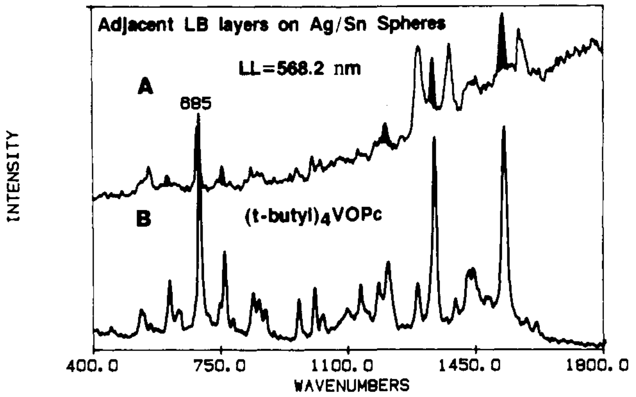

Figure 4. Raman shifts from samples A and B obtained with 568.2-nm laser line.

laser line is shown, where both the vibrational fundamentals of the bottom layer (Oc-PTCDNH) and the upper monolayer of (t-Bu)$_4$VOPc contribute to the Raman spectrum. The sample B with the reverse order of LB layers, under 568.2-nm excitation, gave the spectrum of (t-Bu)$_4$VOPc. This result was in agreement with the fact that 568.2-nm was in preresonance region of the Pc electronic transition, but it was outside of the absorption region of Oc-PTCDNH.

Conclusion

The application of SERRS in the spatial spectroscopic analysis of adjacent LB monolayers has been demonstrated using molecular dyes with distinct electronic absorption in the visible. The spatial spectroscopic tuning may be used to study a variety of sequential monomolecular assemblies, for instance, to follow the interaction and spectral changes in separate monolayers containing donor and acceptor species or a chemical binding (reaction) that could affect one specific layer. In general, SERRS could be used for selective spectroscopic analysis of an LB monolayer in a matrix of spacers of molecules transparent to the exciting electromagnetic field.

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Dioxygen Adsorption on Well-Outgassed and Partially Reduced Cerium Oxide Studied by FT-IR

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Abstract: $^{16}O_2$ ($^{18}O_2$) adsorption on well-outgassed and partially reduced cerium oxide has been investigated by Fourier transform infrared spectroscopy (FT-IR) in the temperature range 200–373 K. Superoxide species ($O_2^-{}_{ads}$) with a pair of characteristic bands at 1126 (1063) and 2237 (2112) cm^{-1} were detected from oxygen adsorption on both surfaces of well-outgassed and partially reduced cerium oxide. One additional band at 883 (835) cm^{-1} attributed to peroxide species ($O_2^{2-}{}_{ads}$) was observed together with the bands at 1129 and 2238 cm^{-1} after oxygen adsorption on partially reduced cerium oxide. The formation of these dioxygen species is strongly dependent on the pretreatment of cerium oxide. In particular, the bands due to peroxide species were only identified on the partially reduced cerium oxide, and the band intensities increased markedly with the prereduction time of cerium oxide. It is concluded that the superoxide species is mainly generated on a coordinatively unsaturated cerium ion while the peroxide species were formed on a pair of surface cerium ions with lower oxidation state created by reduction.

Identification of dioxygen species on surfaces of metals and oxides has long been an attractive subject[1] because the dioxygen species are the most essential intermediates of many heterogeneous oxidation reactions,[2] which consist of the basis for important industrial processes, such as production of oxygen-containing compounds through selective oxidation. Although oxygen adsorption on transition-metal oxides has been extensively examined, the ways how these species form and participate in reactions are still obscure. A detailed study on dioxygen species is therefore necessary for understanding the oxidation mechanism on oxides. Cerium oxide, a rare-earth oxide, has been found to be active for oxidation reactions of hydrocarbons[3,4] and CO.[5,6] The studies of adsorbed oxygen species and their activities on cerium oxide have drawn some attention; for example, ESR (electron spin resonance) investigations[7,8] show that superoxide species, O_2^-, were formed on CeO_2 and on supported CeO_2 with certain pretreatments after oxygen adsorption. Che et al.[9,10] assumed that the O_2^- species adsorbs on Ce^{3+} ion of cerium oxide based on the ESR spectra. O_2^- species were also confirmed[11] on CeO_2/Al_2O_3 and CeO_2Pd/Al_2O_3, and the species were proved to be the active form on the latter during the oxidation reaction of CO and C_2H_4. All above conclusions related to the oxygen species on cerium oxide were drawn only on the basis of ESR results. No IR study of O_2 adsorption on cerium oxide has been reported; especially, no evidence of adsorbed O_2^{2-} species has been obtained for cerium oxide. We reported preliminary oxygen adsorption on ceria by means of IR method.[12]

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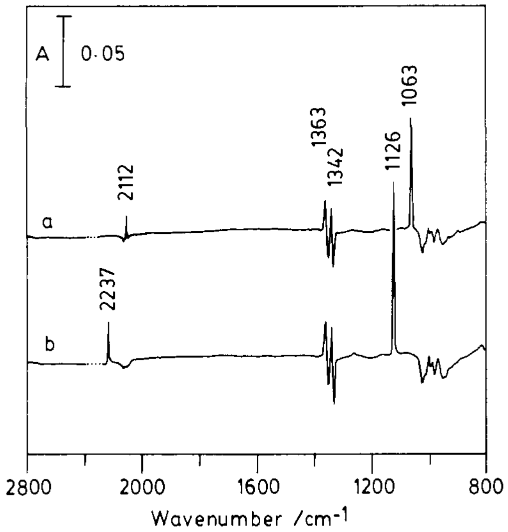

Figure 1. IR spectra of adsorbed dioxygen on CeO_2 (1000 K) at 298 K after admission of O_2 for 1 min: (a) $^{18}O_2$, 4 Torr; (b) $^{16}O_2$, 150 Torr.

One of the powerful techniques for detecting oxygen species is ESR spectroscopy,[13] which has been used to resolve adsorbed O_2^- and O^- species, but the diamagnetic species, O_2^{2-} and O^{2-}, do not give ESR signals. On the other hand, ESR is not successfully applied to the study of oxygen species adsorbed on many paramagnetic oxides. IR method has been often used to characterize the dioxygen species in the matrix[14] and complexes[15] and also has been demonstrated to be very useful in determining the oxygen species formed on oxides.[16]

The present paper reports an attempt to characterize dioxygen adsorption by FT-IR on cerium oxides with various pretreatments. An assignment of dioxygen species (both O_2^- and O_2^{2-}) detected in this study is described, and the nature of the adsorption sites and the effects of different pretreatment of cerium oxide on formation of adsorbed dioxygen species are discussed.

Experimental Section

Materials. A CeO_2 sample for this study was prepared by precipitation via an aqueous solution of cerous nitrate ($Ce(NO_3)_3$) and NH_4OH, and the resulting hydroxide was repeatedly washed with deionized water until NH_4 and NO_3^- ions were entirely eliminated, followed by drying and calcining in air at 393 K for 72 h and at 773 K for 3 h, respectively. The specific surface area (BET) was about 20 m^2/g. The CeO_2 sample was pressed into a self-supporting disk, weight ca. 100–150 mg with a diameter of 20 mm, for IR measurement. H_2 from a cylinder was purified via a Deoxo and further through a liquid-nitrogen trap. $^{16}O_2$ and $^{18}O_2$ (98%) used for the adsorption experiment were refined through a liquid-nitrogen trap in a circulating system.

Apparatus. IR experiments were carried out on a JEOL JIR-100 FT-IR spectrometer with 256 scans at 4-cm^{-1} resolution using a liquid-nitrogen-cooled HgCdTe detector. An IR cell, in which the sample disk can be heated and cooled in the temperature range 150–1000 K with both an external heater wire and a liquid-nitrogen-cooling pipe, was connected to a vacuum system, which can be kept below 10^{-4} Torr (1 Torr = 133.3 Nm^{-2}) by an oil-diffusion pump and a mechanical pump. The spectra in the paper were displayed in absorbance, and their background spectra were recorded before the admission of O_2 at corresponding experimental conditions of the spectra.

Procedures. The sample disk was repeatedly treated in O_2 at 873 K and followed evacuation at 1000 K in the IR cell until surface contaminants such as adsorbed water and carbonate species were completely removed. Surface purity was checked by background spectra. The sample disk after pretreatment in O_2 at 673 K for 12 h and then outgassing at 1000 K for 1 h is considered as a well-outgassed sample and denoted as CeO_2 (1000 K). A partially reduced sample here generally referred to as CeO_2 (673-H) was prepared by treating the CeO_2 (1000 K) in H_2 at 673 K for given time and then evacuated at 1000 K again for 0.5 h in order to remove surface hydroxyl species. In detail, the reduction time (*t*, hour) was also indicated; for example, CeO_2 (673-H-3) means that a well-outgassed cerium oxide sample has been reduced in H_2 at 673 K for 3 h followed by an evacuation at 1000 K for 0.5 h. Either CeO_2 (1000 K) or CeO_2 (673-H) sample was cooled down stepwise to a desired temperature for adsorption experiment, while the background spectra were recorded during the cooling process. The IR cell had been always seated in the sampling chamber of the spectrometer; thereby, all the spectra were taken in situ.

Table I. IR Bands Derived from Adsorption of $^{16}O_2$ and $^{18}O_2$ on Cerium Oxide (cm^{-1})

cerium oxide	$^{16}O_2$	$^{18}O_2$	$^{16}O_2/^{18}O_2$[a]	assignt
CeO_2 (1000 K)	1126	1063	1.059	superoxide, O_2^-
	2237	2112	1.059	
CeO_2 (673-H)	883	835	1.057	peroxide, O_2^{2-}
	1128	1065	1.059	superoxide, O_2^-
	2239	2114	1.059	

[a] Calculated value is 1.060.

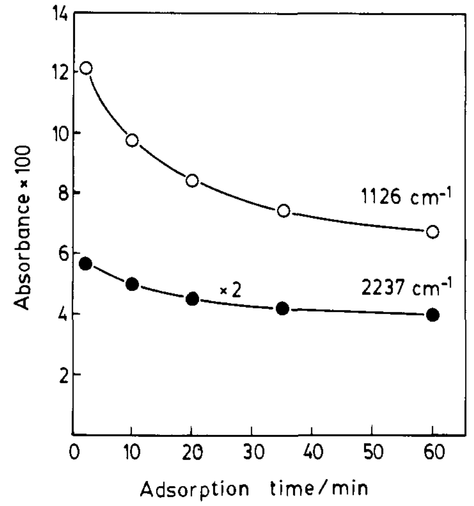

Figure 2. Variation of band intensities vs adsorption time during adsorption of $^{16}O_2$ on CeO_2 (1000 K) at 306 K.

Results

$^{16}O_2$ and $^{18}O_2$ Adsorption on CeO_2 (1000 K). IR spectra of adsorbed O_2 at room temperature on CeO_2 (1000 K) are shown in Figure 1. A pair of bands at 2237 and 1126 cm^{-1} for $^{16}O_2$ adsorption and bands at 2112 and 1063 cm^{-1} for $^{18}O_2$ adsorption were clearly observed after admission of $^{16}O_2$ and $^{18}O_2$, respectively. These bands can be assigned to adsorbed superoxide species ($O_2^-{}_{ads}$) according to the band at 1126 cm^{-1}, which is the characteristic frequency of O–O vibration with bond order of 1.5. This band position is consistent with those of superoxide ligands in the matrixes[14,17,18] and complexes.[15,19] The band at 2237 cm^{-1}, which is almost twice the wavenumber of the band at 1126 cm^{-1}, can be ascribed to the first overtone of that at 1126 cm^{-1}. The assignments are confirmed by the isotopic ratios listed in Table I. Similar spectra have been obtained from the adsorption of O_2 on CeO_2 (1000 K) in the temperature range 200–370 K. At the lower temperature of adsorption, stronger bands have been observed. With elevated temperatures in the presence of O_2, the intensities of the bands due to adsorbed superperoxide species were reduced slightly from 200 to 300 K but markedly from 300 to 373 K. At given adsorption temperature and O_2 pressure, the bands exhibit very high intensities immediately after admitting O_2 and then attenuate gradually with time as illustrated in Figure 2. A similar

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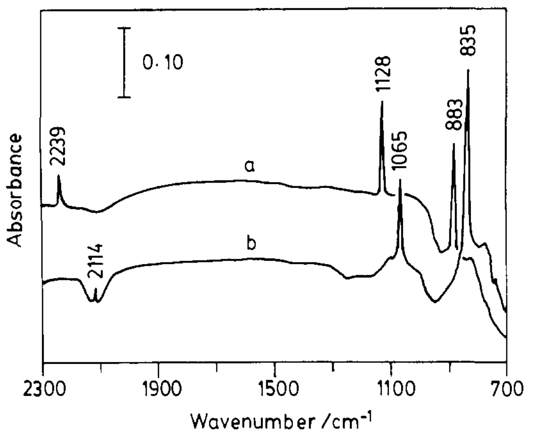

Figure 3. IR spectra of adsorbed dioxygen on CeO_2 (673-H) at 210 K: (a) $^{16}O_2$, 140 Torr, on CeO_2 (673-H-3); (b) $^{18}O_2$, 40 Torr, on CeO_2 (673-H-15).

tendency can be found to be more steep at higher temperatures of O_2 adsorption, while at temperatures below 250 K, the band intensities keep nearly unchanged with adsorption time. It is confirmed that the two bands at 1126 and 2237 cm^{-1} originate from the same species since the two curves of 1126 and 2237 cm^{-1} in Figure 2 show the same trend.

$^{16}O_2$ and $^{18}O_2$ Adsorption on CeO_2 (673-H). Formation of superoxide species is found to be very sensitive to the pretreatment of CeO_2. The bands at 1126 and 2237 cm^{-1} were detected as described above only after the cerium oxide was well outgassed. This might be explained in terms of surface defects or oxygen-deficient sites where the superoxide and other charged oxygen species are produced. We tried to examine the dioxygen species from O_2 adsorption on partially reduced cerium oxide, which has many defects and oxygen vacancies generated after a treatment of prereduction. Figure 3a shows an IR spectrum after adsorption of $^{16}O_2$ on CeO_2 (673-H-3) at 200 K, and Figure 3b presents similar spectrum of $^{18}O_2$ adsorption on CeO_2 (673-H-15). Three sharp bands at 2239, 1128, and 883 cm^{-1} were observed for $^{16}O_2$ adsorption, and these bands correspondingly shift to 2114, 1065, and 835 cm^{-1} for $^{18}O_2$ adsorption. Variation of pressure of O_2 in the range of 140–4 Torr did not cause apparent changes in intensities of these bands. They were gradually reduced when the O_2 pressure was pumped off below 4 Torr, however, still could be detected even after evacuation for 5 min at room temperature. By comparing Figure 3 with Figure 1, the same pair of bands at 2237 (2112) and 1126 (1063) cm^{-1} from $^{16}O_2$ ($^{18}O_2$) adsorption on CeO_2 (1000 K) also appear on CeO_2 (673-H), and one additional band at 883 (835) cm^{-1} was observed on CeO_2 (673-H). This indicates that the superoxide species are able to be formed on both CeO_2 (1000 K) and CeO_2 (673-H) while at least another kind of oxygen species is formed on the latter. The isotopic ratio of the band at 883 cm^{-1} (listed in Table I) is also close to the calculated value for the molecular form of oxygen. This band is attributed to the vibration of dioxygen with a single bond; namely, the band is due to adsorbed peroxide species ($O_2{}^{2-}{}_{ads}$). This wavenumber falls in the region 970–700 cm^{-1} of dioxygen charged with two electrons in metal complexes[15] and also in some matrixes[14] at low temperature. The assignment is consistent with the resuls of O_2 adsorption on metal surface on which bands of adsorbed peroxide species appear at around 850 cm^{-1}.[20,21] Similar curves as shown in Figure 2 were obtained for the three bands of both superoxide and peroxide species on CeO_2 (673-H). The effect of O_2 pressure on the bands due to peroxide and superoxide species on CeO_2 (673-H) is almost the same as the effect on those bands due to superoxide on the CeO_2 (1000 K). The behaviors of the adsorbed superoxide and peroxide species on partially reduced cerium oxide were investigated in the temperature range 200–373 K. Figure 4 exhibits a series of spectra of adsorbed $^{16}O_2$ on CeO_2 (673-H-3) recorded during heating the sample from 200 to 373 K with increasing the temperature by 2.5 K/min in the $^{16}O_2$ gas phase. The three bands are reduced simultaneously when the sample disk is warmed up; especially, the intensities of these bands decrease dramatically above 300 K and finally go to zero at around 420 K. Meanwhile, a pair of broad reverse bands centered at 2115 and 939 cm^{-1} appeared with admission of O_2, and they became more evident at the elevated temperatures. The two bands do not shift on replacing $^{16}O_2$ with $^{18}O_2$ adsorption. We suggest that the two bands arise from cerium oxide but do not from adsorbed oxygen species. With comparing the background spectra, it was found that the two bands are derived from prereduction of the cerium oxide and become stranger when the degree of reduction proceeds. The color of the sample changed from yellow to gray and then to black during H_2 reduction. After introduction of O_2, the sample disk gradually turns gray at room temperature and then to the original yellow at high temperatures. The interpretation of the color changing is straightforward in that the CeO_2 (yellow) is reduced to a nonstiochiometric ceria, CeO_x ($x < 2$, gray or black), and the CeO_x returns to CeO_2 in O_2 at higher temperatures. The two bands are from CeO_x instead of CeO_2; thus, the reverse bands appeared after admission to O_2 to the CeO_x since the spectra of the partially reduced cerium oxide were used as reference spectra.

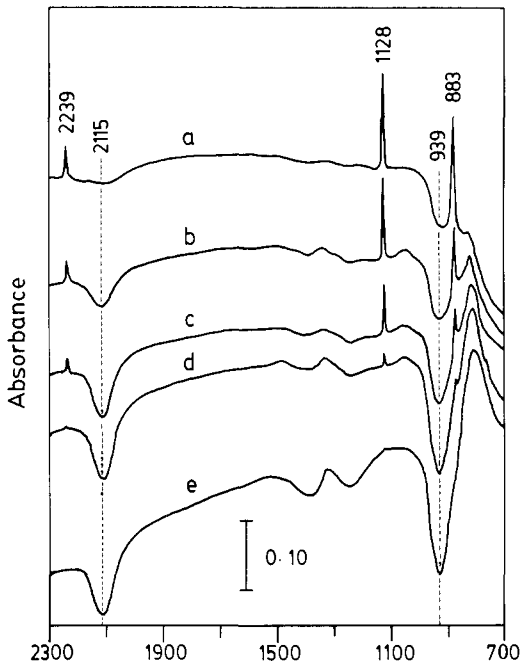

Figure 4. IR spectra of adsorbed dioxygen on CeO_2 (673-H-3) at elevated temperatures (ca. 2.5 K/min) in the presence of $^{16}O_2$: (a) 200 K; (b) 285 K; (c) 323 K; (d) 373 K; (e) 473 K.

$^{16}O_2$ and $^{18}O_2$ Adsorption on Cerium Oxide with Various Extent of Prereduction. It has been found that the band at 883 (835) cm^{-1} due to peroxide is absent on CeO_2 (1000 K) (Figure 1) and appears on CeO_2 (673-H-3) and CeO_2 (673-H-15). In the case of the latter, the intensity of the band at 883 (835) cm^{-1} on CeO_2 (673-H-15) is much stronger than that on CeO_2 (673-H-3). In Figure 5 the results of IR measurements for adsorption of $^{16}O_2$ at 200 K on cerium oxides with the different degree of prereduction are summarized. The band at 1126 cm^{-1} developed when the surface was weakly reduced but declined slightly with prolonged reduction time. On the whole, the band is not affected markedly with the different degrees of prereduction. However, the band at 883 cm^{-1} is absent after O_2 adsorption on well-outgassed cerium oxide, emerges on weakly reduced cerium oxide, and becomes more apparent with an increase of prereduction time. The adsorbed peroxide species are favored on partially reduced cerium oxide. Similar spectra of those on CeO_2 (1000 K) were obtained from

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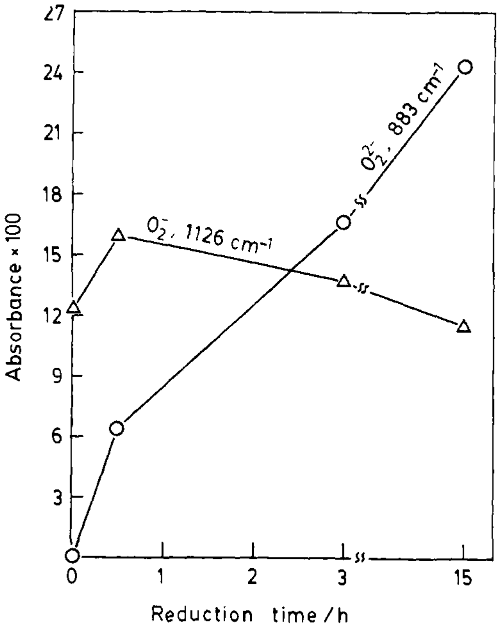

Figure 5. Band intensities of 1126 cm^{-1} due to adsorbed superoxide and 883 cm^{-1} due to peroxide as a function of prereduction time of cerium oxide.

adsorption of $^{16}O_2$ ($^{18}O_2$) on cerium oxide reduced at a temperature below 420 K; i.e., only bands at 2237 (2112) and 1126 (1063) cm^{-1} due to superoxide species appeared, whereas the bands due to peroxide species were absent. Adsorption of $^{16}O_2$ ($^{18}O_2$) on CeO_2 (773-H) gives rise to the spectra similar to those on CeO_2 (673-H) but with a stronger band at 883 (835) cm^{-1}.

Discussion

Adsorbed Superoxide ($O_2^-{}_{ads}$) and Peroxide ($O_2^{2-}{}_{ads}$) Species. Superoxide has been reported to be formed over oxides[1] such as ZrO_2,[27] TiO_2,[23] V_2O_3,[24] MgO,[25] and Al_2O_3,[26] and most of the evidence for superoxide has been obtained by ESR. The IR bands due to superoxide species are estimated to be in the range 1100–900 cm^{-1} according to the O–O band order of 1.5. Davydov et al.[27] have assigned IR bands at around 1180 cm^{-1} to the adsorbed O_2^- species formed via interaction of oxygen with reduced TiO_2. Similar bands attributed to adsorbed O_2^- were detected at 1140 and 1070 cm^{-1} for NiO[28] and at 1160–1015 cm^{-1} for MgO-CoO.[29,30] Obviously the band at 1126 cm^{-1} due to O_2^- species on cerium oxide is in good agreement with above literature results. However, the assignment of adsorbed dioxygen on some oxides[31,32] is controversial because the bands due to M=O or M–O–M (M, metal atom of oxide)[33] are near to those of the O–O vibrations. We believe that the shape of the band and thermal stability of the species should be different between oxygen–metal and oxygen–oxygen species in nature. In general, the former is thermally stable and its IR bands are broad, while the latter is readily removed at elevated temperature and the corresponding bands should be relatively sharp. From the spectra in Figures 1, 3, and 4 the half-widths of bands due to both superoxide and peroxide are within 10 cm^{-1}, which is the typical half-width of a spectrum of molecular form, and the fact that the bands disappear above 420 K (Figure 4) also convinced us of the assignment.

The peroxide species are formed when O_2 gains two electrons, which weaken the O–O bond strength markedly so that the species are easily differentiated from the superoxide by different frequency regions as shown in Figure 3. The species are currently considered as unstable intermediates in the sequence of O_2 dissociation. There is only a detailed study on peroxide species on oxide,[34] and the species is often neglected in discussion of surface oxidation mechanism because of a lack of information about the species. As described previously, the O_2^{2-} species were unambiguously observed on partially reduced cerium oxide even up to 420 K.

Formation of Superoxide and Peroxide Species and Adsorption Sites. Superoxide and peroxide species can be considered as intermediates formed during oxygen dissociation as via the general scheme

$$O_{2\,ads} \xrightarrow{1} O_2^-{}_{ads} \xrightarrow{2} O_2^{2-}{}_{ads} \xrightarrow{3} 2O^-{}_{ads} \xrightarrow{4} 2O^{2-}{}_{lc}$$

where the $O^{2-}{}_{lc}$ is lattice oxygen ion. Obviously the formation of these species mainly depends on the electron donation ability of surface and suitable sites for stabilizing the formed species. On most of the metal surfaces, although oxygen can easily gain electrons from the surface, the dioxygen species are difficult to be detected as a result of the fast dissociation process of O_2. On the contrary, the charged dioxygen species cannot be produced on some oxides due to the very weak electron donation of the surface. The outgassing of cerium oxide at 1000 K really produces surface defects or coordinatively unsaturated surface sites, and the superoxide species are formed on those sites that supply electrons and stabilize the adsorbed species. The surface defects[35,36] produced by removing hydroxyls or surface oxygen might be Ce^{3+} or Ce^{4+} sites with oxygen nests that have also been postulated from the data of NMR and ESR studies[37] on cerium oxide. This can be confirmed by the fact that the charged dioxygen species were not observed even at lower temperature after O_2 doses on hydrated or oxygen-saturated (the sample treated in O_2 at a high temperature and then cooled to a lower temperature) cerium oxide. The intensity decrease in Figure 2 is explained as the superoxide species were formed immediately after O_2 introducing and successively converted into O_2^{2-}, O^-, and finally into $O^{2-}{}_{lc}$ by accepting more electrons from the surface. These changes will make the surface so electron deficient that it is not available for further electron transfer from the surface to dioxygen. The slow decrease in intensity of the band at 1126 cm^{-1} is probably due to the slow step 2 in the above scheme, and this step is accelerated by raising the temperature so that the curve in Figure 2 becomes steep at higher temperatures. The absence of the band due to O_2^{2-} indicates that the step 3 is very fast on well-degassed cerium oxide.

It is well-known that cerium oxide is a nonstoichiometric oxide.[38] The partially reduced cerium oxide can be denoted as CeO_x ($x < 2$) or roughly as a mixture, $CeO_2 + mCe_2O_3$ ($m \ll 1$); i.e., the pretreatment in H_2 at 673 K reduced the surface Ce^{4+} to Ce^{3+} ions[39,40] and produced surface oxygen nests and bulk oxygen vacancies simultaneously. The O_2 adsorption on well-outgassed and partially reduced cerium oxide may be simply generalized

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as the surface oxidation reaction

$$nCeO_x\ (x < 2,\ n > 1) + O_2 \rightarrow [nCeO_x]^+O_2^- \rightarrow [nCeO_x]^{2+}O_2^{2-} \rightarrow [nCeO_x]^{2+} + 2O^- \rightarrow nCeO_y\ (x < y \leqslant 2)$$

Apparently, over the more oxygen-deficient CeO_x, i.e., the smaller x, the reactions proceed more potentially to form O_2^- and O_2^{2-} species. It is quite possible that the peroxide is formed in two ways on the partially reduced cerium oxide. One is via the interaction between two O_2^-, and the other is through the further accepting of an electron of O_2^- by virtue of oxidation of the surface site as described in the above sequence. It is generally considered that O_2^- is bent bonded and O_2^{2-} is side-on bonded on metal surfaces.[41] The abundance of O_2^{2-} on partially reduced cerium oxide may be accounted for by an adsorption model; that is, the peroxide species are formed via the interaction of O_2 with two neighboring Ce^{3+} sites. This can also be explained as follows: the peroxide species are generated via the O_2^- formed on Ce^{3+} or a defect site and subsequently interact with a defect or a Ce^{3+} site in the vicinity where the O_2^{2-} gains its second electron. Since the defect sites on CeO_2 (1000 K) are more sparse than those on CeO_2 (673-H), the peroxide are unfavorable on the former. It is reasonable that the amount of adsorbed peroxide increases with reduction time of cerium oxide (Figure 5) because more surface defects and oxygen vacancy are produced after deeper prereduction. Obviously the CeO_2 (673-H) is more ready to contribute electron to oxygen than is CeO_2 (1000 K); therefore, the O_2^{2-} species are favored on the former. These results are in accordance with the conclusions[42] from molecular orbital calculations for metal complexes in which the peroxide ligand only forms on central metal with low oxidation state. Figure 5 shows that the amount of adsorbed O_2^- remains almost unchanged on various cerium oxide with different degrees of reduction, and this could be interpreted in terms of the conversion from O_2^- to O_2^{2-} that limits the surface concentration of O_2^-.

A similar tendency to the results shown in Figure 2 was found for the band at 883 cm^{-1} in Figure 5, which indicates the conversion from O_2^{2-} to O^- and $O^{2-}{}_{lc}$ and the surface is successively oxidized. The two reverse bands at 2115 and 939 cm^{-1} (Figure 4) appear after admission of O_2 to partially reduced cerium oxide and become more intense with higher adsorption temperature. This fact indicates that the surface is reoxidized at elevated temperatures.

Conclusions

The adsorption of oxygen on well-outgassed cerium oxide gives rise to the IR bands at 2237 and 1126 cm^{-1} attributed to superoxide species and on partially reduced cerium oxide produces the IR bands at 2239, 1128, and 883 cm^{-1} attributed to superoxide and peroxide species, respectively. The assignments are confirmed by the spectra of isotopic $^{18}O_2$ adsorption. The nature of adsorption sites suggests that the superoxide species are formed on the surface defects, namely, the coordinately unsaturated Ce^{4+} ions, and the peroxide species on Ce^{3+} ions or on Ce^{3+} and Ce^{4+} with oxygen nest. The conversion from O_2^- to O_2^{2-} is proposed in two ways: a disproportionation reaction of O_2^- and a successively accepting electron from the surface. The former is universal on both the surfaces of CeO_2 (1000 K) and CeO_2 (673-H); however, the latter particularly happens on the reduced surface.

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Optical Spectra of Transition-Metal Carbonyls: $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$

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Abstract: Near-UV gas-phase optical spectra and absolute absorption cross sections of the transition-metal carbonyls $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$ are presented. They have been recorded using a fast-scanning spectral photometer to minimize heterogeneous decomposition during the measurement. The excited states in the experimental energy range were analyzed employing an INDO/S CI formalism. Calculations on the basis of single excitation CI for singlet–singlet transitions yield good agreement both for transition energies and intensities. From these theoretical models it is deduced that transition-metal carbonyl near-UV spectra are determined exclusively by metal-to-ligand charge-transfer transitions, whereas d → p and d → s excitations do not contribute significantly below 6.2 eV (above 200 nm). The lowest lying singlet excitations in $Cr(CO)_6$ and $Fe(CO)_5$ are predicted to be d → d. Although they are predicted to have little or no dipole allowed character, they should be observable because they are well separated from the first allowed bands. Indeed, they have been detected for $Cr(CO)_6$. The spectra of several substituted complexes $(CO)_5CrR$ (R = CS, PF_3, CHOH) are also calculated and compared with available experimental data.

In the last few years transition-metal carbonyls gained increasing importance in laser chemistry as a source of metal atoms or reactive precursors for chemical vapor deposition of thin films or layers on surfaces.[1] For the analysis of reaction mechanisms it is necessary to understand the electronic structure both of the carbonyls and their fragment molecules. Extended Hückel-type[2] and CNDO CI[3] calculations have been used as basis for the interpretation of experimental UV absorption spectra[4–7] of various

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