Pergamon

Tetrahedron Letters 43 (2002) 7179–7183

TETRAHEDRON
LETTERS

Highly efficient oxidation of alcohols to carbonyl compounds in the presence of molecular oxygen using a novel heterogeneous ruthenium catalyst

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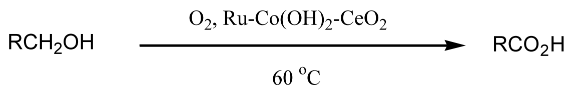
Received 1 July 2002; revised 8 August 2002; accepted 9 August 2002

Abstract—A ruthenium cation combined with microcrystals of cobalt hydroxide and cerium oxide acted as a highly efficient heterogeneous catalyst for the oxidation of various types of alcohols to carbonyl compounds under atmospheric pressure of molecular oxygen at 60°C. Especially, primary aliphatic alcohols could be oxidized to afford the carboxylic acids in high yields.

The selective oxidation of alcohols to the corresponding carbonyl compounds plays an important role in organic synthesis.[1] Even at present, however, stoichiometric amounts of hazardous and/or toxic inorganic oxidants that generate copious amounts of wastes are used.[2] Much attention has been paid to the use of molecular oxygen as a 'green' oxidant to achieve the effective oxidation of alcohols in the presence of transition metal catalysts.[3,4] Recently, we have developed highly active heterogeneous ruthenium catalysts for aerobic alcohol oxidations based on the unique characteristics of inorganic matrices, i.e. hydrotalcites and hydroxyapatites.[4b,d,e] In this paper, a Ru cation combined with cobalt hydroxide and cerium oxide, Ru–$Co(OH)_2$–CeO_2, was found to be an effective heterogeneous catalyst for the oxidation of various alcohols to carbonyl compounds under atmospheric pressure of O_2. Notably, the present catalyst showed high activity for the oxidation of primary aliphatic alcohols to carboxylic acids (Scheme 1).[4c,f]



$$RCH_2OH \xrightarrow[60\ ^{o}C]{O_2,\ Ru\text{-}Co(OH)_2\text{-}CeO_2} RCO_2H$$

Scheme 1.

The Ru–$Co(OH)_2$–CeO_2 catalyst was prepared as follows. To 30 ml of aqueous Na_2CO_3 (13.3 mmol) and NaOH (46.4 mmol) was slowly added a mixture of $Co(NO_3)_2{\cdot}6H_2O$ (10.2 mmol), $Ce(NO_3)_3{\cdot}6H_2O$ (5.1 mmol), and $RuCl_3{\cdot}nH_2O$ (Ru: 1.53 mmol) dissolved in 20 mL of distilled water, and the resultant mixture was heated at 65°C for 18 h with vigorous stirring. The dark brown slurry was filtered, washed with distilled water and dried at 110°C for 12 h, yielding 2.15 g of black powder [Anal. Co, 33.6; Ce, 25.7; Ru, 6.4. XPS: Ru $3p_{3/2} = 464.4$ eV, FWHM = 4.9 eV; Co $2p_{3/2} = 780.8$ eV, FWHM = 2.6 eV].[5]

The black powder exhibited high catalytic activity for the oxidation of various kinds of alcohols in the presence of molecular oxygen as summarized in Table 1.[6] Allylic alcohols (entries 1, 3 and 4), benzylic alcohols (entries 5–8), and secondary alcohols (entries 9–13) gave high yields of the corresponding carbonyl compounds. A heteroaromatic alcohol of 2-thiophenmethanol could be also oxidized quantitatively to 2-thiophencarboxaldehyde (entry 8). The notable ability of the Ru–$Co(OH)_2$–CeO_2 catalyst over other heterogeneous Ru catalysts was the oxidation of cyclohexanol to cyclohexanone in high yield (entry 10). Sterically hindered secondary alcohols, i.e. borneol and adamantanol, could be smoothly converted to the corresponding ketones in quantitative yields (entries 12 and 13). Furthermore, the Ru–$Co(OH)_2$–CeO_2 could be reused with retention of its high catalytic activity (entry 2).[7,8]

Encouraged by the above results, the oxidation of primary aliphatic alcohols, e.g. 1-octanol, was exam-

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Keywords: oxidation; alcohols; carbonyl compounds; molecular oxygen; ruthenium catalyst.

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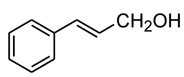
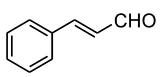
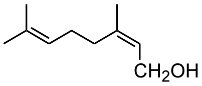
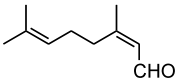
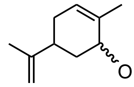
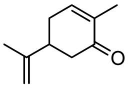
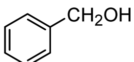
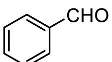
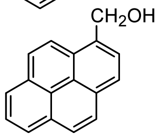
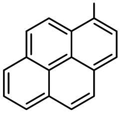
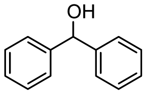
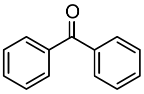
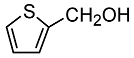
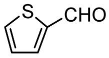
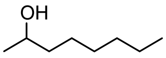
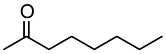
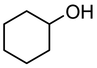
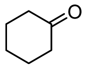
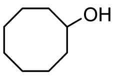
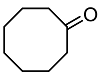
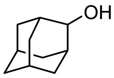
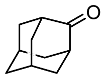
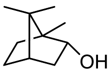
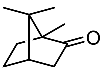
PII: S0040-4039(02)01678-7

Table 1. Aerobic oxidation of various alcohols catalyzed by Ru–$Co(OH)_2$–CeO_2[a]

Entry	Substrate	Product	Time (h)	Conv.(%) [b]	Yield (%) [b,c]
1			1	100	>99 (92)[d]
2[e]			1	100	90
3			4	98	97
4			3	98	98
5			1	100	>99 (96)
6			1	100	>99
7			50 min	100	>99 (95)
8			40 min	100	>99
9			1.5	98	98
10[f]			8	83	81
11[f]			5	85	84
12			2	100	>99 (94)
13			1.5	100	>99

[a] Reaction conditions: substrate (2 mmol), Ru-$Co(OH)_2$-CeO_2 (0.3 g, Ru: 0.2 mmol), benzotrifluoride (5 mL), O_2 flow, 60 °C. [b] Conversion and yield were determined by GC or GC-MS using an internal standard method. [c] Values in parentheses are isolated yields. [d] Large scale oxidation using 20 mmol of substrate (ref. 6). [e] Reuse experiment (ref. 7). [f] Catalyst (0.5 g).

ined using various Ru catalysts under atmospheric O_2 pressure as shown in Table 2. Notably, the Ru–$Co(OH)_2$–CeO_2 was found to be a highly efficient catalyst for the oxidation of 1-octanol to octanoic acid at 60°C (entry 1). This Ru catalyst was more effective for the aerobic oxidation of primary alcohols than the RuHAP and Ru/CeO_2 (entries 3 and 4).[4c,f] In a separate experiment using this Ru–$Co(OH)_2$–CeO_2 catalyst, octanal was smoothly oxidized to octanoic acid even at room temperature in the air (Scheme 2), while slow oxidation occurred with $Co(OH)_2$–CeO_2 catalyst.[4c,9] Without the Ce component, the yield of octanoic acid was low in spite of a high conversion of 1-octanol (entry 2). It can be said that a combination of Ru with both Co and Ce elements is necessary to achieve high yield of the carboxylic acid.

Table 3 shows the results for the oxidation of various primary alcohols using the Ru–$Co(OH)_2$–CeO_2 catalyst.[10] Aliphatic alcohols were smoothly oxidized to the

Table 2. Aerobic oxidation of 1-octanol using various types of heterogeneous Ru catalysts[a]

Entry	Catalyst[b]	Conv. of 1-octanol (%)[c]	Yields (%)[c]	
			Octanoic acid	Octanal
1	Ru–$Co(OH)_2$–CeO_2	100	97	1
2	Ru–Co–Al–CO_3	90	63	26
3	Ru/CeO_2[d]	30	28	0
4[e]	RuHAP	95	0	94
5	Ru–Mg–Ce–CO_3	58	1	48
6	Ru–Mg–Al–CO_3	16	0	15
7	$Co(OH)_2$–CeO_2	<2	0	<1

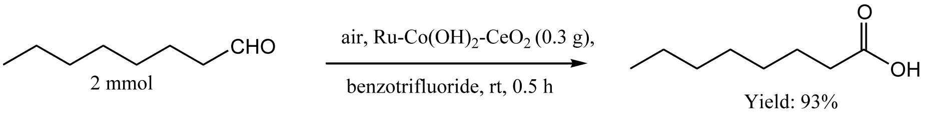
[a] Reaction conditions: 1-octanol (2 mmol), catalyst (0.3 g, Ru: 6 wt%), benzotrifluoride (5 mL), O_2 flow, 60°C, 4 h.

[b] Molar ratio: Co/Ce/Ru = Co/Al/Ru = Mg/Ce/Ru = Mg/Al/Ru = 2/1/0.3.

[c] Conversion and yields were determined by GC using an internal standard method.

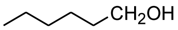
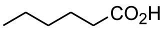
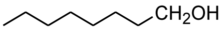
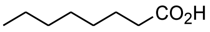
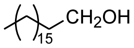
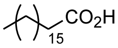
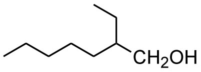
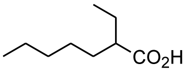
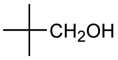
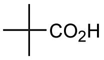
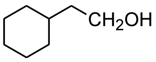
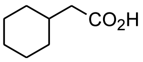
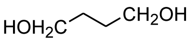
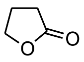
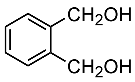
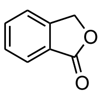
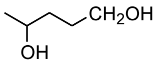
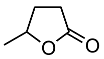
[d] Prepared by the literature procedures (Ref. 4c).

[e] Data from Ref. 4e.



Scheme 2.

Table 3. Oxidation of various primary alcohols catalyzed by Ru–$Co(OH)_2$–CeO_2 in the presence of molecular oxygen[a]

Entry	Substrate	Product	Time (h)	Conv.(%) [b]	Yield (%) [b,c]
1			4	100	89 (80)
2			4	100	97 (90)[d]
3			5	100	82 (78)
4[e]			14	95	79
5			5	100	64
6			4	100	85 (80)
7[f]			6	100	83
8[g]			6	100	77
9[f]			6	100	87

[a] Reaction conditions: substrate (2 mmol), Ru-$Co(OH)_2$-CeO_2 (0.3 g, Ru: 0.2 mmol), benzotrifluoride (5 mL), O_2 flow, 60 °C. [b] Conversion and yield were determined by GC, LC or GC-MS using an internal standard method. [c] Values in parentheses are isolated yields. [d] Large scale oxidation using 20 mmol of substrate (ref. 10). [e] Deionized water (0.2 mL) was added. [f] Diol (1 mmol), 80 °C. [g] Diol (1 mmol), 60 °C.

corresponding carboxylic acids in excellent yields (entries 1–6). Addition of water improved the catalytic activity to attain a high yield of the branched carboxylic acid (entry 4). α,ω-Primary diols were selectively transformed into the corresponding lactones in high yields (entries 7 and 8). Intramolecular competitive oxidation of 1,4-pentanediol having primary and secondary hydroxyls gave methyl-γ-butyrolactone in 87% yield (entry 9). To the best of our knowledge, this Ru–$Co(OH)_2$–CeO_2 is the most effective catalyst for the one-pot oxidation of primary aliphatic alcohols into carboxylic acids using atmospheric pressure of O_2 as a sole oxidant.

When 2,6-di-*tert*-butyl-*p*-cresol as a radical scavenger was added in the oxidation of 1-octanol, octanal was formed in a quantitative yield without formation of the corresponding carboxylic acid. The present oxidation might proceed via a Ru–alkoxide intermediate, followed by β-hydride elimination to give an aldehyde.[11] An efficient transformation of aldehyde to carboxylic acid might involve a free radical process. As previously noted, the oxidation of aldehyde to carboxylic acid was slow using Ce-free Ru catalyst, i.e. Ru–Co–Al–CO_3. High activity of this Ru catalyst might be due to a high oxidation state of the Ru species, e.g. Ru(IV), arising from the Co component.[12] The radical process of the aldehyde oxidation[13] would be also facilitated by the synergism among the Ru, Co, and Ce components.

In conclusion, the Ru cation combined with $Co(OH)_2$ and CeO_2 acted as an excellent heterogeneous catalyst for aerobic oxidation of various types of alcohols, including cyclic alcohols and primary aliphatic alcohols, to the corresponding carbonyl compounds under mild reaction conditions. This heterogeneous Ru catalyst provides a green oxidation protocol for the direct production of aliphatic carboxylic acids from the alcohols using atmospheric pressure of molecular oxygen.

Acknowledgements

This work was supported by the Grant-in-Aid for Scientific Research from Ministry of Education, Culture, Sports, Science and Technology of Japan (11450307). We are grateful to the Department of Chemical Science and Engineering, Graduate School of Engineering Science, Osaka University, for scientific support via 'Gas-Hydrate Analyzing System (GHAS)'.

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5. XRD measurement of the black powder proved the formation of small crystals of $Co(OH)_2$ and CeO_2. Ru K-edge XAFS (Spring-8, BL10B, 2000A0278) revealed that the Ru^{4+} cation exists as a monomeric species on the surface of $Co(OH)_2$ and CeO_2. The curve-fitting analysis of k^3-weighted EXAFS showed that four oxygen atoms surround the isolated Ru species.
6. A typical procedure for the large scale oxidation of alcohols is as follows. A mixture of cinnamyl alcohol (20 mmol, 2.68 g), Ru–$Co(OH)_2$–CeO_2 (0.30 g, Ru 0.20 mmol), and benzotrifluoride (5 mL) was stirred at 80°C for 24 h under atmospheric O_2 pressure. After the reaction, the solid catalyst was separated by filtration, and the Kugelrohr distillation of the residue gave 2.43 g of pure cinnamaldehyde (92%).

7. After the oxidation of cinnamyl alcohol, the solid catalyst was separated by filtration and washed with 10% of aqueous Na_2CO_3 and then deionized water, followed by drying at 110°C. The used catalyst was subjected to the oxidation of cinnamyl alcohol at 60°C for 1 h to give 90% yield of cinnamaldehyde.
8. Filtration of the heterogeneous mixture gave a solution devoid of any oxidizing ability. This result clearly shows that active Ru species did not leach from the Ru–$Co(OH)_2$–CeO_2 catalyst during the oxidation reaction.
9. A temperature of 140°C was required for the oxidation of octanal to octanoic acid when the Ru/CeO_2 catalyst was used.[4c]
10. A typical procedure for the large scale oxidation of primary aliphatic alcohols is as follows. A mixture of 1-octanol (20 mmol, 2.60 g), Ru–$Co(OH)_2$–CeO_2 (0.30 g), and benzotrifluoride (5 mL) was stirred at 80°C under an atmospheric O_2 pressure. After 30 h, the solid catalyst was separated by filtration. Removal of the solvent under the reduced pressure and distillation of the residue gave 2.30 g of pure octanoic acid (90%).
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