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Liquid-phase oxidation of alcohols by oxygen and nitrous oxide catalysed by Ru–Co oxide

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Abstract

Chemoselective catalysts in bulk or supported on γ-Al_2O_3 binary oxides Ru^{IV}–Co^{III} (Ru/Co = 1:1–1:2), prepared by co-precipitation, were used for liquid-phase oxidation of saturated and unsaturated primary and secondary alcohols to aldehydes and ketones with O_2 or N_2O. The catalysts can be separated by filtration and reused. No leaching of Ru or Co in solution was observed. The oxidation is enhanced by the presence of hydration water in the Ru–Co catalyst, which indicates the participation of active Ru^{IV} hydroxo species in the reaction. From XRD and TGA, the Ru–Co oxide can be approximated as a hydrous binary oxide comprising the amorphous RuO_2 and heterogenite-3R cobaltic acid CoO(OH). The alcohol oxidation appears to occur by a nonradical mechanism, which may be viewed as an oxidative dehydrogenation of alcohols to form an aldehyde or ketone. H_2-TPR shows that Co^{III} practically does not affect the oxidising ability of RuO_2. This suggests that the cobalt is likely to enhance catalyst reoxidation by O_2 rather than to play a significant role in the alcohol dehydrogenation. The alcohol oxidation by N_2O exhibits a close similarity to the oxidation by O_2 but is much less efficient. Much more active catalysts are required to make the oxidation with N_2O synthetically useful.

Keywords: Alcohol; Oxidation; Oxygen; Nitrous oxide; Ruthenium oxide; Cobalt

1. Introduction

The catalytic conversion of primary saturated and unsaturated alcohols to aldehydes is essential for the preparation of fragrances, food additives, and 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 with the use of environmentally benign and inexpensive oxidants such as oxygen or air is an important challenge [1,2]. Nitrous oxide is a potentially interesting oxidant for the clean oxidation of organic substrates, as the only by-product in these reactions is dinitrogen [3,4]. Heterogeneous catalysis is generally considered to be the most attractive method for 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 or solid catalysts [1,2,5, and references therein]. Most efficient Ru-based heterogeneous systems for the aerobic oxidation of alcohols in liquid phase include recently developed Ru–Co–Al hydrotalcite [6], Ru-hydroxyapatite [7], Ru–$Co(OH)_2$–CeO_2 [8], and Ru/Al_2O_3 [9]. Frequently, Ru catalysts are sufficiently selective to avoid overoxidation of aldehydes to acids and tolerant toward many other functional groups, including C=C double bonds, that may be present in alcohol molecules [2].

Recently we reported that hydrous Ru^{IV}–M^{III} and Pd^{II}–M^{III} binary oxides (M = Co^{III}, Fe^{III}, and Mn^{III}) are active solid catalysts for the oxidation of primary alcohols to aldehydes with O_2 [10–12] or N_2O [13] in liquid phase, where the Ru^{IV}–Co^{III} oxide is the most efficient catalyst. These cat-

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alysts are robust, purely inorganic materials resistant to oxidative degradation, in contrast to organometallic catalysts. The aim of this work is to investigate in detail the oxidation of saturated and unsaturated primary and secondary alcohols to aldehydes and ketones with O_2 and N_2O in liquid phase with bulk and supported Ru^{IV}–Co^{III} mixed oxide catalysts. The catalyst testing is complemented by mechanistic studies and catalyst characterisation by XRD, TGA, XPS, and H_2-TPR.

2. Experimental

2.1. Materials

Solvents, chemicals, and catalyst supports were purchased from Aldrich, BDH, or Lancaster and used without further purification. Carveol and carvone were kindly donated by Quest International, and $RuCl_3$ and RuO_2 by Johnson Matthey Catalysts. O_2 and N_2O of 99% purity were from BOC Gases.

2.2. Techniques

Thermal gravimetric analysis (TGA) of catalysts was performed on a Setaram TG-DSC 111 analyser. BET surface areas were obtained from nitrogen physisorption measured on a Micromeritics ASAP 2000 instrument. Powder X-ray diffraction (XRD) patterns were obtained with a Siemens D-5005 diffractometer (Co-K_α radiation) and attributed with the use of a JCPDS-ICDD database. The particle size of RuO_2 and CoO(OH) was estimated from the Scherrer equation; no correction for instrumental peak broadening or microstrain was made. X-ray photoelectron spectra (XPS) were measured with an M-Probe SSI spectrometer with the use of monochromated Al-K_α X-rays (1486.6 eV). The catalyst samples were degassed for 24 h under vacuum before analysis. The atomic percentage of Ru and Co at the surface was calculated from the measured XPS peak area corrected for intrinsic sensitivity and spectrometer transmission factors. The metal content in catalyst samples was measured by ICP analysis. Temperature-programmed reduction (TPR) of catalysts was carried out on a Micromeritics 2900 TPD/TPR apparatus equipped with a thermal conductivity detector. Catalyst samples (20–30 mg) were heated to 500 °C at a rate of 10 °C/min in a H_2–Ar (5:95) gas flow (60 cm^3/min).

2.3. Catalyst preparation

Bulk hydrous Ru dioxide was prepared by precipitation from a 0.1 mol/l aqueous solution of $RuCl_3$ with 1 mol/l NaOH at pH 10 and 65 °C. The Ru^{IV}–Co^{III} binary oxides were prepared similarly by co-precipitation of 0.1 mol/l $RuCl_3$ solutions containing appropriate amounts of $CoCl_2$. Supported catalysts were made by (co)precipitation by aqueous NaOH in the presence of a support such as acidic, neutral, or basic γ-alumina (Al_2O_3-a, Al_2O_3-n or Al_2O_3-b) or SiO_2. The suspensions were aged with stirring for 2 h (24 h for supported catalysts), filtered off, washed with water until Cl^- was removed ($AgNO_3$ test; $[Cl^-] < 10^{-8}$ mol/l in washings), and finally dried at 60 °C/0.5 Torr for 2 h, unless stated otherwise. During the preparation, Ru^{III} and Co^{II} underwent aerobic oxidation to Ru^{IV} and Co^{III} [14], respectively. Catalyst characterisation is given in Table 1.

2.4. Oxidation procedure

2.4.1. Oxidation with O_2/air

The oxidation of alcohols was carried out in a 50-ml round-bottomed three-neck glass flask equipped with a reflux condenser, a magnetic stirrer, and a gas inlet allowing a flow of oxygen or air (25 ml/min) to be bubbled into the reaction mixture. *Because of the inherent danger of mixing oxygen with hot organics, appropriate precautions should be taken with this work, particularly if it is scaled up.*

Table 1
Catalyst characterisation

Catalysts and supports[a]	pH[b]	Water content[c] (wt%)	Metal content[d] (wt%)	
			Ru	Co
γ-Al_2O_3-n (neutral), $S_{BET} = 163\ m^2/g$	7.0			
γ-Al_2O_3-a (acidic), $S_{BET} = 155\ m^2/g$	4.5			
γ-Al_2O_3-b (basic), $S_{BET} = 155\ m^2/g$	9.0			
SiO_2, $S_{BET} = 320\ m^2/g$	7.0			
RuO_2/γ-Al_2O_3-n	7.0	4.3	2.00	
$RuO_2 \cdot CoO(OH)/\gamma$-$Al_2O_3$-n	7.0	5.8	2.05	1.12
$RuO_2 \cdot CoO(OH)/\gamma$-$Al_2O_3$-b	9.0	5.7	3.23	1.73
$RuO_2 \cdot CoO(OH)/\gamma$-$Al_2O_3$-a	4.5	5.1	2.66	1.41
$RuO_2 \cdot CoO(OH)/SiO_2$	7.0	5.3	2.99	1.61
$RuO_2 \cdot CoO(OH) \cdot 3H_2O$		21.6	38.0	19.5
$RuO_2 \cdot 1.5CoO(OH) \cdot 4H_2O$		23.0	30.5	24.3

[a] Ru/Co atomic ratios are given from the preparation stoichiometry; the catalyst composition was determined by XRD and TGA.
[b] The pH of 10% aqueous suspension.
[c] From TGA weight loss in the temperature range of 30–300 °C.
[d] From ICP analysis.

Typically, a mixture of an alcohol (2.5 mmol), Ru catalyst (alcohol/Ru = 10:1–45:1 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 it was rapidly and thoroughly stirred. Then the reactor was placed in the oil bath, which was preheated to a certain temperature to start the reaction. We took samples of the reaction mixture at appropriate time intervals to monitor the reaction by GC (Varian 3800 gas chromatograph equipped with a 25 m BP5 capillary column). Reaction products were identified by GC-MS with the use of authentic samples.

2.4.2. Oxidation with N_2O

The oxidation of alcohols with N_2O was carried out in a 50-ml glass-lined stainless-steel autoclave equipped with a pressure gauge and magnetic stirring. Typically, the reaction mixture contained 1.0 mmol substrate and ca. 0.1 mmol dodecane (internal GC standard) in 5.0 ml solvent and an appropriate amount of a catalyst. The mixture was placed in the autoclave, which was then pressurised with N_2O and vented three times at room temperature with stirring to remove air from the system. Finally, the autoclave was pressurised with N_2O and placed in the oil bath, which was preheated to the reaction temperature, to carry out alcohol oxidation with thorough stirring. After that, the reactor was cooled, depressurised, and opened, and the reaction mixture was analysed by GC.

3. Results and discussion

3.1. Catalyst characterisation

The Ru–Co mixed oxide catalysts were characterised by ICP (chemical composition), TGA (water content), XRD (phase analysis), and H_2-TPR (redox properties). Only hydrous oxides were catalytically active in the oxidation of alcohols [11–13]. These oxides were obtained by a mild thermal pretreatment of the precursor hydroxides, typically at 60 °C/0.5 Torr/2 h. From TGA, the active bulk oxides contained three to five water molecules per Ru atom, as determined from weight loss in the temperature range of 30–300 °C (Table 1). Thoroughly dehydrated oxides were inactive in the 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 BET surface area of ca. 200 m^2/g. After dehydration at 130 °C/10 h, the Ru dioxide transformed to the inactive crystalline RuO_2 with the rutile structure (Fig. 1), which had a low surface area (ca. 10 m^2/g), in agreement with the literature [15]. Hydrous RuO_2 has been reported to chemisorb a significant amount of oxygen, whereas the anhydrous form adsorbs little oxygen [15]. These differences might greatly affect the activity of RuO_2 in the oxidation of alcohols [16]. From XRD data (Fig. 2, pattern 1), the hydrous Ru–Co mixed oxide of the optimal 1:1–1:2 atomic ratio comprises an amorphous RuO_2 hydrate and the crystalline cobaltic acid CoO(OH) (heterogenite-3R) with a crystallite size of 100 Å. The peak at 42.6° may indicate the presence of some Co_3O_4. The catalyst might also include a mixed Ru–Co oxide phase. Thus the catalyst composition can be approximated as a binary oxide $RuO_2 \cdot (1\text{–}2)CoO(OH) \cdot (3\text{–}5)H_2O$. The catalyst dehydrated at 130 °C/10 h to an inactive form with the patterns of both rutile RuO_2 and heterogenite-3R CoO(OH) (Fig. 2, pattern 2), with crystallite sizes of 90 and 80 Å, respectively. The hydration water may play an important role, generating active Ru^{IV} hydroxo species (vide infra).

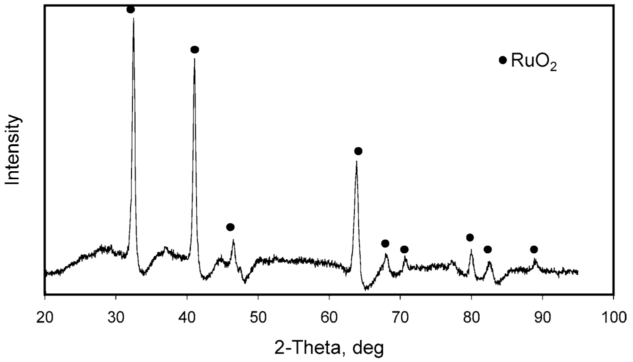


Fig. 1. XRD pattern for RuO_2 pretreated at 130 °C/10 h; matches the pattern of rutile RuO_2.

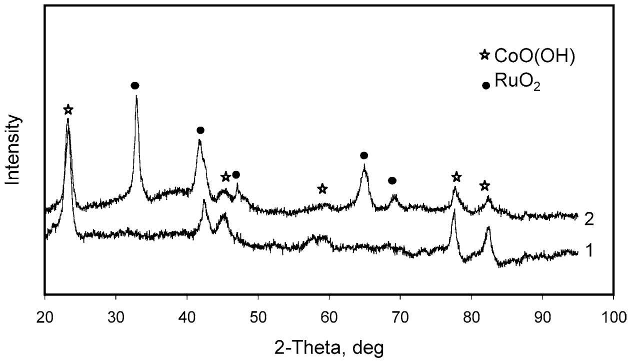


Fig. 2. XRD patterns: 1) Ru–Co (1:1.5) oxide pretreated at 60 °C/0.5 Torr, 2 h; matches the pattern of heterogenite-3R CoO(OH); 2) Ru–Co (1:1.5) oxide pretreated at 130 °C/10 h; shows the patterns of rutile RuO_2 and heterogenite-3R CoO(OH).

The XPS analysis of the oxidation state of Ru in the catalysts, although inconclusive because of the unavoidable carbon contamination [17], was compatible with the presence of Ru^{IV}. The Ru/Co atomic ratio at the surface of Ru–Co oxide (1.55:1) was found to be considerably higher than the bulk ratio (1:1.5). This indicates segregation of Ru and Co in the catalyst, with Ru concentrating at the catalyst surface.

H_2-TPR profiles for bulk and supported catalyst samples are shown in Figs. 3 and 4, respectively. Bulk RuO_2 (rutile) reduces quantitatively to Ru^0 at about 97 °C (Fig. 3, profile 4). A small peak at 176 °C may be due to the reduction of unknown ruthenium species present in the catalyst. $RuCl_3$ reduces to Ru^0 at a higher temperature (215 °C), as expected (profile 1). CoO(OH) exhibits reduc-

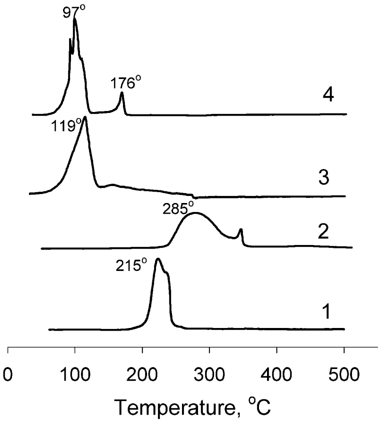


Fig. 3. H_2-TPR profiles: (1) $RuCl_3 \cdot 2H_2O$, (2) CoO(OH), (3) $RuO_2 \cdot CoO(OH) \cdot 3H_2O$, (4) RuO_2.

tion to Co^0 around 285 °C (profile 2), in agreement with previous reports ([18,19] and references therein). In bulk $RuO_2 \cdot CoO(OH)$ catalyst, Ru^{IV} reduces quantitatively to Ru^0 practically in the same temperature range as in the case of RuO_2 (profile 3). Interestingly, no separate peak for Co reduction is observed up to 500 °C. This is not unexpected, as doping Co catalysts with ruthenium has been shown to significantly increase the temperature of Co reduction [18]. In alumina-supported RuO_2 and Ru–Co (1:1) oxide, Ru^{IV} reduces to Ru^0 in the same temperature range as it does in bulk oxides, regardless of the acidity of alumina (Fig. 4, profiles 1–4). On silica, the reduction occurs at a slightly higher temperature, 136 °C (profile 5). No Co reduction peak is observed for the supported Ru–Co catalysts up to 500 °C. This may be explained by the hampering of Co reduction with Ru and the formation of a more stable Co aluminate [18]. The TPR results show that the Co^{III} additives have practically no effect on the oxidizing power of Ru^{IV}.

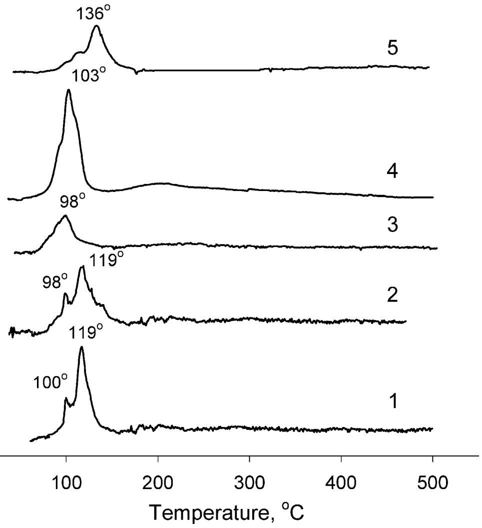


Fig. 4. H_2-TPR profiles for supported Ru–Co catalysts: (1) $RuO_2/\gamma\text{-}Al_2O_3$-n, (2) $RuO_2 \cdot CoO(OH)/\gamma\text{-}Al_2O_3$-a, (3) $RuO_2 \cdot CoO(OH)/\gamma\text{-}Al_2O_3$-n, (4) $RuO_2 \cdot CoO(OH)/\gamma\text{-}Al_2O_3$-b, (5) $RuO_2 \cdot CoO(OH)/SiO_2$.

3.2. *Oxidation of alcohols by O_2*

Table 2 shows representative examples of oxidation of saturated and unsaturated primary and secondary alcohols by O_2 with bulk and supported Ru–Co oxide as the catalyst.

Table 2
Oxidation of alcohols by O_2 catalysed by Ru–Co (1:1) oxide (in toluene, 110 °C)[a]

Entry	Catalyst	Alcohol	Time (h)	Product	Conversion (%)	Selectivity (%)	TOF (h^{-1})
1	Ru–Co[b]	Cinnamyl	0.5	Cinnamaldehyde	96	94	38
2	Ru–Co/Al_2O_3-n	Cinnamyl	0.5	Cinnamaldehyde	100	> 99	40
3	Ru–Co/Al_2O_3-n[c]	Cinnamyl	1.0	Cinnamaldehyde	100	> 99	20
4	Ru–Co/Al_2O_3-n	Cinnamyl	0.25	Cinnamaldehyde	97	98	78
5	Ru–Co/Al_2O_3-a	Cinnamyl	0.25	Cinnamaldehyde	100	> 99	80
6	Ru–Co/Al_2O_3-a[d]	Cinnamyl	0.5	Cinnamaldehyde	76	> 99	68
7	Ru–Co/Al_2O_3-b	Cinnamyl	0.25	Cinnamaldehyde	96	99	77
8	Ru–Co/SiO_2	Cinnamyl	0.5	Cinnamaldehyde	56	> 99	22
9	Ru–Co/Al_2O_3-n	Benzyl	0.25	Benzaldehyde	100	> 99	80
10	Ru–Co/Al_2O_3-n	1-Decanol	3.0	Decanal	86	84	5.6
11	Ru–Co/Al_2O_3-n	1-Decanol[e]	4.0	Decanal	90	> 99	4.5
12	Ru–Co/Al_2O_3-n	9-Decenol	3.0	9-Decenal	75	76	4.9
13	Ru–Co/Al_2O_3-n	9-Decenol[e]	4.0	9-Decenal	92	97	4.6
14	Ru–Co/Al_2O_3-n	2-Decanol	4.0	2-Decanone	87	> 99	4.4
15	Ru–Co/Al_2O_3-n	*t*-Bu(Ph)CHOH	1.0	*t*-Bu(Ph)CO	100	> 99	20
16	Ru–Co/Al_2O_3-n	Carveol[f]	1.0	Carvone	83	> 99	17

[a] Alcohol (1.0 mmol), alcohol/Ru = 20:1 mol/mol, toluene (5 ml) and O_2 (25 ml/min). Turnover frequencies (TOF): mol alcohol reacted per mol Ru and per hour.

[b] Catalyst, $RuO_2 \cdot 1.5CoO(OH) \cdot 4H_2O$; 2.5 mmol alcohol; alcohol/Ru = 20:1 mol/mol [11].

[c] Air (25 ml/min) instead of O_2 as oxidant.

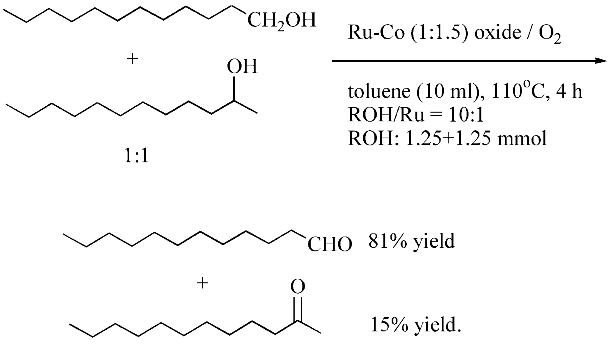
[d] Alcohol/Ru = 45:1 mol/mol.

[e] Radical scavenger 2,6-di-*t*-butyl-*p*-cresol (0.01 M) was added.

[f] Carveol consisted of 57% *trans* and 43% *cis* isomer.

The bulk oxide is useful for catalyst characterisation (vide supra). The supported Ru–Co oxide is a much more efficient catalyst because of the isolation of Ru sites, making more Ru sites available for the reaction. The activated aromatic and allylic alcohols, such as benzyl and cinnamyl alcohol, are oxidised by O_2 with an almost 100% yield of aldehydes in 15 min (entries 5, 9). These last reactions may be affected by oxygen transport into the liquid reaction mixture. The oxidation also proceeds easily when air is used instead of pure O_2, though more slowly, as expected (entry 6). Non-activated primary alcohols (e.g., 1-decanol) are more difficult to oxidise. They, too, give aldehydes in good yields, but overoxidation to acids takes place. Addition of a radical scavenger, such as 2,6-di-*t*-butyl-*p*-cresol, greatly improves the yield of aldehyde (entries 10, 11). This indicates that the overoxidation occurs via a radical mechanism. The oxidation of 9-decenol occurs chemoselectively to 9-decenal without affecting the position of the double bond (entries 12, 13). Therefore, the Ru–Co oxide catalysts possess both high activity and high chemoselectivity for alcohol-to-aldehyde oxidation. It should be noted that the alumina-supported Ru–Co oxide catalyst shows the highest output in the oxidation of cinnamyl alcohol among the most efficient solid Ru catalysts. It has a turnover frequency (TOF) of 80 h^{-1} at 110 °C (entry 5), which is higher than those reported for Ru–Co–Al hydrotalcite (14 h^{-1} at 60 °C) [6], Ru-hydroxyapatite (6 h^{-1} at 80 °C) [7], Ru–Co$(OH)_2$–CeO_2 (10 h^{-1} at 60 °C) [8], and Ru/Al_2O_3 (27 h^{-1} at 83 °C) [9].

The Ru–Co oxide catalysts are also efficient for the oxidation of secondary alcohols to ketones (Table 2, entries 14–16). Interestingly, the aliphatic secondary alcohols oxidise more slowly than the corresponding primary alcohols. Thus the competitive oxidation of an equimolar mixture of 1- and 2-dodecanol gives 81% aldehyde and 15% ketone. This shows that steric effects play a significant role and indicates that alkoxy Ru^{IV} intermediates may be involved in the reaction,



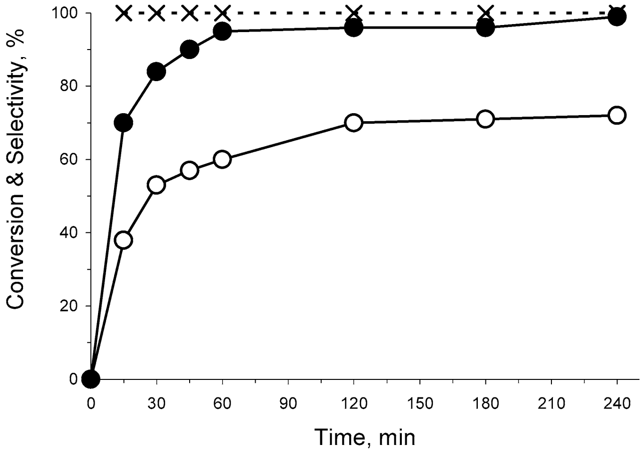


Fig. 5. Oxidation of cis and trans isomers of carveol (0.80 mol/l) with O_2 catalysed by $RuO_2 \cdot CoO(OH)/\gamma$-$Al_2O_3$-n (in toluene, 110 °C, alcohol/Ru = 20:1 mol/mol): conversion of *trans* (open circles) and *cis* (solid circles) carveol; selectivity to carvone (dotted line).

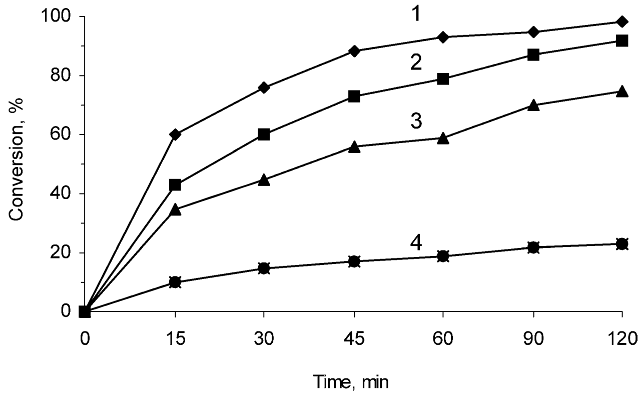
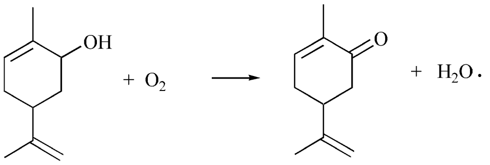


Fig. 6. Oxidation of cinnamyl alcohol (0.20 mol/l) to cinnamaldehyde with O_2 catalysed by supported Ru–Co oxide (in toluene, 110 °C, alcohol/Ru = 45:1 mol/mol): (1) $RuO_2 \cdot CoO(OH)/\gamma$-$Al_2O_3$-a, (2) $RuO_2 \cdot CoO(OH)/\gamma$-$Al_2O_3$-n, (3) $RuO_2 \cdot CoO(OH)/\gamma$-$Al_2O_3$-b, (4) $RuO_2 \cdot CoO(OH)/SiO_2$.

Carveol (*cis*/*trans* = 43:57) is readily oxidised to carvone with almost 100% selectivity (Table 2, entry 16), without double-bond migration,



The *cis*-isomer is more reactive than the *trans*-isomer (Fig. 5).

Catalyst support plays a very important role (Fig. 6). γ-Alumina is much better than silica. This is in agreement with the H_2-TPR results (Fig. 4), as Ru–Co/Al_2O_3 reduces at a lower temperature than Ru–Co/SiO_2. The acidity of alumina is essential too; the acidic alumina is better than the neutral and basic alumina. The acidity of support may affect the state of Ru^{IV} and Co^{III} in the catalyst. It could also facilitate the formation of alkoxy Ru^{IV} intermediate (vide infra).

The Ru–Co catalyst can be reused several times after a simple workup (Fig. 7). In repeated runs, the selectivity re-

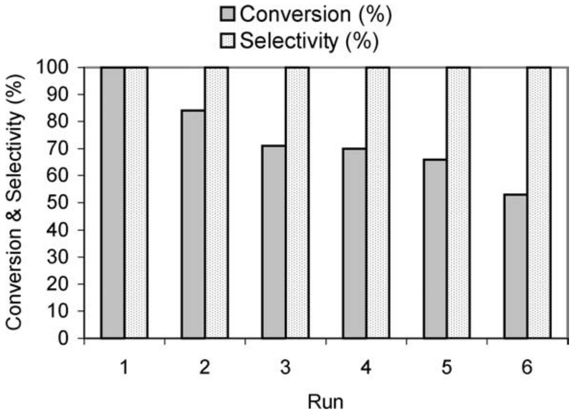


Fig. 7. Catalyst reuse for cinnamyl alcohol oxidation by O_2: $RuO_2 \cdot CoO(OH)/\gamma\text{-}Al_2O_3\text{-n}$, 110 °C, alcohol/Ru = 20:1 mol/mol, 0.5 h. The catalyst was filtered off, washed with CH_2Cl_2, dried in vacuum and reused.

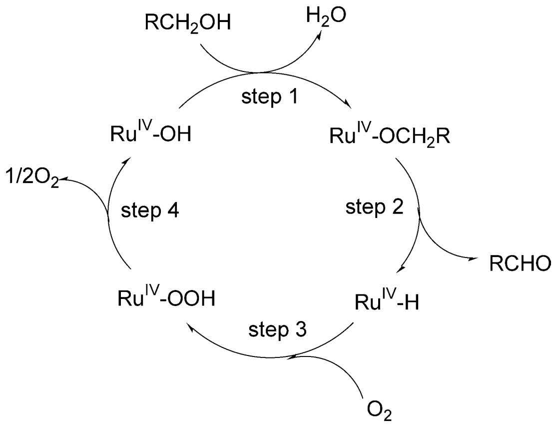
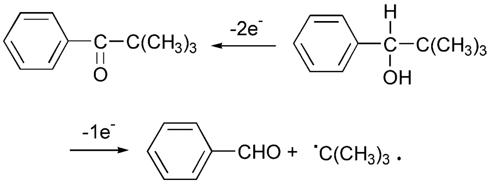


Fig. 8. Mechanism of alcohol oxidation catalysed by Ru^{IV}.

mains almost 100%; the conversion gradually declines, however. This may be due to catalyst dehydration during the workup, which is difficult to avoid in batch operation. Wetting the recovered catalyst with a drop of water improved its reuse to some extent. It should be noted that no leaching of Ru or Co from the catalyst was observed during the reaction (ICP analysis).

3.3. Mechanistic features

The oxidation of alcohols to aldehydes and ketones in the Ru–Co oxide/O_2 system can be viewed as an oxidative dehydrogenation, whereas the formation of acids is an oxygenation; that is, it involves oxygen atom incorporation. The test alcohol t-Bu(Ph)CHOH has been used to probe the mechanism of alcohol oxidation—one-electron versus two-electron transfer ([20] and references therein). With two-electron oxidants, such as Pd^{II}, this alcohol gives the ketone, t-Bu(Ph)CO, with the same carbon backbone. With one-electron oxidants (e.g., Ce^{4+} or $S_2O_8{}^{2-}$) the C–C bond between α and β carbon atoms cleaves to yield benzaldehyde and t-butyl radical as the primary products



With supported Ru–Co oxide catalyst, t-Bu(Ph)CHOH was found to selectively oxidise to t-Bu(Ph)CO (Table 2, entry 15), which indicates that the oxidative dehydrogenation of alcohols to aldehydes or ketones is a two-electron process, and one-electron processes do not play important role in these reactions. Similar behaviour has been observed in alcohol oxidation with O_2 catalysed by $[n\text{-}Pr_4N]RuO_4$ in a homogeneous system [21] and by bulk RuO_2 and Ru–Co oxide in a heterogeneous system [11]. On the other hand, the overoxidation of aldehyde to acid (oxygenation) appears to occur by a free radical mechanism, as it is effectively inhibited by the addition of a radical scavenger (Table 2).

The Ru-catalysed oxidative dehydrogenation of alcohols is likely to occur via the formation of Ru^{IV} alkoxide followed by β elimination of Ru hydride species to yield aldehyde or ketone and subsequent catalyst regeneration by O_2 (Fig. 8) [9]. This mechanism is supported by the following evidence: (i) the results of oxidation of t-Bu(Ph)CHOH favour a two-electron mechanism; (ii) catalyst hydration enhances the reaction that supports the participation of Ru–OH groups; (iii) the substrate activity (primary alcohol > secondary alkohol) is indicative of the participation of Ru^{IV} alkoxide intermediates. In addition, Yamaguchi and Mizuno [9] obtained important evidence supporting the formation of Ru hydride species: they observed transfer hydrogenation of a ketone that was used as the oxidant instead of O_2 for alcohol oxidation catalysed by alumina-supported Ru hydroxide. It should be noted that in this mechanism Ru^{IV} does not change its oxidation state. If the mechanism is correct, the Ru^{IV} acts as a Lewis acid rather than a redox agent.

Another important question is: what is the role of Co^{III}? It is conceivable that Co^{III} could enhance the oxidation power of Ru by increasing its oxidation state or facilitate catalyst regeneration by activating O_2. From H_2-TPR (Figs. 3 and 4), the presence of Co^{III} does not increase the oxidation power of Ru. Hence Co^{III} might facilitate catalyst regeneration (steps 3 and 4). These steps could be rate-controlling in the catalytic process. Such a role of Co is in agreement with the well-known ability of cobalt ions to activate O_2 and peroxides [14].

3.4. Oxidation of alcohols by N_2O

Oxidation by N_2O has attracted considerable interest [3,4]. N_2O is a notorious air pollutant. It is produced in large amounts as a by-product in oxidations by HNO_3, for example, in the production of adipic acid [4]. The use of N_2O for catalytic oxidation will therefore bring “green” benefits by reducing its environmental impact. N_2O is a powerful oxi-

Table 3
Oxidation of cinnamyl alcohol to cinnamaldehyde by N_2O catalysed by Ru–Co (1:1) oxide[a]

Entry	Catalyst	Oxidant	Conversion (%)	Selectivity (%)	TOF (h^{-1})
1	$RuO_2 \cdot CoO(OH)/Al_2O_3$-n	N_2O (10 bar) + air[b]	99	100	9.9
2	$RuO_2 \cdot CoO(OH)/Al_2O_3$-n	N_2 (10 bar) + air[b]	97	98	9.7
3	$RuO_2 \cdot CoO(OH)/Al_2O_3$-n	N_2O (10 bar)[c]	20	100	2.0
4	$RuO_2 \cdot CoO(OH) \cdot 3H_2O$	N_2O (10 bar)[c]	18	100	1.8
5	$RuO_2 \cdot CoO(OH) \cdot H_2O$	N_2O (10 bar)[c,d]	6	100	0.6

[a] Reactions were carried out in 50-ml stirred autoclave in toluene (5 ml) at 110 °C for 2 h; 1.0 mmol alcohol, alcohol/Ru = 20:1 mol/mol. Turnover frequencies (TOF) were defined as mol alcohol reacted per mol Ru and per hour.

[b] The autoclave was pressurised with N_2O or N_2 to 10 bar without removing air.

[c] To remove air, the autoclave was pressurised with N_2O and vented three times then finally pressurised with N_2O to 10 bar.

[d] The catalyst was pre-treated at 110 °C/0.5 Torr for 2 h.

dant ($E_0 = 1.77$ V vs NHE). It is also a clean oxidant—only N_2 forms as a by-product. But N_2O is a quite inert molecule and a poor ligand; hence oxidation with N_2O is very difficult to realise. Very few catalysts are known to activate N_2O for selective oxidation. The best-known catalyst is Fe-zeolite for the gas-phase oxidation of benzene to phenol by N_2O [3]. Some Ru complexes [22] and polyoxometalates [23] catalyse alcohol oxidation by N_2O in a homogeneous solution.

Ru–Co oxide was found to catalyse the oxidation of saturated and unsaturated primary alcohols to aldehydes. Some representative results for the oxidation of cinnamyl alcohol are shown in Table 3. The reaction was carried out in an autoclave at 110 °C in toluene solution under a N_2O pressure of 10 bar. In first experiments, no attempt was made to remove air from the autoclave. Under such conditions, a cinnamaldehyde yield of almost 100% was obtained in 2 h (entry 1). Then the blank experiments with N_2 instead of N_2O were performed, which showed that this result was mainly due to oxidation by the remaining O_2 from air (entry 2). When the air was thoroughly removed, only 20% alcohol-to-aldehyde conversion was observed (entry 3).[1] The oxidation by N_2O, like the oxidation by O_2, was enhanced by the presence of hydration water in the Ru–Co catalyst (entry 5), which suggests the participation of Ru^{IV} hydroxo species in the reaction. Unsaturated alcohols were oxidised chemoselectively by N_2O; for example, 9-decenol gave 9-decenal without migration of the double bond. N_2O was found to selectively oxidise t-Bu(Ph)CHOH to t-Bu(Ph)CO, indicating that the oxidation is a two-electron process, like the oxidation by O_2. Therefore, the oxidation of alcohols by N_2O catalysed by Ru–Co oxide exhibits a close similarity to the corresponding oxidation by O_2. However, N_2O is much less efficient than O_2, which is not unexpected. To make the oxidation by N_2O synthetically useful, much more active catalysts are required.

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[1] The results reported earlier [13] showed higher yields of aldehydes and ketones. These were obtained in the presence of traces of air.