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Catalytic Reactivity of the Lattice Oxygen Atoms of Terbium Oxide

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Lattice oxygen atoms of terbium oxide have been revealed to play an important role in the oxidation of carbon monoxide by using temperature-programmed desorption (TPD) and ^{18}O-tracer techniques. TPD spectra of oxygen from TbO_x were observed as functions of oxygen absorption temperature, pressure, and time. Two main peaks [α(~500°C) and β(~730°C)] were observed in the TPD spectra of oxygen from the oxide between 25 and 820°C, while a small additional peak α' [~550°C] was also observed under certain conditions. The total amount of oxygen desorbed from $TbO_{1.81}$ between 25 and 820°C corresponded to 17% of oxygen atoms in the oxide. When the oxide was allowed an exposure to CO at 320°C, the α peak intensity was decreased by the formation of CO_2 from CO. However, when a gas mixture of CO and O_2 was introduced, the α peak oxygen atoms were not apparently removed by CO although CO_2 was formed. The most of carbon dioxide formed was composed of $C^{16}O_2$, when the terbium oxide was exposed to a mixture of CO and $^{18}O_2$ at 320°C. On the bases of these findings, it was concluded that the lattice oxygen atoms in $TbO_{1.81}$ participated catalytically in the oxidation of carbon monoxide.

INTRODUCTION

Many investigations have been reported on the reactivity and behavior of lattice oxygen atoms in metallic oxides to the catalytic oxidation of olefines or the other oxidation reactions (*1*, *2*). The main interest in these studies is whether the lattice oxygen atoms have better catalytic properties, activity, or selectivity than the oxygen adsorbed over the oxide surface. In previous papers (*3*, *4*), the authors have shown that lattice oxygen atoms of Pr_6O_{11} could be desorbed from the oxide by heating *in vacuo*, and a part of the desorbable lattice oxygen atoms was catalytically active in the oxidation of carbon monoxide. Terbium oxide is also one of the typical nonstoichiometric oxide in a series of the rare earth oxides and the oxide could be catalytically active to some oxidation reactions in case of Pr_6O_{11} (*3*, *5*) as well. Concerning the thermal behavior of the lattice oxygen atoms of terbium oxide, thermodynamic studies have been made by many authors (*6–8*), whereas, kinetic studies on the desorption and absorption of the lattice oxygen atoms have scarcely been performed in relation to their catalytic properties.

In the present study, the thermal behavior and catalytic reactivity of the lattice oxygen atoms in terbium oxide were investigated quantitatively by TPD and ^{18}O-tracer techniques, thermomicrogravimetry, X-ray photoelectron spectroscopy (XPS), and X-ray diffractometry, in order to know the catalytic behavior of lattice oxygen in the oxidation of carbon monoxide.

EXPERIMENTAL

Materials. The terbium oxide (99.9%, 3.2 $m^2\ g^{-1}$) was prepared by calcining the oxalate in a stream of air at 950°C for 6 hr. This oxide was identified as a face-centered cubic $TbO_{1.81}$ by X-ray diffractometry. The oxygen from a commercial cylinder was purified by bulb-to-bulb distillation with liquid nitrogen coolant. Carbon monoxide of a high purity (Takachiho Co.) and $^{18}O_2$ (British Oxygen Co., 99.1%) each in glass cylinders were used without further purification.

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The apparatus and the procedure. The TPD apparatus was a conventional one capable of evacuation to 10^{-5} Torr (1 Torr = 133.3 N m^{-2}) by a diffusion pump, and the schematic diagram of it was described in a previous paper (*4*). The TPD spectra were followed by the variation of pressure with a highly sensitive pirani gauge (Dan Kagaku, Ltd., Model PS-12, 10^{-4} ~10 Torr range) due to desorption of the gases from the sample. The usual procedure of the TPD was as follows: (i) putting 0.0080 g of $TbO_{1.81}$ in the TPD cell which has 24 cm^3 in volume, (ii) heating the cell at 850°C (±1°C) for 1 hr *in vacuo* (~10^{-5} Torr), (iii) cooling to a desired temperature, (iv) introducing of oxygen into the cell, (v) being allowed to stand for the desired time, (vi) pumping off the gaseous phase at the same temperature, (vii) cooling the cell to 25°C, (viii) heating the cell at a rate of 20°C min^{-1} *in vacuo*, and the pressure change due to desorption was recorded. In order to obtain quantitative TPD data, thermomicrogravimetry was adopted by using a handmade Gulbransen-type microbalance set in a high vacuum apparatus which is capable of evacuation to 10^{-5} Torr. The reaction of CO and $^{18}O_2$ over TbO_x was followed by a conventional closed circulating reactor with a volume of 117 cm^3. The XPS spectra were observed with a Vacuum Generator ESCA-3 spectrometer which has a facility of heating the powdered sample *in situ* up to 600°C. TbO_x samples with a desired composition were prepared by heating $TbO_{1.81}$ *in vacuo* in the analyzing chamber at various temperatures for 10 min. The source of the X ray was MgK_α or Al$K\alpha$. The X-ray diffractometry was carried out with a powder method in atmosphere using CuK_α as an X-ray source. The oxygen uptake of the oxide in atmosphere was negligible within 3 hr after the removal of the oxide from the TPD cell. The gas analysis was performed by a small quadrapole mass filter (Spectrum Scientific Co., SM 800) connected to the TPD cell through a variable leak valve.

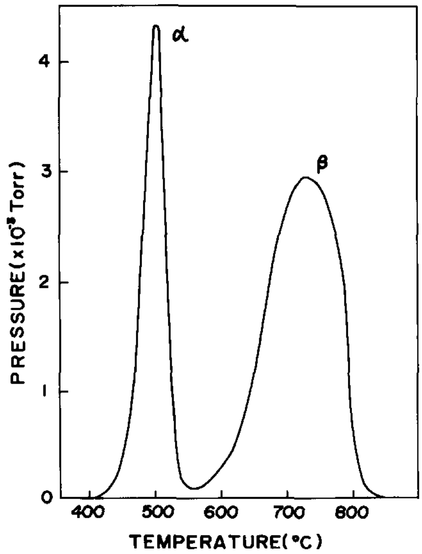

FIG. 1. The TPD spectrum of oxygen from $TbO_{1.81}$. The pretreatment condition was described in the text.

RESULTS AND DISCUSSION

1. TPD Spectra of TbO_x–O_2 System

Figure 1 shows a typical TPD spectrum of oxygen from $TbO_{1.81}$. The temperature, pressure, and time of oxygen absorption to this oxide were 300°C, 400 Torr, and 1 hr, respectively [TPD procedure (iii) ~ (v)]. Two peaks appeared in the spectrum were denoted as α[~500°C] and β[~730°C], respectively. The height of the peak become maximum at an absorption temperature of 300°C. At an oxygen treatment temperature lower than 300°C, the intensities of peaks both in α and in β were weaker than those obtained at higher temperatures of oxygen treatment. At the oxygen treatment temperature higher than 300°C, the peak intensity of α was gradually weakened with the increase of temperature of oxygen treatment, while that of β was almost kept constant up to 500°C. The virgin oxide which was not subjected to either evacuation at 850°C [TPD procedure (ii)] or oxygen absorption at a certain temperature [TPD procedure (iv)] gave almost the same spectrum as this. Then, all of the desorbed gas followed by the TPD spectra was confirmed as oxygen by the mass spectrometry.

Figure 2 shows the influence of oxygen treatment time on the amount of α and β peaks, in which 400 Torr of oxygen was admitted at 320°C for their oxygen treatments [TPD procedure (v) and (vii)]. The absorption rate of the oxygen into the oxide was very fast, i. e., the α and β oxygen peaks were almost saturated within 5 min, however, the absorption rate of the α peak oxygen was slower than that of β peak oxygen. The effect of absorption pressure on the amount of α and β peak oxygens was shown in Fig. 3 in which the sample was treated with oxygen at 320°C for 1 hr [TPD procedure (iv) ~ (vi)]. The absorption pressure of oxygen in the figure was the pressure just before the evacuation at 320°C after the oxygen absorption treatment. When the absorption pressure was 0.3~4 Torr, a new small peak α′ was observed at ~550°C in addition to the α and β peaks. The peak intensity of β oxygen was almost saturated even less than a few Torr of absorption pressure, while the intensity of the α peak increased rather slowly with rise in absorption pressure. The activation energies of oxygen desorption as α and β peaks were calculated by the method proposed by Cvetanović and Amenomiya (*4*, *9*), and the values were found to be 146 and 222 kJ mol^{-1}, respectively. That is, the energy of desorption for the α peak oxygen was much lower than that for the β peak oxygen. As described above, the α peak oxygen has quite different properties from those of the β peak oxygen as to absorption rate, equilibrium pressure, and desorption behavior.

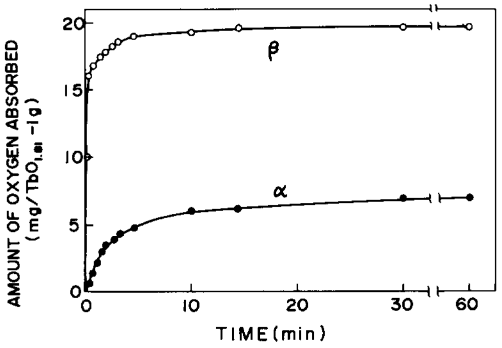

FIG. 2. Relation between the amount of each TPD peak oxygen absorbed in the terbium oxide and the time for absorption in 400 Torr oxygen at 320°C.

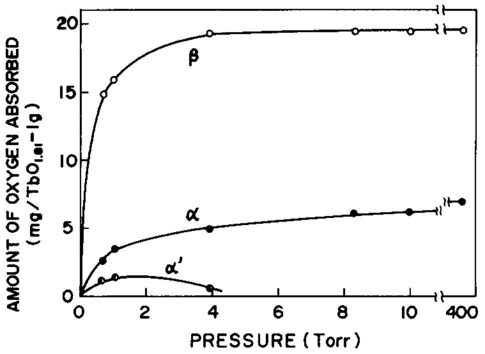

FIG. 3. Relation between the amount of each TPD peak oxygen absorbed in the terbium oxide and the oxygen pressure for absorption at 320°C for 1 hr.

2. *Structural Aspects of TbO_x*

Table 1 presents the lattice parameter and the x values in TbO_x. The sample (a) in the table was the virgin oxide, which was prepared by calcining the terbium oxalate in a stream of air at 950°C for 6 hr. Its lattice constant ($a_{fcc} = 5.280$) agreed well with that of the oxide which was oxygen treated in 400 Torr of oxygen at 300°C for 1 hr after evacuation at 850°C for 1 hr [TPD procedure (i) ~ (vii)], and corresponded to the value obtained by Guth and Eyring (*7*). That is, they reported that a quenched sample of a $TbO_{1.81}$ has a face centered cubic lattice with $a = 5.286 \pm 0.003$ at 25°C. Burham and co-workers (*8*) insisted, however, that a stable oxide in the composition range is triclinic $TbO_{1.818}$ and the lattice parameters are $a = b = c = 5.287 \pm 0.005$, $\alpha = \beta = 90.58°$ and $\gamma = 90.00°$. Furthermore, they indicated in the article that $TbO_{1.714}$ and $TbO_{1.50}$ could also be stable oxides having lattice parameters of 5.319 and 5.359 at 25°C, respectively. Similar values were also reported by Guth and Eyring (*7*), i.e., the oxides to show stability in such range of x in TbO_x were $TbO_{1.7}$ and $TbO_{1.50}$; more-

TABLE 1.

The Structure of Terbium Oxide Having Various Oxygen Peaks at 25°C

	Oxygen peaks found on the TPD spectrum	Lattice parameter by X-ray diffraction	Value of x in TbO_x calculated by gravimetry	Stable form reported by Guth and Eyring (7)
(a)	α and β	$a = 5.280$	1.81	$TbO_{1.81}(Tb_{11}O_{20})$
(b)	β	$a = 5.312$	1.72	$TbO_{1.71}(Tb_7O_{12})$
(c)	no peak	$a = 5.359$	1.46	$TbO_{1.50}(Tb_2O_3)$

over, Gruen and co-workers (*6*) found the lattice parameter of $TbO_{1.50}$ to be 5.359 ± 0.003. On the basis of the above arguments, we should identify the oxide having a lattice parameter $a_{fcc} = 5.280$ in the present experiment as $Tb_{1.81}$ (or, $Tb_{11}O_{20}$, although we had considered it as Tb_4O_7 according to the usually accepted formula for this oxide (*4, 5, 10, 11*). Then, from the phase diagram after Eyring (*12*), the TPD α peak corresponds to thermally induced conversion from the δ-TbO_x phase ($x = 1.818$) to the τ-phase ($x = 1.714$), and TPD β peak to the τ-phase to the ϕ-phase ($x = 1.500$) transition. The close agreement of the value of x determined from X-ray diffractometry and the microgravimetry means that most of the desorbed oxygen from the terbium oxide by heating *in vacuo* has originated from the lattice oxygen atoms in the oxide, however, the oxygen atoms existing in the vicinity of surface layers as lattice oxygen may be more sensitive and removable by the heat treatment of the oxides. Figure 4 shows the XPS spectra of $TbO_{1.81}$ and $TbO_{1.72}$ which were prepared by heat treatment at certain temperatures in the XPS chamber. The spectral features of $Tb3d_{5/2}$ from terbium oxide were scarcely affected by the temperature of the heat treatment, whereas, the spectral features of O_{1S} were strongly affected by these heat treatments. That is, the intensity of the peak having the higher binding energy for $TbO_{1.72}$ was much weaker than that for $TbO_{1.81}$. The ratios of peak intensities at ~531 to ~528 eV of $TbO_{1.81}$ and $TbO_{1.72}$ were 0.68 and 0.38, respectively. This suggests that there were two states of lattice oxygen, at least in the surface layers, and the weakly bounded one (~531 eV) was more easily desorbed by the heating. Since the total amount due to the α peak oxygen corresponds to about 5% of oxygen in $TbO_{1.81}$, the weakly bounded lattice oxygen in the surface layers of $TbO_{1.81}$ was more sensitive and easily removable by heat treatment *in vacuo* than that in the bulk.

3. *Reactivity of the Lattice Oxygen Atoms in $TbO_{1.81}$ with CO*

Figure 5 shows the TPD spectra of oxygen from the $TbO_{1.81}$ treated with 10 Torr of CO at 320°C after reduction. Carbon monoxide could react with α peak oxygen to

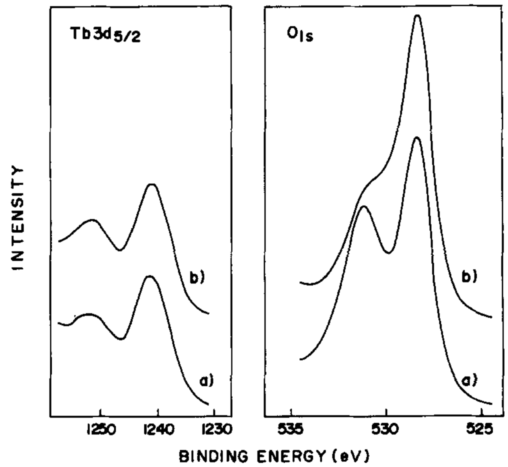

FIG. 4. XPS spectra of TbO_x with various oxygen peaks. The samples were prepared by heating $TbO_{1.81}$ *in vacuo* in the analyzing chamber at 350 and 520°C; the former is denoted (a) and the latter is denoted (b). The (a) and (b) were assigned to be $TbO_{1.81}$ and $TbO_{1.72}$, by the separate experiments (X-ray diffractometry), respectively.

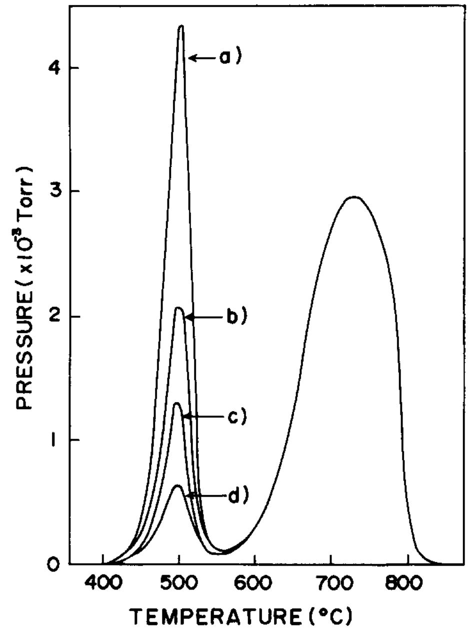

FIG. 5. The TPD spectra of oxygen from TbO$_x$ after the reaction of TbO$_{1.81}$ with 10 Torr CO at 300°C for various time. The reaction time: (a) 0 hr, (b) 1 hr, (c) 4 hr, (d) 6 hr.

form CO$_2$, however, it could not affect the β oxygen peak under this condition. It must be noted that CO did not successively reduce the oxide from the surface to the bulk, but initially reacted with the α peak lattice oxygen atoms. Figure 6 shows the TPD spectra of oxygen from the terbium oxide pretreated under the various conditions. Spectrum (a) was obtained from the oxide which has been treated at 320°C with 10 Torr O$_2$ for 1 hr [TPD procedure (iv)–(vi), this sample was denoted sample (*a*)]. Spectrum (b) was obtained after the exposure of sample (*a*) to 2 Torr CO at 320°C for 2 hr. Obviously, only the α peak oxygen was reduced by the carbon monoxide as in the cases shown in Fig. 5. However, when sample (*a*) was exposed to the gas mixture of CO and O$_2$ (CO, 2 Torr; O$_2$, 10 Torr) at 320°C for 2 hr, the feature of TPD spectrum [spectrum (c)] was almost the same as that of spectrum (a). This suggests that the amount of lattice oxygen atoms did not decrease by exposure to the gas mixture. After the introduction of the gas mixture (CO, 2 Torr; $^{18}O_2$, 10 Torr, in this case) into the cell (the closed circulating reactor, 117 cm^3 in volume, TbO$_{1.81}$, 0.0362 g), the change of composition of the gaseous phase was followed by mass spectrometry. This analysis revealed that the content of CO and $^{18}O_2$ decreased with time, while that of carbon dioxides ($C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$) increased. Figure 7 shows the composition of $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$ in the carbon dioxides during the reaction as well as the conversion of CO into carbon dioxides. As shown in the figure, the content of $C^{16}O_2$ was much higher than those of $C^{16}O^{18}O$ and $C^{18}O_2$. This suggests that some lattice oxygen atoms in TbO$_{1.81}$ takes part in the oxidation of the carbon monoxide as demonstrated by Keulks (*1*) for propylene

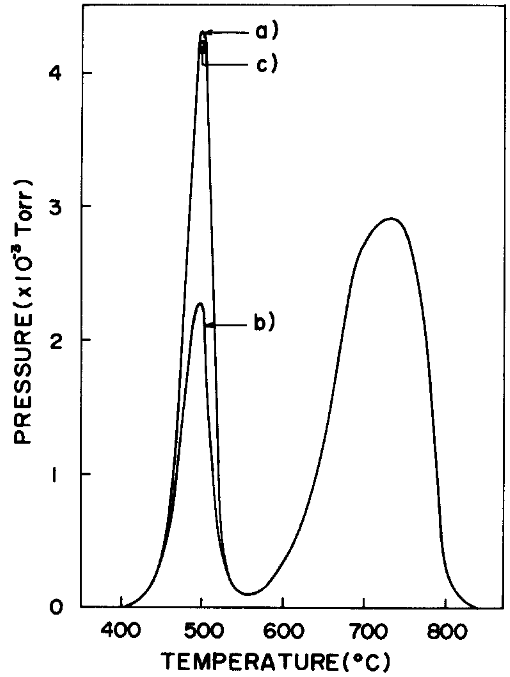

FIG. 6. TPD spectra of oxygen from terbium oxide. The pretreatments were as follows: (a) Oxygen treatment at 320°C with 10 Torr O$_2$ for 1 hr, followed by evacuation at the same temperature [this sample was denoted (*a*)]. (b) Sample (*a*) was exposed under 2 Torr CO at 320°C for 2 hr, and then evacuated at the same temperature. (c) Sample (*a*) was exposed under 2 Torr CO and 10 Torr O$_2$ at 320°C for 2 hr, and then evacuated at the same temperature.

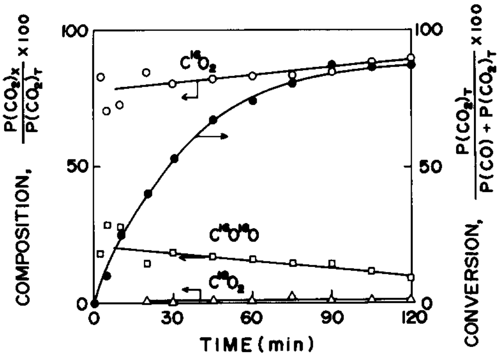

FIG. 7. Composition of the $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$ in the total carbon dioxides formed by the oxidation of CO with $^{18}O_2$ over $TbO_{1.81}$ at 320°C. P_{CO}, 2 Torr; $P_{^{18}O_2}$, 10 Torr; catalyst weight, 0.0362 g; volume of the reactor, 117 cm^3. Conversion of CO into carbon dioxides was also presented. $(CO_2)_x$, $C^{16}O_2$, $C^{16}O^{18}O$, or $C^{18}O_2$; $(CO_2)_t$, $C^{16}O_2$ + $C^{16}O^{18}O$ + $C^{18}O_2$.

oxidation over bismuth molybdate. In this case, the preadsorbed oxygen, even if it might exist, should be negligible, because the number of terbium ions on the top layer of the oxide surface corresponds to only about 10% of CO introduced. The reason why the content of $C^{16}O^{18}O$ was so low during the reaction must be due to fast migration of oxide ions in the oxide. The fast migration of oxide ions of the α and β peaks was confirmed by TPD and the mass spectrometry. That is, even after a labeling procedure of the α and β peak oxygen atoms with ^{18}O, only a few percent to the whole desorbed oxygens was found to be $^{16}O^{18}O$ and $^{18}O_2$ in each of the TPD oxygen peaks. The amount of the lattice oxide ions reacted with carbon monoxide after 2 hr corresponded to about 3.3% of the lattice oxide ions of the oxide, so that the amount of $C^{16}O^{18}O$ formed was much less than that of $C^{16}O_2$.

In conclusion, carbon monoxide was catalytically oxidized with the surface lattice oxygen atoms of $TbO_{1.81}$, probably a part of the α peak oxygen atoms, which was continuously supplied from the bulk. The oxygen incorporated into the terbium oxide from the gaseous phase migrated immediately into the bulk.

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