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Absorption and Desorption Behavior of Unstable Lattice Oxygen in Praseodymium Oxide

Catalytic reactivities of the lattice oxygen of metal oxides in the oxidation of olefins or in other oxidation reactions have been reported by many investigators (*1*). In connection with this, some rare earth oxides of nonstoichiometric composition, e.g., praseodymium oxide and terbium oxide, sometimes showed higher catalytic activity than the other rare earth sesquioxides in the catalytic oxidation of nitric oxide (*2*) or butane (*3*).

The unstable lattice oxygen of praseodymium oxide was detected quantitatively by using a temperature-programmed desorption (TPD) method, and the lattice oxygen was found to react with nitric oxide (*2*) and carbon monoxide (*4–6*) to form nitrogen dioxide and carbon dioxide, respectively. Concerning the thermal behavior of the lattice oxygen in praseodymium oxide, many thermodynamic studies have been made (*7–10*); however, few kinetic data for the absorption and desorption of lattice oxygen have been reported. In a previous paper (*5*), the authors found five different TPD oxygen peaks [α(~340°C), α'(~380°C), β(~400°C), γ(440°C), and δ(500°C)] from the praseodymium oxide, and investigated the thermal behavior of the β, γ, and δ peak oxygens as functions of oxygen absorption temperature, pressure, and time. Moreover, only the β peak oxygen was shown to react with nitric oxide (*4*) and carbon monoxide (*5*) at 300°C.

In the present work, the thermal behavior of the lattice oxygen of α' (or α and β) peak oxygen in praseodymium oxide in the composition range $PrO_{1.83}$–PrO_2 was examined by TPD and X-ray diffractometry.

Praseodymium oxide was prepared by calcining an oxalate in a stream of air at 950°C for 6 h. This oxide was identified by X-ray diffraction analysis as a face-centered cubic $PrO_{1.83}$. The purity of the oxide was higher than 99.9%. The surface area determined by the BET method was 2.3 m^2 g^{-1} using nitrogen adsorption at 77 K. Highly pure oxygen from a commercial cylinder was purified by bulb-to-bulb distillation with liquid nitrogen coolant.

The TPD apparatus was a conventional one capable of evacuation to 1×10^{-5} Torr (1 Torr = 133.33 N m^{-2}) by an oil diffusion pump (*4*). The usual procedure for TPD was as follows: (1) placing 0.014 g of $PrO_{1.83}$ in the TPD cell, (2) heating the cell at 750°C for 1 h under vacuum, (3) cooling to a desired temperature, (4) introducing oxygen into the cell, (5) allowing the cell to stand for a desired time, (6) pumping off the gaseous phase at the same temperature, (7) cooling the cell to 25°C, (8) heating the cell at a rate of 20°C min^{-1} under vacuum; the pressure change due to desorption from the oxide was followed with a highly sensitive pirani gauge (Dan Kagaku Ltd., PS-12, 10^{-4}–10 Torr range). The desorbed gas was also analyzed with a quadrupole mass filter attached to the TPD apparatus. X-ray diffractometry was carried out with a powder method in atmosphere at room temperature using Cu$K\alpha$ as an X-ray source (30 kV, 40 mA). The oxygen uptake of the oxide in atmosphere was negligible in the X-ray analysis within 3 h after removal of the oxide sample from the TPD cell.

Figure 1 shows the TPD spectra of oxygen from praseodymium oxide treated with oxygen (heated in oxygen; see above) at various temperatures in 400 Torr of O_2 for 1

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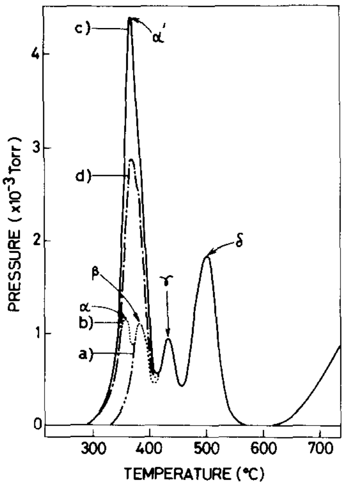

Fig. 1. TPD spectra of oxygen from praseodymium oxide oxygen-treated in 400 Torr of O_2 for 1 h at various temperatures: (a) 320°C, (b) 304°C, (c) 300°C, (d) 200°C.

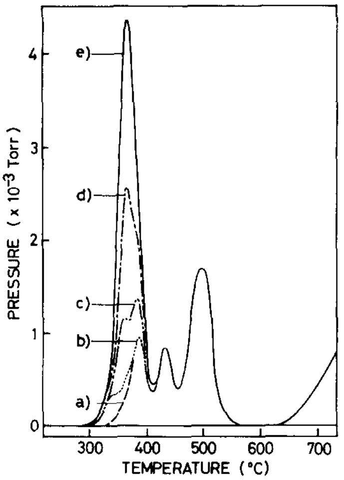

Fig. 2. TPD spectra of oxygen from praseodymium oxide oxygen-treated at 300°C in 400 Torr of O_2 for various times: (a) 30 s, (b) 1 min, (c) 2 min, (d) 15 min, (e) 1 h.

h. Spectrum a, obtained from the sample treated with oxygen at 320°C, gave peaks β, γ, and δ. When praseodymium oxide was treated with oxygen at temperatures between 302 and 308°C, the α peak appeared around 360°C. When it was treated at temperatures lower than 300°C, however, a large α' peak appeared around 380°C in which both α and β peaks were included. In the case in which the oxide was oxygen-treated at a temperature lower than 200°C, the intensity of the α' peak was much weaker than that of the oxide treated at 300°C. Virgin praseodymium oxide prepared by calcining the oxalate in atmosphere at 950°C for 6 h and cooling to room temperature gave only β, γ, and δ peaks on the TPD spectrum. Praseodymium oxide prepared under similar conditions, but calcined in 1 atm of O_2 instead of atmosphere, also gave the same TPD spectrum with β, γ, and δ peaks. Either the α or the α' peak appeared after evacuation of the sample at 750°C (procedure 2) before the oxygen-absorption treatments (procedures 3–7). Then all of the desorbed gas followed on the TPD spectra was assigned as oxygen by mass spectrometry.

Figure 2 shows the influence of oxygen treatment time on TPD spectra, in which 400 Torr of oxygen was introduced at 300°C. The intensities of the β, γ, and δ oxygen peaks were saturated within 30 s after introducing oxygen into the cell. The intensity of the α' peak increased rather slowly with an increase in the pressure of oxygen introduced, and saturated after ca. 1 h. Figure 3 shows the effect of oxygen

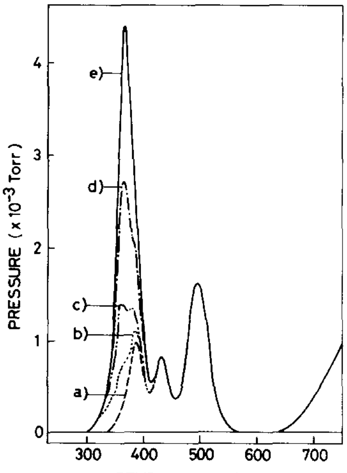

Fig. 3. TPD spectra of oxygen from praseodymium oxide oxygen-treated at 300°C for 1 h in various O_2 pressures: (a) 50 Torr, (b) 250 Torr, (c) 280 Torr, (d) 290 Torr, (e) 400 Torr.

pressure on features of TPD spectra, in which the praseodymium oxide sample was treated with oxygen in various oxygen pressures at 300°C for 1 h. Quantitative relationships between oxygen pressure and amount of each TPD peak oxygen are shown in Fig. 4. The intensities of the γ and δ oxygen peaks rapidly increased with an increase in the absorption pressure of oxygen and were almost saturated at higher than 50 Torr of absorption pressure (*4*), while the intensity of the α' oxygen peak was ultimately saturated at 400 Torr. One can see from this figure that the critical pressure for the formation of PrO_2 at 300°C is about 400 Torr. From the desorption spectrum, the activation energies of the desorption of each peak oxygens could be calculated by the method proposed by Cvetanović and Amenomiya (*11*). Those values for the α', γ, and δ peak oxygens of the praseodymium oxide were estimated to be 33, 43 (*4*), and 43 (*4*) kcal mol^{-1}, respectively. As has been revealed in a previous paper (*5*), the β peak oxygen is catalytically active for the oxidation of carbon monoxide; this α' peak oxygen may also be catalytically active for the oxidation of carbon monoxide or other reactants.

Praseodymium oxides having β–δ peak oxygens and α'–δ peak oxygens are identified as $PrO_{1.83}$ (or, Pr_6O_{11}) and PrO_2, respectively (*4*). As shown in Figs. 5 and 6, the

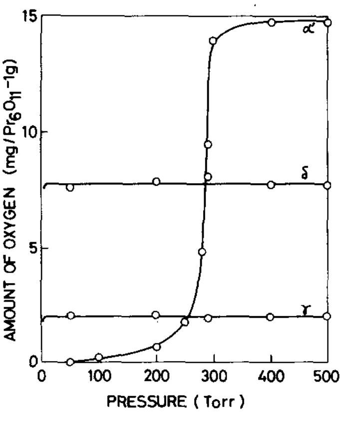

FIG. 4. Relationship between amount of each TPD peak oxygen absorbed in the praseodymium oxide and ambient oxygen pressure in the oxygen treatment at 300°C for 1 h.

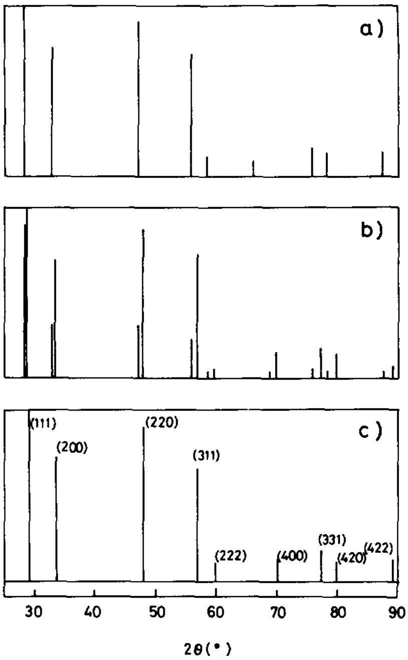

FIG. 5. X-ray diffraction spectra of some typical praseodymium oxides oxygen-treated in 400 Torr of O_2 for 1 h at various temperatures: (a) 320°C, (b) 308°C, (c) 300°C. The oxides in (a), (b), and (c) are identified as $PrO_{1.83}$ (or Pr_6O_{11}), $PrO_{1.83}$ + PrO_{2-x} ($x \approx 0$), and PrO_2, respectively.

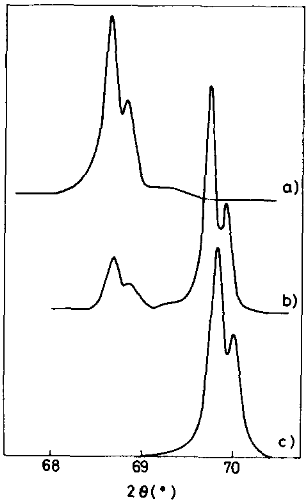

FIG. 6. X-ray diffraction spectra from the (400) plane of fcc praseodymium oxides oxygen-treated in 400 Torr of O_2 for 1 h at various temperatures: (a) 320°C, (b) 308°C, (c) 300°C.

oxide with α, β, γ, and δ peak oxygens can be identified as a mixture of $PrO_{1.83}$ and PrO_{2-x} ($x \approx 0$). Siegraff and Erying (*12*) obtained two crystalline oxide phases, Pr_6O_{11} and PrO_2, even when they oxidized Pr_6O_{11} at 350°C under an oxygen pressure of 4.25 atm. It is worth noting in this study that PrO_2 could be formed when Pr_6O_{11} was heated under 400 Torr of O_2 at 250–300°C after evacuation of the oxide at 750°C for 1 h. If the evacuation treatment at 750°C was not performed, PrO_2 was not formed even when the oxide was oxygen-treated under the same conditions (P_{O_2} = 400 Torr, 250–300°C, for 1 h). Evacuation at a high temperature promotes oxygen uptake into the lattice. The reason for this phenomenon is now under investigation.

The results obtained in this work can be summarized as follows.

(1) PrO_2 could easily be formed when $PrO_{1.83}$ (viz., Pr_6O_{11}) is heated in 400 Torr of O_2 at 250–300°C after evacuation of the oxide at 750°C for 1 h. If the evacuation treatment at 750°C is not performed, no PrO_2 is formed even if the oxide is heated in 400 Torr of O_2 at temperatures between 250 and 300°C.

(2) The critical pressure for the formation of PrO_2 at 300°C is about 400 Torr.

(3) A mixed oxide of $PrO_{1.83}$ and PrO_{2-x} ($x \approx 0$) is formed when praseodymium oxide is heated in 400 Torr of O_2 at temperatures between 302 and 308°C. This oxide gives two peaks, α (320–340°C) and β (~390°C), on a TPD spectrum below 410°C.

(4) The α′ peak oxygen in PrO_2 may be catalytically active for the oxidation of carbon monoxide and other reactants; however, a high oxygen partial pressure may be needed to prevent reduction of the oxide during the oxidation reactions.

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