JOURNAL OF SOLID STATE CHEMISTRY 4, 370–373 (1972)

The Study of Oxygen Sorption on Cerium(IV) Oxide by Electron Spin Resonance

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Received September 7, 1971

The presence of paramagnetic species on the surface of cerium(IV) oxide prepared by the thermal decomposition of the oxalate at low temperatures (375°) was shown by ESR. The sorption of oxygen at room temperature showed a new signal having $g_\perp = 2.0137$ and $g_\parallel = 2.0312$. This signal is ascribed to the formation of the anionic radical O_2^- on the surface. The origin of the paramagnetic species is ascribed to quasi-free electrons in the *n*-type nonstoichiometric cerium(IV) oxide.

Introduction

Cerium oxide is fairly extensively used in heterogeneous catalysis (*1*), but very little work has been done to explain its surface activity.

The stable oxide of cerium is CeO_2. It is well known, however, that this oxide is a nonstoichiometric compound (*2*) described by the formula CeO_{2-x}. The concentration of defects depends on the oxygen partial pressure at constant temperature.

Although the use of ESR spectroscopy in studies of surface defects and oxygen adsorption in oxides has been demonstrated (*3*) in some oxides used as catalysts, very few publications have appeared on cerium(IV) oxide (*4*). In some of these studies the oxide was prepared by the thermal decomposition of cerium(III) oxalate at high and low temperatures (*4a*, *4c*), while in another (*4b*) the oxide was prepared by the thermal decomposition of cerium nitrate at 500°. The effect of the crystal field on impurities deliberately introduced into solids was also studied (*5*) for cerium by ESR. Work on glasses containing cerium has also been published (*6*).

ESR spectroscopy has been used in this work to study oxygen sorption on ceria. The spectra were recorded simultaneously with adsorption measurements.

Experimental

Materials

Cerium(IV) Oxide. The CeO_2 samples (P.59 and P.69) were prepared by decomposing cerium(III) oxalate in air at 375° for one hour (*7*) and leaving the oxide at this temperature for an additional one hour. The cerium(III) oxalate was prepared by dissolving either ceria 99.999% (code 217.92) in concentrated nitric acid, without using reducing agents (sample P.59) or from cerium(III) nitrate 99.9999% (code 277.93) (sample P.69). The nitrate solution was evaporated to a volume of 15 ml and diluted, and the oxalate was precipitated by oxalic acid. The precipitate was filtered on a Selas crucible and washed with a dilute solution of oxalic acid until no nitrate ion could be detected. All the reagents used in these preparations were of analytical grade, and the cerium starting materials were supplied by the American Potash and Chemical Corporation.

Gases. All the gases employed were of analytical purity, supplied by Matheson Company, Inc. Some of the experiments were carried out with oxygen prepared *in situ* by the thermal decomposition of degassed potassium permanganate; the results were identical to those attained when cylinder gas was used.

Apparatus

Electron spin resonance data were obtained with a Varian V 4502 X band spectrometer at a cavity

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* Taken partly from M. G.'s Ph.D. thesis, June 1970.

† In part, under Grant DA-ARO-D-31-124 G83 of the Army Research Office at the University of California, Santa Barbara.

resonance frequency of 9.178 GHz. The magnetic field was modulated at 100 kHz, with precautions concerning saturation. Calibration for g values was carried out by occasionally impregnating the outer walls of the reactor with an acetone solution of α,α'-diphenyl-β-picrylhydrazyl (DPPH). The DPPH value was taken as 2.0036.

X-Ray analyses were carried out with a Phillips diffractometer (Cu$K\alpha$ nickel filtered radiation). Both P.59 and P.69 gave a diffraction pattern typical of cerium(IV) oxide.

Procedure

The ceria were transferred to a slender-trap-shaped quartz reactor as described by Andreev and Selwood (*8*) with a modification described elsewhere (*4c*). This reactor can be inserted in the ESR cavity, connected to a vacuum line, and evacuated while still inserted in the cavity. Gases can also be supplied to or pumped from the sample while the reactor is in the cavity without removing it from the line. In most experiments precautions were taken to prevent contact between ceria and grease vapour (Westeff greaseless stopcocks were used). However, this procedure was seen to be unnecessary, the same results being obtained from the stopcocks and joints lubricated with Apiezon L grease when the sample was not protected by a liquid-nitrogen-cooled trap. Some of the runs were carried out in an ESR tube (3 mm i.d.) connected to a vacuum line by an O-ring connector. Measurements up to a temperature of 298° were carried out with a V-4540 Variable Temperature Controller. Outgassings and pretreatments at high temperatures were performed by replacing the cavity and the Dewar of the variable temperature controller by a furnace without breaking the vacuum. This was possible because the magnet could be slid away from the sample cavity on rails.

Unless otherwise stated all measurements were carried out at room temperature.

Results

CeO_2 (P.59)

A very diffuse (signal I) $g = 1.96$ was observed in the spectrum of the freshly prepared sample. The intensity remained unchanged after 4 days of continuous pumping at 10^{-5} Torr. Exposing this sample to dry air for several days, signal I almost disappeared, and no other signal was detectable; upon recommencement of pumping, however, the sample immediately gave a very weak signal (II), with a g value around that of a free electron. The exact value is not given here as the signal was observed in these runs only on the scope. As the pumping progressed, the peak intensity of signal II increased significantly, reaching a maximum and finally disappearing while the pumping was continued. Again, when the sample was removed from the vacuum line and exposed to dry air for several days the same cycle was observed. A somewhat similar phenomenon was observed with ultra high purity alumina (*9*).

Identical results were obtained with samples P.59 and P.69. It may be remarked here that when cerium(IV) oxide was obtained directly by the decomposition of cerium(III) nitrate 99.9999% even at 375°, a very significant signal with $g_{av} = 1.961$ was obtained.

Simultaneous Oxygen Sorption and ESR Studies

Signal II was obtained when oxygen was adsorbed on the oxide. The runs described in the present report were carried out at oxygen pressures around 300×10^{-3} Torr. Pumping desorbs the sorbed oxygen with simultaneous diminishing of the peak intensity of signal II, which finally disappears. With the sorption of oxygen, signal II is enhanced at the expense of the diffuse signal I, while as a result of evacuation, signal I is restored and signal II diminishes. Such cycles of sorption and desorption always yield the same result.

The Effect of Oxygen Pressure on Signal II

The peak intensity of this signal obtained at oxygen pressures around 300×10^{-3} Torr ($g = 2.02$) showed a tendency to split (Fig. 1). The peak-to-peak width was 34 G. This signal is reduced to a single broad and unresolved line with increase of oxygen pressure to 1–2 Torr (Fig. 2). At oxygen pressures higher than 10 Torr the signal becomes so diffuse as to be hardly detectable. The effect was reversible, i.e., when oxygen is pumped off, signal II becomes pronounced as displayed on the scope. The signal splits at low oxygen pressures (Fig. 3) having $g_{\perp} = 2.0137$, $g_{\parallel} = 2.0312$. This signal disappears when oxygen is evacuated.

Discussion

The quadrivalent cerium ion has the electronic configuration Xe $4f^0 5d^0 6s^0$. This configuration does not suggest likelihood of the obtaining of an ESR signal. On the other hand, compounds of trivalent cerium are expected to show absorptions in the ESR spectrum (Ce^{3+} $4f^1\,{}^2F_{5/2}$). However, in polycrystalline trivalent cerium compounds a signal

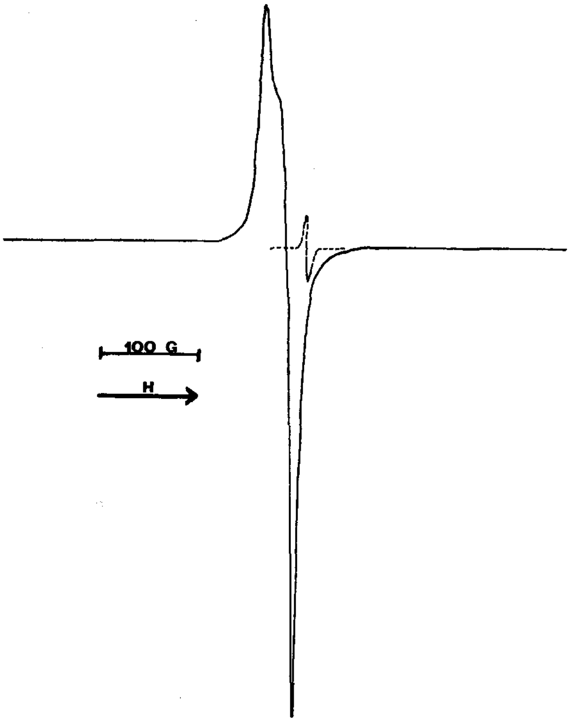

FIG. 1. Electron Spin Resonance Signal obtained from CeO_2 (P.59). Oxygen pressure 270 × 10^{-3} Torr. $g_{av} = 2.02$. The broken line is the spectrum for DPPH.

is not obtained because of the dipolar effects and exchange interaction. This effect of the interaction can be overcome by the "dilution" of these dipoles in matrices of other salts. However, because of the fast spin lattice relaxation, a signal can be observed only at temperatures less than 20°K (*10*). ESR measurements were reported on trivalent cerium in various single crystals (*5c*) at low temperature, and no signal of the trivalent cerium were observed at higher temperatures, according to these reports.

Cerium is an oxygen-deficient *n*-type semiconductor (CeO_{2-x}). There are several theories concerning the structure of this nonstoichiometric oxide (*2*) based mostly on electrical conductivity measurements. The two prevailing opinions (*11*) indicate that the cerium in nonstoichiometric ceria is not present in the trivalent state. It is suggested here that signal I ($g_{av} = 1.96$) may be ascribed to the quasi-free electron (e') as described in the equation

$$CeO_2 = Ce_i + 4e' + O_2(g), \qquad (1)$$

where Ce_i is an interstitial quadrivalent cerium ion.

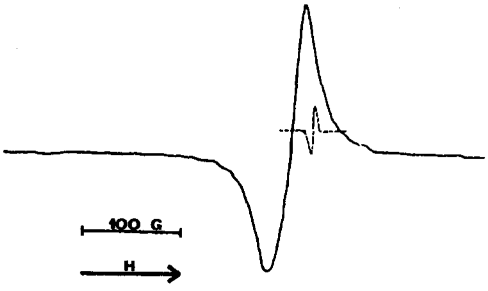

FIG. 2. Electron Spin Resonance Signal obtained from CeO_2 (P.59). Oxygen pressure 2 Torr. $g_{av} = 2.02$. The broken line is the spectrum for DPPH.

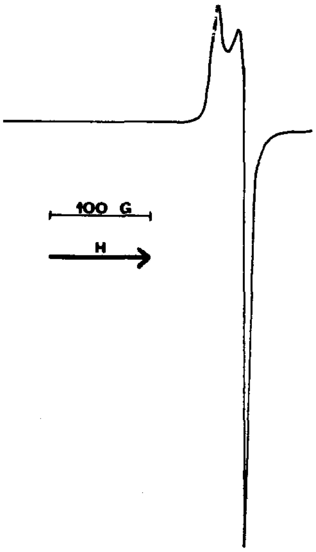

FIG. 3. Electron Spin Resonance Signal obtained from CeO_2 (P.59). Oxygen pressure 65 × 10^{-3} Torr. $g_{\parallel} = 2.0312$, $g_{\perp} = 2.0137$.

The recent suggestion (*4b*) that signal I originates in trivalent cerium ions in CeO_{2-x} seems unlikely for the following reasons: (a) The g of trivalent cerium differs from the value obtained for signal I reported here and elsewhere (*4b*). (b) The integrated intensity of signal I decreases simultaneously with the sorption of oxygen while the signal II increases. However, signal I is restored easily by pumping at room temperature while signal II diminishes. Oxidation and reduction of cerium are hardly likely to take place under the conditions described above. It may thus be suggested that the decrease in intensity of signal I is not caused by oxidation of a lower-valent cerium ion and hence that signal I is not due to trivalent cerium. The decrease in signal I described below (2) is caused by the depletion of electron concentration.

The asymmetric signal $g_{\parallel} = 2.0312$, $g_{\perp} = 2.0137$ is ascribed to O_2^- formed on the surface (*13*), and was not obtained after preparation of CeO_2 (P.59) and

CeO_2 (P.69). After exposure to air for several days of this sample, no signal was observed when the spectrum was taken on the sample right from the storing vial, but was observed after pumping, when it eventually disappeared. In the run where oxygen was applied to the sample, the signal showed up as oxygen was sorbed, reached a maximum and then broadened until it could not be observed at high pressures. Pumping this sample showed identical behaviour to the sample stored in air. It is suggested that the O_2^- ion is formed on the surface according to

$$O_2(g) + e' = O_2^-(ads). \qquad (2)$$

The adsorption is reversible. The formation of O_2^- suggests a reduction in the concentration of conduction electrons and hence a lowering in the electrical conductivity of the ceria. A qualitative indication of the change in the conductivity was shown by the change in the cavity Q by sorption and desorption of oxygen at room temperature, which also indirectly supports our conclusion that signal I cannot be ascribed to trivalent cerium ions.

It may also be mentioned here that signal II does not originate from gaseous molecular oxygen (*14*).

The broadening of signal II at higher oxygen pressures may be ascribed to a fast exchange interaction

$$O_2^-(ads) + O_2(g) = O_2(g) + O_2^-(ads). \qquad (3)$$

Acknowledgments

The authors wish to thank L. Webber (University of California, Santa Barbara), Dr. I. Mayer and I. Felner (The Hebrew University of Jerusalem) for X-ray analyses. Some of the ESR runs at various microwave powers were carried out by Miss Nurit Kaufherr.

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