

# Reactivity of Ru=O species in RuO<sub>2</sub>/CeO<sub>2</sub> catalysts prepared by a wet reduction method

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## Abstract

The paper deals with the reactivity of RuO<sub>2</sub>/CeO<sub>2</sub> prepared by a wet reduction method: ruthenium was supported on Ce(OH)<sub>3</sub>, which was precipitated by alkali-hydrolysis of Ce(NO<sub>3</sub>)<sub>3</sub>, under a reduction condition with formaldehyde at pH 11 and transformed into RuO<sub>2</sub>/CeO<sub>2</sub> catalysts by calcination in air at 773 K. The catalysts were investigated with an ESR technique and were tested for oxidation of propylene. They had no ESR signals by themselves at room temperature, but gave two sets of anisotropic signals upon contact with propylene. These signals were derived from the reaction products between Ru=O and propylene. The intensities of the signals were kept unchanged at room temperature for more than 1 h in the absence of excess propylene. The signals decayed in the presence of excess propylene and the upfield signal decayed more rapidly. A prior heating of the catalyst in air at 473 K or above caused the increase in the intensity of the upfield signal. The time course of the signal changes discriminated between ethylene and olefins with allylic hydrogen toward Ru=O species.

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**Keywords:** RuO<sub>2</sub>/CeO<sub>2</sub>; Ru=O; ESR; DRIFT; XANES; Oxidation; C<sub>3</sub>H<sub>6</sub>

## 1. Introduction

Ruthenium dioxide is known to catalyze many types of reactions including organic and inorganic oxidations [1–8]. We reported that Ru=O species in RuO<sub>2</sub>/CeO<sub>2</sub> prepared by a wet reduction method played an important role in the N<sub>2</sub>O decomposition with propylene [9] and oxidation of propylene [10]. The method is an effective and easy-to-operate method of preparing supported precious metal catalysts. The Ru=O species, which were inherently present in RuO<sub>2</sub>/CeO<sub>2</sub> were produced more by the treatment of oxygen at 473 K or above, and were responsible for the activation of propylene

[9,10]. Sommerfeld and Parravano observed that oxygen was chemisorbed on RuO<sub>2</sub> in the temperature range 373–658 K at 1.3–66 Pa of O<sub>2</sub> pressure [11]. Over, Jacobi and co-workers have investigated that there were several oxygen species on the surface of RuO<sub>2</sub>(110) by the treatment with oxygen [12,13]. The oxygen species on top of coordinatively unsaturated RuO<sub>2</sub>(110) which they cited in their papers should be Ru=O in our view [9,10]. They supposed several oxygen species and set up a model of products between their oxygen species and ethylene. Wan et al. reported that partial oxidation of methane over Ru/SiO<sub>2</sub> was caused by O<sup>2-</sup> species of low concentration over the catalyst, while complete oxidation by O<sup>2-</sup> species of high concentration [14].

In this paper, we have been investigating the reactivity of Ru=O species of RuO<sub>2</sub>/CeO<sub>2</sub> catalysts prepared by the wet reduction method by using an ESR technique for the reactions between Ru=O species and propylene or other olefins.

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## 2. Experimental

### 2.1. Materials

Cerium(III) nitrate, formaldehyde and sodium hydroxide were obtained from Nacalai Tesque Co. Ruthenium trichloride hydrate containing 39.7% ruthenium by weight was purchased from Tanaka Kinzoku Kogyo K.K.  $\text{Zr}(\text{OH})_4$  was purchased from Kojundo Chemical Laboratory Co.  $\gamma\text{-Al}_2\text{O}_3$  was supplied from Taimei Chemicals Co.

### 2.2. Preparation of catalysts

Catalysts were prepared by two methods: a wet reduction method and a dry reduction method, which we tentatively called. Wet stands for that colloidal ruthenium is treated with in situ prepared wet  $\text{Ce}(\text{OH})_3$ , and dry stands for that colloidal ruthenium is treated with previously calcined dry  $\text{CeO}_2$ .

*Wet reduction method:* Cerium hydroxide was precipitated from 500 ml of aqueous cerium(III) nitrate ( $6.0 \times 10^{-2}$  mol/l) at pH of about 11 by adding 3N NaOH. After the precipitates were filtered, they were dispersed in 500 ml of deionized water. Aqueous  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  (0.682 g) and formaldehyde solutions ( $\text{HCHO}/\text{Ru}$  (molar ratio) = 5) were added to the dispersion, and the mixed suspension was stirred for 1 h at 363 K. Then, 3N NaOH was added until the pH of the solution was about 11. The solid portion was filtered and washed with deionized water until the pH of the filtrate was below 9. It was dried at 363 K overnight and transformed into a  $\text{RuO}_2/\text{CeO}_2$  catalyst by calcination in air at 773 K for 3 h. The loading of  $\text{RuO}_2$  is 5 wt.% on metal basis.

*Dry reduction method:* Cerium hydroxide was precipitated from 500 ml of aqueous cerium(III) nitrate ( $6.0 \times 10^{-2}$  mol/l) at pH of about 11 by adding 3N NaOH. The precipitates were filtered, and washed with deionized water until the pH of the filtrate was below 9. It was dried at 363 K and calcined in air at 673 K for 3 h. The obtained  $\text{CeO}_2$  was added to a mixture of aqueous  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  (0.682 g) and formaldehyde ( $\text{HCHO}/\text{Ru}$  (molar ratio) = 5), and the mixed suspension was stirred for 1 h at 363 K. Then, 3N NaOH was added until the pH of the solution was about 11. The solid portion was filtered and washed with deionized water until the pH of the filtrate was below 9. It was dried at 363 K overnight followed by calcination in air at 773 K for 3 h.  $\text{RuO}_2/\text{ZrO}_2$  and  $\text{RuO}_2/\gamma\text{-Al}_2\text{O}_3$  were prepared in a similar manner using  $\text{Zr}(\text{OH})_4$  and  $\gamma\text{-Al}_2\text{O}_3$ . The loading of  $\text{RuO}_2$  is 5 wt.% on metal basis.

### 2.3. Reaction apparatus and procedure

Oxidation of propylene was carried out using a continuous flow reactor. The catalyst (0.5 g) was milled with quartz and molded into a pellet. The pellet was ground

and sieved in 14–28 mesh size. The catalyst was pre-treated with dry air at 573 K for 1 h. Forty-five milliliters of a mixture of propylene (4000 ppm) and helium and 10 ml of  $\text{O}_2$  were introduced to the reactor at room temperature. The reaction temperature was increased at the rate of 2.5 K/min (295–423 K) and 5 K/min (above 423 K). Propylene and  $\text{CO}_2$  were analyzed with an on-line TCD gas-chromatograph (Shimadzu GC-8A, Porapak Q column, 1 m) at 363 K.

### 2.4. Characterization

Diffuse reflectance infrared Fourier transform (DRIFT) spectra of the catalysts were recorded in the range  $4000\text{--}700\text{ cm}^{-1}$  on a Nicolet spectrophotometer (Model Magna-IR 560) and the background spectrum employed was that of KBr. ESR spectra were obtained with a JEOL TE-300 ESR spectrometer. The catalyst (64–66 mg) was put into an ESR tube and heated at 473 K for 30 min while a stopcock open in the air to have adsorbed water condensed above the furnace. The tube was evacuated to remove water, and heated at 473 K in 300 Torr of  $\text{O}_2$  for 1 h. The tube was cooled to room temperature and evacuated. When 25 Torr of  $\text{C}_3\text{H}_6$  was added, gradual decrease of pressure was observed. After pressure drop ceased (about 30 s), excess propylene was evacuated. ESR measurements were run at room temperature or 77 K. XAFS measurements for Ru K-edge were carried out by a transmission mode at the BL-10B station of the Photon Factory in the High Energy Accelerator Research Organization (Tsukuba, Japan). The ring energy was 2.5 GeV and the ring current was 350–420 mA. The catalyst was mixed with boron nitride and was molded into a disk (diameter: 14 mm). A Si(3 1 1) double crystal was used to monochromatize the X-ray. In situ XAFS was carried out with a self-designed cell for in situ IR measurements [15].  $\text{Ru}/\text{CeO}_2$  was heated at prescribed temperatures in the flow of  $\text{O}_2$  (5 ml/min) up to 573 K.

## 3. Results and discussion

### 3.1. IR spectra of supported $\text{RuO}_2$ catalysts

Fig. 1 shows DRIFT spectra of supported  $\text{RuO}_2$  catalysts. As reported earlier [16–18], the vibration bands of  $940\text{--}1000\text{ cm}^{-1}$  observed for supported  $\text{RuO}_2$  catalysts were assigned to bridge and surface Ru–O species. We previously reported that this vibration bands is due to Ru=O species, which have five coordinated structure on the support [9]. A vibration band was observed at  $984\text{ cm}^{-1}$  in  $\text{RuO}_2/\text{CeO}_2$ . In the spectrum of  $\text{RuO}_2/\text{ZrO}_2$ , a shoulder peak was slightly observed at  $1000\text{ cm}^{-1}$ . A broad and big signal obscured vibration bands of ruthenium oxide if any. Therefore, we considered that Ru=O species were present in  $\text{RuO}_2/\text{CeO}_2$ , which was prepared by the wet reduction method and might be in  $\text{RuO}_2/\text{ZrO}_2$ .

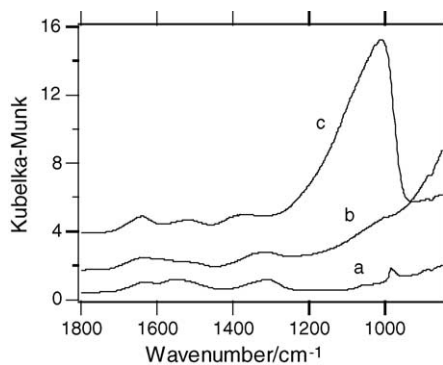


Fig. 1. DRIFT spectra of supported RuO<sub>2</sub> (5 wt.%) catalysts. Support: (a) CeO<sub>2</sub>, (b) ZrO<sub>2</sub> and (c) γ-Al<sub>2</sub>O<sub>3</sub>.

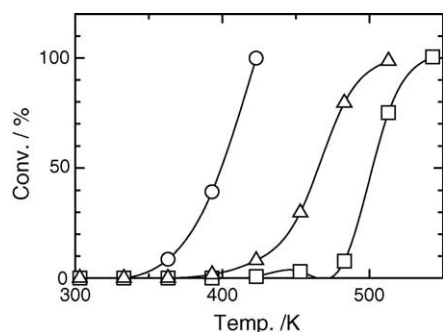


Fig. 2. Oxidation of propylene over supported RuO<sub>2</sub> (5 wt.%) catalysts. Support: (○) CeO<sub>2</sub>, (△) ZrO<sub>2</sub> and (□) γ-Al<sub>2</sub>O<sub>3</sub>.

### 3.2. Oxidation of propylene over supported RuO<sub>2</sub> catalysts

Total oxidation of propylene was carried out over 5 wt.% RuO<sub>2</sub>/CeO<sub>2</sub>, RuO<sub>2</sub>/ZrO<sub>2</sub> and RuO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>, whose reactivity decreases in that order (Fig. 2). The oxidation of propylene was completed at 423, 483 and 543 K over 5 wt.% RuO<sub>2</sub>/CeO<sub>2</sub>, RuO<sub>2</sub>/ZrO<sub>2</sub> and RuO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>, respectively. The higher reactivity of RuO<sub>2</sub>/CeO<sub>2</sub> than RuO<sub>2</sub>/ZrO<sub>2</sub> and RuO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> is the same as in the case of the reaction between N<sub>2</sub>O and C<sub>3</sub>H<sub>6</sub> [9]. The high reactivity of

RuO<sub>2</sub>/CeO<sub>2</sub> was explained to be ascribed to the Ru=O species susceptible to olefins. The view supports the relatively high reactivity of RuO<sub>2</sub>/ZrO<sub>2</sub>, which has a shoulder band of Ru=O as shown in Fig. 1.

### 3.3. XANES spectra of 5 wt.% RuO<sub>2</sub>/CeO<sub>2</sub> heated in O<sub>2</sub>

Fig. 3 shows the X-ray absorption near edge structure (XANES) spectra of 5 wt.% RuO<sub>2</sub>/CeO<sub>2</sub> heated in O<sub>2</sub> from 295 to 573 K. We assigned that the pre-edge peak was due to asymmetric Ru<sup>4+</sup> species having Ru=O bond [9]. The pre-edge peak of 5 wt.% RuO<sub>2</sub>/CeO<sub>2</sub> heated in O<sub>2</sub> at 373 K is almost the same as that of the untreated. The pre-edge peak increased for 5 wt.% RuO<sub>2</sub>/CeO<sub>2</sub> heated at 473 K and no further increase was observed on heating at 573 K.

### 3.4. ESR spectra of supported RuO<sub>2</sub> catalysts

No ESR-signals were observed at room temperature for any RuO<sub>2</sub> catalysts without treatment of propylene. After an ESR-tube containing 5 wt.% RuO<sub>2</sub>/CeO<sub>2</sub> was carefully evacuated for 2 min, propylene (25 Torr) was introduced. A slight pressure decrease was observed. When the pressure drop ceased (about 30 s), excess propylene was evacuated. A small ESR signals (a) were observed at room temperature (Fig. 4). Evacuation was continued for the catalyst to remove adsorbed water for 2 h, and propylene was added. The intensity of the ESR-signal (b) with  $g_1 = 2.079$ ,  $g_2 = 1.946$  and  $g_3 = 1.881$  was larger than that of the signal (a) by three times. Evacuation of a thin ESR-tube containing catalyst powders causes sudden fly-off, especially for powders with adsorbed water. To prevent it the tube was heated to 473 K while the stopcock was left open. A few water droplets were condensed on the tube wall just above the end of a furnace. After the tube was cooled to room temperature, it was evacuated to remove the water for 1 h. Propylene was added and excess propylene was evacuated. The ESR intensity of the signal (c) increased twice that of (b). Another anisotropic signal with  $g'_1 = 2.040$ ,  $g'_2 = 1.916$  and  $g'_3 = 1.825$  was observed. These results indi-

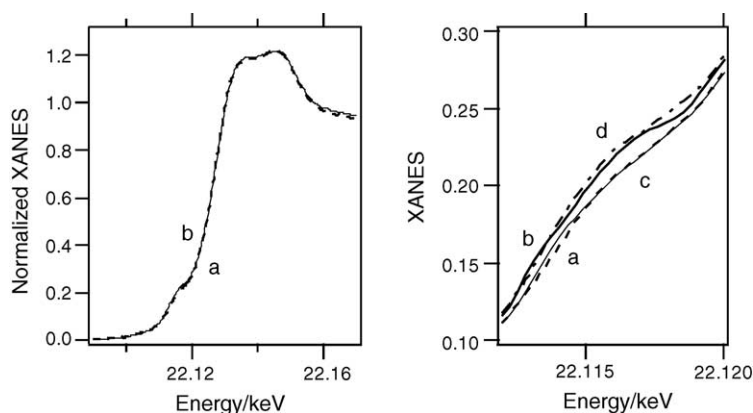


Fig. 3. XANES spectra of 5 wt.% RuO<sub>2</sub>/CeO<sub>2</sub> heated in situ in O<sub>2</sub>. (a) 295 K, (b) 473 K, (c) 373 K and (d) 573 K.

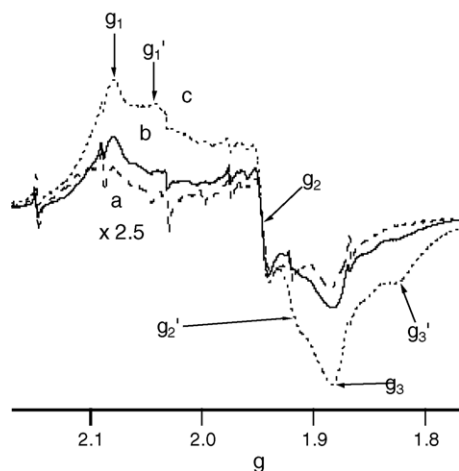


Fig. 4. ESR spectra of 5 wt.% RuO<sub>2</sub>/CeO<sub>2</sub> treated with propylene. Pretreatment: (a) evacuation for 2 min, (b) evacuation for 2 h and (c) heating at 473 K while the stopcock was left open and evacuation for 1 h.

cate that adsorbed water prevents the reaction of propylene with the catalyst at room temperature.

XANES spectra of these original catalysts showed that the oxidation states of ruthenium were 4+ (4d<sup>4</sup> configuration) [9]. The reasons why no ESR signals of Ru<sup>4+</sup> are observed are explained in terms of a strong zero-field splitting and/or a strong relaxation because of the strong coupling between spin and orbital momentum [19]. The ESR-signals in Fig. 4 are assigned to Ru<sup>3+</sup> species on supports [19–23].

To avoid the effect of adsorbed water, catalysts were pretreated before the reaction with olefins as follows: after 5 wt.% RuO<sub>2</sub>/CeO<sub>2</sub> catalyst was heated in air at 473 K for 30 min while the stopcock was open and then water and air were evacuated, they were again heated at 473 K in O<sub>2</sub> (300 Torr) for 1 h. The reaction between the catalyst and propylene at room temperature was ascertained by the gradual pressure decrease of propylene. Excess propylene was evacuated after the cease of pressure drop. Two sets of anisotropic signals were observed at room temperature as shown in Fig. 5.

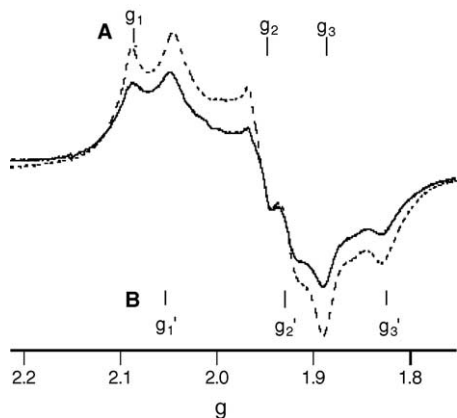


Fig. 5. ESR spectra of 5 wt.% RuO<sub>2</sub>/CeO<sub>2</sub> treated with olefins. Olefin: (---) C<sub>2</sub>H<sub>4</sub> and (—) C<sub>3</sub>H<sub>6</sub>.

Table 1  
ESR parameters of 5 wt.% RuO<sub>2</sub>/CeO<sub>2</sub> catalysts treated with olefins<sup>a</sup>

	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	CH <sub>2</sub> =C(CH <sub>3</sub> ) <sub>2</sub>	Me <sub>2</sub> C=CMe <sub>2</sub>	Toluene
<i>g</i> <sub>1</sub>	2.087	2.087	2.086	2.079	2.084
<i>g</i> <sub>2</sub>	1.955	1.950	1.949	1.947	1.949
<i>g</i> <sub>3</sub>	1.888	1.890	1.887	1.882	1.888
<i>g</i> ' <sub>1</sub>	2.044	2.049	2.055	2.060	2.056
<i>g</i> ' <sub>2</sub>	1.926	1.926	1.924	1.921	1.924
<i>g</i> ' <sub>3</sub>	1.829	1.829	1.828	1.828	1.830

<sup>a</sup> Before treating with olefins, the catalysts were heated at 473 K in 300 Torr of O<sub>2</sub> for 1 h.

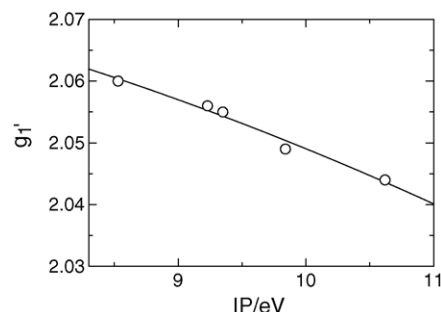


Fig. 6. Plots of *g*'<sub>1</sub> values vs. ionization potentials of olefins.

The set of the downfield signal is designated as A, and the set of the upfield signal as B. The *g* values of these signals are almost the same as those observed in Fig. 4c. The heating at 473 K in O<sub>2</sub> resulted in the large intensity of the B signal. The intensities of A and B were kept unchanged for more than 1 h unless excess propylene was present in the gas phase. Other olefins and even toluene similarly gave two sets of signals (Table 1). The parameters of the signal A are almost unchanged among olefins, but the *g*'<sub>1</sub> values of the signal B change with the ionization potentials of olefins as shown in Fig. 6. There are little or no differences in *g*'<sub>2</sub> and *g*'<sub>3</sub> values.

When excess propylene (20 Torr) was contacted with the catalyst, both sets of signals decayed (Fig. 7). Especially, the signal B was lowered within minutes, giving two new broad signals at the lower-magnetic field (Fig. 8). The signal A also decayed rather slowly. The decay processes with

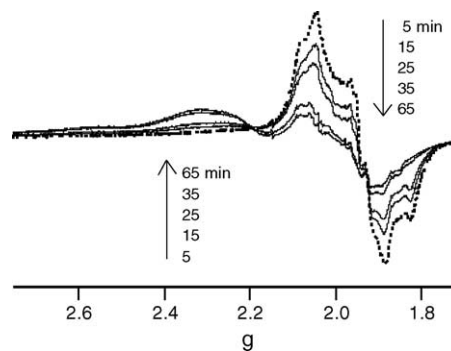


Fig. 7. Changes of ESR signals of 5 wt.% RuO<sub>2</sub>/CeO<sub>2</sub> with time in the presence of C<sub>3</sub>H<sub>6</sub> (20 Torr).

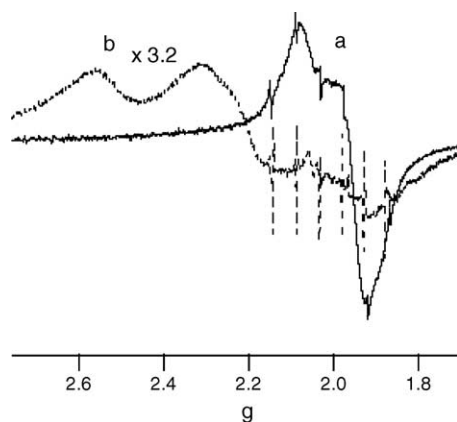


Fig. 8. The ESR spectra of 5 wt.% RuO<sub>2</sub>/CeO<sub>2</sub> in the presence of olefins after 6 days. (a) C<sub>2</sub>H<sub>4</sub> and (b) C<sub>3</sub>H<sub>6</sub>. Six lines in (b) are due to Mn<sup>2+</sup> contaminated in CeO<sub>2</sub>.

isobutene and 2,3-dimethyl-2-butene were almost the same as that with propylene. However, the decay process for ethylene was different from that of propylene. No signals at the lower-magnetic field was formed regardless of the contact of excess ethylene with the catalyst for a long time. The difference of the ESR spectra between ethylene and propylene was also observed in their temperature programmed desorption (TPD) patterns [9]. This was caused by the lack of allylic hydrogen in ethylene. Since toluene gave no lower-magnetic field signal on longer contact (one month) with RuO<sub>2</sub>/CeO<sub>2</sub>, methyl group of toluene did not behave like that of propylene. After 5 wt.% RuO<sub>2</sub>/CeO<sub>2</sub> catalyst was heated in O<sub>2</sub> at 473 K for 1 h and cooled to room temperature, evacuation was continued at room temperature for 14 h. The catalyst gave the same ESR signals shown in Fig. 5 when contacted with propylene. This implies that the oxygen species formed when treated with O<sub>2</sub> at 473 K are not loosely adsorbed oxygen, but firmly fixed ruthenium oxide species, which are inherently present in the catalyst and produced by heating at 473 K in O<sub>2</sub>.

Temperature programmed reduction was conducted with 2% hydrogen diluted with argon resulting in two reduction peaks in the range of 339–359 and 359–378 K for 6.5 wt.% RuO<sub>2</sub>/CeO<sub>2</sub> [24]. ESR signals were detected at 77 K and room temperature for the catalyst reacted with 150 Torr of hydrogen at 339 K for 15 min. The ESR spectrum measured at 77 K is shown in Fig. 9. There included the spectrum (77 K) of 5 wt.% RuO<sub>2</sub>/CeO<sub>2</sub> reacted with propylene at room temperature for 7 days. The coincidence of the signals at the lowest magnetic field shows that the signal should be that of Ru<sup>3+</sup>OH species. The large downfield shift of the *g*<sub>1</sub> value was observed in the replacement of one NH<sub>3</sub> group in Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>/H-X zeolite with OH group [25]. The expanded ordinate of the initial ESR spectrum for the 5 wt.% RuO<sub>2</sub>/CeO<sub>2</sub> reacted with C<sub>3</sub>H<sub>6</sub> showed a signal with the similar *g* value. The lack of the signal in RuO<sub>2</sub>/CeO<sub>2</sub> treated with C<sub>2</sub>H<sub>4</sub> indicates that the hydrogen of OH group is derived from allylic hydrogen of olefins.

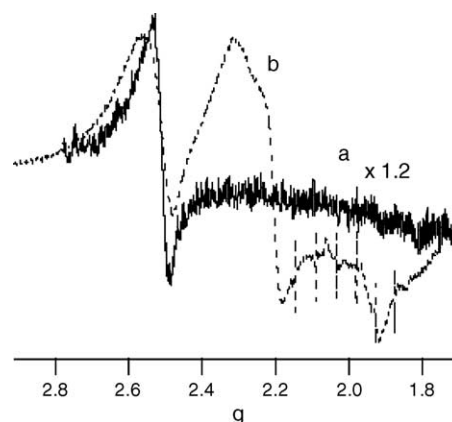


Fig. 9. ESR spectra (77 K) of 5 wt.% RuO<sub>2</sub>/CeO<sub>2</sub> treated with H<sub>2</sub> at 339 K for 15 min and C<sub>3</sub>H<sub>6</sub> for 7 days. (a) H<sub>2</sub> and (b) C<sub>3</sub>H<sub>6</sub>.

Ruthenium oxide catalysts prepared by a different method or on different supports gave different ESR spectra. Fig. 10 shows ESR spectra of 5 wt.% RuO<sub>2</sub>/CeO<sub>2</sub> prepared by the dry reduction method and RuO<sub>2</sub>/ZrO<sub>2</sub> prepared by the wet reduction method with the ESR parameters of A signals of *g*<sub>1</sub> = 2.091, 2.085, *g*<sub>2</sub> = 1.949, 1.963, *g*<sub>3</sub> = 1.895, 1.864, respectively. No B signals were observed for both catalysts. There are small differences in *g*<sub>2</sub> and *g*<sub>3</sub> values. No such signal was observed for RuO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> on contact with propylene.

Catalysts (5 wt.% RuO<sub>2</sub>/CeO<sub>2</sub>) prepared by the wet reduction method were calcined at 573, 773 and 1073 K in air for 3 h. Color deterioration was observed for the catalyst calcined at 1073 K. Fig. 11 shows ESR spectra of these catalysts treated with propylene. The signal intensity was obviously decreased for the catalyst calcined at 1073 K. The intensity of the B signal is larger than that of the A signal. The B signal was hardly observed for the catalyst calcined at 573 K. Two types of Ru=O species are observed in the ESR spectrum. The distribution of two Ru=O species is dependent on heat treatment. Both signals are produced for the catalysts calcined at 753 K. The Ru=O species giving the B signal are not

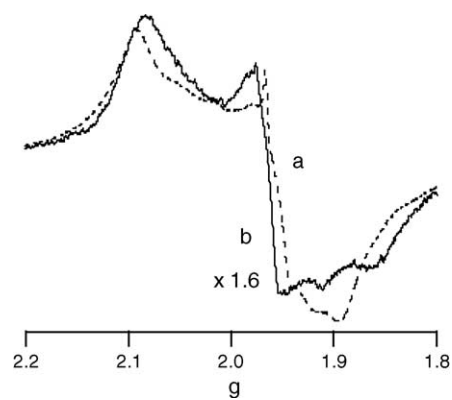


Fig. 10. ESR spectra of supported RuO<sub>2</sub> (5 wt.%) catalysts treated with propylene. (a) RuO<sub>2</sub>/CeO<sub>2</sub> prepared by the dry reduction method and (b) RuO<sub>2</sub>/ZrO<sub>2</sub> prepared by the wet reduction method.



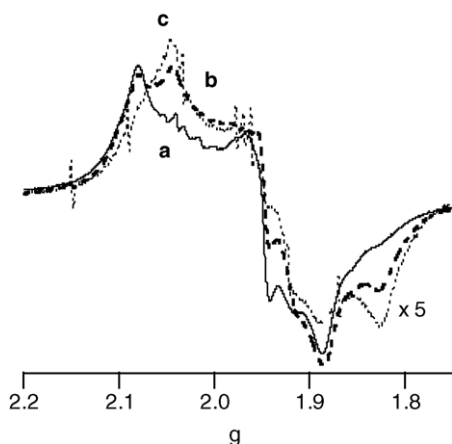


Fig. 11. ESR spectra of 5 wt.% RuO<sub>2</sub>/CeO<sub>2</sub> calcined at different temperatures on contact with propylene. (a) 573 K, (b) 773 K and (c) 1073 K.

formed by the calcination at as low as 573 K. Paulus et al. set up two model structures for the reaction products between O-rich RuO<sub>2</sub>(1 1 0) and ethylene as intermediately forming RuCH<sub>2</sub>CH<sub>2</sub>ORu (**1**) and RuO=CHCH<sub>2</sub>Ru (**2**) + RuOH (**3**) [7]. The  $g_1'$  values of the B signal relate with the ionization potentials of olefins (Fig. 6). The signal can be rather related with **1** as far as all of  $\pi$ -electrons are not transferred to form Ru–C bond.

IR spectra of RuO<sub>2</sub>/CeO<sub>2</sub> catalysts indicated absorption band of ruthenium oxide assigned as Ru=O, but did not show how many types of Ru=O species there are. The ESR data gave two types of Ru=O species. Their formation is dependent on the kind of supports, preparation methods, calcination temperatures and treatment with oxygen at 473 K or above. Elucidation of the reaction mechanism between propylene and RuO<sub>2</sub>/CeO<sub>2</sub> prepared by the wet reduction method is currently under way.

#### 4. Conclusion

The various oxygen species on RuO<sub>2</sub>(1 1 0) surfaces were characterized [12,13]. We assigned the IR absorption band of RuO<sub>2</sub>/CeO<sub>2</sub> prepared by the wet reduction method at 984 cm<sup>-1</sup> as that of Ru=O. Two sets of anisotropic ESR signals appeared at room temperature when RuO<sub>2</sub>/CeO<sub>2</sub> was treated with propylene. They were assigned as Ru<sup>3+</sup> species, which were formed from the reaction between Ru=O and propylene. The intensity of the upfield signal was increased by heating RuO<sub>2</sub>/CeO<sub>2</sub> in O<sub>2</sub> at 473 K. Both signals were kept unchanged more than 1 h without excess propylene. On exposure to excess propylene both signals decayed, especially the upfield signal more rapidly and instead the new broad signal appeared at lower-magnetic field. We assigned it as Ru<sup>3+</sup>OH. Two anisotropic signals were observed for RuO<sub>2</sub>/CeO<sub>2</sub> treated with ethylene, but no Ru<sup>3+</sup>OH signal

was formed. The hydrogen in the OH group was derived from allylic hydrogen of propylene.

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