Scope, Kinetics, and Mechanistic Aspects of Aerobic Oxidations Catalyzed by Ruthenium Supported on Alumina

Kazuya Yamaguchi and Noritaka Mizuno*[a]

Abstract: The Ru/Al_2O_3 catalyst was prepared by modification of the preparation of $Ru(OH)_3 \cdot nH_2O$. The present Ru/Al_2O_3 catalyst has high catalytic activities for the oxidations of activated, nonactivated, and heterocyclic alcohols, diols, and amines at 1 atm of molecular oxygen. Furthermore, the catalyst could be reused seven times without a loss of catalytic activity and selectivity for the oxidation of benzyl alcohol. A catalytic reaction mechanism involving a ruthenium alcoholate species and β-hydride elimination from the alcoholate has been proposed. The reaction rate has a first-order dependence on the amount of catalyst, a fractional order on the concentration of benzyl alcohol, and a zero order on the pressure of molecular oxygen. These results and kinetic isotope effects indicate that β-elimination from the ruthenium alcoholate species is a rate-determining step.

Keywords: alcohols · amines · heterogeneous catalysis · molecular oxygen · supported catalysts

Introduction

Ketones and aldehydes are an important class of industrial chemicals that have been widely used as chemical intermediates or solvents; for example, more than 8×10^5 tons of C_4 ketones and 2×10^6 tons of C_1-C_3 aldehydes have been produced in one year.[1] Alcohol oxidations are traditionally carried out with stoichiometric metal oxidants, particularly dichromate and permanganate, to produce enormous amounts of heavy metal salts as wastes.[2] In this context, the development of catalytic oxidation systems with molecular oxygen is intrinsically "non-waste producing" and of great importance.[3]

Many methods used for the homogeneous oxidation of alcohols catalyzed by transition metals such as ruthenium,[4] palladium,[5] copper,[6] cobalt,[7] and vanadium[8] have recently been reported; however, these systems have disadvantages: large quantities of catalysts and sometimes co-catalysts such as NaOAc, NaOH, K_2CO_3, *N*-hydroxyphthalimide (NHPI), hydroquinone, and 2,2′,6,6′-tetramethylpiperidinyloxy (TEMPO) are needed, and/or kinds of substrate alcohols are limited. $CuCl/Phen/K_2CO_3$[6a,d,e] and $Pd(OAc)_2$/PhenS*/NaOAc[5d,h] are examples of systems used for efficient aerobic alcohol oxidations. With the former system, the turnover number (TON) and turnover frequency (TOF) for the oxidation of 2-undecanol are low, that is, 9 and 5 h^{-1}, respectively. With the latter system, those for the oxidation of 2-pentanol are 400 and 100 h^{-1}, respectively. Even with these systems, large quantities of co-catalysts such as NaOAc, NaOH, and K_2CO_3 (0.05–2 equivalents with respect to the alcohol) are needed to achieve high yields of carbonyl compounds. In addition, the $Pd(OAc)_2$/PhenS*/NaOAc system cannot oxidize carbon–carbon double bond, sulfur, or nitrogen-containing alcohols because of strong coordination to the Pd center.[5d,h] Therefore, little is known of widely usable oxidations of alcohols with molecular oxygen alone.

In addition, if these oxidations could be performed with solid (supported) catalysts, they would be environmentally friendly because of the easy isolation of catalysts from the products and the recycling.[9] nPr_4NRuO_4/MCM-41,[10a] Ru/CeO_2,[10b] Ru–hydrotalcite,[10c,d] $[(RuCl)_2Ca_8(PO_4)_6(OH)_2]$,[10e] $[RuCl_2(p\text{-cymene})]_2$/activated carbon,[10f] Ru–Mn–Fe–Cu mixed oxide,[10g,h] zeolite-confined RuO_2 (RuO_2-FAU),[10i] Pd or Pt on activated carbon,[11a] Pd–hydrotalcite,[11c,d] Pd–hydroxyapatite,[11e] and polymer-supported Pd[11f] are examples. However, the heterogeneous oxidations are limited to activated alcohols and/or the TONs and TOFs are very low.[10, 11] Furthermore, although heterogeneous catalytic oxidations of alcohols with molecular oxygen without additives in water or without solvents are environmentally and technologically the most desirable methods, efficient, widely usable catalysts are hitherto unknown.

We have very recently reported effective aerobic heterogeneous oxidations of alcohols and amines with molecular oxygen or air alone catalyzed by a supported ruthenium catalyst (Ru/Al_2O_3).[12] In this paper, we expand the scope and

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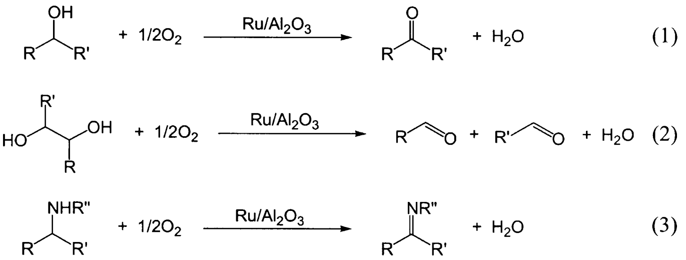
discuss the kinetic and mechanistic aspects of the aerobic oxidations [Eqs. (1)–(3)].



Results and Discussion

Scope of the Ru/Al$_2$O$_3$-catalyzed aerobic oxidation: First, the catalytic activity and selectivity for the oxidation of benzyl alcohol with 1 atm of molecular oxygen as the sole oxidant were compared with various ruthenium catalysts. The results are shown in Table 1. No oxidation proceeded in the absence of the catalyst or in the presence of γ-Al$_2$O$_3$ (entries 15 and 16). Among various ruthenium catalysts tested, Ru/Al$_2$O$_3$ had the highest catalytic activity and selectivity for the oxidation of benzyl alcohol to benzaldehyde (entry 1). Neither benzoic acid nor benzyl benzoate could be detected. When the reactions were carried out in toluene, *p*-xylene, and ethyl acetate, the reaction rates and the selectivity to benzaldehyde were almost the same as those in trifluorotoluene. Under the present conditions, the initial rate (R_0) for the oxidation of benzyl alcohol for Ru/Al$_2$O$_3$ was 1.93×10^{-2} M min^{-1}, which is higher than that of the active homogeneous catalyst *n*Pr$_4$NRuO$_4$ (1.44×10^{-2} M min^{-1}; entry 8).[4e,f] In the case of the catalyst precursor of RuCl$_3 \cdot n$H$_2$O, Friedel–Crafts-type reaction to afford *o*-, *m*-, and *p*-benzyltrifluorotoluenes proceeded (entry 9). [RuCl$_2$(PPh$_3$)$_3$] gave only stoichiometric amounts of benzaldehyde (entry 11) and 18-electron ruthenium complexes such as [RuCl$_2$(dmso)$_4$], RuCl$_2$(bpy)$_2$, and [RuCl$_2$(*p*-cymene)]$_2$ were completely inactive (entries 12–14). The increase in the reaction temperature above 423 K resulted in the successive oxidation of benzaldehyde and decrease in the selectivity.

Table 1. Oxidation of benzyl alcohol with molecular oxygen.[a]

	Catalyst	Solvent	Conversion [%]	Selectivity [%]	$R_0 \times 10^2$ [M min^{-1}]
1	Ru/Al$_2$O$_3$	PhCF$_3$	> 99	> 99	1.93
2	Ru/Al$_2$O$_3$	toluene	> 99	> 99	1.88
3	Ru/Al$_2$O$_3$	*p*-xylene	> 99	> 99	1.84
4	Ru/Al$_2$O$_3$	ethyl acetate	> 99	> 99	1.99
5	Ru/Al$_2$O$_3$	acetonitrile	50	> 99	0.77
6	Ru(OH)$_3 \cdot n$H$_2$O	PhCF$_3$	2	> 99	0.03
7	RuO$_2$ anhydrous	PhCF$_3$	no reaction	–	–
8	[*n*Pr$_4$NRuO$_4$]	PhCF$_3$	79	> 99	1.44
9	RuCl$_3 \cdot n$H$_2$O	PhCF$_3$	> 99	< 1[b]	–
10	[Ru(acac)$_3$]	PhCF$_3$	no reaction	–	–
11	[RuCl$_2$(PPh$_3$)$_3$]	PhCF$_3$	5	> 99	0.08
12	[RuCl$_2$(dmso)$_4$]	PhCF$_3$	no reaction	–	–
13	[RuCl$_2$(bpy)$_2$]	PhCF$_3$	no reaction	–	–
14	[RuCl$_2$(*p*-cymene)]$_2$	PhCF$_3$	no reaction	–	–
15[c]	Al$_2$O$_3$	PhCF$_3$	no reaction	–	–
16	none	PhCF$_3$	no reaction	–	–

[a] Benzyl alcohol (1 mmol), Ru catalyst (2.5 mol% Ru), PhCF$_3$ (1.5 mL), 356 K, O$_2$ atmosphere, 1 h. Conversion and selectivity were determined by GC using naphthalene as an internal standard. [b] Friedel–Crafts-type products (*o*-, *m*-, and *p*-benzyltrifluorotoluenes) were formed as byproducts. [c] Al$_2$O$_3$ (0.2 g).

We used inductively coupled plasma combined with atomic emission spectroscopy (ICP-AES) to confirm that the Ru content of the used Ru/Al$_2$O$_3$ catalyst was the same as that of the fresh catalyst and that no Ru was detected in the filtrate (below a detection limit of 7 ppb). In addition, the oxidation of benzyl alcohol was completely stopped by the removal of Ru/Al$_2$O$_3$ from the reaction solution as shown in Figure 1. These results indicate that any Ru species that leached into the reaction solution is not an active homogeneous catalyst and that the observed catalysis is truly heterogeneous in nature.[13] The Ru/Al$_2$O$_3$ could be reused; when the oxidation of benzyl alcohol was repeated even seven times, benzaldehyde was quantitatively produced at the same rate as that for the first run. It is noted that air can be used instead of molecular oxygen in the present system without changes in conversions and selectivities for the oxidation of benzyl alcohol.

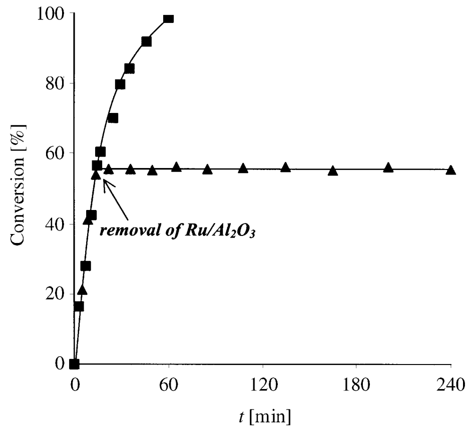


Figure 1. Effect of removal of Ru/Al$_2$O$_3$ on the oxidation of benzyl alcohol. Without removal of Ru/Al$_2$O$_3$ (■); an arrow indicates the removal of Ru/Al$_2$O$_3$ (▲). Reaction conditions were the same as those in Table 1.

Next, the scope of the present Ru/Al$_2$O$_3$ catalyst system towards various kinds of alcohols was examined. The results are summarized in Table 2. Ru/Al$_2$O$_3$ has high catalytic activities for the oxidations of activated, nonactivated, and heterocyclic alcohols and diols with only 1 atm of molecular oxygen. All primary and secondary benzylic alcohols were converted into the corresponding benzaldehydes and ketones, respectively, in quantitative yields (entries 1–11). The present catalytic system was not affected by the presence of carbon–carbon double bonds in the substrates. Primary and secondary α,β-unsaturated alcohols afforded the corresponding α,β-unsaturated aldehydes and ketones, respectively, without intramolecular hydrogen transfer, geometrical isomerization, or epoxidation of the carbon–carbon double bonds (entries 12–14). The present system could also oxidize linear

Table 2. Oxidation of various alcohols with molecular oxygen catalyzed by Ru/Al$_2$O$_3$.[a]

	Substrate	t [h]	Conversion [%]	Product	Selectivity [%]
1	benzyl alcohol	1	>99	benzaldehyde	>99
2	2-methylbenzyl alcohol	1	>99	2-methylbenzaldehyde	>99
3	3-methylbenzyl alcohol	1	>99	3-methylbenzaldehyde	>99
4	4-methylbenzyl alcohol	1	>99	4-methylbenzaldehyde	>99
5	4-methoxybenzyl alcohol	1	>99	4-methoxybenzaldehyde	>99
6	4-chlorobenzyl alcohol	1	>99	4-chlorobenzaldehyde	>99
7	4-nitrobenzyl alcohol	3	97	4-nitrobenzaldehyde	>99
8	1-phenylethanol	1	>99	acetophenone	>99
9	cyclopropylphenylmethanol	1	>99	cyclopropylphenylketone	>99
10	2,2-dimethyl-1-phenyl-1-propanol	1.5	>99	2,2-dimethyl-1-phenyl-1-propanone	>99
11	benzhydrol	7	>99	benzophenone	>99
12	cinnamyl alcohol	1.5	>99	cinnamaldehyde	98
13[b]	3-penten-2-ol	6	84	3-penten-2-one	>99
14	geraniol	6	89	geranial	97
15	2-pentanol	5	90	2-pentanone	>99
16	2-octanol	2	91	2-octanone	>99
17[b]	cyclobutanol	8	85	cyclobutanone	99
18[b]	cyclopentanol	8	92	cyclopentanone	>99
19[b]	4-*tert*-butylcyclohexanol	8	90	4-*tert*-butylcyclohexanone	95
20[b]	cyclooctanol	6	81	cyclooctanone	>99
21	2-adamantanol	7	>99	2-adamantanone	>99
22[b]	(−)-borneol	2	>99	camphor	99
23[b,c]	1-octanol	4	87	*n*-octanal	98
24[b,c]	1-decanol	4	71	*n*-decanal	99
25	2-thiophenemethanol	1.5	>99	2-thiophenecarboxaldehyde	>99
26[b]	3-pyridinemethanol	2	93	3-pyridinecarboxaldehyde	>99
27[d]	4-(1-hydroxyethyl)benzyl alcohol	1	>99	4-(1-hydroxyethyl)benzaldehyde	94
28[e]	1,4-benzenedimethanol	2	>99	terephthalaldehyde	>99
29[e]	1,2-benzenedimethanol	2	>99	phthalide	98
30[e]	styrene glycol	16	>99	benzaldehyde	90
31[e]	hydrobenzoin	2	>99	benzaldehyde	92[f]
32[e]	1,2-octanediol	24	80	*n*-heptanal	26
				2,4-dihexyl-1,3-dioxolane	60[g]
33[e]	*cis*-1,2-cyclooctanediol	6	98	1,2-cyclooctanedione	59
				1,8-octanedial	30

[a] Substrate (1 mmol), Ru/Al$_2$O$_3$ (2.5 mol% Ru), PhCF$_3$ (1.5 mL), 356 K, O$_2$ atmosphere. Conversion and selectivity were determined by GC or ^{1}H NMR using naphthalene or nitrobenzene as an internal standard. [b] Ru/Al$_2$O$_3$ (5 mol% Ru). [c] Hydroquinone (1 equivalent with respect to Ru) was added. [d] Substrate (0.25 mmol), Ru/Al$_2$O$_3$ (10 mol% Ru), DMSO (3 mL), 356 K, O$_2$ atmosphere. [e] Substrate (0.5 mmol), Ru/Al$_2$O$_3$ (4 mol% Ru), toluene (3 mL), 373 K, O$_2$ atmosphere. [f] Selectivity [%] = benzaldehyde [mol]/(2 × substrate consumed [mol]) × 100. [g] Selectivity [%] = (2 × dioxolane [mol])/substrate consumed [mol]) × 100.

secondary and cyclic aliphatic alcohols in high yields (entries 15–20). Furthermore, Ru/Al$_2$O$_3$ efficiently catalyzed the oxidation of nonactivated linear aliphatic 2-octanol without solvents. The solvent-free oxidation of 2-octanol at 423 K (0.1 mol% Ru) had a TOF of 300 h^{-1} and the TON reached 950. The TOF and TON are the highest among those reported for the aerobic oxidation of 2-octanol by the following Ru or Pd catalysts: [RuCl$_2$(PPh$_3$)$_3$]/TEMPO (TON and TOF, 466 and 104 h^{-1}),[4i,k] Ru/quinone/Co–salen (194, 97 h^{-1}),[4n] [nPr$_4$NRuO$_4$] (20, 6 h^{-1}),[4e,f] Ru/CeO$_2$ (30, 5 h^{-1}),[10b] Ru–Co–hydrotalcite (9, 5 h^{-1}),[10d] [(RuCl)$_2$Ca$_8$(PO$_4$)$_6$(OH)$_2$] (6, 1 h^{-1}),[10e] Ru–Mn–Fe–Cu mixed oxide (4, 1 h^{-1}),[10g,h] zeolite-confined RuO$_2$ (RuO$_2$-FAU) (9, 2 h^{-1} for 2-heptanol),[10i] Pd(OAc)$_2$/PhenS*/NaOAc (400, 10 h^{-1} for 2-hexanol),[5d] Pd–hydrotalcite (20, 2 h^{-1} for 2-dodecanol),[11c,d] Pd–hydroxyapatite (152, 6 h^{-1}),[11e] and polymer-supported Pd (4, 0.2 h^{-1} for cyclooctanol).[11f]

Sterically hindered alcohols such as 2-adamantanol and (−)-borneol were also efficiently oxidized to the corresponding ketones (entries 21 and 22). The less reactive aliphatic primary alcohols 1-octanol and 1-decanol could also be oxidized. Extended reaction times did not improve the yields of the aldehydes because of successive oxidation to the corresponding carboxylic acids. Addition of a small amount of hydroquinone (1 equivalent with respect to Ru) completely suppressed the successive oxidation to afford only aliphatic aldehydes in fairly good yields (entries 23 and 24). Ru/Al$_2$O$_3$ successfully catalyzed the oxidation of alcohols containing heteroatoms (oxygen, sulfur, and nitrogen) to the corresponding aldehydes in high yields (entries 5, 25, and 26), while monomeric complexes such as Ru and Pd could not catalyze oxidations of these alcohols because of the strong coordination to the metallic center.

The present procedure was further applied to the oxidation of various kinds of diols. In the intramolecular competitive oxidation of the primary/secondary diol 4-(1-hydroxyethyl)benzyl alcohol, the Ru/Al$_2$O$_3$ catalyst chemoselectively gave 4-(1-hydroxyethyl)benzaldehyde in 94% yield (entry 27). The oxidation of the α,ω-primary diol 1,4-benzenedimethanol gave terephthalaldehyde (entry 28). In contrast, a quantitative lactonization occurred in the case of 1,2-benzenedimethanol (entry 29). In the case of 1,2-diols, the product selectivities depended upon the kinds of substrates. For 1,2-diols with phenyl rings at α-positions, only the carbon–carbon bond cleavage was observed (entries 30 and 31). For the aliphatic linear 1,2-diol 1,2-octanediol, carbon–carbon bond cleavage to give *n*-heptanal occurred together with the formation of significant amounts of 2,4-dihexyl-1,3-dioxolane by the reaction of *n*-heptanal and the starting diol (entry 32). The oxidation of *cis*-1,2-cyclooctanediol afforded the corresponding 1,2-diketone and the carbon–carbon bond cleaved product (entry 33).

The present Ru/Al_2O_3 catalyst also has high catalytic activity for the oxidation of amines with molecular oxygen. The results are summarized in Table 3. All primary benzylic amines tested were converted into the corresponding benzonitriles in high yields (entries 1–6). The carbon–carbon double bond did not affect the oxidation under the reaction conditions (in a similar way to that observed for the oxidation of alcohols) and only the amino function was dehydrogenated to the nitrile without isomerization of the double bond or intramolecular hydrogen transfer (entry 7). Primary aliphatic amines such as *n*-octylamine and *n*-dodecylamine were effectively oxidized to the corresponding nitriles (entries 8 and 9). Not only primary amines but also secondary and heterocyclic amines were selectively oxidized. In the case of the secondary amines *N*-benzylaniline and dibenzylamine, the corresponding imines were obtained in high yields (entries 10 and 11). The heterocyclic amines indoline and 1,2,3,4-tetrahydroquinoline gave indole and quinoline in >99% and 95% yields, respectively (entries 12 and 13).

Kinetics and mechanism: It has been reported that 2,2-dimethyl-1-phenyl-1-propanol was oxidized to give the corresponding ketone with the two-electron transfer oxidant Pd^{II}, and that the one-electron-transfer oxidant Ce^{IV} gave benzaldehyde and the *tert*-butyl radical as primary products.[14] The Ru/Al_2O_3-catalyzed oxidation of 2,2-dimethyl-1-phenyl-1-propanol was found to yield the corresponding ketone with >99% selectivity at 100% conversion (entry 10 in Table 2). Also, the oxidations of radical clock substrates such as cyclopropylphenyl carbinol and cyclobutanol exclusively produced cyclopropylphenyl ketone and cyclobutanone, respectively (entries 9 and 17 in Table 2). The lack of ring-opened products indicates that free radical intermediates are not involved in the oxidation of these substrates. When the free radical initiator 2,2′-azobis(isobutyronitrile) (2.5 mol%) was used instead of Ru/Al_2O_3, insignificant amounts of benzaldehyde (11% yield) and benzyl benzoate (8% yield) were produced after 48 h. Furthermore, the addition of radical scavengers such as 2,6-di-*tert*-butyl-4-methylphenol, hydroquinone, TEMPO, and garvinoxyl (2.5 mol%) did not affect the reaction rates or the product selectivity for oxidations of benzyl alcohol. These results show that free radical intermediates are not involved in the present alcohol oxidation and that the abstraction of an α-hydrogen from an alcohol is not caused by Ru/Al_2O_3.

The reaction rates for the oxidation of 1-octanol, 2-octanol, benzyl alcohol, and 1-phenylethanol were 1.38×10^{-2}, 1.98×10^{-2}, 1.93×10^{-2}, and 2.81×10^{-2} M min^{-1} at 356 K, respectively, indicating that the oxidations of secondary alcohols proceeded faster than primary ones. In contrast, the oxidation of primary alcohols proceeded faster than secondary alcohols for their mixtures (competitive oxidations). For example, an equimolar mixture of benzyl alcohol and 1-phenylethanol gave a mixture of benzaldehyde and acetophenone in 90% and 24% yields, respectively, at 356 K for 1 h. The ratio of the oxidation rate of benzyl alcohol to that of 1-phenylethanol was 8.2. Similarly, the oxidation of 1-octanol was 12 times faster than that of 2-octanol for the competitive oxidation. In addition to the intermolecular competitive oxidations, the same phenomenon was observed for the intramolecular competitive oxidation of the primary–secondary diol of 4-(1-hydroxyethyl)benzyl alcohol (entry 27 in Table 2). These faster oxidations of primary alcohols support the formation of ruthenium alcoholate through the ligand exchange of the ruthenium hydroxide species with alcohols (step 1), since the formation of metal alcoholate species is well known for the selective oxidation of the primary hydroxyl group.[4e–g, 10e, 15] Under anaerobic conditions, the amount of acetone produced

Table 3. Oxidation of various amines with molecular oxygen catalyzed by Ru/Al_2O_3.[a]

	Substrate	*t* [h]	Conversion [%]	Product	Selectivity [%]
1	benzylamine	1	>99	benzonitrile	82
2	2-methoxybenzylamine	1	>99	2-methoxybenzonitrile	97
3	3-methoxybenzylamine	1	94	3-methoxybenzonitrile	93
4	4-methoxybenzylamine	1	>99	4-methoxybenzonitrile	96
5	4-methylbenzylamine	1	>99	4-methylbenzonitrile	93
6[b]	3-chlorobenzylamine	1	>99	3-chlorobenzonitrile	90
7	geranylamine	10	98	geranyl nitrile	90
8	*n*-octylamine	2	>99	*n*-octanenitrile	96
9	*n*-dodecylamine	3	84	*n*-dodecanenitrile	90
10	*N*-benzylaniline	15	85	*N*-benzylideneaniline	94
11[b]	dibenzylamine	16	85	*N*-benzylidenebenzylamine	84[c]
12	indoline	2	>99	indole	>99
13	1,2,3,4-tetrahydroquinoline	7	95	quinoline	>99

[a] Substrate (1 mmol), Ru/Al_2O_3 (2.8 mol% Ru), $PhCF_3$ (5 mL), 373 K, O_2 flow (1 atm). Conversion and selectivity were determined by GC using naphthalene or diphenyl as an internal standard. The main byproducts were *N*-alkylimines. [b] *p*-Xylene (5 mL) was used as a solvent, and the reaction temperature was 403 K. [c] Benzonitrile (7% selectivity) and benzaldehyde (6% selectivity) were formed as byproducts.

was approximately the same as those of Ru loaded and water produced for the oxidation of 2-propanol. These facts also support the proposed step 1.

Figure 2 shows the relationship between $\log(k_X/k_H)$ and the Brown–Okamoto σ^+ [16] (or σ) for the oxidation of benzyl alcohols catalyzed by Ru/Al_2O_3. The order of reactivity for benzyl alcohol was p-CH_3O ($k_X/k_H = 2.27$) > p-CH_3 (1.55) > p-H (1.00) > p-Cl (0.96) > p-NO_2 (0.45). The slope of the linear line in Figure 2 gave a Hammett ρ^+ value of -0.461 ($r^2 = 0.99$). The moderate negative value of Hammett ρ^+ values can be interpreted in terms of a positively charged transition state at the α-carbon atom adjacent to the phenyl ring.[17] The correlation with the Brown–Okamoto σ^+ constants had better fits than that with σ constants particularly for electron-donating substituents such as p-CH_3O and p-CH_3 (Figure 2, $r^2 = 0.93$). This fact indicates that the formation of a carbocation transition state, which is stabilized by electron-donating substituents, is involved in the oxidation path (step 2).[17]

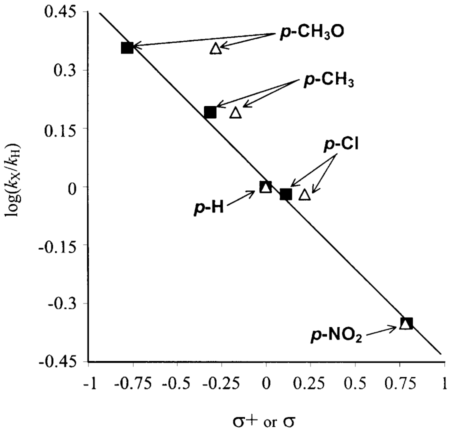


Figure 2. Hammett plots for competitive oxidation of benzyl alcohol and p-substituted benzyl alcohols. $\log(k_X/k_H)$ versus σ^+ (■) and $\log(k_X/k_H)$ versus σ (△). Reaction conditions: benzyl alcohol (0.5 mmol), p-substituted benzyl alcohol (0.5 mmol), Ru/Al_2O_3 (1.0 mol% Ru), $PhCF_3$ (1.5 mL), 333 K, O_2 atmosphere.

When acetophenone (1 M) was treated in 2-propanol under Ar at 343 K for 12 h, almost equimolar amounts of acetone and 1-phenylethanol were produced (93% yield), which is consistent with the formation of the ruthenium hydride species as an intermediate.[18] This also shows that the hydride ion transfer from alcohol to Ru may take place (step 2).

The dependence of k_H/k_D values on the reaction temperature was examined for Ru/Al_2O_3-catalyzed oxidation of α-deuterio-p-methylbenzyl alcohol. Moderate k_H/k_D values were obtained ($k_H/k_D = 4.2$–5.0 at 373–333 K) and the experimental data can be expressed by the equation $\ln(k_H/k_D) = \ln(A_H/A_D) - \Delta E_a/RT$ (Figure 3). Here, the ΔE_a value is $4.82\,kJ\,mol^{-1}$ and is nearly equal to the zero-point energy difference for the respective C–H and C–D bonds ($E_0^H - E_0^D = 4.90\,kJ\,mol^{-1}$), and A_H/A_D and $\Delta(\Delta S^{\ddagger})$ are 0.92 and 0, respectively. These values mean that the difference between the k_H and k_D ratio stems only from the zero-point energies ($E_0^H - E_0^D$), and indicates that the hydride ion transfer proceeds through a symmetrical transition state in step 2.[19]

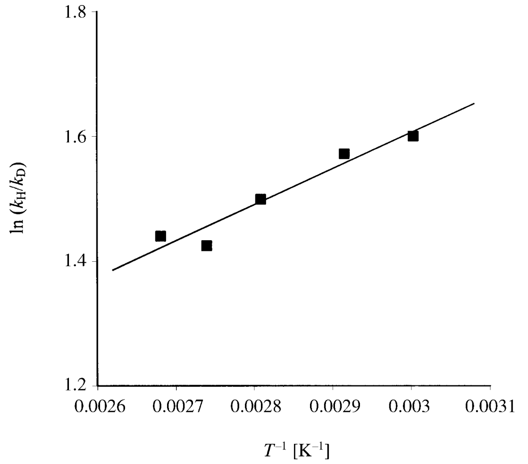


Figure 3. Temperature dependence of intramolecular kinetic isotope effects (k_H/k_D) on the reaction temperatures (333–373 K) for the oxidation of α-deuterio-p-methylbenzyl alcohol. Reaction conditions: α-deuterio-p-methylbenzyl alcohol (1 mmol), Ru catalyst (2.5 mol% Ru), $PhCF_3$ (1.5 mL), 333–373 K, O_2 atmosphere. Line fit: $\ln(k_H/k_D) = -0.08 + 580.73/T$ ($r^2 = 0.94$).

While step 3 may proceed via the formation of hydrogen peroxide, the filtrate for the oxidation of benzyl alcohol with molecular oxygen displayed a negative peroxide test (Quantofix test stick; detection limit, $1\,mg\,L^{-1}$ hydrogen peroxide). The catalytic oxidation of benzyl alcohol with hydrogen peroxide hardly proceeded because of the rapid decomposition of hydrogen peroxide, in accordance with the rapid decomposition of Ru^{n+}–OOH without the contribution to oxidations of alcohols in step 4.

On the basis of all these results, we propose the mechanism given in Scheme 1 for the Ru/Al_2O_3-catalyzed aerobic oxidations of alcohols. This catalytic oxidation can be divided into steps (1–4): the Ru^{n+}–alcoholate species is formed through the ligand exchange between Ru^{n+}–hydroxide and the alcohol (step 1). The alcoholate species undergoes typical β-hydride elimination to afford the corresponding carbonyl compound and the Ru^{n+}–hydride species (step 2). The hydride species is then reoxidized by molecular oxygen (step 3). Reoxidation of Ru^{n+}–hydride is likely to proceed through the insertion of molecular oxygen into Ru^{n+}–hydride. The formation of water in the oxidation of 2-propanol with molecular oxygen was monitored at various temperatures (333–356 K) and revealed that the amount of water produced was the same as the amount of acetone produced (Figure 4). The measurement of molecular oxygen uptake during the oxidation of benzyl alcohol was also carried out. As shown in Figure 5, the amount of molecular oxygen consumed was half that of benzaldehyde produced. These respective 1:1 (H_2O:product) and 1:2 (O_2:product) stoichiometries indicate that a simple dehydrogenation does not proceed and support the overall reaction summarized in Scheme 1.

The dependence of the rate of oxidation of benzyl alcohol on the amount of catalyst was investigated in the range 1.25–5 mol% catalyst. As shown in Figure 6, the concentration of benzaldehyde produced was proportional to time. Therefore, the slope can be recognized as the rate (R_0), and this was proportional to the amount of catalyst (inset in Figure 6). This

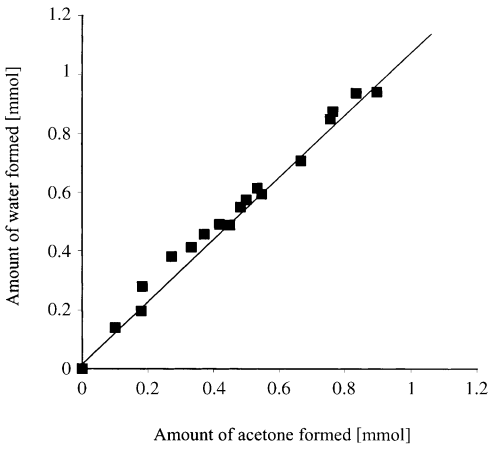


Figure 4. Relationship between amounts of water and acetone formed in the oxidation of 2-propanol with molecular oxygen by Ru/Al_2O_3. Reaction conditions: 2-propanol (19.6 mmol), Ru/Al_2O_3 (0.13 mol% Ru), 333–356 K, O_2 atmosphere. Slope (water formed/acetone formed) = 1.12 (r^2 = 0.98).

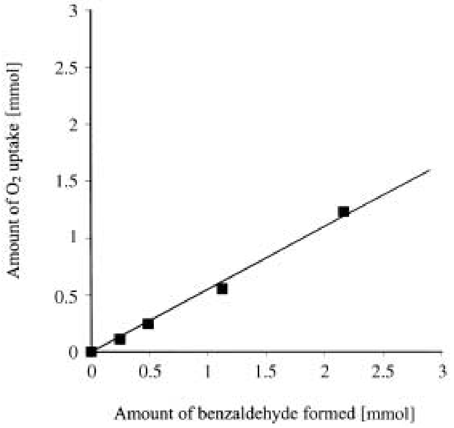
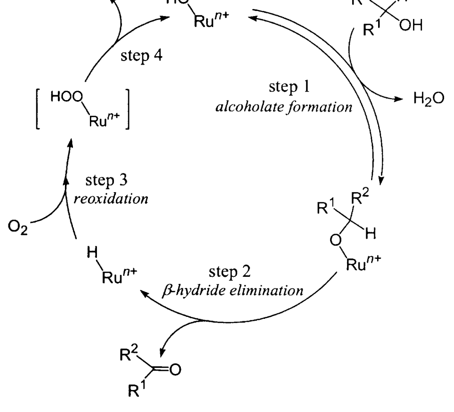


Figure 5. Relationship between amounts of benzaldehyde and O_2 uptake for the oxidation of benzyl alcohol with molecular oxygen by Ru/Al_2O_3. Reaction conditions: benzyl alcohol (3 mmol), Ru/Al_2O_3 (1.0 mol%), $PhCF_3$ (1.5 mL), 356 K, O_2 atmosphere. Slope (O_2 uptake/benzaldehyde formed) = 0.54 (r^2 = 0.99).



Scheme 1. Proposed mechanism for the Ru/Al_2O_3-catalyzed aerobic oxidations of alcohols.

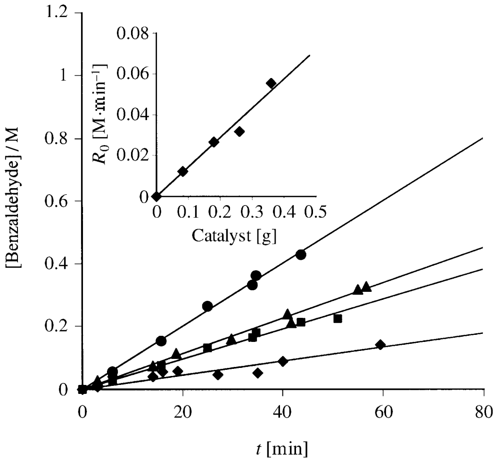


Figure 6. Effect of amount of catalyst on the oxidation of benzyl alcohol. Reaction conditions: benzyl alcohol (1 mmol), Ru/Al_2O_3 (0.09 (◆), 0.18 (■), 0.27 (▲), 0.36 g (●), $PhCF_3$ (1.5 mL), 333 K, O_2 atmosphere. Inset, reaction rate (R_0) versus amount of catalyst.

indicates the first-order dependence of R_0 on the amount of catalyst. Figure 7 shows the dependence of R_0 on the pressure of molecular oxygen (P_{O_2}). The slope of $\ln R_0$ versus $\ln P_{O_2}$ plots was -0.03 (inset in Figure 7), showing that R_0 was almost independent of P_{O_2}. The zero-order dependence on the pressure of molecular oxygen shows that the reoxidation smoothly proceeds and is not a rate-determining step. Ruthenium complexes have been widely studied as catalysts for aerobic alcohol oxidations. However, the oxidation catalysis does not often cycle because of the slow reoxidation. The reoxidation step is usually promoted by the addition of electron–proton transfer mediators such as quinone[4d,g,n] and TEMPO.[4i,k] It is notable that the present Ru/Al_2O_3 catalyst does not need such mediators.

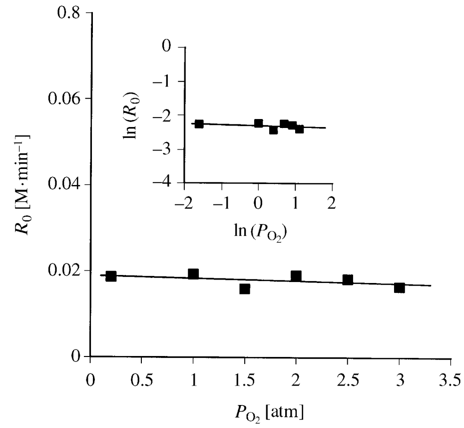


Figure 7. Reaction rate as a function of the oxygen pressure. Reaction conditions: benzyl alcohol (1 mmol), Ru/Al_2O_3 (2.5 mol%) $PhCF_3$ (1.5 mL), 356 K, P_{O_2} = 0.2–3.0 atm. Slope from the inset = -0.03.

Figure 8a illustrates the dependence of R_0 on the concentration of benzyl alcohol at various temperatures. Good linear correlations were observed between $1/R_0$ versus 1/[alcohol]

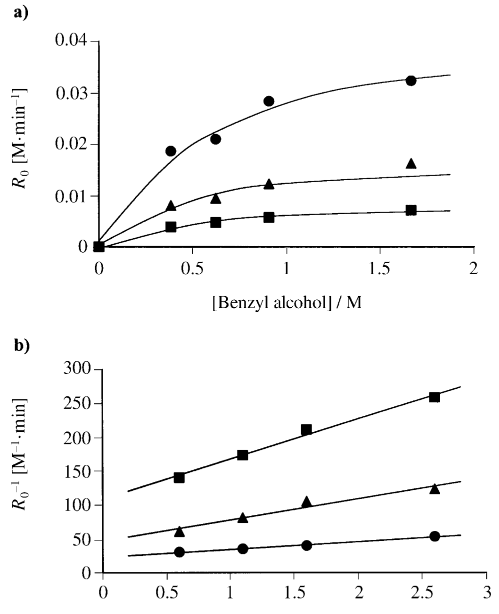


Figure 8. a) Dependence of reaction rate on concentration of benzyl alcohol and b) Lineweaver–Burk plots. Reaction conditions: benzyl alcohol (0.6–3 mmol), Ru/Al_2O_3 (2.5 mol%), $PhCF_3$ (5 mL), 333 (■), 343 (▲), 356 K (●), O_2 atmosphere.

(Lineweaver–Burk plots) as shown in Figure 8b. These show that the oxidation follows Michaelis–Menten-type kinetics as a function of alcohol: first-order dependence on alcohol at the low concentrations and zero-order dependence at higher concentrations. The effects of reaction temperature on the Ru/Al_2O_3-catalyzed oxidation of benzyl alcohol are shown in Figure 9, and the Arrhenius plots are shown in the inset. Good

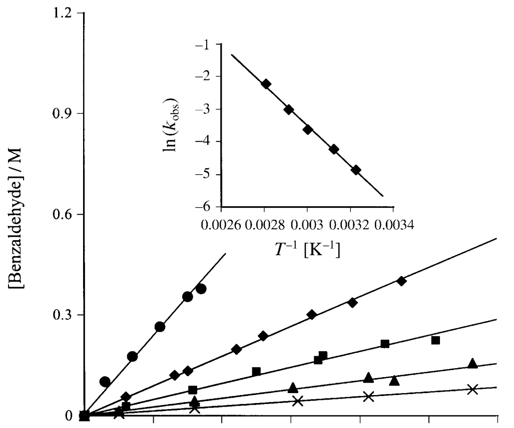


Figure 9. Effect of reaction temperature on the oxidation of benzyl alcohol. Reaction conditions: benzyl alcohol (1 mmol), Ru catalyst (2.5 mol% Ru), $PhCF_3$ (1.5 mL), 310 (×), 320 (▲), 333 (■), 343 (◆), 356 K (●), O_2 atmosphere. Inset: Arrhenius plots for the oxidation of benzyl alcohol. R_0 values were regarded as the pseudo-zero-order rate constants (k_obs) because the concentration of benzaldehyde produced was proportional to time. Line fit: $\ln(k_\text{obs}) = 15.05 - 6180.40/T$ ($r^2 = 0.99$).

linearity was observed and afforded the following activation parameters: $E_a = 51.4\ \text{kJ mol}^{-1}$, $\ln A = 15.1$, $\Delta H^{\ddagger}_{298\,K} = 48.9\ \text{kJ mol}^{-1}$, $\Delta S^{\ddagger}_{298\,K} = -128.1\ \text{J mol}^{-1}\text{K}^{-1}$, and $\Delta G^{\ddagger}_{298\,K} = 87.1\ \text{kJ mol}^{-1}$. The activation energy (E_a) was close to that reported for the $[RuCl_2(PPh_3)_3]$/TEMPO-catalyzed aerobic alcohol oxidation.[4i,k] From the kinetic data, the reaction rate (R_0) can be expressed as follows [Eq. (4)]:

$$R_0 = -d[\text{alcohol}]/dt = k_\text{obs}[\text{catalyst}]^1[\text{alcohol}]^{1\rightarrow 0}, \quad \text{where}$$
$$k_\text{obs} = 3.44\times10^6\exp(-6.18\times10^3/T) \tag{4}$$

Kinetic isotope effects (k_H/k_D) at 333 K were 5.0 and 2.4 for the intramolecular competitive oxidation of α-deuterio-p-methylbenzyl alcohol and for the intermolecular competitive oxidation of benzyl alcohol and $[D_7]$benzyl alcohol ($C_6D_5CD_2OH$), respectively. Equation (4) and the kinetic isotope effects show that step 2 is a rate-determining step.[17]

Conclusion

In summary, the present Ru/Al_2O_3 catalyst can act as an efficient heterogeneous catalyst for the oxidations of alcohols and amines. The catalyst's performance raises the prospect of using this type of simple supported catalyst for organic syntheses and industrial alcohol oxidation processes because of 1) its applicability to a wide range of alcohols and amines, 2) the use of molecular oxygen or even air as an oxidant, 3) simple workup procedures (products/catalyst separation), and 4) reusability of Ru/Al_2O_3. The kinetic and mechanistic investigations show that Ru/Al_2O_3-catalyzed aerobic alcohol oxidation proceeds through an alcoholate/β-hydride elimination mechanism and that the β-hydride elimination is a rate-limiting step.

Experimental Section

Preparation of Ru/Al_2O_3 catalyst: The Ru/Al_2O_3 catalyst was prepared by a modification of the preparation of $Ru(OH)_3 \cdot n H_2O$ according to ref. [20]. Thus, γ-Al_2O_3 (2.0 g, JRC-ALO-4, BET surface area: 174 m^2g^{-1}) was vigorously stirred with an aqueous solution of $RuCl_3$ (60 mL, 8.3×10^{-3} M) for 15 min at room temperature. The initially brown aqueous phase became lighter, and the powder turned dark gray. The powder was filtered, washed with a large amount of water, and then dried in vacuo. The obtained powder was added into deionized water (30 mL) and the pH value of the solution was slowly adjusted to 13.2 by addition of an aqueous solution of NaOH (1.0 M), and the resulting slurry was stirred for 24 h. The powder's color changed from dark gray to dark green. The solid was filtered off, washed with a large amount of water, and dried in vacuo to afford Ru/Al_2O_3 (2.1 g) as a dark green powder. The contents of ruthenium and chloride were 1.4 and 0 wt%, respectively. The BET surface area was 182 m^2g^{-1}. The ESR spectrum had a signal at $g = 2.11$, which was assigned to Ru^{3+} with a low-spin d^5 electron configuration.[21] The XRD pattern was the same as that of the γ-Al_2O_3 support and no signals due to ruthenium metal or dioxide were observed. Particles of ruthenium metal or dioxide were not detected by the TEM micrograph. The IR spectrum showed a very broad ν(OH) band in the range 2900–3700 cm^{-1}. These facts suggest that ruthenium(III) hydroxide is highly dispersed on γ-Al_2O_3. Thus, the Ru/Al_2O_3 catalyst can be easily prepared in a quantitative yield and the content of Ru is controllable. The catalyst should be considerably less expensive than organometallic and inorganic compounds.

Typical procedures for the aerobic oxidations of alcohols: A suspension of Ru/Al_2O_3 (0.18 g, 2.5 mol% Ru) in trifluorotoluene (1.5 mL) was stirred for 5 min. Benzyl alcohol (0.11 g, 1 mmol) was added and molecular oxygen was passed through the suspension. The resulting mixture was then heated at 356 K for 1 h with azeotropic removal of water formed under an O_2 flow (ca. 1 mL min^{-1}) and benzaldehyde was produced in >99% GC yield. After the reaction, the catalyst was separated by filtration (or centrifugation) and was further washed with acetone. The filtrate was evaporated in vacuo, and the crude product was further purified by column chromatography on silica gel to give pure benzaldehyde (0.10 g, 95% isolated yield). The separated Ru/Al_2O_3 was washed with an aqueous solution of NaOH (1.0 M) and water (30 mL), and dried in vacuo before recycling.

Synthesis of α-deuterio-*p*-methylbenzyl alcohol: α-Deuterio-*p*-methylbenzyl alcohol was synthesized by the reduction of *p*-methylbenzaldehyde using lithium aluminum deuteride by a modification of the procedure reported for the synthesis of deuterium-labeled toluene.[22] Thus, a solution of *p*-methylbenzaldehyde (3.2 g, 26.7 mmol) in dry THF (20 mL) was added slowly to a suspension of lithium aluminum deuteride (0.33 g, 7.9 mmol) in dry THF (20 mL) at room temperature, and then the resulting mixture was stirred vigorously under Ar atmosphere at 333 K. After 8 h, the mixture was cooled to 273 K and unreacted lithium aluminum deuteride was destroyed by the addition of water (500 μL). Then, an aqueous solution of NaOH (50 mL, 0.1 M) was added slowly to the mixture. The resulting white solid was removed by filtration and washed with THF, and the filtrate was extracted with chloroform (100 mL × 4). The combined extract was dried with $CaCl_2$ and evaporated to give crude α-deuterio-*p*-methylbenzyl as a white powder. The crude product was recrystallized from petroleum ether/chloroform solution (97:3) to give the purified compound (1.4 g, 43%) as a white sticky crystal. The product was identified by comparison of the physical and spectral data with those of the authentic unlabelled material. The deuterium content was estimated to be >99% by mass spectrometry and ^{1}H NMR spectroscopy. ^{1}H NMR (270 MHz, [D$_1$]chloroform, 25 °C, TMS): $\delta = 7.21$ (d, $^3J(H,H) = 7.82$ Hz, 2H; aromatic H), 7.13 (d, $^3J(H,H) = 7.10$ Hz, 2H; aromatic H), 4.54 (s, 1H, CHDO), 2.33 (s, 3H; CH_3), 2.25 ppm (d, $^3J(H,H) = 4.80$ Hz, 1H; OH); ^{13}C NMR (67.5 MHz, [D$_1$]chloroform, 25 °C, TMS): $\delta = 137.8$, 137.2 (C^{para}), 129.1 ($2C^{meta}$), 127.1 ($2C^{ortho}$), 64.7 (t, $^1J(C,D) = 25.7$ Hz; CHDOH), 21.1 ppm (CH_3); MS (70 eV, EI): m/z (%): 124 (19) [M^++H], 123 (100) [M^+], 121 (18), 108 (84), 106 (44), 94 (54), 93 (43), 92 (54), 91 (77), 80 (77), 78 (52), 77 (70), 65 (52); elemental analysis calcd (%) for C_8H_9DO (123.2, deuterium was calculated as hydrogen): C 78.65, H 8.25; found: C 78.50, H 8.24.

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