Surface Reducibility of Cerium Oxide Modified with Palladium

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Three peaks at 530, 532, and 534 eV in the X-ray photoelectron spectrum of O 1s region for palladium-modified cerium oxide after reduction with hydrogen at 573 K can be attributed to Ce^{4+}–O–Ce^{4+}, Ce^{4+}–O–Ce^{3+}, and Ce^{3+}–O–Ce^{3+} on the surface, respectively.

Cerium oxide is often employed as a component of catalysts in various reactions such as reduction of nitrogen oxides, oxidation of hydrocarbons, and hydrogenation of carbon oxides.[1] Since the redox behavior of cerium oxide seriously affects the catalytic processes, the reducibility of cerium oxide has been widely studied by several techniques,[1,2] and it can be directly monitored by the X-ray photoelectron spectrum (XPS) in Ce 3d region.[3–9] Shyu et al. proposed that the relative intensity of the peak at 917 eV (referred as u''') in the whole Ce 3d region can be used as a parameter of reducibility of Ce^{4+} to Ce^{3+} in cerium oxide,[3] while the region is so wide that the base line is fluctuated and the determination of quantitative intensity for the whole Ce 3d region is often difficult.

The electronic states of the surface oxygen should be affected by the reduction; however, the detailed study has not been carried out. In the present paper, we will show that XPS of O 1s region for cerium oxide sensitively relates to the reducibility. The samples of cerium oxide were modified with palladium which enhances reduction of cerium oxide in the presence of chlorine ions.[1,10–12]

Cerium oxide was modified with palladium by different methods. A sample was prepared by the deposition–precipitation method from an aqueous solution of $Pd(NO_3)_2$ (Kishida Chemicals, GR grade) in which CeO_2 (Daiichi Kigenso Kagaku Kogyo) was dispersed. Palladium hydroxide was exclusively precipitated on the surface of CeO_2 (Daiichi Kigenso Kagaku Kogyo) dispersed in the palladium solution by gradual addition of 1 M NaOH solution under mechanical stirring and the pH value of the mixture was maintained at 10 for 1 h. The resulting solids washed with distilled water were dried at 393 K for 5 h, then calcined at 723 K for 5 h in air (Pd–CeO_2-1). Two samples were prepared from 0.01 M HCl aqueous solution of $PdCl_2$ (Kishida, GR) by the deposition–precipitation method. In this procedure one sample (Pd–CeO_2-2) was prepared with stirring by ultrasonic also with mechanical stirring, and the other (Pd–CeO_2-3) was only with a magnetic stirrer. Another sample (Pd–CeO_2-4) was prepared by the conventional impregnation technique from the same starting mixture for Pd–CeO_2-2 or -3. After cerium oxide was impregnated with $PdCl_2$ by evaporation of the mixture at 353 K, the wet solid was dried at 393 K for 5 h and calcined at 723 K for 5 h in air. All the palladium contents in the samples were 3 wt%.

The contents of chlorine in the samples were determined by the fluorescent X-ray analysis method (Table 1). Trace amounts of sodium less than 0.01 wt% were detected in the samples prepared by deposition–precipitation by ICP emission spectrometry.

Table 1. Surface properties of CeO_2 modified with palladium[a]

Sample	Cl / wt%	BET / m^2g^{-1}	%u''' / %	O/Ce	O 1s peak intensity[b] a	b	c	Ce^{3+} / %
Pd-CeO_2-1	0	105	7.2	3.4	0.74	0.24	0.02	15
Pd-CeO_2-2	0.020	102	10.7	2.9	0.66	0.29	0.05	22
Pd-CeO_2-3	0.033	92	7.5	2.5	0.41	0.44	0.15	38
Pd-CeO_2-4	0.38	70	6.9	2.0	0.26	0.51	0.23	48

[a] Reduced with hydrogen at 573 K for 1 h.
[b] Normarized intensities for the peaks at 530 (a), 532 (b), and 534 eV (c).

X-Ray photoelectron spectra were recorded in situ at room temperature with a Shimadzu ESCA–KM. The samples were pretreated with hydrogen (ca. 30 kPa) at 573 K for 1 h in the spectrometer and evacuated at the same temperature for 0.5 h. Binding energies were determined by reference to the C 1s line at 284.6 eV. The surface molar ratio of O/Ce was calculated from the peak areas using the atomic sensitivity factors of O 1s (0.66) and Ce 3d (10).[13]

In the Ce 3d region XPS peaks at ca. 917 eV (u''') attributed to Ce^{4+} species were recorded with the Pd-CeO_2 samples reduced in situ at 573 K (Figure 1).[3,4] The percent areas of u''' in the whole Ce 3d region (%u''') for Pd–CeO_2-1, -2, -3, and -4 were 7.2, 10.7, 7.5, and 6.9%, respectively, whereas the areas were determined by assuming the baselines shown in the figure with broken lines. Since the value for oxidized CeO_2 was reported to be 13.4%,[3] it would be suggested that the ceria surfaces except for Pd–CeO_2-2 are highly reduced. However, in the XPS for Pd–CeO_2-1 the peak at ca. 885 eV (v') associated with Ce^{3+} states was not clearly present.[7–9] In addition the sample is free from chlorine ions which promote the reduction of cerium oxide.[10–12] Hence, the surface of ceria on Pd–CeO_2-1 is not reduced highly, and the parameter of %u''' is not always reliable probably because of uncertainty of the baseline in the spectrum.

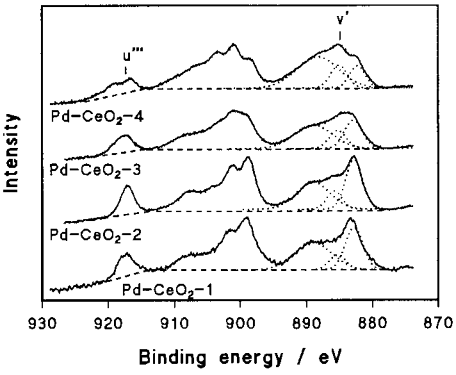

Figure 1. XPS of Ce 3d region for 3 wt% Pd/CeO_2 reduced with hydrogen at 573 K for 1 h.

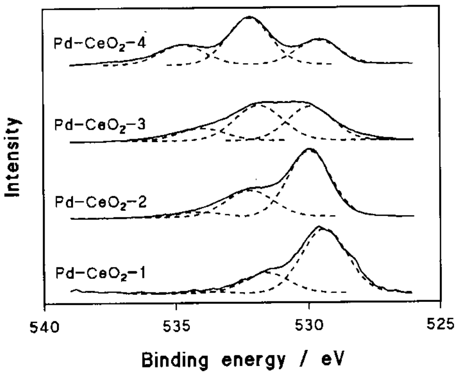

Figure 2. XPS of O 1s region for 3 wt% Pd/CeO$_2$ reduced with hydrogen at 573 K for 1 h.

On the other hand overlapped three peaks were seen in the O 1s region of the XPS for these samples and the spectra can be deconvoluted into three Gaussian peaks with 2.0 ± 0.1 eV of peak width at half height. The peaks were at 529.7 ± 0.3 eV, 531.9 ± 0.3 eV, and 534.3 ± 0.4 eV (Figure 2). The presence of three peaks evidently show that there are at least three different oxygen species on the surface of cerium oxide. The presence of chlorine ions may directly affect the XPS of O 1s; however, the number of chloride ions is significantly smaller than that of surface oxygen atoms estimated from the BET surface area (Table 1) assuming that the atomic cross sections of O^{2-} and Ce^{4+} are 0.050 nm^2 and 0.037 nm^2, respectively.[14] For example, the chlorine contents of Pd–CeO$_2$-3 and -4 are 0.009 mmol g^{-1} and 0.1 mmol g^{-1}, respectively, and the corresponding quantities of the surface oxygen atoms are estimated as 2.4 mmol g^{-1} and 1.2 mmol g^{-1}, respectively. Thus, the effect of chlorine, if present, is negligible. Small peaks at ca. 289 eV attributed to residual carboxyl groups on the surface were found in the XPS of C 1s for the samples except Pd–CeO$_2$-4, but the quantities of the oxygen species estimated from the surface concentration of the carboxyl species using the atomic sensitivity factor of C 1s (0.25)[13] were less than 5% of the total number of oxygen atoms on the surface. Although the binding energy of O 1s for a carboxyl group is ca. 531 eV,[13,15] the peak at 530 eV or 532 eV cannot be attributed to the carboxyl group. The binding energy of O 1s for the hydroxyl groups on metal oxides is usually higher than that for the lattice oxygen.[13,15] It was reported that the number of the surface hydroxyl groups depends on the surface reducibility of cerium oxide,[8,16] but the number of hydroxyl groups on the surface is considered to be small. On the basis of the data reported by Laachir et al. the number of the hydroxyl groups on the surface of cerium oxide with 35–36% reduction (BET surface area, 115 m^2 g^{-1}) can be estimated to be 0.05 mmol g^{-1}.[8] The ratio of O/Ce decreases with an increase in the chlorine content of the sample (see Table 1), suggesting that oxygen vacancies are mainly formed after the reduction treatment.[16] Hence, the contribution of hydroxyl groups to the XPS of O 1s region is determined to be small.

Here, we can find interesting relationship in the normalized peak intensities described in Table 1. That is, the value of $a^{1/2} + c^{1/2}$ was always 0.98–1.03, where a and c are the peak intensities at 530 and 534 eV, respectively. In the crystalline structure of cerium oxide (e.g., fluorite structure for CeO$_2$), an oxygen atom is surrounded by four cerium atoms.[1] However, the oxygen atoms lack the coordination structure on the surface. Hence, it is supposed that the coordination number of the oxygen atom on the surface is less than four and the bonds between surface oxygen and cerium are disproportional. Assuming that each oxygen atom interacts with two cerium atoms on the surface, the fractions of oxygen atoms connecting to two Ce^{4+} and to two Ce^{3+} will be x^2 and $(1 - x)^2$, respectively, where a value, x, is the fraction of Ce^{4+} to whole cerium atoms on the surface. If a and c are equal to x^2 and $(1–x)^2$, respectively, the value of $a^{1/2} + c^{1/2}$ will be one. Hence, the peaks at 530 and 534 eV can be attributed to Ce^{4+}–O–Ce^{4+} and Ce^{3+}–O–Ce^{3+} on the surface, respectively, while the peak at 530 eV is major in Pd–CeO$_2$-1 of which the reducibility should be small. The peaks at 532 eV can be attributed to Ce^{4+}–O–Ce^{3+} on the surface. Since the lower electron density usually results in the higher binding energy, the density on the oxygen atom mainly connecting to two Ce^{3+} is probably the lowest. The reducibility of ceria (surface fraction of Ce^{3+}) can be calculated as 15%, 22%, 38%, and 48% for Pd–CeO$_2$-1, -2, -3, and -4, respectively, from the peak intensities of the O 1s peaks. The values correspond to the intensities of the v' peak found in the XPS of Ce 3d region (see Figure) and also to the chlorine contents. Thus, the lattice oxygen species are estimated to be responsible for the O 1s peaks, and the reduction of cerium oxide probably produces oxygen with the lower electron density.

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