. *Alcohol oxidation*

The supported ruthenium compounds were investigated as catalysts for the oxidation of alcohols with various co-oxidants (table 2). It was observed that 1-hexanol underwent rapid oxidation with the polymer-supported sodium ruthenate using either iodosyl benzene (PhIO) or tetrabutyl ammonium periodate (TBAP) as co-oxidants in dichloromethane. The primary oxidation to the aldehyde proceeded selectively and in excellent yields for the 2% loaded polymer. PhIO has been reported to be an effective co-oxidant for the oxidation of alcohols by $RuCl_2(PPh_3)_3$ [22]. However, with primary aliphatic alcohols this latter system, apart from giving the aldehydes, also gave the over-oxidation products, i.e., the carboxylic acids. Furthermore, complete conversion to the acids with an excess of PhIO was reported. Both the 1% and 2% ruthenium loaded polymers, reported here, are thus milder and more selective, since no acids were

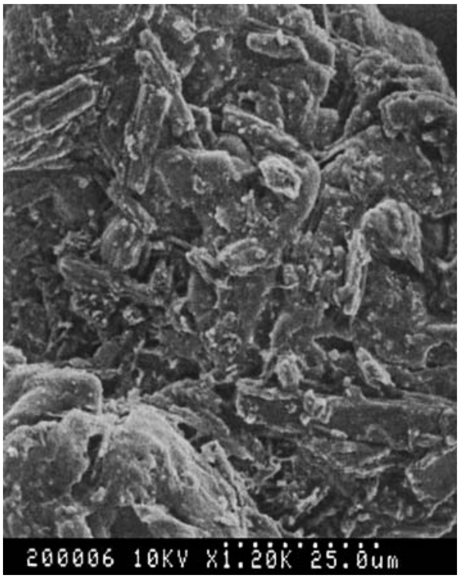

Figure 2. SEM image of the 2% RuP4VP (2% cross-linked).

Figure 4. SEM image of ruthenate on 25% cross-linked P4VP.

Table 2
Oxidation of 1-hexanol to hexanal using the one and two percent Ru loaded polymer and in the absence of a catalyst in CH_2Cl_2

Co-oxidant	Time (h)	1% Loaded Yield (%)[a]	2% Loaded Yield (%)[a]	No catalyst Yield (%)[a]
Stoichiometric[b]	0.1	12	16	
	24	16	19	
NaOCl	0.1	39	27	
	24	53	51	
NaOCl (excess)[c]	0.1	8	29	
	24	51	53	
NaOCl (40 °C)	0.1	4		
	24	35		
H_2O_2	0.1	0	11	
	24	0	18	
t-BuOOH	0.1	5	32	
	24	6	33	
NMO	0.1	12	23	0
	24	30	30	15
Me_3NO	0.1	8	14	0
	24	18	33	0
PhIO	0.1	32	86	0
	24	69	93	20
TBAP	0.1	35	95	50
	24	73	100	52
	48	73		
O_2	0.1	17	15	
	48	17	15	

[a] Yield and conversion are identical since only hexanal is formed.
[b] No co-oxidant.
[c] One equivalent excess.

observed to form. The 2% loaded RuP4VP–TBAP system was the only combination that effected total conversion of 1-hexanol to hexanal within 24 h, possibly partially due to the high activity of TBAP with the primary alcohol in the absence of the primary oxidant. The RuP4VP–NaOCl combination was significantly less effective as conversions of only 53% and 51% were obtained after 24 h with the 1% and 2% loaded polymers, respectively. Adding a further equivalent of NaOCl did not affect the conversion of the alcohol to the aldehyde. This may be due to a limited interaction between the co-oxidant with the solvent containing the polymer-supported oxidant and the substrate as the NaOCl used was a 15% solution in water and was therefore, not miscible with the organic solvent.

Hydrogen peroxide, *t*-butyl hydroperoxide (*t*-BuOOH), trimethylamine-N-oxide (Me_3NO) and methyl morpholine-N-oxide (NMO) were found not to be very active with either the 1% or 2% loaded polymers, despite them being widely used with other ruthenium-based catalysts [23]. The amount of water present in the H_2O_2 and *t*-BuOOH solutions is unlikely to account for the lower activities of these two co-oxidants relative to other ruthenium species, since results for the CrO_3 catalysed oxidation of indan in CH_2Cl_2 by either aqueous 30% or 70% *t*-BuOOH afforded similar results [24]. The higher conversions obtained by *t*-BuOOH rather than H_2O_2 as the oxygen source could be rationalised by its higher stability and better solubility in the solvent. The difference in basicity between the hydroperoxides, $pK_a(t-\mathrm{BuOOH}) = 12.8$, $pK_a\ (H_2O_2) = 11.6$ could also play an important role [24]. The RuP4VP – molecular oxygen combination was poor for 1-hexanol, with conversions being similar to those obtained in stoichiometric oxidations.

A similar trend was observed for the oxidation of the secondary alcohol, 2-hexanol, to 2-hexanone with PhIO or TBAP being the best co-oxidants of those investigated with both the 1% and 2% loaded polymers (table 3). It was observed that the rate at which maximum conversion was obtained, when using the 2% RuP4VP with either PhIO or TBAP, was greater for the primary alcohol than for the secondary alcohol. This is also observed for the majority of the other co-oxidants. However, trimethylamine-N-oxide was also found to be very effective, being significantly more active than for the oxidation of 1-hexanol. This co-oxidant (Me_3NO) had also been found to be active with supported perruthenate [18]. H_2O_2, though a poorer co-oxidant than Me_3NO, was also more active with the secondary alcohol.

Maximum conversion of 2-hexanol to 2-hexanone was achieved using 2% RuP4VP with PhIO as co-oxidant (or 1% RuP4VP and TBAP) and warming the reaction mixture to 45 °C. This increase in the conversion at an elevated temperature may be due to greater movement of the polymeric chains, thereby enabling a

Table 3
Oxidation of 2-hexanol to 2-hexanone using the 1% and 2% Ru loaded polymer in CH_2Cl_2 or toluene

Solvent	Co-oxidant	Time (h)	1% Loaded Yield (%)[a]	2% Loaded Yield (%)[a]	No catalyst Yield (%)[a]
CH_2Cl_2	Stoichiometric	0.1	12	20	
		48	17	25	
Toluene	Stoichiometric	0.1	0		
		3	8		
		24	14		
		48	19		
CH_2Cl_2	NaOCl	0.1	24	20	
		24	52	44	
		48	54	53	
CH_2Cl_2	NaOCl (excess)	0.1	20	18	
		24	50	48	
		48	55	55	
CH_2Cl_2	NaOCl (40 °C)	0.1	30	40	
		24	58	52	
CH_2Cl_2	H_2O_2	0.1	17	20	
		48	17	29	
CH_2Cl_2	*t*-BuOOH	0.1	22	18	
		48	26	21	
CH_2Cl_2	NMO	0.1	11	7	0
		24	16	34	0
		48	21	36	
CH_2Cl_2	Me_3NO	0.1	41	38	0
		24	63	85	14
		48	64	85	
CH_2Cl_2	PhIO	0.1	41	73	0
		3	83	84	
		48	85	89	0
Toluene	PhIO	0.1	68		
		3	75		
		24	77		
CH_2Cl_2	PhIO(45 °C)	0.1		73	
		24		80	
		48		100	
CH_2Cl_2	TBAP	0.1	39	34	7
		24	46	71	16
		48	51	91	
Toluene	TBAP	0.1	8		
		3	32		
		24	51		
		48	74		
CH_2Cl_2	TBAP (45 °C)	0.1	73		
		24	80		
		48	100		
CH_2Cl_2	DCP–N–O[b]	0.1		21	
		24		24	
		48		24	
CH_2Cl_1	O^2	0.1	21	22	
		48	20	24	

[a] Yield and conversion are identical since only 2-hexanone is formed.
[b] 2,6-dichloropyridine-N-oxide.

greater interaction between the active site and the substrate and would be consistent with the findings of Pittman and Hanes [25]. According to this theory the oxidation of 1-hexanol should occur more rapidly than 2-hexanol with the same catalyst and co-oxidant, due to the 'bulky' nature of the secondary alcohol. The secondary alcohol should experience a greater steric hindrance than the primary alcohol as it penetrated through the cross-linked polymeric chains. However, as the ruthenate loading increased (from 1% to 2%), more surface deposition was found to occur, which would weaken the shape selectivity effect discussed above. The lack of any clear trend for the 1% RuP4VP may indicate that, although the ruthenium loading is lower, most of the active ruthenium is present on the surface of the support.

Although the co-oxidant 2,6-dichloropyridine-N-oxide was shown to be very efficient in conjunction with ruthenium containing porphyrins, not damaging the catalysts and thereby decreasing turnover numbers [26], our results show it to be a poor co-oxidant for the RuP4VP systems. As with 1-hexanol, molecular oxygen was a poor co-oxidant, giving results close to those of the stoichiometric oxidation. The stoichiometric oxidations of both 1- and 2-hexanol to hexanal and 2-hexanone respectively, gave turnovers (calculated on the assumption that all the ruthenium present was involved in the catalysis) marginally greater than one, indicating a small degree of autocatalysis occurring [27].

Although the 2% RuP4VP catalyst, in general, performs better than the 1% RuP4VP catalyst because there is effectively more ruthenium at the bead surface, the efficiency of the catalyst per ruthenium atom is lower. This agrees with the findings of Nicolaides and Coville who reported that increasing ruthenium loading resulted in a decrease in the effective surface area of the ruthenium in an olefin hydrogenation catalyst [28].

The sodium ruthenate supported on 25% cross-linked P4VP with Me_3NO and PhIO as co-oxidants was also investigated for the oxidation of 2-hexanol (table 4). Lower yields, when compared to 2% RuP4VP were observed and this is in accordance with the literature, namely that an increase in divinyl benzene content, and hence cross-linking, causes the internal viscosity to increase, restricting the accessibility of the active sites [29].

The 2% polymer-supported sodium ruthenate catalyst was recycled three times with PhIO as co-oxidant. A slight decrease in efficiency and rate of oxidation was observed between the initial reaction and the first recycle, after which the catalyst's performance appeared to be stable. This recycling is in contrast to the reported chromium supported on P2VP and P4VP oxidants, where only the polymer is recycled [11,12]. Characterisation data (IR, SEM, XPS) of recovered used catalysts were very similar to those of new catalysts, strongly suggesting that the polymeric back-bone is not attacked by the oxidation systems. The catalysts thus appear to be chemically and mechanically stable.

Typical experiments to determine the extent of catalyst leaching from the support during the reaction, involved filtering off the catalyst approximately 1 h after the start of the reaction (ca. 30% conversion) and to continue stirring the reaction mixture. No further reaction was observed, suggesting that the catalyst does not leach or that the leached species is inactive [30]. In a separate experiment, the catalyst was filtered off after 48 h of stirring and the solution examined by flame emission spectroscopy. A 0.00025% ruthenium contamination of the solvent was determined, meaning that 0.46% of the total ruthenium present was lost from the 2% loaded polymer.

Since the 2% loaded P4VP was the best catalyst and PhIO and TBAP were the most effective co-oxidants, we decided to investigate these further in the oxidation of a range of alcohols. Two different solvents were chosen, dichloromethane and toluene, the latter because it is a solvent that causes polymers such as PVP to swell. The results are shown in table 5. Whilst no clear trend could be seen for the oxidation reactions in the different solvents, CH_2Cl_2 and toluene, this may be due to the different solubilities and reactivities of the co-oxidants in these solvents. In general PhIO shows activity as a primary oxidant of alcohols in both solvent systems, whilst TBAP shows no activity in toluene, and lower activity than PhIO in CH_2Cl_2. The stoichiometric oxidations of cinnamyl alcohol by 2% RuP4VP in both toluene and CH_2Cl_2 allowed a comparison without interfering effects due to the co-oxidants. Here, conversions were higher when using toluene as solvent. This effect could be attributed to the swelling of the polymeric chains, thereby allowing the substrate to interact with the active sites of the polymer to a greater extent. The use of CH_2Cl_2, in contrast, does not cause the polymer to swell and hence cinnamyl alcohol, a bulky alcohol, is likely to experience steric constraints within the polymeric chains.

In the catalytic reactions, a variety of alcohols was selectively oxidised to their corresponding oxidation

Table 4

Comparison between the Ru loaded 2% and 25% cross-linked polymers for the oxidation of 2-hexanol to 2-hexanone in CH_2Cl_2

Polymeric system	Co-oxidant	Time (h)	Yield (%)[a]
2% RuP4VP	Me_3NO	0.1	38
		24	85
2% RuP4VP	PhIO	0.1	73
		24	84
25% RuP4VP	Me_3NO	0.1	23
		24	36
25% RuP4VP	PhIO	0.1	37
		24	66

[a] Yield and conversion are identical since only 2-hexanone is formed.

Table 5
Oxidation to the corresponding aldehydes and ketones, with various co-oxidants by the 2% loaded polymeric oxidant and in the absence of the primary oxidant

Substrate	Product	Solvent	Co-oxidant	Time (h)	2% RuP4VP Yield (%)[a]	No catalyst Yield (%)[a]
Cinnamyl alcohol	A	Toluene	Stoichiometric	0.1	22	
				24	34	
				48	35	
Cinnamyl alcohol	A	CH_2Cl_2	Stoichiometric	0.1	20	
				24	25	
				48	26	
Cinnamyl alcohol	A	Toluene	PhIO	0.1	75	0
				3	88	0
				24	100	23
Cinnamyl alcohol	A	CH_2Cl_2	PhIO	0.1	89	24
				3	100	27
Cyclohexanol	K	CH_2Cl_2	PhIO	0.1	69	1
				3	76	5
				24	81	27
Cinnamyl chloride	A	CH_2Cl_2	PhIO	0.1	0	0
				24	0	0
Cyclobutanol	K	CH_2Cl_2	PhIO	0.1	98	0
				3	100	12
Furfuryl alcohol	A	CH_2Cl_2	PhIO	0.1	66	0
				3	79	10
				24	82	15
4-Nitrobenzyl alcohol	A	CH_2Cl_2	PhIO	0.1	44	2
				3	54	4
				24	55	28
Geraniol	A	CH_2Cl_2	PhIO	0.1	67	4
				24	70	18
				48	88	
Crotyl alcohol	A	CH_2Cl_2	PhIO	0.1	12	0
				3	58	0
				24	65	30
Cinnamyl alcohol	A	Toluene	TBAP	0.1	61	0
				3	100	0
Cinnamyl alcohol	A	CH_2Cl_2	TBAP	0.1	79	10
				3	83	32
				24	100	36
Cyclobutanol	K	CH_2Cl_2	TBAP	0.1	74	0
				3	80	0
				24	85	0
				48	85/100[b]	
Cyclohexanol	K	Toluene	TBAP	0.1	27	0
				3	69	0
				24	100	0
Cyclohexanol	K	CH_2Cl_2	TBAP	0.1	67	
				3	73	
				24	77	
Cinnamyl chloride	A	Toluene	TBAP	0.1	0	0
				24	0	0
Cinnamyl chloride	A	CH_2Cl_2	TBAP	0.1	0	
				24	0	
Furfuryl alcohol	A	CH_2Cl_2	TBAP	0.1	60	0
				3	93	11
				24	100	13
4-Nitrobenzyl alcohol	A	CH_2Cl_2	TBAP	0.1	48	22
				3	57	25
				24	98	27
Geraniol	A	CH_2Cl_2	TBAP	0.1	85	0
				3	93	0
				24	93	0

Table 5
continued

Substrate	Product	Solvent	Co-oxidant	Time (h)	2% RuP4VP Yield (%)[a]	No catalyst Yield (%)[a]
Crotyl alcohol	A	CH_2Cl_2	TBAP	0.1	90	
				3	93	
				24	93	

[a] Yield and conversion are identical since only the carbonyl compounds are formed.

[b] After the addition of acetonitrile.

A: corresponding aldehyde

K: corresponding ketone

products (aldehydes or ketones) without any over-oxidation products being formed or attack at double bonds occurring. Geraniol was oxidised to geranial only, whereas isomerisation to citronellal can occur using perruthenate catalysts [31]. Double bond isomerisation during the oxidation of crotyl alcohol was also not observed. The catalyst's inactivity towards cinnamyl chloride and the selective conversion of the hydroxyl group to a carbonyl unit in furfuryl alcohol and 4-nitrobenzyl alcohol show that heteroatoms or sensitive functional groups are not attacked.

Halving the usual amount of primary oxidant (2% RuP4VP) still gave total conversion of cinnamyl alcohol in conjunction with TBAP, whilst 2% RuP4VP with PhIO gave an 80% yield of cinnamaldehyde.

The 2% loaded RuP4VP–PhIO system achieved total conversion of cyclobutanol within 3 h, whilst the 2% loaded RuP4VP–TBAP system achieved total conversion once acetonitrile was added to the reaction mixture. This technique had been applied successfully in the homogeneous tetrapropylammonium perruthenate catalysed oxidation of a number of alcohols and was attributed to a solvent coordination effect [32]. The quantitative oxidation of cyclobutanol to cyclobutanone, with no acyclic products being formed, strongly suggests that the polymer-supported ruthenate is a two electron oxidant [14,15]. These polymer supported ruthenate systems were also observed to be milder than unsupported ruthenate, since unsupported ruthenate oxidises crotyl alcohol, cinnamyl alcohol and 4-nitrobenzyl alcohol to carboxylic acids [15]. The general enhancement of selectivity for the polymer-supported sodium ruthenate over unsupported ruthenate could be attributed to the proposal that the catalytically active sites are both surface and internally associated with the cross-linked polymeric chains. This affects the catalyst on a shape selective basis. The 'co-ordination' of the ruthenate to the polymer may also weaken the ruthenate slightly as an oxidant, thereby preventing the formation of carboxylic acids. The net result, as shown in table 5, is that the 2% RuP4VP catalyst compares very favourably with all other polymer-supported oxidants for the alcohol to carbonyl transformation [11,12,18].

3. Conclusions

In conclusion, the poly(4-vinylpyridine) supported sodium ruthenate was found to be an easily synthesised, recyclable polymeric two electron oxidant for the efficient and highly selective oxidation of a wide range of alcohols to their corresponding carbonyl products. These reactions occur at room temperature without heteroatom oxidation, double bond isomerisation or cleavage and no acid formation is observed.

4. Experimental

4.1. Materials

Poly(4-vinylpyridine) cross-linked with 2% divinyl benzene (Acros or Aldrich), poly(4-vinylpyridine) cross-linked with 25% divinyl benzene (Aldrich), *iso*-butyl methacrylate (Acros), powdered 4 Å molecular sieves (Aldrich), cinnamyl alcohol (Acros Organics), cinnamaldehyde (Acros Organics), cinnamyl chloride (Aldrich), citral (BDH), crotyl alcohol (Aldrich), crotonaldehyde (Acros Organics), cyclobutanol (Acros Organics), cyclohexanol (BDH), cyclohexanone (Kleber), geraniol (Acros Organics), furfuryl alcohol (H & W Fine Chemicals), furfuraldehyde (BDH), 1-hexanol (Acros), hexanal (Aldrich), hexanoic acid (Aldrich), 2-hexanol (Aldrich), 2-hexanone (Aldrich), 4-nitrobenzyl alcohol (Acros), 4-nitrobenzaldehyde (Aldrich), 2,6-dichloropyridine (Acros) and iodosobenzene diacetate (Acros) were obtained commercially. Iodosylbenzene and 2,6-dichloropyridine-N-oxide were prepared as previously reported [33]. The other co-oxidants used, tert-butyl hydroperoxide (70% m/v, Aldrich), sodium hypochlorite (15% m/v, Associated Chemical Enterprises), hydrogen peroxide (30% m/v, Saarchem), trimethylamine-N-oxide dihydrate (Aldrich), 4-methylmorpholine-N-oxide (Aldrich) and tetrabutylammonium periodate (Acros) were used as supplied.

4.2. Techniques

SEM and energy dispersive X-ray spectroscopy (EDS) analyses were carried out on a Hitachi S520. The

EDS was done using a LINK ISIS energy dispersive x-ray analysis system, which was fitted to the SEM. The extent of metal loading was determined by flame emission spectroscopy and conducted in triplicate. Flame emission analyses were carried out on a Perkin Elmer Aanalyst. XPS data was obtained from a Physical Electronics (PHI) Quantum 2000 Scanning XPS (X-Rays: Al k(Alpha) @ 15 kV beam energy and 20 W beam power; Spot Size: 100 micron; Pressure: 2×10^{-8} Torr). IR spectra were recorded on a Nicolet 5DX FT-spectrometer as KBr disks. DRIFT spectra and IR microscope images were recorded on a Perkin Elmer Spectrum GX FT-IR system. Gas chromatography was carried out on Pye Unicam GCD, Fisons GC 8000 and Perkin Elmer XL Autosystem instruments.

All catalytic and stoichiometric reactions were carried out a minimum of three times to ensure reproducibility. All alcohol oxidation reactions were carried out in the dark to prevent free radical oxidation reactions initiated by UV radiation and under a N_2 atmosphere to prevent possible oxidation by air.

4.3. Catalyst preparation

4.3.1. Preparation of RuO_4

RuO_4 was prepared as previously reported [34]. Thus $RuCl_3{\cdot}3H_2O$ (1.54 g, 5.88 mmol) and $NaIO_4$ (5.50 g, 25.7 mmol) in de-ionised water (40 mL) were stirred overnight in a round-bottomed flask with a Teflon stopper (greasing the stopper should be avoided). The RuO_4 formed was extracted into CCl_4 (40 mL) and stored under an aqueous $NaIO_4$ solution (1.00 g $NaIO_4$ in 30 mL water).

4.3.2. Preparation of 2% ruthenium loaded polymer-supported sodium ruthenate

A solution of sodium ruthenate was prepared by stirring 7.8 mL of a 1 M NaOH solution with an equivolume of the RuO_4 in CCl_4 from the above stock solution under N_2 for 24 h. A colour change from yellow to deep red was observed. 1 g of 2% cross-linked poly(4-vinylpyridine) was then added to this ruthenate solution and the mixture stirred for a further 6 h. It was observed that the white beads changed colour to dark brown, which were suspended in a now colourless liquid. The loaded polymer was dried under vacuum and stored under N_2.

4.3.3. Preparation of 1% ruthenium loaded polymer-supported sodium ruthenate

3.9 mL of RuO_4 in CCl_4 was stirred with an equivolume of 1 M NaOH for 24 h. 1 g of 2% cross-linked poly(4-vinylpyridine) was then added to this solution and the mixture stirred for a further 6 h. The loaded polymer was dried under vacuum and stored under N_2.

4.3.4. Preparation of sodium ruthenate supported on 25% cross-linked P4VP

The method is similar to that mentioned above, except that 25% cross-linked poly(4-vinylpyridine) is added instead of the 2% cross-linked polymer.

4.4. Oxidation procedures

4.4.1. Typical catalytic oxidation procedure of alcohols using the polymer-supported oxidant

Activated 4 Å powdered molecular sieves (180 mg) and 6 mL solvent (CH_2Cl_2 or toluene) were added to a nitrogen filled Schlenk tube. The alcohol (0.478 mmol) and isobutyl-methacrylate (80 μL, 0.5 mmol) as the internal standard were then added. A 1.5-fold excess, relative to the substrate, (0.717 mmol) of the appropriate co-oxidant and the catalyst (200 mg) was added and the mixture stirred at room temperature under N_2. Aliquots were sampled at the start of the reaction, after 3, 24 and 48 h. The aliquots were dried with anhydrous magnesium suphate and filtered through cotton wool. The filtrate was then immediately analysed by gas-chromatography.

4.4.2. Typical isolation of reaction products (e.g. cinnamaldehyde)

The reaction mixture, double the scale described above, was stirred for 24 h. Thereafter, the molecular sieves and catalyst were filtered off and the solvent eluted through a silica column in order to remove the co-oxidant (TBAP) and any possible traces of leached ruthenium. The product was then isolated by fractional distillation and quantified gravimetrically (92%). TLC and NMR were used to further confirm the identity of the product.

4.5. Procedure for recycling the loaded polymer

After the oxidation reaction mixture was stirred for 28 h, the mixture was filtered through a sintered glass crucible to separate the catalyst from the reaction products. The supported catalyst was then added to a new Schlenk tube prepared as above. The recycling procedure was repeated three times with a minimal mechanical loss of catalyst.

4.5.1. Typical stoichiometric oxidation procedure of alcohols using the polymer-supported oxidant

This procedure was identical to the procedure using the polymer-supported catalysts with the only difference being that no co-oxidant was added.

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