

# Highly active trimetallic Ru/CeO<sub>2</sub>/CoO(OH) catalyst for oxidation of alcohols in the presence of molecular oxygen

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## Abstract

The trimetallic Co-Ce-Ru compound acted as a highly efficient heterogeneous catalyst for the oxidation of various alcohols into the corresponding carbonyls, including less-reactive *primary* alcohols, in the presence of molecular oxygen under mild reaction conditions. Characterization of the catalyst using the K-edge X-ray absorption technique revealed that a monomeric Ru(IV) species was immobilized on the surface of CeO<sub>2</sub>/CoO(OH) support. The role of each metal component of the catalyst in the alcohol oxidation is discussed in relation to their local structure.

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**Keywords:** Alcohol oxidation; Molecular oxygen; Ruthenium; Heterogeneous catalyst; X-ray absorption fine structure

## 1. Introduction

Oxidation of alcohols into carbonyl compounds is one of the most pivotal functional group transformations in organic synthesis [1]. Today's environmental concerns demand clean oxidation reactions that minimize or eliminate the wastes, by replacing the conventional stoichiometric methods with atom-efficient catalytic protocol using molecular oxygen as a sole oxidant [2]. Use of some homogeneous metal complexes of Ru [3], Pd [4], Co [5], Os [6], and Cu [7] has achieved high catalytic activity and selectivity, but there is a strong demand for a highly efficient protocol using heterogeneous catalysts that offer significant advantages not only of being operationally simple [8], but also of enabling unprecedented reactions based on multi-functions at the surface [9]. Accordingly, the heterogeneous alcohol oxidation to the corresponding carbonyl compounds has progressed substantially by solid catalysts of Ru [10] and Pd [9b,11], to the best of our knowledge, however, there are few excellent heterogeneous catalysts

for the one-pot oxidation of *primary* aliphatic alcohols into carboxylic acids using atmospheric pressure of O<sub>2</sub> as a sole oxidant.

We are currently developing high-performance heterogeneous metal catalysts using inorganic crystallines, i.e. hydroxyapatite [10e,11d,12] and hydrotalcite [10c,10d,13], as macroligands for the catalytic active center. Especially, isomorphic substitution of the metal cations in the Brucite-layer of hydrotalcite compounds [14] by a ruthenium one provides highly-functionalized catalysts for the alcohol oxidation based on the interaction between metal species [10c,10d]. Herein, we present our studies demonstrating that the material composed of ruthenium, cobalt, and cerium elements, designated as Co-Ce-Ru, acted as a highly efficient heterogeneous catalyst for one-pot synthesis of carboxylic acids from the *primary* alcohols without any additives. Further, the reaction mechanism for the above oxidation is discussed based on the structures of the Co-Ce-Ru catalyst evaluated by means of K-edge X-ray absorption for fine structure (XAFS) that is a powerful technique for determining the local structure of heterogeneous catalysts [15]. A preliminary result of the oxidation reaction has previously been communicated [16].

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## 2. Experimental

### 2.1. General

All organic reagents were purified before use [17]. 4-Phenyl-but-3-en-2-ol was synthesized according to the literature procedure [18].  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  (Ru; 42.3 wt.%) was obtained from N.E. Chemcat. Co. Ltd. Other inorganic reagents were purchased from Wako Pure Chemical Co. Ltd. as special grade, and were used as received.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  at 400 and 100 MHz, respectively, on a JNM AL-400 spectrometer. Chemical shifts are reported in parts per million (ppm,  $\delta$ ) relative to  $\text{Me}_4\text{Si}$ . All the products were identified by GC-MS or NMR in comparison with those of authentic samples. X-ray diffraction (XRD) was measured on the X'pert diffractometer (Phillips Co. Ltd.). X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCA-2000 (Shimadzu Co. Ltd.).

### 2.2. Catalyst preparation

The Co-Ce-Ru catalyst was prepared as follows: to a mixture of aqueous  $\text{Na}_2\text{CO}_3$  (30 ml, 13.3 mmol) and  $\text{NaOH}$  (46.4 mmol) was slowly added a solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (10.2 mmol),  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (5.1 mmol), and  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  (Ru: 1.53 mmol) in deionized water (20 ml). After vigorous stirring the mixture at  $65^\circ\text{C}$  for 18 h, the resulting dark brown slurry was filtered, washed with distilled water, and dried at  $110^\circ\text{C}$  for 12 h to yield a 2.15 g of black powder (Anal. Co, 33.6 wt.%; Ce, 25.7 wt.%; Ru, 6.4 wt.%; XPS: Ru  $3p_{3/2}$ : 464.4 eV, FWHM = 4.9 eV. The XPS peak position is referred to C 1s at 283.0 eV). XRD measurement of the Co-Ce-Ru showed that the layered-structure of hydrotalcites was not formed, however, the diffraction peaks were observed at  $2\theta$  of  $20^\circ$ ,  $39^\circ$ ,  $28^\circ$ , and  $48^\circ$ . The former two peaks are assignable to the diffraction of  $\text{CoO}(\text{OH})$  and the latter peaks are identified to the  $\text{CeO}_2$  phase [19]. No peaks were detected due to the Ru species. It should be noted that the FWHM value of ca.  $1.0^\circ$  for the  $\text{CeO}_2$  phase in the Co-Ce-Ru catalyst was larger than that of ca.  $0.1^\circ$  for bulk  $\text{CeO}_2$ .

For comparison, the Mg-Al-Ru- $\text{CO}_3$  catalyst was obtained by replacing a part of Al cations in the Brucite-like layer of the hydrotalcite, Mg-Al- $\text{CO}_3$ , with Ru [10c]. Substitution of Co and Ce for Mg and Al of the Mg-Al-Ru- $\text{CO}_3$  gave Co-Al-Ru- $\text{CO}_3$  [10d] and Mg-Ce-Ru- $\text{CO}_3$ , respectively.

### 2.3. General procedure for oxidation of alcohols

A typical example for the oxidation of 1-octanol by the Co-Ce-Ru catalyst is as follows. Into a reaction vessel equipped with a reflux condenser were placed the Co-Ce-Ru (0.30 g, Ru: 0.20 mmol) and benzotrifluoride (5 ml). After the reaction vessel was filled with  $\text{O}_2$ , 1-octanol (2.60 g,

20 mmol) was added. Then, the reaction mixture was vigorously stirred at  $80^\circ\text{C}$  under atmospheric pressure of  $\text{O}_2$  for 30 h. The solid catalyst was removed by filtration. Evaporation of solvent under reduced pressure and Kugelrohr distillation of the residue afforded 2.30 g of pure octanoic acid (90%).

The spent catalyst was washed with 10% of aqueous  $\text{Na}_2\text{CO}_3$  and deionized water, followed by drying at  $110^\circ\text{C}$ , and then subjected to the alcohol oxidation under identical conditions.

### 2.4. X-ray absorption measurements

Ru K-edge X-ray absorption spectra were measured at room temperature in a transmission mode at the EXAFS facilities installed at BL01B1 line of SPring-8 at JASRI, Harima, Japan using a Si(311) monochromator (2001B0179-NX-np). Co K-edge X-ray absorption was recorded at room temperature in a transmission mode at the EXAFS facilities of BL-7C line of KEK-PF, Tsukuba, Japan with a Si(111) monochromator (2002G102). A detailed procedure for data reduction is described in elsewhere [20].

## 3. Results

The Co-Ce-Ru catalyst was prepared by a co-precipitation method using  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , and  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  under aqueous base conditions. The Co-Ce-Ru had no longer the layered-structure of hydrotalcites, however, it proved to exhibit a strong ability of alcohol oxidation as described below.

### 3.1. Aerobic oxidation of alcohols

As shown in Table 1, oxidation of various allylic alcohols smoothly proceeded in the presence of the Co-Ce-Ru catalyst under an atmospheric pressure of molecular oxygen at  $60^\circ\text{C}$ . Cinnamyl alcohol and its derivative were readily oxidized to give the corresponding  $\alpha,\beta$ -unsaturated aldehydes in almost quantitative yields (entries 1 and 3). The Co-Ce-Ru catalyst was also effective for the oxidation of aliphatic allylic alcohols (entry 4). Although the oxidation of a secondary allylic alcohol such as 4-phenyl-but-3-en-2-ol proceeded slowly, prolonged reaction times afforded the corresponding ketone in a high yield (entry 5). The spent Co-Ce-Ru catalyst was easily separated from the reaction mixture by filtration and could be reused with retention of its high activity and selectivity (entry 2). To confirm whether the alcohol oxidation occurs on the Co-Ce-Ru surface, the catalyst was removed by filtration after ca. 50% conversion. No oxidation proceeded when the colorless filtrate was further reacted under similar reaction conditions.

Benzyl alcohol and its *para*-substituted derivatives were converted smoothly to the corresponding aldehydes in quantitative yields (entries 6–8). Secondary benzylic alcohols

Table 1  
Oxidation of allylic and benzylic alcohols catalyzed by Co-Ce-Ru in the presence of molecular oxygen<sup>a</sup>

Entry	Substrate	Product	Time (h)	Conversion (%) <sup>b</sup>	Yield (%) <sup>b, c</sup>
1			1	100	>99 (92)
2 <sup>d</sup>			1	100	90
3			2	100	99
4			4	98	97
5			24	94	93
6			1	100	100(96)
7			1	100	>99
8			0.5	100	>99
9			0.83	100	>99(95)
10			0.5	100	>99
11			13	100	99
12			0.66	100	>99

<sup>a</sup> Reaction conditions: substrate (2 mmol), Co-Ce-Ru (0.3 g, Ru: 0.20 mmol), benzoic acid (5 ml), O<sub>2</sub> flow, and 60 °C.

<sup>b</sup> Conversion and yield were determined by GC or GCMS using an internal standard method.

<sup>c</sup> Values in parentheses are isolated yields using 20 mmol of substrate.

<sup>d</sup> The spent catalyst from entry 1 was used.

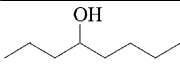
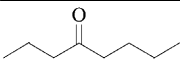
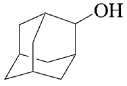
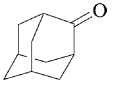
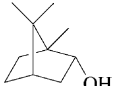
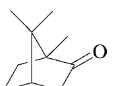
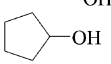
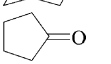
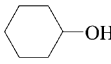
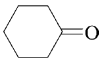
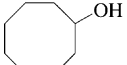
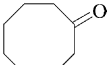
were readily oxidized to the corresponding ketones in high yields within short reaction times (entry 9). A  $\alpha$ -hydroxy ketone such as benzoin gave benzil as a sole product within 30 min (entry 10). This catalyst was also effective in oxidizing heteroaromatic alcohols such as 2-pyridinemethanol and 2-thiophenemethanol to the corresponding aldehydes, whereas the oxidation of 2-pyridinemethanol required a long reaction time (entries 11 and 12).

As summarized in Table 2, the Co-Ce-Ru catalyst was also effective in oxidizing aliphatic secondary alcohols, including cyclic ones, in the presence of molecular oxygen to afford the corresponding ketones. Oxidation of linear alcohols proceeded smoothly with a high yield (entry 1). It should be emphasized that *cyclic secondary alcohols were converted into the corresponding ketones in high yields* (entries 2–6). In the cases of sterically hindered cyclic alcohols such as 2-adamantanol and borneol, the Co-Ce-Ru exhibited extraordinary high catalytic activity (entries 2 and 3). Note

that the Co-Ce-Ru catalyst acted effectively in the oxidation of cyclohexanol to cyclohexanone within 6 h. To the best of our knowledge, this is the first example for the highly efficient oxidation of cyclohexanol to cyclohexanone using heterogeneous ruthenium catalyst in the presence of molecular oxygen.

The above results have encouraged us to apply the Co-Ce-Ru catalyst to the oxidation of less-reactive aliphatic *primary* alcohols. To evaluate the catalytic properties of the Co-Ce-Ru, the oxidation of 1-octanol was carried out using various Ru catalysts under an atmospheric O<sub>2</sub> pressure, and the results are listed in Table 3. Among the hydrotalcite- and hydroxyapatite-immobilized Ru catalysts [10c-e], and Ru/CeO<sub>2</sub> [10b], the trimetallic Co-Ce-Ru exhibited the highest catalytic activity for the oxidation of 1-octanol into octanoic acid. In the cases of the Mg-Ce-Ru-CO<sub>3</sub> and Mg-Al-Ru-CO<sub>3</sub> catalysts, the conversion of 1-octanol was low to give only octanal as a product. Using the Co-Ce-CO<sub>3</sub>

Table 2  
Aerobic oxidation of secondary alcohols catalyzed by Co-Ce-Ru<sup>a</sup>

Entry	Substrate	Product	Time (h)	Conversion (%) <sup>b</sup>	Yield (%) <sup>b,c</sup>
1			2	95	95
2			2	100	>99(94)
3			1.5	100	>99
4 <sup>d</sup>			8	90	88
5 <sup>d</sup>			6	91	89
6 <sup>d</sup>			4	94	93

<sup>a</sup> Reaction conditions: substrate (2 mmol), Co-Ce-Ru (0.3 g, Ru: 0.20 mmol), benzotrifluoride (5 ml), O<sub>2</sub> flow, and 60 °C.

<sup>b</sup> Conversion and yield were determined by GC, LC or GCMS using an internal standard method.

<sup>c</sup> Values in parentheses are isolated yields using 20 mmol of substrate.

<sup>d</sup> Substrate (1 mmol).

without Ru component, the oxidation of 1-octanol scarcely proceeded. 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. Obviously, the Ru species acts as catalytically active sites for this alcohol oxidation and the Co component plays an essential role in the production of carboxylic acid.

Subsequently, the Co-Ce-Ru catalyst was applied to the oxidation of aliphatic *primary* alcohols, and typical results are shown in Table 4. Linear *primary* alcohols were readily oxidized to the corresponding carboxylic acids in excellent yields without formation of esters (entries 1 and 2). Branched and cyclic *primary* aliphatic alcohols were oxidized in the presence of the Co-Ce-Ru catalyst in moderate yields (entries 3–5). In case of a branched *primary* alcohol,

the addition of water improved the yield of the branched carboxylic acid (entry 3). A 20 mmol scale oxidation of 1-octanol proceeded at 80 °C to afford octanoic acid in 90% yield after 30 h.  $\alpha,\omega$ -Diols were also selectively oxidized using the Co-Ce-Ru catalyst to form the corresponding lactones in moderate yields (entries 6 and 7). The high chemoselectivity for the *primary* hydroxyl function is exemplified in the following competitive oxidations. An intramolecular competitive oxidation of 1,4-pentanediol afforded methyl- $\gamma$ -butyrolactone in 87% yield at 80 °C for 6 h (entry 8). When an equimolar mixture of 1-octanol and 4-octanol was used as substrates, 80% of octanoic acid was selectively obtained together with 5% of 4-octanone for 7 h at 60 °C.

To the best of our knowledge, the Co-Ce-Ru catalyst is the most effective catalyst for the one-pot oxidation of *primary* aliphatic alcohols into carboxylic acids using atmospheric pressure of O<sub>2</sub> as a sole oxidant. Although the use of other homogeneous transition metal complexes and heterogeneous catalysts can also achieve the effective oxidation of *primary* alcohols using O<sub>2</sub> as a sole oxidant [3b-d,4-7,10b,10e,10g,10j,11a,11e], the major products are aldehydes; only a few reports can be found on the selective formation of carboxylic acid [4c,5,10b,11a,11e].

The time profile of the oxidation of 1-octanol catalyzed by the Co-Ce-Ru was plotted in Fig. 1. It is evident that the yield of octanal reached a maximum at 2 h, and the yield of octanoic acid increased rapidly thereafter. When 2,6-di-*tert*-butyl-*p*-cresol as a radical scavenger was added in the oxidation of 1-octanol using the Co-Ce-Ru catalyst, octanal was formed quantitatively without formation of octanoic acid. An efficient transformation of aldehyde to carboxylic acid might involve a free radical process associated with Co species.

Table 3  
Effect of catalysts in aerobic oxidation of 1-octanol<sup>a</sup>

Entry	Catalyst	Conversion (%) <sup>b</sup>	Yield (%) <sup>b</sup>	
			Octanoic acid	Octanal
1	Co-Ce-Ru	100	97	1
2	Co-Al-Ru-CO <sub>3</sub>	90	63	26
3	Ru/CeO <sub>2</sub> <sup>c</sup>	30	28	0
4	Mg-Ce-Ru-CO <sub>3</sub>	58	1	48
5	Ru-hydroxyapatite <sup>d</sup>	95	0	94
6	Mg-Al-Ru-CO <sub>3</sub>	16	0	15
7	Co-Ce-CO <sub>3</sub>	<2	0	<1

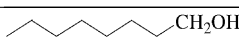
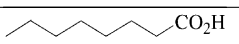
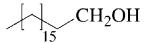
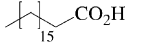
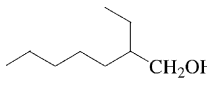
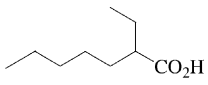
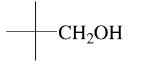
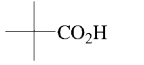
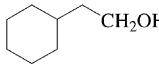
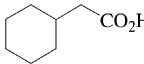
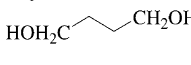

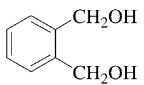

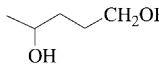

<sup>a</sup> Reaction conditions: 1-octanol (2 mmol), catalyst (0.3 g, Ru: 6 wt.%), benzotrifluoride (5 ml), O<sub>2</sub> flow, 60 °C, and 4 h.

<sup>b</sup> Conversion and yields were determined by GC using internal standard method.

<sup>c</sup> Prepared by literature procedure ([10b]).

<sup>d</sup> Cited from [10e]; Ru hydroxyapatite (0.2 g), 16 h.

Table 4  
Oxidation of primary alcohols by Co-Ce-Ru catalyst using molecular oxygen<sup>a</sup>

Entry	Substrate	Product	Time (h)	Conversion (%) <sup>b</sup>	Yield (%) <sup>b, c</sup>
1			4	100	97 (90)
2			5	100	82 (78)
3 <sup>d</sup>			14	95	79
4			5	100	64
5			4	100	85 (80)
6 <sup>e</sup>			6	100	83
7 <sup>f</sup>			6	100	77
8 <sup>e</sup>			6	100	87

<sup>a</sup> Reaction conditions: substrate (2 mmol), Co-Ce-Ru (0.3 g, Ru: 0.20 mmol), benzotrifluoride (5 ml), O<sub>2</sub> flow, and 60 °C.

<sup>b</sup> Conversion and yield were determined by GC, LC, or GCMS using internal standard method.

<sup>c</sup> Values in parentheses are isolated yields using 20 mmol of substrate.

<sup>d</sup> Deionized water (0.2 ml) was added.

<sup>e</sup> Diol (1 mmol) 80 °C.

<sup>f</sup> Diol (1 mmol).

We have demonstrated the high performance of the trimetallic Co-Ce-Ru catalyst in the aerobic oxidation of various kinds of alcohols to the corresponding carbonyl compounds. Especially, less-reactive primary alcohols could be effectively converted into carboxylic acids. Since the above highly efficient alcohol oxidation might relate to the oxidation states and local structure of Ru and Co components in the Co-Ce-Ru catalyst, the fine structure around Ru and Co species was straightforwardly determined by X-ray absorption spectroscopy in the next section.

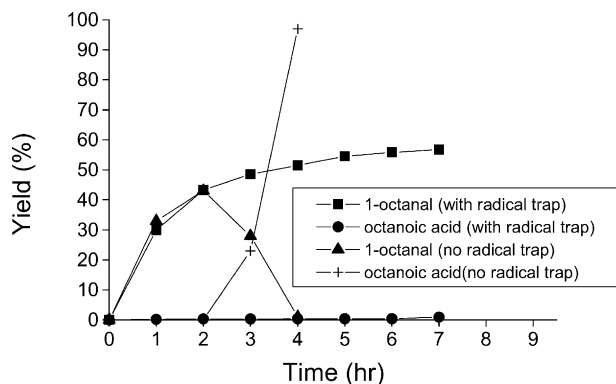


Fig. 1. Time profiles of oxidation of 1-octanol catalyzed by Ru-CoO(OH)-CeO<sub>2</sub> in the absence and presence of 2,6-di-*tert*-butyl-*p*-cresol. Reaction conditions: 1-octanol (2 mmol), Ru-CoO(OH)-CeO<sub>2</sub> (0.3 g, Ru: 0.20 mmol), benzotrifluoride (5 ml), 2,6-di-*tert*-butyl-*p*-cresol (0.05 mmol), O<sub>2</sub> flow, and 60 °C.

### 3.2. K-edge XAFS measurements

The XANES spectrum of the Co-Ce-Ru catalyst was compared with those of Ru(acac)<sub>3</sub> and anhydrous RuO<sub>2</sub>. The edge position of the Co-Ce-Ru sample overlies those of anhydrous RuO<sub>2</sub> and Ru(acac)<sub>3</sub>, showing that the oxidation state of Ru element in the Co-Ce-Ru is +3 or +4. Since the edge position hardly distinguishes between Ru<sup>3+</sup> and Ru<sup>4+</sup> [21], this technique cannot be used to determine the fractions of Ru<sup>3+</sup> and Ru<sup>4+</sup> in the Co-Ce-Ru sample. However, XPS characterization showed that the electron binding energy of Ru 3p<sub>3/2</sub> is higher than that of the Mg-Al-Ru-CO<sub>3</sub>, where the trivalent Ru cations exist in the Brucite-layers of the hydroxalcite [10c], implying the formation of tetravalent Ru species in the Co-Ce-Ru catalyst.

Fig. 2 depicts Fourier transforms of *k*<sup>3</sup>-weighted Ru K-edge EXAFS of the RuO<sub>2</sub> and the Co-Ce-Ru(IV). The RuO<sub>2</sub> has the rutile structure composed of RuO<sub>6</sub> octahedra, possessing four oxygen ions at 1.984 Å and two axial oxygen ions at 1.942 Å from the Ru<sup>4+</sup> center [22]. The octahedra are linked in chains by sharing two oxygen ions with each of two neighboring octahedra to form a three-dimensional network, creating eight Ru-Ru distances at 3.535 Å. The above peaks could be clearly observed in the FT EXAFS of the RuO<sub>2</sub>, as shown in Fig. 2A. On the other hand, the peak ascribed to the Ru-Ru bond was hardly detected in the FT EXAFS of the Co-Ce-Ru(IV) sample (Fig. 2B). Such a situation has been already observed for Ru(III)-hydroxyapatite [10e] and the Co-Al-Ru(IV)-CO<sub>3</sub>

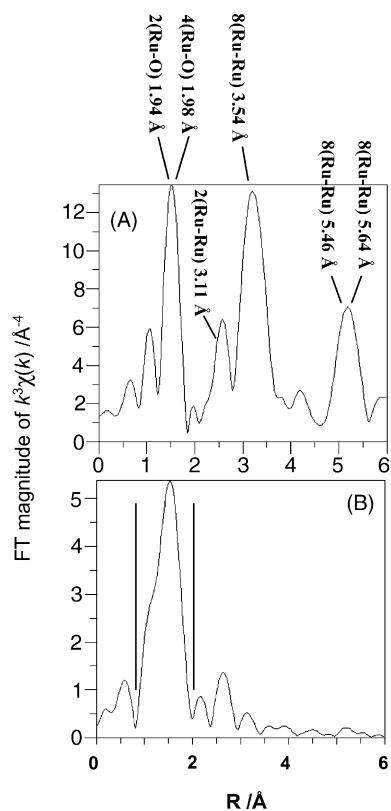


Fig. 2. Fourier transforms of  $k^3$ -weighted Ru K-edge EXAFS of (A) anhydrous  $\text{RuO}_2$  and (B) Co-Ce-Ru. Phase shift was not corrected.

samples [13], and shows that the Ru cation species in the Co-Ce-Ru(IV) catalyst exists as a monomer.

The peak around  $1.5 \text{ \AA}$  was inversely Fourier transformed for curve-fitting analysis using Ru–O shell parameters to obtain distance between Ru and oxygen atoms and their coordination number. The experimental data were well fitted by using two sets of Ru–O bond. In Table 5, the results of curve-fitting analysis of the Co-Ce-Ru(IV) sample are summarized together with those of the Co-Al-Ru(IV)- $\text{CO}_3$  [13]. The cationic Ru species had a coordination with one short Ru–O distance ( $1.81 \text{ \AA}$ ) and four long Ru–O dis-

Table 5

Results of curve-fitting analysis of the Co-Ce-Ru(IV) and Co-Al-Ru(IV)- $\text{CO}_3$

Sample	Shell	$R \text{ (\AA)}^a$	C.N. <sup>b</sup>	$\Delta\sigma \text{ (\AA}^2)^c$
Co-Ce-Ru(IV)	Ru–O(1)	1.81	0.9	–0.00449
	Ru–O(2)	1.97	4.0	–0.00038
Co-Al-Ru(IV)- $\text{CO}_3$	Ru–O(1)	1.89	1.1	0.00001
	Ru–O(2)	1.999	5.1	0.00001
$\text{RuO}_2^d$	Ru–O(1)	1.94	2	–
	Ru–O(2)	1.98	4	–

<sup>a</sup> Interatomic distance.

<sup>b</sup> Coordination number.

<sup>c</sup> Difference between Debye–Waller factor of the catalysts and that of the reference sample.

<sup>d</sup> From the crystallographic data ([22]).

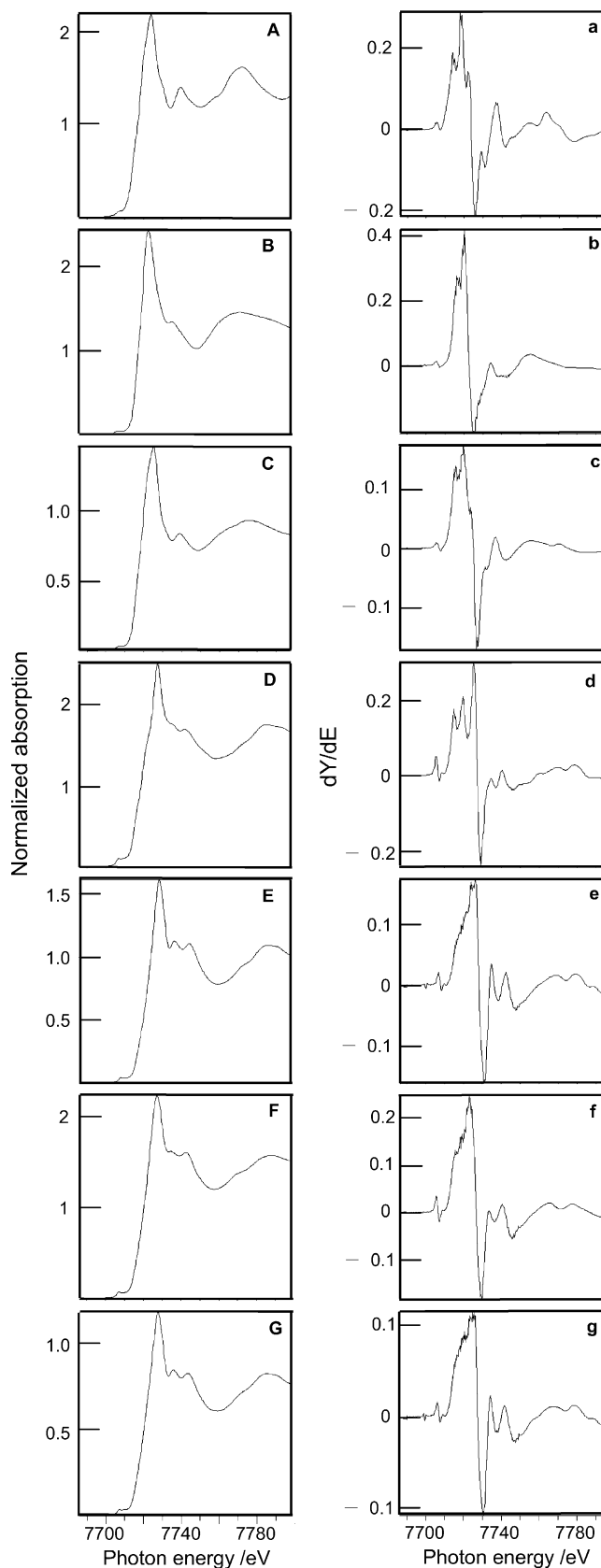


Fig. 3. Co K-edge XANES spectra and their first derivatives of (A, a) CoO, (B, b)  $\text{Co}(\text{NO}_3)_2$ , (C, c) Co-Al- $\text{CO}_3$ , (D, d)  $\text{CO}_2\text{O}_3$ , (E, e) Co-Ce-Ru, (F, f) Co-Al-Ru- $\text{CO}_3$ , and (G, g) Co-Ce- $\text{CO}_3$ .

tances (1.97 Å). The above results show that the isolated Ru(IV) species in the Co-Ce-Ru catalyst is surrounded by five oxygen atoms. The short Ru–O bond is assignable to Ru(IV)–OH species because the distance is slightly longer than that of the Ru(IV)=O observed in the Ru complexes with  $\sigma$ -saturated tertiary amine ligands (1.765 Å) [23] but shorter than the Ru(II)–OH bond in the nitrosylruthenium porphyrin complex (1.956 Å) [24]. Therefore, we think that the short Ru–O bond of the Co-Ce-Ru(IV) catalyst might originate from a Ru(IV)–OH moiety.

Fig. 3 shows Co K-edge XANES spectra and their first derivatives of reference samples, e.g. CoO, Co(NO<sub>3</sub>)<sub>2</sub>, and Co<sub>2</sub>O<sub>3</sub>, and Co-containing catalysts. The absorption, arising from the 1s → 4p transition, is known to be sensitive to the oxidation state and coordination sphere [25], and the chemical shift between Co<sup>2+</sup> and Co<sup>3+</sup> was observed in the edge position of each spectrum of reference compounds. Moreover, oxygen ligands reflect the complicated feature around the edge (a, d versus b). The edge position of the Co-Al-CO<sub>3</sub> sample was similar to those of divalent Co compounds. In contrast, the positions of the Co-Ce-Ru(IV), the Co-Al-Ru(IV)-CO<sub>3</sub>, and the Co-Ce-CO<sub>3</sub> were similar to that of Co<sub>2</sub>O<sub>3</sub>. Furthermore, their first derivatives resembled

those of Co<sub>2</sub>O<sub>3</sub>. These results indicate that the Co atoms in the Co-Al-Ru(IV)-CO<sub>3</sub> and Co-Ce-CO<sub>3</sub> catalysts might be present as a trivalent form, and surrounded by several oxygens.

In Fig. 4, Fourier transforms of  $k^3$ -weighted Co K-edge EXAFS spectra of Co references and catalyst samples are shown. In the radial structure functions for the Co compounds, two distinct peaks appeared around 1.5 and 2.5 Å. The peak around 1.5 Å is due to oxygen scatterers, and the latter peak is assignable to back scattering from neighboring Co atoms. The inverse Fourier transform of the peak around 1.5 Å of the Co(III)-Ce-Ru(IV), shown in Fig. 4D, can be fitted using Co–O shell parameters. The trivalent cobalt species in the Co-Ce-Ru(IV) had a coordination with four short Co–O distances (1.86 Å) and two long Co–O distances (1.998 Å), as summarized in Table 6. The interatomic distance between two Co ions and the coordination number were 2.87 Å and 6, respectively.

For the Co–O shell of all the catalyst samples, each estimated parameter is identical within the calculation errors. As shown in Table 6, the interatomic distances and coordination numbers are very close to those of CoO(OH) [26], where the environment around Co<sup>3+</sup> is six-fold coordination.

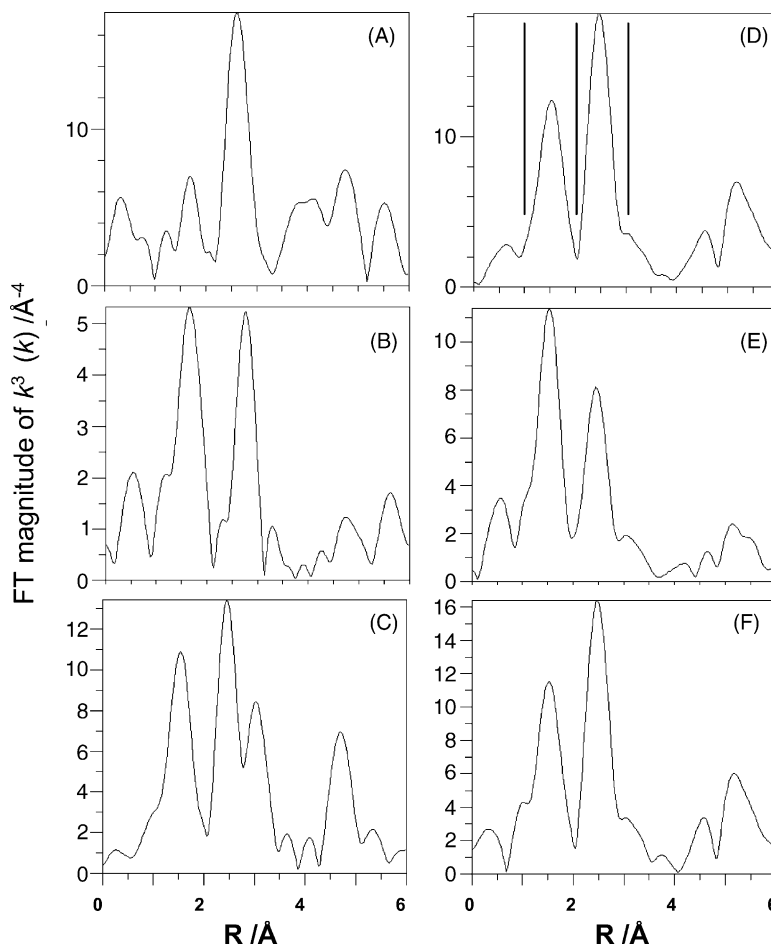


Fig. 4. Fourier transforms of Co K-edge EXAFS of (A) CoO, (B) Co-Al-CO<sub>3</sub>, (C) Co<sub>2</sub>O<sub>3</sub>, (D) Co-Ce-Ru, (E) Co-Al-Ru-CO<sub>3</sub>, and (F) Co-Ce-CO<sub>3</sub>. Phase shift was not corrected.

Table 6  
Results of curve-fitting analysis of Co–O and Co–Co shells for Co-containing catalysts

Sample	Shell	$R$ (Å) <sup>a</sup>	C.N. <sup>b</sup>	$\Delta\sigma$ (Å <sup>2</sup> ) <sup>c</sup>
Co-Ce-Ru(IV)	Co–O(1)	1.86	4.0	–0.0086
	Co–O(2)	1.998	2.5	–0.00115
	Co–Co	2.87	5.9	–0.00411
Co-Al-Ru(IV)-CO <sub>3</sub>	Co–O(1)	1.86	4.0	–0.0069
	Co–O(2)	1.995	2.5	–0.0098
	Co–Co	2.85	2.9	–0.0035
Co-Ce-CO <sub>3</sub>	Co–O(1)	1.86	4.0	–0.0076
	Co–O(2)	2.00	2.5	–0.0106
	Co–Co	2.87	5.8	–0.00365
CoO(OH) <sup>d</sup>	Co–O	1.897	6.0	–
	Co–Co	2.851	6.0	–

<sup>a</sup> Interatomic distance.

<sup>b</sup> Coordination number.

<sup>c</sup> Difference between Debye–Waller factor of the catalysts and that of the reference sample.

<sup>d</sup> From the crystallographic data ([26]).

The above estimated EXAFS parameter strongly suggests that Co<sup>3+</sup> cations in the catalysts are present at the center of the oxygen octahedron. The 2.87 Å Co–Co distance of the Co–Ce–Ru(IV) and the Co–Ce–CO<sub>3</sub> samples is associated with a Co–Co bond in the CoO(OH) phase, where the CoO<sub>6</sub> octahedra are linked by sharing two oxygen ions with each of six neighboring octahedra to create a two-dimensional network. Conclusively, the CoO(OH) phase is formed in the presence of Ru and Ce elements.

#### 4. Discussion

Mixed oxides between Co and Ce elements in the Co(III)-Ce-Ru(IV) sample were not detected by both XAFS and XRD measurements. The large FWHM value of the CeO<sub>2</sub> phase compared with bulk phase suggested small CeO<sub>2</sub> crystals. Therefore, the main phase of this catalyst is composed of the CoO(OH) crystals physically mixed with a small CeO<sub>2</sub> particles. Here, we propose a plausible structure of the Co(III)-Ce(IV)-Ru(IV) catalyst based on the above characterizations as illustrated in Fig. 5, where the monomeric Ru(IV) cation species is located on the surface of the CeO<sub>2</sub>/CoO(OH) support. At present, we think that the most Ru species are incorporated into the CoO(OH) structure in the vicinity of the CeO<sub>2</sub> particles. A similar ionic radii of Ru(IV) (65 pm) and Co(III) (64 pm) [27] supports an incorporation of the Ru(IV) species into the CoO(OH) crystal. The inverse FT of the peak around 2.7 Å in Fig. 2B, however, cannot be fitted using Ru–Co shell parameters. This might be caused by an inhomogeneous distribution of bond distance between Ru and Co cations on the surface.

It has been reported that the CoO(OH) can be obtained by oxidation of CoCl<sub>2</sub> under strong alkali conditions in the pres-

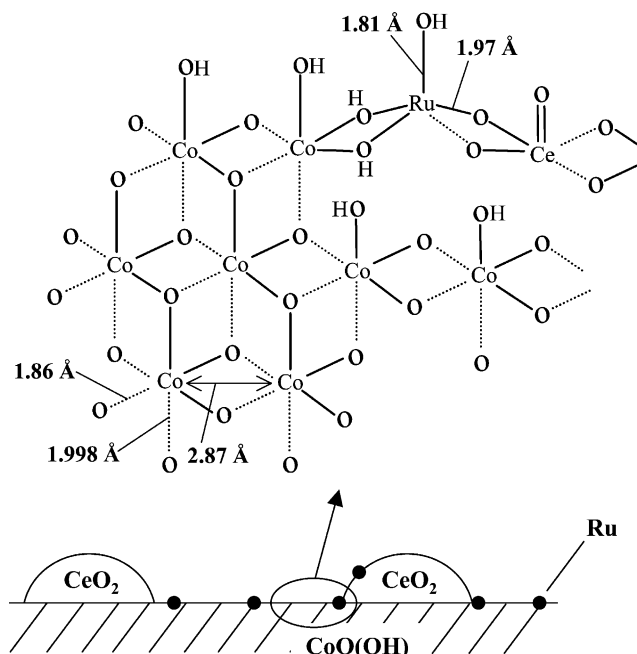


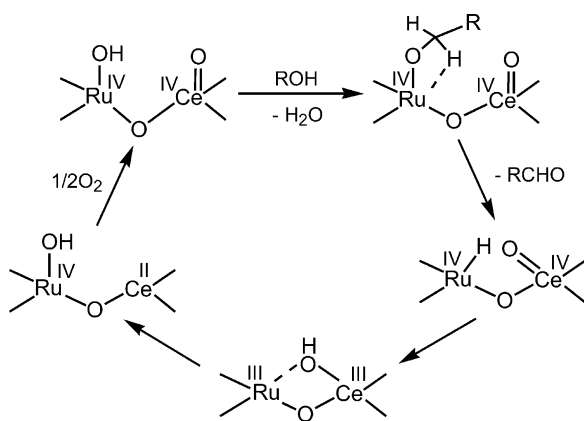
Fig. 5. Proposed structure of the Co(III)-Ce(IV)-Ru(IV) trimetallic catalyst. The small particles of CeO<sub>2</sub> are combined with the CoO(OH) crystalline. Most part of monomeric Ru(IV) species, as shown by black circle, are located at the surface of the CoO(OH) and in the vicinity of the CeO<sub>2</sub> particles. The hydrogen atoms of the CoO(OH) crystal are located at the interlayer space between the two-dimensional CoO<sub>6</sub> layer.

ence of molecular oxygen [26]. However, under the present conditions, the oxidation state of Co species remained divalent without Ru nor Ce element, e.g. the Co–Al–CO<sub>3</sub>. The Co(III) species in the Co(III)-Ce(IV)-Ru(IV) catalyst was formed during the preparation in the presence of Ru and/or Ce components. Therefore, Ru or Ce cations catalytically promote the oxidation of Co(II) to Co(III) species under aerobic conditions. Judging from the standard redox potentials [27], the resultant Co(III) cation can have oxidizing ability of Ru(III) to Ru(IV), and Ce(III) to Ce(IV) to afford Co(II) species. The Co(II) species was reoxidized into Co(III) during the treatment at 110 °C under aerobic conditions.

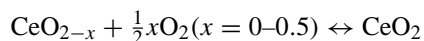
As shown in Table 6, the small coordination number of Co–Co shell, e.g. 2.9, for the Co(III)-Al-Ru(IV)-CO<sub>3</sub> might be ascribed to highly distorted structure or incomplete crystal of the CoO(OH) phase. This accords with the XRD of the Co(III)-Al-Ru(IV)-CO<sub>3</sub> showing no diffraction peak due to the CoO(OH) phase. However, the presence of Ce enlarged the coordination number of the Co–Co bond from 2.9 to 5.9; a high crystallinity of the CoO(OH) phase was achieved in the presence of Ce component. Displacement of Al by Ce cation inhibits the formation of the Brucite-layer due to larger ionic radii of Ce (94 pm for Ce<sup>4+</sup>; 107 pm for Ce<sup>3+</sup>) than that of Al<sup>3+</sup> (57 pm), which resulted in an aggregation of Co(III) species to large crystallines of the CoO(OH). Since the ionic radii of Ce is also larger than that of Co<sup>3+</sup> (64 pm), Ce cations could be expelled from the crystal structure of the CoO(OH).



Vide supra, the surface Ru(IV) species is responsible for the oxidation of alcohols to aldehydes. The alcohol oxidation involves the formation of a Ru-alcoholate species, which undergoes  $\beta$ -elimination to produce the aldehyde and a Ru-hydride species. Reaction of the hydride species with  $O_2$  affords a Ru-hydroperoxide species, followed by the ligand exchange to regenerate Ru-alcoholate species together with the formation of  $O_2$  and  $H_2O$  [10e]. In the intermolecular competitive oxidation between benzyl alcohol and benzyl [ $D_7$ ] alcohol ( $C_6D_5CD_2OH$ ) using the Co(III)-Ce(IV)-Ru(IV) catalyst at  $60^\circ C$ , the kinetic isotope effect ( $k_H/k_D$ ) was found to be 2.5. Therefore, the elimination of  $\beta$ -hydrogen of the Ru-alcoholate species is the rate-determining step. The high activity of the Co(III)-Ce(IV)-Ru(IV) catalyst in the alcohol oxidation is attributable to the promotion of the  $CeO_2$  in this elimination step. Presumably, a Ru(IV)-O-Ce(IV) bond could accelerate the  $\beta$ -elimination to afford a Ru(IV)-O-Ce(II) moiety as well as the formation of a Ru-alcoholate species.

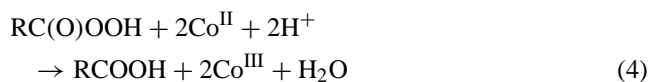
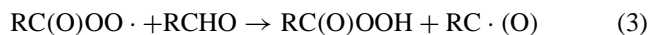
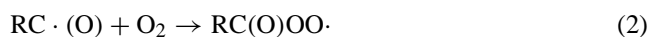
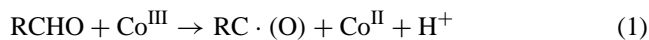


The bridging oxygen atom between metals in the heterobimetallic complexes has been proposed to promote the alcohol oxidation via elimination of  $\beta$ -hydrogen of metal-alcoholate species [3d]. A subsequent oxidation of the Ce(II) species with molecular oxygen regenerates the Ru(IV)-O-Ce(IV) species. It has been well known that the Ce component activates molecular oxygen based on the following reversible redox reaction [28]:



In the Co(III)-Ce(IV)-Ru(IV) trimetallic catalyst, the CoO(OH) phase plays an essential role in the production of carboxylic acids from aldehydes via free-radical pathway [29]. It is well known that the Co(III) species mediates the formation of peracids by radical chain reaction of aldehydes with molecular oxygen [30]. We consider the reaction pathway for oxidation of aldehydes to carboxylic acids as follows. Aliphatic aldehyde reacts with the surface Co(III) species to give an acyl radical,  $RC \cdot (O)$ , and a Co(II) species and  $H^+$  (Eq. (1)). Reaction of an acyl radical with molecular oxygen affords an acylperoxy radical that abstracts a

hydrogen from the aldehyde giving the peracid,  $RC(O)OOH$  (Eqs. (2) and (3)). Co(III) species is regenerated by the reaction of the peracid and the Co(II)/ $H^+$  together with a formation of carboxylic acid and  $H_2O$  (Eq. (4)) [31].



Correspondingly, the Co(III)-Ce(IV)-Ru(IV) efficiently catalyzed the oxidation of aliphatic aldehydes into the carboxylic acids even at room temperature [16]. The peracid may participate in the oxidation of alcohol in combination with the Ru species [30b], and in the reoxidation of the Ce(II) to Ce(IV) species.

## 5. Conclusions

The structure of ruthenium and cobalt cations in the Co-Ce-Ru catalyst was determined by means of K-edge XAFS technique to elucidate the origin of prominent catalysis for one-pot synthesis of carboxylic acids from *primary* alcohol under an atmospheric pressure of  $O_2$ . The isolated Ru(IV) species is immobilized on the surface of  $CeO_2/CoO(OH)$  support where each metal species works cooperatively in the above aerobic oxidation. We expect that the precise control of redox interactions among surface metal cations can provide highly-functionalized solid catalysts for oxidation reactions using molecular oxygen as a sole oxidant.

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## References

- [1] (a) R.A. Sheldon, J.K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981; (b) R.A. Sheldon, I.W.C.E. Arends, G.-J. ten Blink, A. Dijkman, *Acc. Chem. Res.* 35 (2002) 774;

- (c) G.-J. ten Brink, I.W.C.E. Arends, R.A. Sheldon, *Adv. Synth. Catal.* 344 (2002) 355.
- [2] B.M. Trost, *Science* 254 (1991) 1471;  
R.A. Sheldon, *Chemtech* (1994) 38;  
P.T. Anastas, J.C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, Oxford, 1998;  
M. Lancaster, *Green Chemistry: An Introductory Text*, Royal Society of Chemistry, Cambridge, 2002.
- [3] (a) J.-E. Bäckvall, E.L. Chowdhury, U. Karlsson, *J. Chem. Soc. Chem. Commun.* (1991) 473;  
(b) I.E. Markó, P.R. Giles, M. Tsukazaki, I. Chellé-Regnaut, C. Urch, S.M. Brown, *J. Am. Chem. Soc.* 119 (1997) 12661;  
(c) A. Hanyu, E. Takezawa, S. Sakaguchi, Y. Ishii, *Tetrahedron Lett.* 39 (1998) 5557;  
(d) P.A. Shapley, N. Zhang, J.L. Allen, D.H. Pool, H.C. Liang, *J. Am. Chem. Soc.* 122 (2000) 1079;  
(e) A. Dijksman, A. Marino-González, A.M.I. Payeras, I.W.C.E. Arends, R.A. Sheldon, *J. Am. Chem. Soc.* 123 (2001) 6826;  
(f) G. Csajenyik, A.H. Éll, L. Fadini, B. Pugin, J.-E. Bäckvall, *J. Org. Chem.* 67 (2002) 1657;  
(g) J.B. Johnson, J.-E. Bäckvall, *J. Org. Chem.* 68 (2003) 7681.
- [4] (a) K.P. Peterson, R.C. Larock, *J. Org. Chem.* 63 (1998) 3185;  
(b) T. Nishimura, T. Onoue, K. Ohe, S. Uemura, *J. Org. Chem.* 64 (1999) 6750;  
(c) G.-J. ten Brink, I.W.C.E. Arends, R.A. Sheldon, *Science* 287 (2000) 1636.
- [5] (a) T. Iwahama, S. Sakaguchi, Y. Nishiyama, Y. Ishii, *Tetrahedron Lett.* 36 (1995) 6923;  
(b) T. Iwahama, Y. Yoshino, T. Keitoku, S. Sakaguchi, Y. Ishii, *J. Org. Chem.* 65 (2000) 6502.
- [6] C. Dobler, G.M. Mehlretter, U. Sundermeier, M. Eckert, H.C. Mil- itzer, M. Beller, *Tetrahedron Lett.* 42 (2001) 8447.
- [7] I.E. Markó, P.R. Giles, M. Tsukazaki, S.M. Brown, C.J. Urch, *Science* 274 (1996) 2044;  
P. Gamez, I.W.C.E. Arends, J. Reedijk, R.A. Sheldon, *Chem. Commun.* (2003) 2414.
- [8] R.A. Sheldon, H. van Bekkum, *Fine Chemicals through Heterogeneous Catalysts*, Wiley, New York, 2001.
- [9] (a) K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida, K. Kaneda, *J. Am. Chem. Soc.* 121 (1999) 4526;  
(b) K.-M. Choi, T. Akita, T. Mizugaki, K. Ebitani, K. Kaneda, *New J. Chem.* 27 (2003) 324;  
(c) K. Mori, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.*, in press.
- [10] (a) M. Matsumoto, M. Watanabe, *J. Org. Chem.* 49 (1984) 3435;  
(b) F. Vocanson, Y.P. Guo, J.L. Namy, H.B. Kagan, *Synth. Commun.* 28 (1998) 2577;  
(c) K. Kaneda, T. Yamashita, T. Matsushita, K. Ebitani, *J. Org. Chem.* 63 (1998) 1750;  
(d) T. Matsushita, K. Ebitani, K. Kaneda, *Chem. Commun.* (1999) 265;  
(e) K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* 122 (2000) 7144;  
(f) K. Yamaguchi, N. Mizuno, *New J. Chem.* 26 (2002) 972;  
(g) K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* 41 (2002) 4538;  
(h) B.-Z. Zhan, M.A. White, T.K. Sham, J.A. Pincock, R.J. Doucet, K.V.R. Rao, K.N. Robertson, T.S. Cameron, *J. Am. Chem. Soc.* 125 (2003) 2195;
- (i) M. Musawir, P.N. Davey, G. Kelly, I.V. Kozhevnikov, *Chem. Commun.* (2003) 1414;  
(j) K. Yamaguchi, N. Mizuno, *Chem. Eur. J.* 9 (2003) 4353.
- [11] (a) M. Akada, S. Nakano, T. Sugiyama, K. Ichitoh, H. Nakao, M. Akita, Y. Moro-oka, *Bull. Chem. Soc. Jpn.* 66 (1993) 1511;  
(b) K. Ebitani, Y. Fujie, K. Kaneda, *Langmuir* 15 (1999) 3557;  
(c) T. Nishimura, N. Kakiuchi, M. Inoue, S. Uemura, *Chem. Commun.* (2000) 1245;  
(d) K. Mori, K. Yamaguchi, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* 124 (2002) 11572;  
(e) Y. Uozumi, R. Nakao, *Angew. Chem. Int. Ed.* 42 (2003) 194.
- [12] K. Mori, K. Yamaguchi, T. Mizugaki, K. Ebitani, K. Kaneda, *Chem. Commun.* (2001) 461.;  
K. Mori, M. Tano, T. Mizugaki, K. Ebitani, K. Kaneda, *New J. Chem.* 26 (2002) 1536;  
M. Murata, T. Hara, K. Mori, M. Ooe, T. Mizugaki, K. Ebitani, K. Kaneda, *Tetrahedron Lett.* 44 (2003) 4981;  
T. Hara, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, *Tetrahedron Lett.* 44 (2003) 6207.
- [13] K. Kaneda, K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani, *Catal. Surv. Jpn.* 4 (2000) 31.
- [14] S. Miyata, *Clays Clay Miner.* 28 (1980) 50;  
F. Cavani, F. Trifiró, A. Vaccari, *Catal. Today* 11 (1991) 173.
- [15] J.H. Sinfelt, G.H. Via, F.W. Lytle, *Catal. Rev.* 26 (1984) 81.
- [16] H.-B. Ji, K. Ebitani, T. Mizugaki, K. Kaneda, *Tetrahedron Lett.* 43 (2002) 7179.
- [17] D.D. Perrin, W.L.F. Armarego (Eds.), *Purification of Laboratory Chemicals*, third ed., Pergamon Press, Oxford, UK, 1988.
- [18] W.G. Brown, *Organic Reactions*, vol. VI, Wiley, New York, 1951.
- [19] Powder Diffraction File, *Alphabetical Index Inorganic Phases*, JCPDS, Pennsylvania, USA, 1980.
- [20] T. Tanaka, H. Yamashita, R. Tsuchitani, T. Funabiki, S. Yoshida, *J. Chem. Soc., Farad. Trans.* 84 (1988) 2987.
- [21] D.A. McKeown, P.L. Hagans, L.P.L. Carette, A.E. Russell, K.E. Swider, D.R. Rolison, *J. Phys. Chem. B* 103 (1999) 4825.
- [22] P. Triggs, *Helv. Phys. Acta* 58 (1985) 657.
- [23] C.-M. Che, T.-F. Lai, K.-Y. Wong, *Inorg. Chem.* 26 (1987) 2289.
- [24] K.M. Miranda, X. Bu, I. Lorković, P.C. Ford, *J. Am. Chem. Soc.* 36 (1997) 4838.
- [25] P.A. Barrett, G. Sanker, R.H. Jones, C.R.A. Catlow, J.M. Thomas, *J. Phys. Chem. B* 101 (1997) 9555;  
G. Sanker, J.M. Thomas, F. Rey, G.N. Greaves, *J. Chem. Soc. Chem. Commun.* (1995) 2549.
- [26] R.G. Delaplane, J.A. Ibers, J.R. Ferraro, J.J. Rush, *J. Chem. Phys.* 50 (1969) 1920.
- [27] J. Emsley, *The Elements*, third ed., Oxford University Press, 1998.
- [28] H.C. Yao, Y.F. Yao, *J. Catal.* 86 (1984) 254;  
Y. Nagai, T. Yamamoto, T. Tanaka, S. Yoshida, T. Nonaka, T. Okamoto, A. Suda, M. Sugiura, *Catal. Today* 74 (2002) 225.
- [29] B. Bhatia, J. Iqbal, *Tetrahedron Lett.* 33 (1992) 7961;  
A.N. Kharat, P. Pendleton, A. Badalyan, M. Abedini, M.M. Amini, *J. Mol. Catal. A* 175 (2001) 277.
- [30] (a) C.E.H. Bawn, J.B. Williamson, *Trans. Faraday Soc.* 47 (1951) 721;  
(b) S.-I. Murahashi, T. Naota, N. Hirai, *J. Org. Chem.* 58 (1993) 7318;  
(c) R.A. Sheldon, J.K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981, Chapter 5, p.140.
- [31] G.H. Jones, *J. Chem. Soc., Chem. Commun.* (1979) 536.