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Effects of Additives on the Reduction and Oxidation of Terbium Oxides

Catalytic oxidations of hydrocarbons or the other catalytic oxidation reactions are generally believed to proceed via the reduction and oxidation cycles of catalysts (redox mechanism). The catalytic activities of the oxides of Ce, Pr, and Tb in the oxidations of hydrogen, hydrocarbons, or NO are quite high compared to those of the other rare earth metal oxides (*1*). This can be ascribed to the nature of the former three oxides that the $Ln^{3+} \rightleftarrows Ln^{4+}$ interconversion occurs readily. The rapid diffusion of oxygen in the bulk is also responsible for the high catalytic activities of Pr- and Tb oxides (*1–3*). Takasu *et al.* (*3*) investigated thermal behavior and catalytic reactivity of the latice oxygen atoms in terbium oxides by temperature-programmed desorption (TPD) and ^{18}O-tracer techniques. They clarified that the lattice oxygen atoms in $TbO_{1.81}$ participated catalytically in the oxidation of CO. Therefore, the enhancement in the kinetic behavior of lattice oxygen atoms results in improvement of the catalytic activity of terbium oxide. It may be expected that some solid additives would enhance the kinetics of the lattice oxygen atoms. Thus, in the present study, we describe the effect of solid additives on the kinetic behavior of lattice oxygen atoms of terbium oxides, i.e., the effect on the rates of reduction and oxidation of the oxides. The effect of additives may be either favorable or deleterious.

Thermodynamic studies on the TbO_x–O_2 systems ($1.50 < x < 2.00$) have been made by Eyring *et al.* (*4, 5*). They have demonstrated the temperature–composition projection of the TbO_x–O_2 phase diagram (*4, 5*). The Tb–O system at oxygen pressures below 1 atm has three phases, $TbO_{1.5+x}(\phi)$, $TbO_{1.74}(\iota)$, and $TbO_{1.818}(\delta)$ (*4, 5*).

The terbium oxide (Tb_4O_7) used was a reagent grade power (purity > 99.9%) obtained from Soekawa Chemical Company. The BET surface area was 19.2 $m^2\ g^{-1}$. The samples with solid additives were prepared as follows: the terbium oxide was immersed in aqueous solutions of nitrates, chlorides, or ammonium salts of the metal elements of the additives. Then, the samples were calcined at 873 K in a flow of oxygen. After this treatment, the additives may be assumed to become their stable oxides, except for Pt and Ag which are metallic states. The weight percentage of the additives was adjusted to 2.0 when they were in metallic state.

The procedure of the TPD measurement was as follows. (i) The samples (40 mg) in the TPD cell of 35 cm^3 volume, were treated in an oxygen atmosphere (12 kPa) for 60 min at 873 K using a closed gas circulation system and degassed for 90 min at the same temperature. (ii) Oxygen (12 kPa) was readmitted to the system and the gas–solid equilibrium was achieved at 573 K. The composition of the terbium oxide without additives was determined as $TbO_{1.82}$ by the method described later. (iii) After cooling the cell to 298 K, the gaseous phase was pumped out. (iv) The temperature of the sample was raised at a rate of 20 K min^{-1} under vacuum and the relative pressure of oxygen desorbed was measured by quadrupole mass spectrometer.

The apparatus employed for the measurement of oxygen absorption by TbO_x

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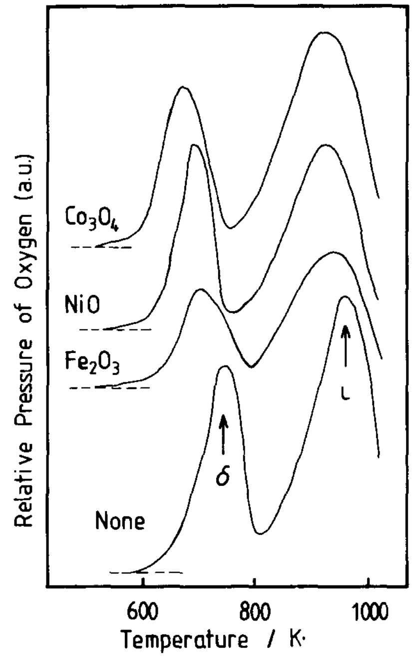

FIG. 1. Effect of additives on the TPD spectra of lattice oxygen of Tb oxides.

was a conventional closed system. The kinetic curves of the oxygen absorption were recorded by reading the pressure drop of the gas. Before the experiment, the samples (200 mg) in a U-shaped quarts reactor was treated in the same way as (i) for the TPD measurement. The composition of the sample without additives after this pretreatment was $TbO_{1.55\pm0.01}$.

The composition of TbO_x after the pretreatment was determined as follows. (i) Terbium oxide is readily reduced by hydrogen to a sesquioxide at 873 K, but never to a lower oxide at this temperature. Therefore, the initial x in TbO_x can be determined by measuring the final quantity of hydrogen consumed in the reduction at 873 K. (ii) According to Kordis and Eyring (*6*) terbium oxide is in δ-phase ($TbO_{1.818}$) at 573 and 673 K in an equilibrium pressure of oxygen above 7 kPa. Hence, the measurement of the quantity of oxygen transferred into the crystal or desorbed from the crystal makes it possible to estimate the initial O/Tb ratio of the sample. Both methods of (i) and (ii) gave good agreement in the experimental error of ±0.01 in x.

Effect of Additives on the Rate of Reduction

Figure 1 shows the TPD spectra for the terbium oxides with or without additives. The horizontal dotted-lines in Fig. 1 are the baselines for each spectrum. Two peaks observed for each sample can be ascribed to the desorption of the lattice oxygen atoms of δ- and ι-phases which can be seen in the phase diagram for TbO_x–O_2 system (*4*, *5*). The TPD peaks appeared at lower temperature for each spectrum were denoted as δ-peaks since they were ascribed to the desorption of the oxygen of δ-phase. The peaks due to the desorption of the oxygen of the ι-phase appeared at higher temperatures were denoted as ι-peaks. Figure 1 shows that the addition of Co, Ni, and Fe (all in the state of oxides) decreases the temperatures for the δ-peaks remarkably compared to the peak observed for the terbium oxide alone (the bottom spectrum). The shifts in the temperatures of the peak-maxima for δ-peaks were as large as 80 and 60 degrees for Co and Ni, respectively. The beginning temperatures for the desorption of oxygen giving δ-peaks are also shifted to lower temperatures for the samples containing Co, Ni, and Fe. These facts indicate that these additives enhance greatly the reduction (desorption) of the lattice oxygen.

Figure 2 shows the effects of additives of Cu, Ag, Pt, Pd, V, and Mo on the TPD spectra. Cu and Ag shifted the beginning temperatures and maxima of δ-peaks to lower temperatures as much as 40 and 35 degrees, respectively, compared to the position of the peak for the terbium oxide alone, but the shift was very small on the ι-peaks. In the case of the Pt-containing sample, the maxima of the two peaks (δ and ι) seem to be shifted to lower temperatures. However, the beginning temperature of the δ-peak is not lowered at all by addition of Pt, which suggests that Pt does not accelerate the reduction of lattice oxygens. The

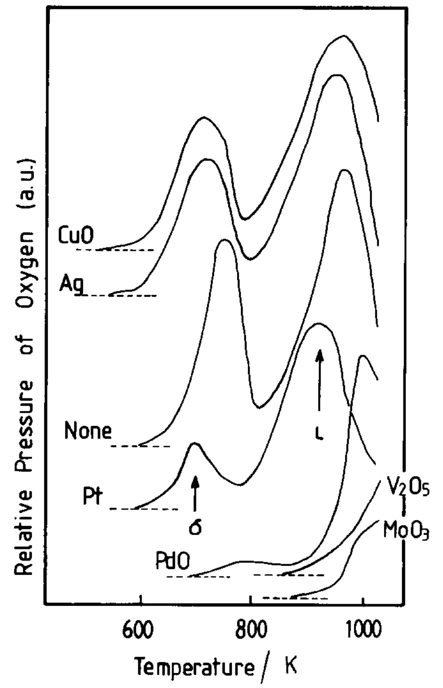

FIG. 2. Effect of additives on the TPD spectra of lattice oxygen of Tb oxides.

fact that the intensity of the δ-peak spectrum for the Pt-containing sample is unusually weaker than that for the sample without additives suggests that the quantity of lattice oxygens in the former sample has been missing considerably compared to the quantity in the latter. The TPD spectra for the samples with the additives of V, Mo, and Pd showed no δ-peak or only a very weak one (in the case of Pd at 793 K). If the oxygen desorption spectra appeared above 873 K for these samples are caused by the lattice oxygen of ι-phase, the additives should be considered as strong poisons for the reduction of ι-phase oxygen because the desorption of ι-phase oxygen for terbium oxide alone begins above 773 K.

Effect of Additives on the Rate of Oxidation

Figure 3 shows the effect of additives (2 wt%) on the kinetic curves of oxidation of TbO_x. The experiments were started at 473 K under the initial oxygen pressure of 11.6 kPa. The pressure of oxygen finally decreased to 10.2 kPa. The temperature of the reactor was raised finally to 573 K (to 673 K in the case of TbO_x only). The final value of x at 573 or 673 K were assumed to be 1.818 for all the samples in Fig. 3. X-Ray diffraction spectra observed for these samples supported that the composition of the host oxide was of $TbO_{1.818}$ according to ASTM cards No. 16-97 and 16-130. Thus, the x for each sample at time t can be calculated on the basis of the difference in the quantity of oxygen adsorbed between the final and at t. The kinetic curves in Fig. 3 show that the presence of Co, Ni, Fe, and Cu clearly enhances the rate of oxidation of TbO_x. In the case of Ag, the acceleration was observed at the early stage of the reaction. As described earlier (Figs. 1 and 2), these additives also enhanced the reduction of the crystal oxygens of TbO_x.

X-Ray diffraction spectra and XPS spectra for the samples containing Ni, Co, and Fe after the pretreatment showed that the oxidation states of the additives were NiO, Co_3O_4, and Fe_2O_3, respectively. The formation of mixed oxides such as perovskite-

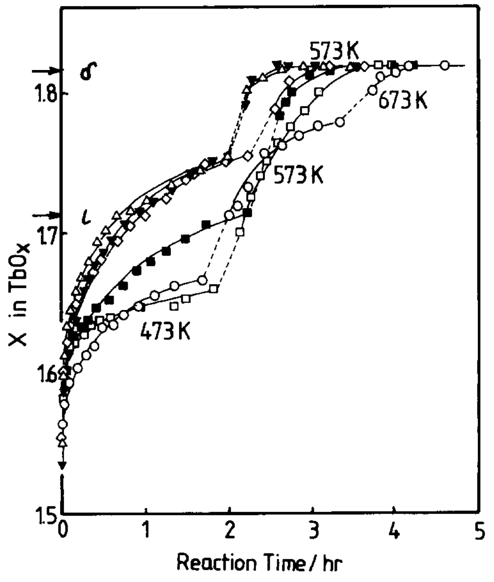

FIG. 3. Effects of additives on the kinetic curves of oxidation of TbO_x. Additives: (○) none, (△) Co_3O_4, (▼) NiO, (◇) Fe_2O_3, (■) CuO, (□) Ag.

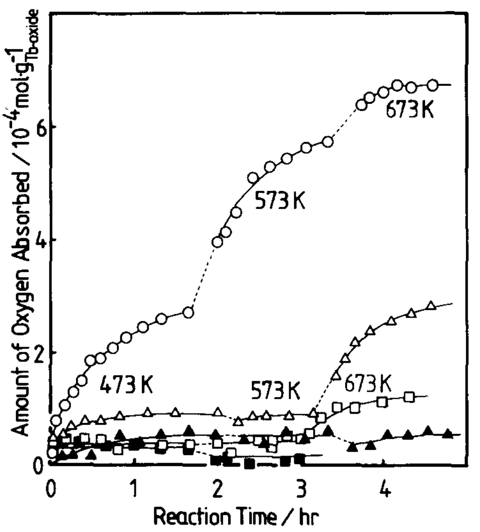

FIG. 4. Effects of additives on the kinetic curves of oxidation of TbO_x. Additives: (○) none, (△) Pt, (□) PdO, (▲) MoO_3, (■) V_2O_5.

type oxides was not observed. Therefore, the exact nature of the interaction between the additives and terbium oxide is not known at the moment. The favorable effects of the additives on reduction (Figs. 1 and 2) and oxidation (Fig. 3) can be ascribed to the increase in the number of active sites for the adsorption and desorption of oxygen. Alternatively, the active sites might decrease the activation energies in the transfer of oxygen atoms from the sites to the lattice of TbO_x and vice versa.

Figure 4 shows the effect of additives of Pt, Pd, Mo, and V on the kinetic curves of oxidation of the terbium oxides. Here the amount of oxygen absorbed instead of x in TbO_x is plotted against time. The kinetic curve for the terbium oxide alone is also shown in Fig. 4 for comparison. X-Ray diffraction spectra for the samples observed after the experiments shown in Fig. 4 indicated that the oxidation state of the host oxide was close to the composition of Tb_4O_7 ($TbO_{1.75}$) (referring to ASTM card No. 13-387) irrespective of the kind of additives. This indicates that the additives of Pt, Pd, Mo, and V inhibit the oxidation of the host oxide to $TbO_{1.818}$. Obviously the kinetic curves in Fig. 4 show that these additives strongly reduce the rate of oxidation of TbO_x compared to the kinetic curve for TbO_x without additives. As already described, the TPD spectra for the samples with Pt, Pd, Mo, or V (Fig. 3) showed only a weak or no δ-peaks. This can be ascribed to the strong retardation by these additives for oxidation of the host oxide to δ-phase ($TbO_{1.818}$) during the pretreatment of the samples in the atmosphere of oxygen. The retardation may be caused by the mixed oxide formed between the additive and terbium oxide. X-Ray diffraction spectra for the samples with Mo and V showed new diffraction peaks probably due to the compound oxides formed between TbO_x and Mo or V. Although we have not yet succeeded the identification of the products, the product oxides coating the surface of terbium oxides might inhibit further oxidation of terbium oxides. The retardation by Pt and Pd was not easy to be explained. No compound oxides between TbO_x and Pt or Pd were observed by X-ray diffraction analysis. Further studies on these points are definitely needed.

REFERENCES

1. Rosynek, M. P., *Catal. Rev.* **16,** 111 (1977).
2. Takasu, Y., Matsui, M., and Matsuda, Y., *J. Catal.* **76,** 61 (1982).
3. Takasu, Y., Yokoo, T., Matsui, M., Matsuda, Y., and Toyoshima, I., *J. Catal.* **77,** 485 (1982).
4. Hyde, B. G., and Eyring, L., "Rare Earth Research III" (L. Eyring, Ed.), p. 623. Gordon & Breach, New York, 1965.
5. Burnham, D. A., Eyring, L., and Kordis, J., *J. Phys. Chem.* **72,** 4424 (1968).
6. Kordis, J., and Eyring, L., *J. Phys. Chem.* **72,** 2044 (1968).

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