I.r. Spectra of Dioxygen Species Formed on CeO_2 at Room Temperature

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I.r. bands at 1126 and 2237 cm^{-1} attributed to adsorbed superoxide ions (O_2^-), were observed on CeO_2 by Fourier transform i.r. spectroscopy at room temperature.

Oxygen (di-, mono-oxygen) species on the surface of metals and oxides are of great interest in a variety of catalytic oxidation reactions. There has been much effort to detect and characterize the oxygen species by i.r. spectroscopy,[1] but no i.r. study of the oxygen species has been reported on CeO_2. Here we present the i.r. spectra of surface dioxygen species formed on CeO_2 at room temperature *via* O_2 adsorption. On the basis of isotopic substitution experiments and from literature results, it is concluded that the dioxygen species adsorbed is the superoxo (O_2^-) type.

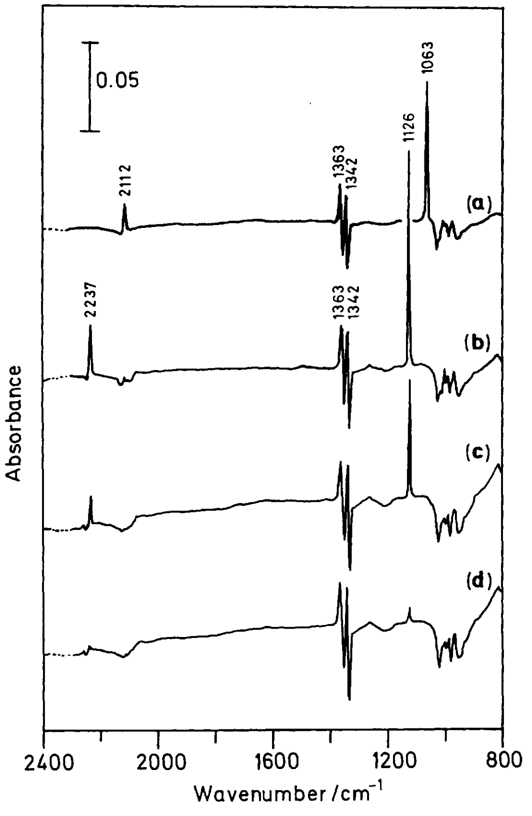

Figure 1. I.r. spectra of adsorbed O_2 on CeO_2 at room temperature. (a) adsorbed $^{18}O_2$ (4 Torr) (1 Torr = 133·322 Pa); (b) adsorbed $^{16}O_2$ (140 Torr), 1 min after admission of $^{16}O_2$; (c) 60 min, and (d) evacuation for 30 min after (c).

The CeO_2 sample was prepared by precipitation from aqueous cerium nitrate with NH_4OH and the resultant hydroxide was calcined at 773 K for 3 h. $^{16}O_2$ and $^{18}O_2$ (>98%) used in this study were purified in a circulation system through a liquid nitrogen trap. A self-supporting disc of the sample was placed in an i.r. cell which was connected to a vacuum system. The sample was dehydroxylated at 1000 K for 1 h in the i.r. cell before the adsorption experiments took place. The spectra were recorded at 4 cm^{-1} resolution using a JEOL JIR-100 Fourier-transform i.r. spectrometer, relative to spectra of the sample prior to O_2 adsorption and plotted in absorbance mode.

A typical spectrum of $^{16}O_2$ adsorbed on CeO_2 at room temperature is shown in Figure 1b. Two very sharp peaks at 2237 and 1126 cm^{-1} appeared simultaneously as soon as the CeO_2 was exposed to $^{16}O_2$ at room temperature and then tended to decline progressively with time (from Figure 1b to 1c). When the gas phase was evacuated, the intensities of both bands were reduced significantly, whereas the residuals of the peaks could still be detected after pumping for 30 min (Figure 1d). Under an atmosphere of $^{16}O_2$, the two bands could be observed up to 373 K. These features indicated that the two bands may be from the same adsorbed species which are quite stable on the surface of CeO_2.

Figure 1a displays a spectrum of adsorbed $^{18}O_2$ and this can be compared with that of adsorbed $^{16}O_2$ (Figure 1b) under the same conditions. It is clear that the bands at 2237 and 1126 cm^{-1} of adsorbed $^{16}O_2$ shift to bands at 2112 and 1063 cm^{-1} of adsorbed $^{18}O_2$ respectively. The isotopic ratios for both bands are 1.059, nearly equal to the square root of the reduced mass ratio for the harmonic vibrational model of dioxygen.

The band at 1126 cm^{-1} is exactly in the region of 1020—1180 cm^{-1} for superoxide ion species on other oxides[2—5] and in a matrix.[6] This wavenumber is also in excellent agreement with the estimation for superoxide ions with an oxygen–oxygen bond order of 1.5. For physically adsorbed molecular oxygen, the oxygen–oxygen stretching frequency is about 1500 cm^{-1} which is close to that of the free oxygen molecule.[5] Another dioxygen species is the peroxide ion ($O_2{}^{2-}$)[7,8] which generally shows an oxygen–oxygen vibration around 850 cm^{-1}. The band at 1126 cm^{-1} is thus clearly due to adsorbed superoxide ions ($O_2{}^{-}$). It is also reasonable to assign the band to adsorbed dioxygen species in view of its narrow half width. The band at 2237 cm^{-1} which has not been reported before is at almost twice the wavenumber of the 1126 cm^{-1} bond, and its isotopic shift (125 cm^{-1}) is twice that of the 1126 cm^{-1} band (63 cm^{-1}); therefore it can be attributed to the first overtone of the band at 1126 cm^{-1}. The fact that the intensity of the two bands during evacuation showed a constant ratio confirmed that the two bands are due to the same species. Superoxide species on pure and supported CeO_2 were also proposed in the light of the e.s.r. signals[9,10] derived from adsorption of O_2.

The reverse bands in the range 1400—1300 and 1000—800 cm^{-1} occur as a result of the O_2 admission, but no isotopic shift was found due to $^{18}O_2$ adsorption (Figure 1a). The two sections cannot be recovered after evacuation of the gas phase (Figure 1d). These peaks arise from the original CeO_2, not from O_2 adsorption. A careful check of the background spectrum of the sample shows some sharp peaks in the two regions. It is found that the adsorption of O_2 will slightly affect the shape and position of the peaks in the two regions, so the ratioed spectra will show the reverse bands. No peaks were observed in the regimes around 1126 and 2237 cm^{-1} in the background spectrum before adsorption of O_2.

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