

Highly Dispersed Ruthenium Hydroxide Supported on Titanium Oxide Effective for Liquid-Phase Hydrogen-Transfer Reactions

Kazuya Yamaguchi, Takeshi Koike, Jung Won Kim, Yoshiyuki Ogasawara, and Noritaka Mizuno*^[a]

Abstract: Supported ruthenium hydroxide catalysts ($\text{Ru}(\text{OH})_x/\text{support}$) were prepared with three different TiO_2 supports (anatase TiO_2 ($\text{TiO}_2(\text{A})$), BET surface area: $316 \text{ m}^2 \text{ g}^{-1}$), anatase TiO_2 ($\text{TiO}_2(\text{B})$, $73 \text{ m}^2 \text{ g}^{-1}$), and rutile TiO_2 ($\text{TiO}_2(\text{C})$, $3.2 \text{ m}^2 \text{ g}^{-1}$), as well as an Al_2O_3 support ($160 \text{ m}^2 \text{ g}^{-1}$). Characterizations with X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), electron spin resonance (ESR), and X-ray absorption fine structure (XAFS) showed the presence of monomeric ruthenium(III) hydroxide and polymeric ruthenium(III) hydroxide species. Judging from the coordination numbers of the nearest-neighbor Ru atoms and the intensities of the

ESR signals, the amount of monomeric hydroxide species increased in the order of $\text{Ru}(\text{OH})_x < \text{Ru}(\text{OH})_x/\text{TiO}_2(\text{C}) < \text{Ru}(\text{OH})_x/\text{Al}_2\text{O}_3 < \text{Ru}(\text{OH})_x/\text{TiO}_2(\text{B}) < \text{Ru}(\text{OH})_x/\text{TiO}_2(\text{A})$. These supported ruthenium hydroxide catalysts, especially $\text{Ru}(\text{OH})_x/\text{TiO}_2(\text{A})$, showed high catalytic activities and selectivities for liquid-phase hydrogen-transfer reactions, such as racemization of chiral secondary alcohols and the reduction of carbonyl compounds and allylic alcohols. The catalytic activities of

$\text{Ru}(\text{OH})_x/\text{TiO}_2(\text{A})$ for these hydrogen-transfer reactions were at least one order of magnitude higher than those of previously reported heterogeneous catalysts, such as $\text{Ru}(\text{OH})_x/\text{Al}_2\text{O}_3$. These catalysts were truly heterogeneous, and the catalysts recovered after the reactions could be reused several times without loss of catalytic performance. The reaction rates monotonically increased with an increase in the amount of monomeric ruthenium hydroxide species, which suggests that the monomeric species are effective for these hydrogen-transfer reactions.

Keywords: alcohols • carbonyl compounds • heterogeneous catalysis • racemization • reduction

Introduction

Homogeneous catalysts of inorganic salts and organometallic complexes have been used for many bulk and fine chemicals syntheses. They are usually dissolved in solvents to make all the catalytic sites accessible to substrates, and they show high catalytic activity and selectivity. Despite these advantages, homogeneous catalysts are used in only 20–30% of industrial processes because separation of the catalyst from the product(s) (problem of product contamination)

and the reuse of (expensive) catalysts are very difficult. Therefore, the development of easily recoverable and recyclable heterogeneous catalysts has received a particular research interest and could solve the problems of the homogeneous systems.^[1] Although the immobilization of homogeneous catalysts onto inert solid supports and attachment of the catalytically active species through covalent or ionic bonds with (modified) supports have been extensively studied, the intrinsic catalytic activities and selectivities of the homogeneous catalysts are usually considerably lowered by the heterogenization. Furthermore, leaching of the heterogeneous catalysts is frequently observed and is a severe drawback. Therefore, the design of true efficient heterogeneous catalysts with activities and selectivities comparable to or higher than those of the corresponding homogeneous analogues is one of the most important challenges in modern organic synthesis, especially for fine chemicals.^[1] Our strategy to design efficient heterogeneous catalysts for various functional group transformations is the creation of metal hydroxide species on the appropriate supports.^[2–5] The metal hydroxide

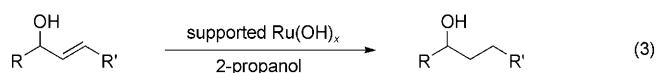
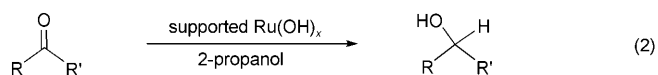
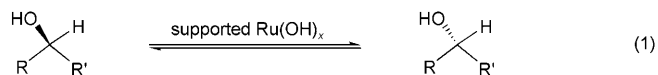
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species possess both Lewis acid and Brønsted base sites, and the various functional group transformations are likely to be promoted through the concerted activation of these groups.

Racemization is a very important reaction; the remaining enantiomer from a stereoselective reaction can be recycled by racemization to overcome this disadvantage of kinetic resolution.^[6] Transition-metal-catalyzed Meerwein–Ponndorf–Verley-type (MPV-type) reduction with an alcohol as a hydrogen source is one of the most convenient methods for large-scale production because it is not necessary to use high-pressure molecular hydrogen or hazardous reduction reagents.^[7] Although many efficient methods for homogeneous hydrogen-transfer reactions catalyzed by transition-metal complexes have been developed,^[7–9] these systems often need additives such as hydrogen acceptors or bases to promote the reactions and have the above-mentioned disadvantages, namely, the difficulty of catalyst/product(s) separation and reuse of catalysts. To the best of our knowledge, there are few examples of the heterogeneously catalyzed racemization of alcohols and amines^[2,10] and only one example of the selective reduction of allylic alcohols with an alcohol as the hydrogen source.^[3]

We prepared three kinds of supported ruthenium hydroxide catalysts with different TiO₂ supports: Ru(OH)_x/TiO₂(A), Ru(OH)_x/TiO₂(B), and Ru(OH)_x/TiO₂(C) (see later section), and these catalysts could act as efficient, reusable heterogeneous catalysts for various hydrogen-transfer reactions, such as the racemization of chiral secondary alcohols [Eq. (1)], as well as the reduction of carbonyl compounds [Eq. (2)] and allylic alcohols [Eq. (3)]. In particular,



the highly dispersed ruthenium hydroxide species supported on high-surface area TiO₂, Ru(OH)_x/TiO₂(A), showed very high catalytic activity for these hydrogen-transfer reactions—much higher than those of the previously reported heterogeneous catalysts including Ru(OH)_x/Al₂O₃.^[2,3] Herein, we report the characterization of these supported ruthenium catalysts, the scope of the above-mentioned transformations, and the relationship between the catalytic activities and the structure of the active sites in detail.

Results and Discussion

Preparation and characterization of supported ruthenium hydroxide catalysts: The supported ruthenium hydroxide

catalysts (Ru(OH)_x/support) were prepared with three different TiO₂ supports, anatase TiO₂ (TiO₂(A), Ishihara Sangyo Kaisya Ltd., ST-01, 316 m²g⁻¹), anatase TiO₂ (TiO₂(B), the Catalysis Society of Japan, JRC-TIO-1, 73 m²g⁻¹), and rutile TiO₂ (TiO₂(C), Showa Denko K. K., SUPER-TITANIA G-2, 3.2 m²g⁻¹). For comparison, supported ruthenium hydroxide on Al₂O₃ (Sumitomo Chemical, KHS-24, BET surface area: 160 m²g⁻¹) was prepared according to the same procedure.^[2–4] The catalysts were prepared by the reaction of TiO₂ (or Al₂O₃) with RuCl₃ in aqueous medium followed by the treatment with NaOH. The powder TiO₂ (or Al₂O₃) (2.0 g) pretreated at 823 K for 3 h was vigorously stirred with 60 mL of an aqueous solution of RuCl₃ (8.3 mM, ca. pH 2.0) at room temperature (ca. 293 K). After 15 min, the solution was adjusted to pH 13.2 by addition of an aqueous solution of NaOH (1 M), and the resulting slurry was stirred for 24 h. The solid was then filtered off, washed with a large amount of water (ca. 4 L), and dried in vacuo to afford supported ruthenium hydroxide catalysts. The ruthenium contents in Ru(OH)_x/TiO₂(A), Ru(OH)_x/TiO₂(B), Ru(OH)_x/TiO₂(C), and Ru(OH)_x/Al₂O₃ were 2.1, 2.2, 2.2, and 2.1 wt %, respectively (Table 1). The preparation of (highly dispersed) supported ruthenium hydroxide catalysts with SiO₂ and MgO was unsuccessful because SiO₂ and MgO supports are somewhat soluble in the ruthenium solution.

Table 1. Various supported ruthenium hydroxide catalysts.

Catalyst ([wt %])	Support ^[a]	BET surface area [m ² g ⁻¹]	Catalyst
Ru(OH) _x /TiO ₂ (A) (2.1)	anatase TiO ₂	316	298
Ru(OH) _x /TiO ₂ (B) (2.2)	anatase TiO ₂	73	74
Ru(OH) _x /TiO ₂ (C) (2.2)	rutile TiO ₂	3.2	7.0
Ru(OH) _x /Al ₂ O ₃ (2.1)	Al ₂ O ₃	160	163
Ru(OH) _x	–	–	15

[a] See the Experimental Section.

The BET surface areas of the supported ruthenium hydroxide catalysts were very close to those of the parent supports (Table 1). The XRD patterns of supported ruthenium hydroxide catalysts were the same as those of the parent supports and no signals due to Ru metal clusters and RuO₂ were observed. These facts suggest that ruthenium species are highly dispersed on the surface of supports.

To clarify the ruthenium species on the supports, ruthenium hydroxide (Ru(OH)_x) prepared by the treatment of RuCl₃ with base (without support, see the Experimental Section) was first characterized. The XPS spectrum of Ru(OH)_x showed the binding energies of Ru 3p_{3/2} and Ru 3p_{1/2} core level at 462.9 and 484.8 eV, respectively, which shows that the average oxidation state of the ruthenium species is +III (Figure 1a).^[11] The O 1s spectrum could be resolved into three constituents assignable to the bridged Ru–O–Ru oxygen atom (62%), the Ru–OH oxygen atom (35%), and water (3%) with binding energies at 530.4, 532.7, and 534.9 eV, respectively (Figure 1b).^[12] This result

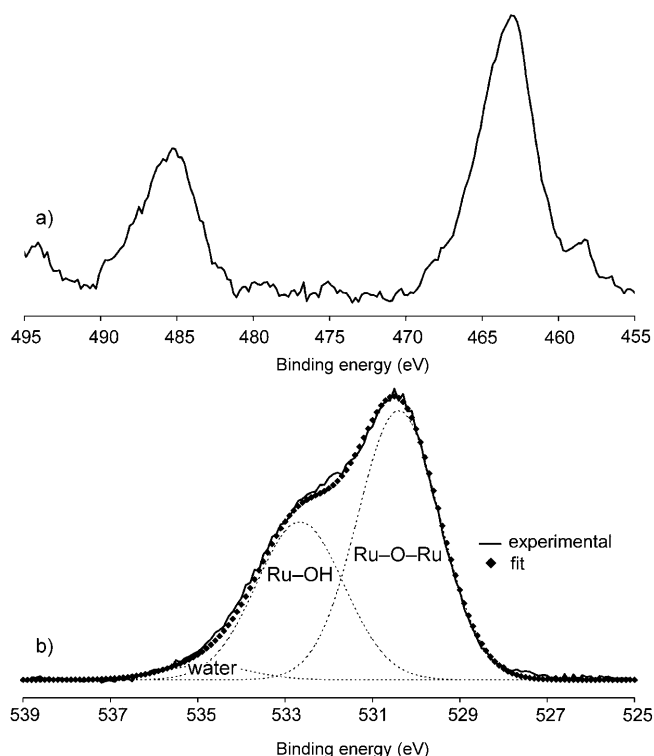


Figure 1. XPS spectra of Ru(OH)_x in the a) Ru 3p and b) O 1s regions. The O 1s spectrum (solid line in (b)) could be well reproduced by the sum of the three contributions from bridged Ru–O–Ru, Ru–OH, and water oxygen atoms (broken lines in (b)).

shows that the ratio of bridged Ru–O–Ru oxygen atoms to Ru–OH oxygen atoms in Ru(OH)_x is approximately 2:1.

Figure 2e and f shows the radial distribution functions (RDFs) from the Fourier transformation of the *k*³-weighted

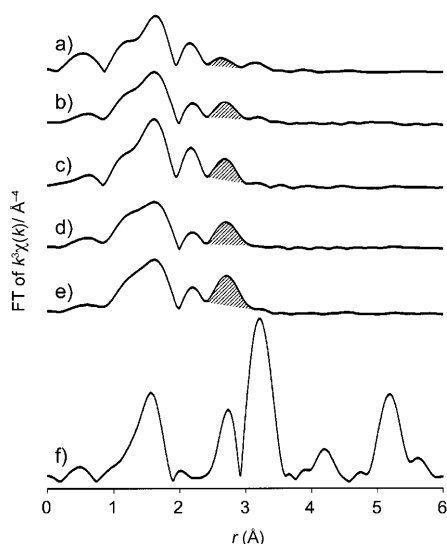


Figure 2. RDFs from the Fourier transformation of the *k*³-weighted EXAFS spectra of a) Ru(OH)_x/TiO₂(A), b) Ru(OH)_x/TiO₂(B), c) Ru(OH)_x/Al₂O₃, d) Ru(OH)_x/TiO₂(C), e) Ru(OH)_x, and f) anhydrous RuO₂. The phase shift was not corrected.

extended X-ray absorption fine structure (EXAFS) for Ru(OH)_x and anhydrous RuO₂. Curve-fitting analysis for the first Ru–O shell parameters for Ru(OH)_x shows that the coordination number (C.N.) was six, which is similar to that of anhydrous RuO₂.^[13] However, the RDFs exhibited significant differences for longer range Ru···Ru interactions. The intensity of the Ru···Ru shell signal at *r* = 2.8 Å (the phase shift was not corrected) for Ru(OH)_x was considerably damped relative to that for anhydrous RuO₂. Curve-fitting analysis of the signal showed that the interatomic distance between two ruthenium cations was (3.10 ± 0.01) Å and the C.N. was 1.4(±0.2) (Table 2). This

Table 2. Curve-fitting analysis for various supported ruthenium hydroxide catalysts.

Catalyst	Shell	<i>d</i> [Å] ^[a]	C.N. ^[b]	σ [Å ²] ^[c]
Ru(OH) _x /TiO ₂ (A)	Ru–O	2.01 (±0.01)	5.9 (±0.7)	0.0108
	Ru···Ru	3.07 (±0.02)	0.37 (±0.17)	0.0052
Ru(OH) _x /TiO ₂ (B)	Ru–O	2.03 (±0.01)	6.1 (±0.7)	0.0117
	Ru···Ru	3.09 (±0.01)	0.76 (±0.21)	0.0059
Ru(OH) _x /Al ₂ O ₃	Ru–O	2.03 (±0.01)	5.7 (±0.5)	0.0083
	Ru···Ru	3.08 (±0.01)	0.91 (±0.20)	0.0058
Ru(OH) _x /TiO ₂ (C)	Ru–O	2.02 (±0.01)	6.6 (±0.9)	0.0142
	Ru···Ru	3.10 (±0.01)	0.94 (±0.22)	0.0061
Ru(OH) _x	Ru–O	2.02 (±0.01)	6.3 (±0.7)	0.0117
	Ru···Ru	3.10 (±0.01)	1.4 (±0.2)	0.0061

[a] *d* = average interatomic distance. [b] C.N. = average coordination number. [c] σ = Debye–Waller factor.

distance is associated with the Ru···Ru interatomic distance in anhydrous RuO₂ with rutile structure, in which each ruthenium cation is bound by two oxygen ions at the corners (Figure 3a).^[13] The absence of the Ru···Ru shell signal at *r* = 3.3 Å (the phase shift was not corrected) in the RDF of Ru(OH)_x suggests that no three-dimensional networks of the ruthenium hydroxide species are present in Ru(OH)_x. Thus, in the present Ru(OH)_x species, it is most likely that

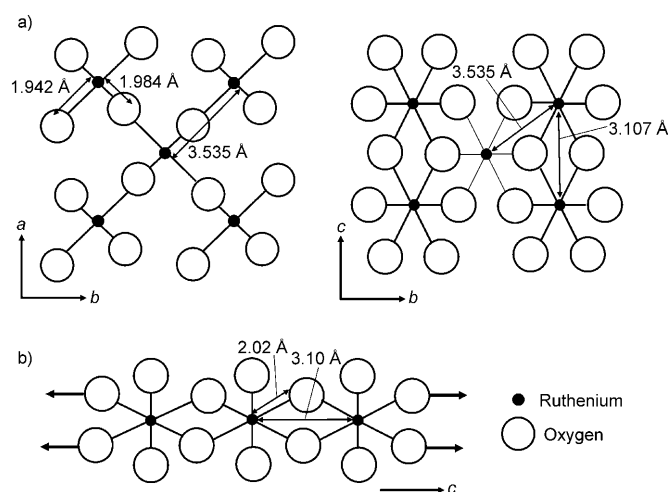


Figure 3. a) Crystal structure of anhydrous RuO₂ with rutile^[13] structure and b) a possible structure of the Ru(OH)_x species.

two ruthenium cations are bound by two oxygen ions to form the one-dimensional chainlike core structure (Figure 3b). The above-mentioned ratio of bridged Ru–O–Ru oxygen atoms to Ru–OH oxygen atoms in Ru(OH)_x determined by the XPS analysis also supports this idea (Figure 1b). A similar one-dimensional chainlike structure is proposed for ruthenium hydrate oxide.^[14]

The X-ray absorption near-edge structure (XANES) spectra of the supported ruthenium hydroxide catalysts were

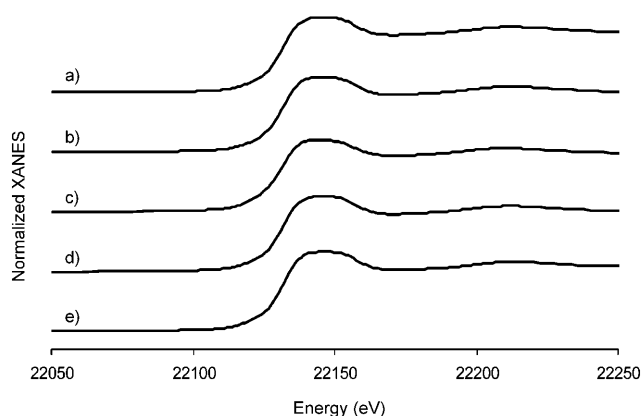


Figure 4. XANES spectra of a) Ru(OH)_x/TiO₂(A), b) Ru(OH)_x/TiO₂(B), c) Ru(OH)_x/TiO₂(C), d) Ru(OH)_x/Al₂O₃, and e) Ru(OH)_x.

very similar to that of Ru(OH)_x (Figure 4), which suggests that the catalysts have similar oxidation states and RuO₆ octahedral environments to those of Ru(OH)_x. As shown in the RDFs of the supported ruthenium hydroxide catalysts and Ru(OH)_x species (Figure 2), the local structure of all supported ruthenium hydroxide catalysts prepared in this study was intrinsically identical to that of Ru(OH)_x. A difference in the C.N.s of the Ru···Ru shell signals at $r=2.8$ Å was observed (Figure 2 and Table 2). The C.N.s (≤ 0.94) show the presence of a mixture of monomeric ruthenium hydroxide species and polymeric species in the supported hydroxide catalysts. Judging from the C.N.s of the Ru···Ru shell signals, the amounts of the monomeric hydroxide species increased in the order of Ru(OH)_x < Ru(OH)_x/TiO₂(C) < Ru(OH)_x/Al₂O₃ < Ru(OH)_x/TiO₂(B) < Ru(OH)_x/TiO₂(A). The ESR spectrum of Ru(OH)_x/TiO₂(A) (Figure 5a) showed an intense signal with rhombic g tensors characteristic of a low-spin Ru³⁺ species ($g_1=2.07$, $g_2=1.98$, $g_3=1.92$).^[15] The signal intensity increased in the same order as that of the amounts of monomeric hydroxide species (Figure 5).^[16]

Although the BET surface area of TiO₂(B) (73 m² g⁻¹) was lower than that of Al₂O₃ (160 m² g⁻¹), and the ruthenium content of Ru(OH)_x/TiO₂(B) (2.2 wt %) was almost the same as that of Ru(OH)_x/Al₂O₃ (2.1 wt %), the C.N. of the nearest-neighbor Ru atoms of Ru(OH)_x/TiO₂(B) (0.76) was lower than that of Ru(OH)_x/Al₂O₃ (0.91) (Tables 1 and 2). Therefore, TiO₂ stabilizes the monomeric ruthenium species.

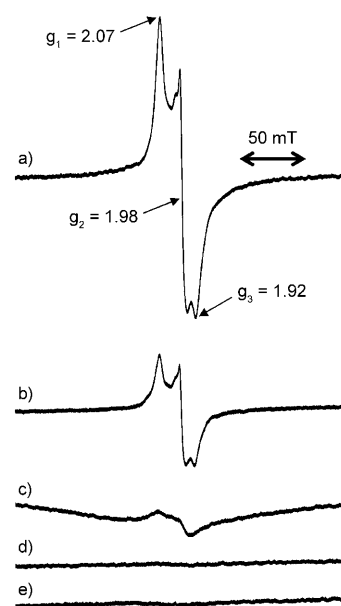


Figure 5. ESR spectra of a) Ru(OH)_x/TiO₂(A), b) Ru(OH)_x/TiO₂(B), c) Ru(OH)_x/Al₂O₃, d) Ru(OH)_x/TiO₂(C), and e) Ru(OH)_x.

Hydrogen-transfer reactions by supported ruthenium hydroxide catalysts: First, the catalytic activities of the supported ruthenium hydroxide catalysts for the racemization of (*R*)-1-phenylethanol were examined (Table 3).^[17] Under

Table 3. Racemization of (*R*)-1-phenylethanol.^[a]

Entry	Catalyst	t [h]	ee [%]	Selectivity [%]	TOF ^[b] [h ⁻¹]
1	Ru(OH) _x /TiO ₂ (A)	1	2	92	380
2	Ru(OH) _x /TiO ₂ (B)	1	30	88	120
3	Ru(OH) _x /TiO ₂ (C)	1	98	95	3
4	Ru(OH) _x /Al ₂ O ₃	1	79	95	23
5	Ru(OH) _x	1		no reaction	–
6	RuO ₂ (anhydrous)	5		no reaction	–
7	RuHAP	5	95	98	1
8	RuCl ₃ · n H ₂ O	5	1	6 ^[c]	–
9	[RuCl ₂ (PPh ₃) ₃]	5		no reaction	–
10	[RuCl ₂ (bpy) ₃]	5		no reaction	–
11	[RuCl ₂ (dmsO) ₄]	5		no reaction	–
12	[Ru(acac) ₃] ^[d]	5		no reaction	–
13	K ₂ [RuCl ₆] $\cdot n$ H ₂ O	5		no reaction	–
14	n Pr ₄ NRuO ₄	5	83	88	4
15	[Ru ₃ (CO) ₁₂]	5		no reaction	–
16 ^[e]	TiO ₂ (A)	5		no reaction	–
17 ^[e]	Al ₂ O ₃	5		no reaction	–
18	none	5		no reaction	–

[a] Reaction conditions: (*R*)-1-phenylethanol (1 mmol), catalyst (Ru: 1 mol %), toluene (3 mL), 353 K, in 1 atm of Ar. The enantiomeric excess (ee) and selectivity to racemization were determined by GC (Rt β -CDEXM column) or HPLC (Chiralcel-OD column) analyses with an internal standard. [b] The TOF values were calculated by the following recursion formula: $\text{TOF}[\text{h}^{-1}] = \{\log(ee/100)\} / \{\log(1 - (x/100))\} / t$, where ee , x , and t are the enantiomeric excess [%], the amount of catalyst [mol %], and reaction time [h], respectively. [c] 1-Phenyl-1-tolylethane and 1,1'-(oxydiethylidene)bisbenzene were formed as byproducts. [d] acac = acetylacetonate. [e] 40 mg.

the present conditions, no reaction occurred in the absence of catalyst, or in the presence of only TiO₂, anhydrous RuO₂, or Ru(OH)_x. In the case of RuCl₂·*n*H₂O, the selectivity for racemization was very low because of the formation of 1-phenyl-1-tolylethane and 1,1'-(oxydiethylidene)bisbenzene as byproducts. Although ruthenium complexes such as [RuCl₂(PPh₃)₃], [RuCl₂(bpy)₂], and [RuCl₂(dmsO)₄] (bpy = 2,2'-bipyridine; dmsO = dimethyl sulfoxide) have been reported to be active for racemization in the presence of bases such as NaOH and Na₂CO₃,^[8] they were inactive in the absence of bases under the present reaction conditions. Among the supported ruthenium hydroxide catalysts tested, the reaction rates decreased in the order of Ru(OH)_x/TiO₂(A) (turnover frequency (TOF) = 380 h⁻¹) > Ru(OH)_x/TiO₂(B) (120 h⁻¹) > Ru(OH)_x/TiO₂(C) (3 h⁻¹), whereas the selectivities for racemization were 88–95% and did not vary greatly. The Ru(OH)_x/TiO₂(A) catalyst showed the highest TOF, more than sixteen times higher than those of heterogeneous catalysts,^[10] including RuHAP (TOF = 1 h⁻¹; HAP = [RuCl]²⁺ species on hydroxyapatite)^[10] and Ru(OH)_x/Al₂O₃ (TOF = 23 h⁻¹).^[2,10b] Moreover, the TOF reached up to 1061 h⁻¹ when the racemization of (*R*)-1-phenylethanol was carried out with 0.5 mol% of Ru(OH)_x/TiO₂(A) at 373 K [Eq. (4)].

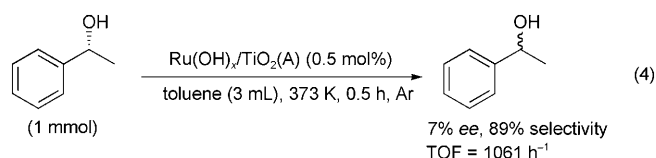


Table 4 shows the results of the racemization of various chiral secondary alcohols with the most active catalyst Ru(OH)_x/TiO₂(A). Ru(OH)_x/TiO₂(A) had high catalytic ac-

Table 4. Ru(OH)_x/TiO₂(A)-catalyzed racemization of various chiral secondary alcohols.^[a]

Entry	Substrate	Product	<i>t</i> [h]	<i>ee</i> [%]	Selectivity [%]
1			3	<1	83
2			3	<1	83
3 ^[b]			4	6	76
4			8	<1	76
5 ^[b]			4	4	84
6 ^[b]			4	2	85

[a] Reaction conditions: substrate (1 mmol), Ru(OH)_x/TiO₂(A) (Ru: 1 mol%), toluene (3 mL), 353 K, in 1 atm of Ar. The enantiomeric excess (*ee*) and selectivity for racemization were determined by GC or HPLC with an internal standard. The main byproducts were ketones. [b] Ru: 2 mol%.

tivities for the racemization of activated chiral secondary alcohols as well as non-activated ones. Chiral phenylethanol derivatives were smoothly converted into the corresponding racemic alcohols with good *ee* values and selectivities (Table 4, entries 1–3). Not only aromatic alcohols, but also less reactive aliphatic chiral secondary alcohols could be racemized to the corresponding alcohols (Table 4, entries 4–6). A major advantage of using Ru(OH)_x/TiO₂(A) is its heterogeneous nature, which was confirmed by the fact that the reaction did not proceed after removal of the catalyst at the reaction temperature, and no leaching of the ruthenium species was observed.^[18] It was confirmed by XANES and EXAFS spectra that the local structure of the ruthenium species in used Ru(OH)_x/TiO₂(A) catalyst was the same as that in the fresh catalyst. Furthermore, the Ru(OH)_x/TiO₂(A) catalyst could be reused for the racemization of (*R*)-1-phenylethanol at least three times with retention of its high catalytic performance (<1% *ee*, 86% selectivity for the 3rd reuse).

Next, the catalytic activities of a series of the supported ruthenium hydroxide catalysts for the MPV-type reduction of acetophenone with 2-propanol were examined (Table S1 in the Supporting Information).^[17] Among the supported catalysts tested, the reaction rates decreased in the order of Ru(OH)_x/TiO₂(A) (TOF = 118 h⁻¹) > Ru(OH)_x/TiO₂(B) (44 h⁻¹) > Ru(OH)_x/TiO₂(C) (6 h⁻¹). The selectivities for conversion into the corresponding alcohols were greater than 99% in all cases. The Ru(OH)_x/TiO₂(A) catalyst also showed the highest catalytic activity, and the reaction rate with Ru(OH)_x/TiO₂(A) was about one order of magnitude higher than that with previously reported catalyst Ru(OH)_x/Al₂O₃ (TOF = 13 h⁻¹).^[2]

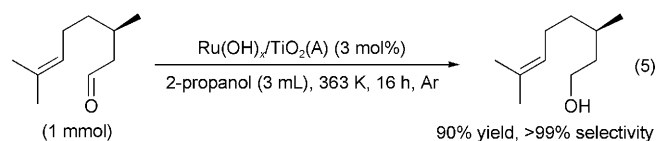
In the presence of the most active catalyst Ru(OH)_x/TiO₂(A), the scope of the present system towards various kinds of structurally diverse carbonyl compounds was examined (Table 5). The present system did not need any base, and the reduction proceeded under relatively mild reaction conditions with only 1 mol% of the catalyst. Acetophenone derivatives were smoothly converted into the corresponding 1-phenylethanols in excellent yields (Table 5, entries 1–4). Not only aromatic ketones, but also non-activated aliphatic ones could be reduced to the corresponding aliphatic secondary alcohols in excellent yields (Table 5, entries 5–8). The present system was also applicable to the reduction of heteroatom-containing substrates such as 2-thiophenecarboxaldehyde and 3-pyridinecarboxaldehyde (Table 5, entries 9 and 10). Furthermore, the chemoselective reduction of (*R*)-(+)-citronellal could be realized [Eq. (5)]. When the reduction of (*R*)-(+)-citronellal was carried out with molecular hydrogen in the presence of the most widely used catalysts, such as Pd/C and PtO₂·*n*H₂O (Adam's catalyst), the corresponding saturated aldehyde was obtained as a major product (Scheme S1 in the Supporting Information).

The present reduction was also heterogeneously catalyzed, and the Ru(OH)_x/TiO₂(A) catalyst could be reused for the reduction of acetophenone with retention of its high catalytic performance (93% yield for the 3rd reuse). The

Table 5. Ru(OH)_x/TiO₂(A)-catalyzed reduction of various carbonyl compounds with 2-propanol as a hydrogen donor.^[a]

Entry	Substrate	Product	<i>t</i> [h]	Yield [%]
1			1	95
2			3	82
3			1	89
4			3	83
5			1	96
6			2	92
7			3	91
8			12	99
9			24	78
10			24	64

[a] Reaction conditions: substrate (1 mmol), Ru(OH)_x/TiO₂(A) (Ru: 1 mol %), 2-propanol (3 mL), 363 K, in 1 atm of Ar. The yields were determined by GC with an internal standard.



Ru(OH)_x/TiO₂(A) catalyst could also act as an effective heterogeneous catalyst for the reduction of various kinds of allylic alcohols to saturated alcohols under similar reaction conditions (Table 6).^[17]

Figure 6 shows the relationship between relative reaction rates and C.N.s of nearest-neighbor Ru atoms for the above hydrogen-transfer reactions. The reaction rates monotonically increased with the decrease in C.N.s (the increase in the amounts of the monomeric ruthenium hydroxide species), suggesting that the monomeric ruthenium hydroxide species are effective for the present hydrogen-transfer reactions.

Conclusion

The supported ruthenium hydroxide catalyst Ru(OH)_x/TiO₂(A) showed the highest catalytic activity for hydrogen-transfer reactions, such as the racemization of chiral secondary alcohols and the reduction of carbonyl compounds and allylic alcohols—at least one order of magnitude higher than those with heterogeneous catalysts such as Ru(OH)_x/Al₂O₃. It is likely that the monomeric Ru³⁺ hydroxide spe-

Table 6. Ru(OH)_x/TiO₂(A)-catalyzed selective reduction of various allylic alcohols.^[a]

Entry	Substrate	Product	<i>t</i> [h]	Yield [%]
1			1	98
2			1.5	96
3			3	95
4 ^[b]			2	94
5 ^[c]			1	93
6 ^[c]			2	76

[a] Reaction conditions: substrate (1 mmol), Ru(OH)_x/TiO₂(A) (Ru: 1 mol %), 2-propanol (3 mL), 363 K, in 1 atm of Ar. The yields were determined by GC with an internal standard. [b] Ru: 5 mol %. [c] Ru: 3 mol %.

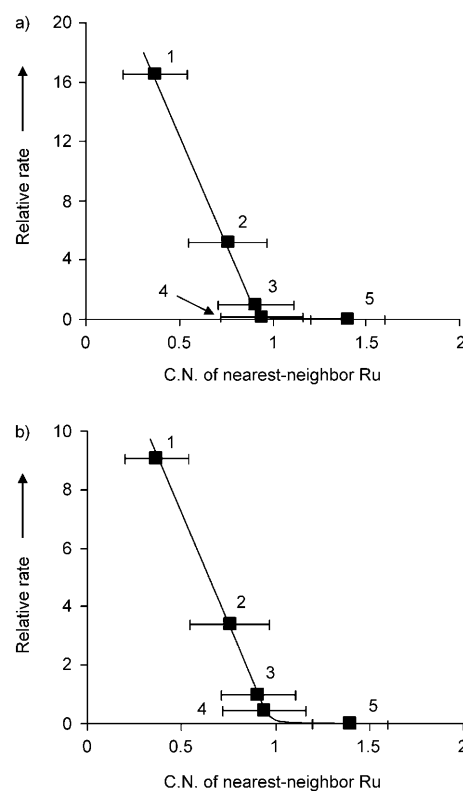


Figure 6. Relationship between relative reaction rates and coordination numbers (C.N.) of nearest-neighbor Ru atoms for a) the racemization of (*R*)-1-phenylethanol and b) the reduction of acetophenone with 2-propanol by various ruthenium hydroxide catalysts. The reaction rate with Ru(OH)_x/Al₂O₃ was taken as unity. 1: Ru(OH)_x/TiO₂(A), 2: Ru(OH)_x/TiO₂(B), 3: Ru(OH)_x/Al₂O₃, 4: Ru(OH)_x/TiO₂(C), and 5: Ru(OH)_x.

cies are effective for the present hydrogen-transfer reactions. The above-mentioned catalysts were truly heterogeneous and the catalysts recovered after the reactions could be reused with retention of their high catalytic performance.

Experimental Section

General: NMR spectra were recorded on a JEOL JNM-EX-270 instrument. ^1H and ^{13}C NMR spectra were measured at 270 and 67.8 MHz, respectively, in $[\text{D}_2]$ chloroform with tetramethylsilane (TMS) as an internal standard. GC analyses were performed on a Shimadzu GC-17 A instrument with a flame ionization detector (FID) equipped with a Rt β -CDEXM capillary column (internal diameter=0.25 mm, length=30 m) or a DB-WAX capillary column (internal diameter=0.25 mm, length=30 m). HPLC analyses were performed on a Shimadzu LC-10A instrument with a UV detector equipped with a Chiralcel-OD column (internal diameter=46 mm, length=25 cm) using *n*-hexane/2-propanol (95:5 v/v) as an eluent. Mass spectra were recorded on a Shimadzu GCMS-QP2010 instrument equipped with a TC-5HT capillary column (internal diameter=0.25 mm, length=30 m). The ICP-AES analyses were performed with a Shimadzu ICPS-8100 instrument. The ESR measurements (X-band) were performed with a JEOL JES-RE-1X instrument at 103 K under an Ar atmosphere. The XRD patterns were measured with a Rigaku MultiFlex instrument by using $\text{Cu}_{\text{K}\alpha}$ radiation (40 kV-50 mA). The X-ray absorption spectra were recorded at the NW10A beam line of PF at KEK, Japan (proposal No. 2007G096). A Si(311) single crystal was used to obtain the monochromated X-ray beam. Two ion chambers filled with Ar and Kr were used as I_0 and I detectors, respectively. For EXAFS analysis, the oscillation was first extracted from the EXAFS data by a spline smoothing method. The Fourier transformation of the k^3 -weighted EXAFS oscillation from k space to r space was performed over the range $3.0\text{--}16.5 \text{ \AA}^{-1}$ to obtain an RDF. For the curve-fitting analysis, the empirical phase shift and amplitude functions for Ru–O and Ru–Ru were extracted from the data for RuO_2 and Ru metal. The data were analyzed by using REX2000 software (version 2.5, Rigaku). The XPS measurements were carried out on a JEOL JPS-90 instrument by using monochromated $\text{Al}_{\text{K}\alpha}$ radiation ($h\nu=1486.6 \text{ eV}$). The X-ray anode was run at 200 W and the voltage was kept at 10 kV. The pass energy was fixed at 10.0 eV to ensure sufficient resolution to determine peak positions accurately. The binding energies were calibrated by using the $\text{Au } 4f_{7/2}$ signal at 84.0 eV.

Reagents: Reagents and substrates were obtained from Tokyo Kasei, Aldrich, and Fluka (reagent grade) and used without further purification. 2-Propanol (Kanto), however, was carefully purified (degassed) before use.^[19] Anatase TiO_2 (ST-01, $316 \text{ m}^2 \text{ g}^{-1}$), anatase TiO_2 (JRC-TIO-1, $73 \text{ m}^2 \text{ g}^{-1}$), rutile TiO_2 (SUPER-TITANIA G-2, $3.2 \text{ m}^2 \text{ g}^{-1}$), and Al_2O_3 (KHS-24, BET surface area: $160 \text{ m}^2 \text{ g}^{-1}$) were obtained from Ishihara Sangyo Kaisya Ltd., the Catalysis Society of Japan, Showa Denko K. K., and Sumitomo Chemical respectively. RuHAP ($[\text{RuCl}]^{2+}$ species on hydroxyapatite, 9.1 wt %) was purchased from Wako.

Preparation of $\text{Ru}(\text{OH})_x$: An aqueous solution of RuCl_3 (8.3 mM) was adjusted to pH 13.2 by addition of an aqueous solution of NaOH (1M), and the resulting solution was stirred at room temperature (ca. 293 K) for 24 h. The solid was then filtered off, washed with a large amount of water, and dried in vacuo to afford $\text{Ru}(\text{OH})_x$ in approximately 80% yield (based on RuCl_3).

Procedures for catalytic reactions: All operations were carried out in a glove box under Ar for the hydrogen-transfer reactions. A typical procedure is as follows: $\text{Ru}(\text{OH})_x/\text{TiO}_2(\text{A})$ (Ru: 1 mol %), (*R*)-1-phenylethanol (1 mmol), and toluene (3 mL) were successively placed into a pyrex vial. A teflon-coated magnetic stirrer bar was added, and the reaction mixture was vigorously stirred (800 rpm) at 353 K under 1 atm of argon. After 3 h, the catalyst and the product(s) were separated by filtration (or centrifugation), and the solid mixture was washed with toluene. Then, diphenyl (internal standard, 0.3 mmol) was added to the combined organic solution, and the solution was analyzed by GC on a chiral column. The separated catalyst was washed with an aqueous solution of NaOH (1M) and water, and then dried in vacuo before being recycled.

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