Oxidation and Reduction of Praseodymium Oxides at Low Temperatures

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The praseodymium oxides form a homologous series of intermediate phases with formula Pr_nO_{2n-2} ($n = 4,7,9-12$), based on ordering of the oxygen vacancies in oxygen-deficient fluorite structure at temperatures below 773 K [1–3]. The phase transition reactions between these phases have been extensively studied by Eyring *et al.* [4–6]. However, detailed studies at temperatures below 523 K have not been reported. Therefore, we will describe in this communication the characteristic features for the oxidation–reduction of praseodymium oxides observed at low temperatures.

Experimental

The praseodymium oxide used was a reagent-grade powder (purity > 99.9%) obtained from Asahi Chemical Industry Co. The BET surface area of the sample was 11.9 $m^2 g^{-1}$. Kinetic measurements for the oxidation and reduction of praseodymium oxides with O_2 and CO, respectively, were carried out in a conventional gas-circulation apparatus of *ca.* 380 ml. During the reduction with CO, the CO_2 formed was always condensed in a trap which had been placed in the gas-circulation line and cooled at 77 K. The changes in the O/Pr ratio with time were calculated on the basis of the quantity of O_2 (oxidation) or of CO (reduction) consumed with the progress of the reactions. The method for the determination of the initial O/Pr ratios was described elsewhere [7]. The experimental error for the O/Pr ratios determined in this work was ±0.005.

Results and Discussion

Figure 1 shows the kinetic curves of oxidation of PrO_x at different temperatures under oxygen pressure of 20.6–1.3 kPa. The kinetic curves show several breaks at the O/Pr ratios which correspond to the intermediate phases of $\iota(Pr_7O_{12}, x = 1.714)$, $\zeta(Pr_9O_{16}, x = 1.778)$, $\epsilon(Pr_{10}O_{18}, x = 1.800)$, and $\beta(Pr_{12}O_{22}, x = 1.833)$. Moreover, the kinetic curves show that the oxidation proceeds stepwise through these phases as $\iota \rightarrow \zeta \rightarrow \epsilon \rightarrow \beta$. The kinetic curve for 393 K indicates the steps at ratios of O/Pr around 1.87–1.88 and 1.91.

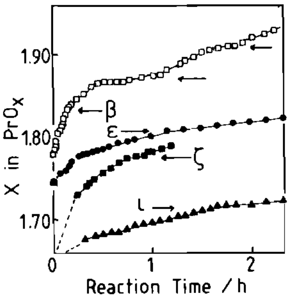

Fig. 1. Kinetic curves of oxidation of PrO_x at different temperatures: ▲; 323 K, ■; 353 K, ●; 373 K, □; 393 K.

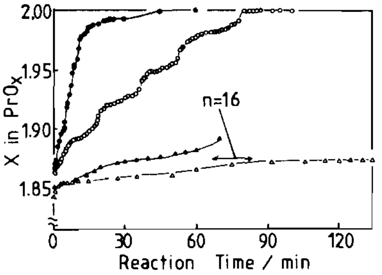

Fig. 2. Kinetic curves of oxidation of PrO_x at 513 K at different oxygen pressures. Oxygen pressures: △; 3.5 kPa, ▲; 5.1 kPa, ○; 13.3 kPa, ●; 47.9 kPa.

Figure 2 shows the oxidation curves obtained at 513 K under different pressures of oxygen. The curves clearly indicate many breaks or steps. The oxidation above the composition of $PrO_{1.875}$ ($n = 16$) did not proceed when the oxygen pressure was lower than 4.0 kPa at 513 K. Moreover, at temperatures higher than 533 K, the oxidation never proceeded under oxygen pressure of 8.0 kPa. These observations strongly suggest the existence of the intermediate phase $Pr_{16}O_{30}$. Many breaks or steps are also seen on the kinetic curves for the reduction shown in Fig. 3. The steps at the composition of $PrO_{1.875}$ ($Pr_{16}O_{30}$), $PrO_{1.833}$ ($Pr_{12}O_{22}$), and $PrO_{1.800}$ ($Pr_{10}O_{18}$) can always be seen on the kinetic curves in both reduction and oxidation. However, for the oxygen composition above $PrO_{1.90}$, the oxygen composition for the steps observed on the kinetic curves were not always identical for each run.

Figure 4 shows the X-ray powder diffraction (Cu Kα) peaks in the range of diffraction angles (2θ) 86–90 and 75–80 degrees for the quenched specimen

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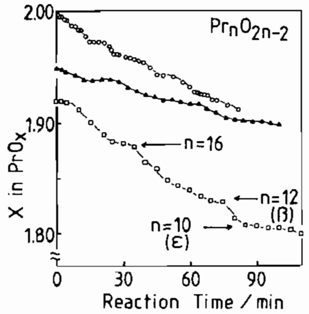

Fig. 3. Kinetic curves of reduction of PrO_x. CO pressures and temperatures: ○; 21.3 kPa, 513 K, ▲; 13.3 kPa, 493 K, □; 20.0 kPa, 513 K.

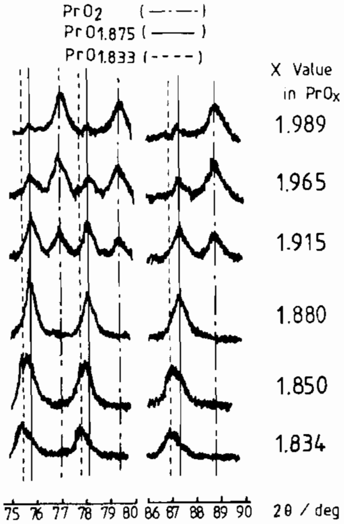

Fig. 4. X-ray diffraction spectra for PrO_x specimen with different *x*.

at the O/Pr compositions indicated in the figure. Since the diffraction positions for the specimen are close to each other, only the spectra at high diffraction angles were shown in the figure. The compositions of the specimen were adjusted at 513 K by reduction or oxidation and quenched to room temperature. There was no change in composition of the specimen during the quenching, as confirmed by measuring oxygen absorbed. The diffraction angles for PrO_2 and $PrO_{1.833}$ ($Pr_{12}O_{20}$, β-phase) from the ASTM card (No. 24-1006 and (6-329) are indicated by (—–—) and (-----), respectively, in the figure. The X-ray diffraction spectrum observed for the specimen $PrO_{1.834}$ can be ascribed to that of the β-phase stoichiometric oxide. The X-ray spectrum for the specimen $PrO_{1.880}$ clearly shows the existence of a single phase around this composition (probably $Pr_{16}O_{30}$). The intermediate composition $PrO_{1.850}$ must be the two phase mixtures of β and $Pr_{16}O_{30}$; in fact, the corresponding X-ray diffraction spectrum for the specimen $PrO_{1.850}$ can be explained in terms of the overlap of the spectra for the latter two phases. The spectra observed for $PrO_{1.915}$, $PrO_{1.965}$, and $PrO_{1.989}$ show only the diffraction peaks of $Pr_{16}O_{30}$ and PrO_2. These observations indicate that the intermediate compositions between $PrO_{1.880}$ and PrO_2 are the mixtures of $Pr_{16}O_{30}$ and PrO_2.

The observation of the steps and breaks on the kinetic curves for the oxygen compositions above $Pr_{16}O_{30}$ can not be explained by the idea that the reactions proceed stepwise through the stoichiometric phases (Pr_nO_{2n-2}) with $n > 16$, because the X-ray analysis indicated that there are no single phase oxides between the compositions $Pr_{16}O_{30}$ and PrO_2. This observation may be interpreted by the concept of phase-transition of domains between $Pr_{16}O_{30}$ and PrO_2 exhibiting hysteresis in their phase transition [8]. The completion of the phase transition in a domain may stimulate the successive transition of nearest-neighbor domains. Thus, the kinetic curves of oxidation for the composition greater than $Pr_{16}O_{30}$ would show several sigmoid curves, according to the initiation and the aided transition of the domains. Further studies are definitely needed to support the explanation described above.

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