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Highly efficient liquid-phase oxidation of primary alcohols to aldehydes with oxygen catalysed by Ru–Co oxide

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Ru^{IV}–Co^{III} (1 : 1.5) binary oxide, prepared by co-precipitation, is a highly efficient solid catalyst for the oxidation of primary alcohols to aldehydes with O_2 (76–95% selectivity at 54–100% conversion) in a liquid phase under atmospheric pressure.

The catalytic conversion of primary alcohols to aldehydes is essential for the preparation of fragrances and food additives as well as many organic intermediates.[1,2] Traditional methods for the synthesis of aldehydes involve the use of stoichiometric amounts of inorganic oxidants, *e.g.* Cr(VI), and generate large quantities of waste. The development of effective catalytic aerobic oxidation of alcohols using environmentally benign and inexpensive oxidants such as oxygen or air is an important challenge.[1] Heterogeneous catalysis is generally considered to be the most attractive method to effect the aerobic oxidation. Typically, the aerobic oxidation of alcohols involves the use of catalysts based on platinum group metals.[1,2] Supported platinum and palladium catalysts have long been used for alcohol oxidation.[2] More recently, ruthenium catalysts have attracted significant interest. These involve soluble complexes[3–8] or solid catalysts.[9–14] the most efficient Ru-based heterogeneous systems for the aerobic oxidation of alcohols in a liquid phase include recently developed Ru–Co–Al hydrotalcite,[10] Ru–hydroxyapatite[11] and Ru/Al_2O_3.[12] Frequently, Ru catalysts are sufficiently selective to avoid over-oxidation of aldehydes to acids and are tolerant towards many other functional groups that may be present in the alcohol molecules.

In this work, we report that both saturated and unsaturated primary alcohols can be heterogeneously oxidised to aldehydes by O_2 or air in a liquid phase with a very high efficiency using binary oxide catalysts based on Ru^{IV} and another transition metal ion.† The oxidation was carried out at 80–110 °C in organic solvents such as toluene, acetonitrile or dichloroethane, toluene being the best solvent. Ruthenium dioxide hydrate has been reported as a stoichiometric oxidant and a selective catalyst for the heterogeneous oxidation of allylic alcohols to aldehydes with O_2 in a liquid phase.[9] We found that Ru dioxide was also quite efficient when using air instead of O_2 for such oxidations, as exemplified by the oxidation of cinnamyl alcohol (Table 1, entries 1 and 2). It could be reused several times, the catalytic activity being gradually reduced, however (entry 3). Further, we attempted modification of Ru dioxide with various transition metal cations (M), such as Co^{III}, Cu^{II}, Fe^{III}, *etc.* These cations were introduced simply by co-precipitation from aqueous solutions with NaOH to form binary Ru^{IV}–M oxides. Addition of M was found to improve the activity of Ru catalysts; the effect of additives depended upon the nature of M. In the absence of Ru, the M oxides showed no catalytic activity. Co^{III} introduced in a Ru : Co atomic ratio of 2 : 1–1 : 5, preferably 1 : 1–1 : 2, caused the most remarkable acceleration (entries 4 and 5). In the oxidation of cinnamyl alcohol with O_2, the Ru^{IV}–Co^{III} (1 : 1.5) system gave 92% yield of cinnamaldehyde at 100% conversion in 0.5 h (entry 4; *cf.* RuO_2, entry 1). In the oxidation with air, Ru–Co oxide was also more efficient than RuO_2 (*cf.* entries 2 and 6). Like RuO_2, the Ru–Co oxide was reusable, albeit with gradually declining activity.

It should be noted that the Ru–Co oxide catalyst showed the highest output in the oxidation of cinnamyl alcohol amongst the most efficient solid Ru catalysts. It had a turnover frequency (TOF) of 38 h^{-1} at 110 °C (entry 5) which is higher than those reported for Ru–Co–Al hydrotalcite (14 h^{-1} at 60 °C),[10] Ru–hydroxyapatite (6 h^{-1} at 80 °C)[11] and Ru/Al_2O_3 (27 h^{-1} at 83 °C).[12] The selectivity of Ru–Co oxide catalyst (up to 95%) is practically the same as that of Ru–Co–Al hydrotalcite (94%),[10] which is somewhat lower than those reported for Ru–hydroxyapatite and Ru/Al_2O_3 (98–99%).[11,12] This may be explained by the presence of cobalt in the first two catalysts.

The oxidation of alcohols to aldehydes by RuO_2/O_2 and Ru–Co/O_2 systems does not appear to involve one-electron processes because these systems selectively oxidised the test alcohol *t*-Bu(Ph)CHOH to the ketone *t*-Bu(Ph)CO in refluxing

Table 1 Ru-catalysed oxidation of alcohols to aldehydes by O_2 in toluene, 110 °C[a]

Entry	Catalyst[b]	Alcohol	Time/h	Aldehyde	Conversion %	Selectivity (%)	TOF/h^{-1}
1	RuO_2	Cinnamyl	2.0	Cinnamaldehyde	100	79	5.0
2	RuO_2[c]	Cinnamyl	2.0	Cinnamaldehyde	50	80	2.5
3	RuO_2[d]	Cinnamyl	2.0	Cinnamaldehyde	80	79	4.0
4	Ru–Co	Cinnamyl	0.5	Cinnamaldehyde	100	92	20
5	Ru–Co[e]	Cinnamyl	0.5	Cinnamaldehyde	96	94	38
6	Ru–Co[c]	Cinnamyl	0.5	Cinnamaldehyde	72	94	14
7	Ru–Co[f]	Cinnamyl	0.5	Cinnamaldehyde	100 (100)	95 (92)	20
8	Ru–Co[f]	Cinnamyl	1.0	Cinnamaldehyde	100 (100)	95 (47)	10
9	Ru–Cu	Cinnamyl	2.0	Cinnamaldehyde	100	85	5.0
10	Ru–Co[f]	1-Dodecanol	4.0	Dodecanal	52	83	1.3
11	Ru–Co[f]	9-Decenol	4.0	9-Decenal	54	93	1.4

[a] A mixture of alcohol (2.5 mmol), Ru catalyst (alcohol : Ru = 10 : 1 mol/mol) and toluene (10 ml) was treated with O_2 (25 ml min^{-1}). Conversions and selectivities were measured by GC with internal standard. Turnover frequencies (TOF) were defined as mol alcohol reacted per mol Ru and per hour. [b] Hydrous Ru, Ru–Co (1 : 1.5) and Ru–Cu (1 : 2) oxides pre-treated at 60 °C/0.5 Torr for 2 h. [c] Air (25 ml min^{-1}) instead of O_2 as oxidant. [d] Reuse of entry 1. [e] 2.5 mmol alcohol, alcohol : Ru = 20 : 1 mol/mol, 5 ml toluene. [f] Radical scavenger 2,6-di-*tert*-butyl-*p*-cresol (0.11 mmol) was added; in brackets are conversions and selectivities corresponding to maximum yields obtained without the scavenger.

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toluene. Similar behaviour has been observed for $[n\text{-}Pr_4N]RuO_4$ in a homogeneous system.[8]

Being highly active for alcohol-to-aldehyde oxidation (oxidative dehydrogenation), Ru–Co oxide also accelerated the consecutive oxidation of the aldehyde to acid (oxygenation), as can be seen in Fig. 1. Hence a strict control of the reaction course is required. Addition of a radical scavenger (*e.g.*, 2,6-di-*tert*-butyl-*p*-cresol) almost completely inhibited the over-oxidation (Fig. 1; Table 1, entries 7 and 8).[9] This is indicative of a free radical mechanism for the aldehyde-to-acid oxidation.

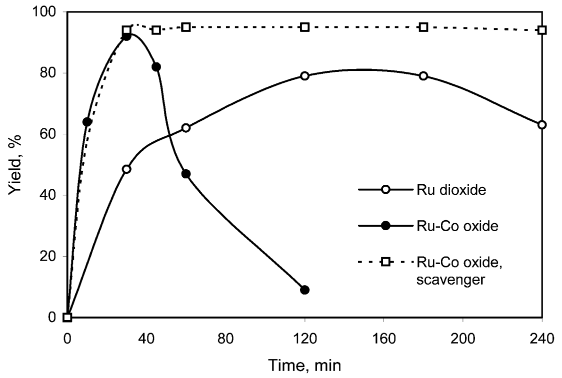

Fig. 1 Yield of cinnamaldehyde *vs.* time for the aerobic oxidation of cinnamyl alcohol (2.5 mmol) catalysed by RuO_2 or by Ru–Co (1 : 1.5) oxide with and without radical scavenger (0.11 mmol) in toluene (10 ml) at 110 °C (alcohol : Ru = 10 : 1).

The Ru–Co oxide was also found to be active for the aerobic oxidation of non-activated saturated and unsaturated primary alcohols such as 1-dodecanol and 9-decenol to the corresponding aldehydes (entries 10 and 11). In the latter case, no double bond migration was observed. It should be noted, however, that the cobalt-free catalysts, Ru–hydroxyapatite and Ru/Al_2O_3, give higher selectivities to aldehydes in the oxidation of saturated primary alcohols.[11,12]

It should be pointed out that only hydrous oxides, RuO_2 or Ru–Co, were catalytically active (Fig. 2). These were obtained by a mild thermal pre-treatment of the precursor hydroxides at 60 °C/0.5 Torr/2 h. From thermogravimetric analysis (TGA), the active oxides contained 3–5 water molecules per Ru atom. Thoroughly dehydrated oxides were inactive in the aerobic oxidation of alcohols. The hydrous RuO_2 has been reported to be different from the anhydrous form.[15] As shown by powder XRD, the hydrous RuO_2 was amorphous; it had a Brunauer–Emmett–Teller (BET) surface area of *ca.* 200 $m^2\ g^{-1}$. After dehydration at 130 °C/10 h, the Ru dioxide transformed to the inactive crystalline RuO_2 with the rutile structure, which had a low surface area (*ca.* 10 $m^2\ g^{-1}$), in agreement with the literature.[15] The hydrous RuO_2 has been found to chemisorb a significant amount of oxygen, whereas the anhydrous form has little chemisorbed oxygen.[15] These differences might greatly affect the activity of RuO_2 in the oxidation of alcohols.[9] The mechanism of the enhancing effect of cobalt in alcohol oxidation is not yet clear. The Ru–Co synergism has been found in the homogeneous co-oxidation of alcohols and aldehydes[4] and in the oxidation of alcohols on Ru–Co–Al hydrotalcite.[10] From X-ray diffraction (XRD) and TGA data, the hydrous Ru–Co (1 : 1.5) oxide could be approximated as a binary oxide $RuO_2{\cdot}1.5CoO(OH){\cdot}3\text{–}5H_2O$ comprising the amorphous RuO_2 hydrate and the crystalline cobaltic acid CoO(OH). It might also include a mixed Ru–Co oxide phase. Detailed characterisation of this catalyst is in progress.

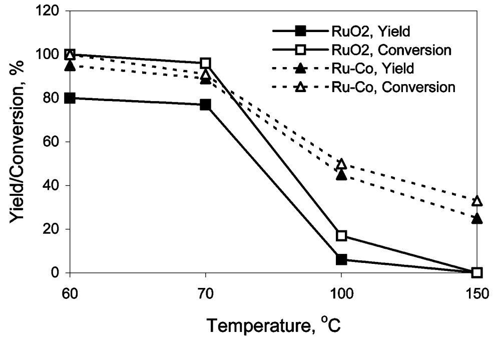

Fig. 2 Effect of pre-treatment temperature (0.5 Torr, 2 h) on catalytic activity of hydrous RuO_2 and Ru–Co (1 : 1.5) oxide in the oxidation of cinnamyl alcohol by O_2 in toluene (110 °C, alcohol : Ru = 10 : 1, 2 h for RuO_2 and 0.5 h for Ru–Co oxide).

The mechanism of alcohol oxidation on the hydrous Ru–Co oxide may be viewed as an oxidative dehydrogenation involving the formation of a Ru^{IV} alkoxide intermediate from Ru^{IV} hydroxo species, *e.g.* $Ru^{IV} - OH + RCH_2OH \rightarrow Ru^{IV} - OCH_2R + H_2O$, followed by β elimination to give the aldehyde and a ruthenium hydride species. The latter is then oxidised by oxygen. Cobalt might play a significant role in the activation of oxygen in catalyst reoxidation.

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Notes and references

† *Experimental*. All alcohols were used as received without further purification. Solvents were dried over 4 Å molecular sieves. Ru dioxide hydrate was prepared by precipitation from 0.2 M aqueous solution of $RuCl_3$ with 1 M NaOH at pH 10. The Ru^{IV}–Co^{III} binary oxides were prepared similarly by co-precipitation of 0.2 M $RuCl_3$ solutions containing appropriate amounts of $CoCl_2$. The suspensions were aged with stirring for 2 h, filtered off, washed with water until Cl^- was removed (test with $AgNO_3$) and finally dried at 60 °C/0.5 Torr for 2 h. During the preparation, Ru^{III} was oxidised to Ru^{IV} and Co^{II} to Co^{III} by air. The oxidation of alcohols was carried out in a 50 ml round-bottom three-neck glass flask equipped with a reflux condenser, a magnetic stirrer and a gas inlet allowing bubbling a flow of oxygen or air (25 ml min^{-1}) into the reaction mixture. Because it is inherently unsafe to mix oxygen with hot organics, appropriate precautions should be taken when carrying out this work, particularly if scaling it up. Typically, a mixture of an alcohol (2.5 mmol), Ru catalyst (alcohol : Ru = 10 : 1 mol/mol) and decane (GC internal standard) in toluene (10 ml) was charged in the reactor and saturated with oxygen at room temperature for 5 min while being intensely stirred. Then the reactor was placed into the oil bath preheated to a certain temperature to start the reaction. Samples of the reaction mixture were taken out at appropriate time intervals to monitor the reaction by GC.

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