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CATALYTIC REACTIVITY OF THE LATTICE OXIDE IONS OF PRASEODYMIUM OXIDE

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Lattice oxide ions of praseodymium oxide, Pr_6O_{11} , have been revealed to play an important role in the oxidation of carbon monoxide using $^{18}O_2$ tracer and a TPD(temperature-programmed-desorption) techniques.

Participations of lattice oxide ions of oxide catalysts, such as bismuth-molybdate catalyst, in the oxidation of propylene have been reported by Keulks$^{1)}$, Moro-oka$^{2)}$, and other investigators. The main interest in such study is whether the lattice oxide ions show better catalytic properties, activity or selectivity, than the adsorbed oxygen on the oxide. In the previous paper$^{3)}$, the authors presented that a few percent of the lattice oxide ions of Pr_6O_{11} could be desorbed by heating the oxide in vacuo above ~590K, and the desorbable oxide ions could be removed with nitric oxide at 573K forming nitrogen dioxide. In the present letter, catalytic behavior of the lattice oxide ions have been presented using a TPD and $^{18}O_2$ tracer techniques in the oxidation of carbon monoxide as a fundamental investigation to develop a new oxidation catalyst.

Praseodymium oxide(99.9%) was prepared by calcining the oxalate in a stream of air at 1223K for 6h. This oxide was identified as Pr_6O_{11} by a X-ray diffractometry. The surface area was $2.3m^2g^{-1}$ by the BET method using nitrogen adsorption at 77K. 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%) in glass cylinders were used without further purification. The TPD apparatus was a conventional one$^{3)}$ capable of evacuation to $\sim 10^{-5}$ Torr(1 Torr $=133.3Nm^{-2}$) by a diffusion pump. The TPD spectra were obtained by following the variation of pressure with a highly sensitive pirani gauge due to desorption of the gases from the sample. 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.

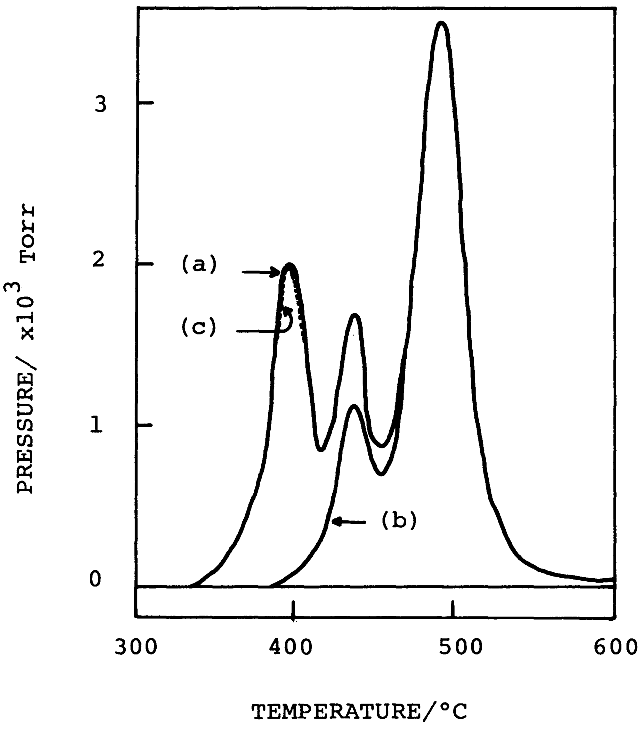

Fig.1. TPD spectra of oxygen from a praseodymium oxide.

The pre-treatments were as follows: (a): Oxygen treatment at 593K with 10 Torr of O_2 for 1h, followed by evacuation at the same temperature[This sample was denoted (a)]. The total amount of oxygen desorbed between 593 and 893K corresponds to 7.5% of oxide ions in the oxide; (b): Sample (a) was exposed under 2 Torr of CO at 593K for 6h, and then evacuated at the same temperature; (c): Sample (a) was exposed under 2 Torr of CO and 10 Torr of $^{18}O_2$ at 593K for 6h, and then evacuated at the same temperature.

Figure 1 shows the TPD spectra of oxygen from the praseodymium oxide pre-treated under various conditions. The spectrum (a) was obtained by the following procedure: (1) putting 0.0067g of Pr_6O_{11} in the TPD cell which has 24cm^3 in volume, (2) heating the cell at 1023K for 1h in vacuo, (3) cooling to 593K, (4) introducing 10 Torr of oxygen(O_2) into the cell, (5) being allow to stand for 1h, (6) pumping off the gaseous phase at 593K, (7) cooling the cell to 298K, (8) heating the cell at a rate of 20 Kmin^{-1} during evacuation, and the pressure change due to desorption of oxygen from the oxide was recorded. The oxide after the pre-treatment of the TPD procedure (7)[This sample was denoted sample (a)] was also identified as Pr_6O_{11} by the X-ray diffractometry. Each peaks found in these spectra were termed from the lower temperature β, γ, and δ according to the previous papers[3,4]. The total amount of oxygen from β, γ, and δ peaks corresponded to 7.5% of total oxide ions in Pr_6O_{11}. The sample (a) was exposed to 2 Torr of CO at 593K, and then evacuated the gaseous phase at the same temperature after 6h[spectrum (b)]. Obviously, β peak oxygen was reduced by the carbon monoxide. On the other hand, when a mix gas of CO and $^{18}O_2$(CO: 2.0 Torr, $^{18}O_2$: 10 Torr) was introduced into the TPD cell at 593K after the same pre-treatment as for (a), and then evacuated the gaseous phase at the same temperature after 6h[spectrum (c)], the spectrum feature was almost same as that of (a). According to the mass spectrometry during the TPD measurement[spectrum (c)], a few percent of $^{18}O^{16}O$ and $^{18}O_2$ was detected in the desorbed gases from the each TPD peaks; β, γ, and δ, while neither carbon monoxide nor carbon dioxide was found in the desorbed gases. Prior to the above TPD measurement, the change of composition of the gaseous phase after the introduction of the mix gas into the cell was followed by the mass spectrometry. This analysis showed that the content of CO and $^{18}O_2$ decreased with time, while that of carbon dioxide($C^{18}O^{16}O$ and $C^{16}O^{16}O$) increased. Figure 2 shows the composition of $C^{18}O^{16}O$ and $C^{16}O^{16}O$ in the carbon dioxide formed during the reaction. Obviously, the content of $C^{16}O^{16}O$ was much higher than that of $C^{18}O^{16}O$. About 70% of CO was oxidized to carbon dioxide at 6h; however, $C^{18}O^{18}O$ was not found in the gaseous phase. These findings for the composition of gaseous phase and the TPD analysis[Fig.1. (a) and (c)] should suggest that the carbon monoxide

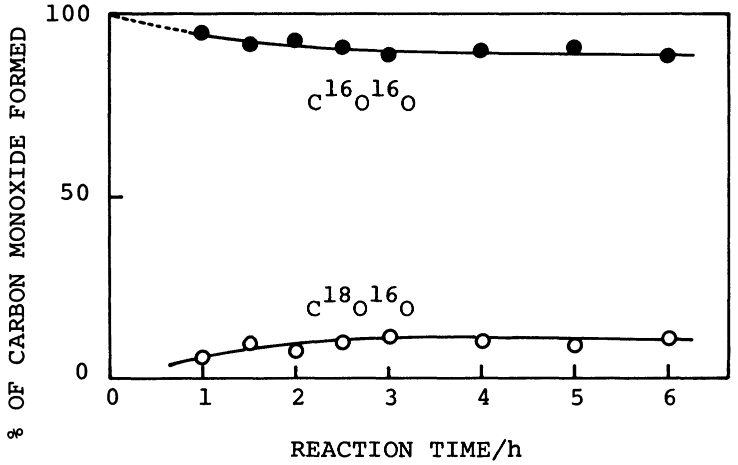

Fig.2. Composition of the $C^{18}O^{16}O$ and $C^{16}O^{16}O$ in the total carbon dioxide formed by the oxidation of CO with $^{18}O_2$ over Pr_6O_{11} at 593K. P_{CO} : 2.0 Torr; $P_{^{18}O_2}$: 10 Torr; Catalyst weight : 0.0067g; volume of the reaction cell : 24cm^3.

catalytically reacted with the lattice oxide ions of Pr_6O_{11} to form carbon dioxide. In this case, the preadsorbed oxygen, even if it might exist, should be negligible, because the number of the praseodymium ions on the top layer of the oxide corresponds to only about 6.7% of carbon monoxide introduced. The reason why the content of $C^{18}O^{16}O$ was so low during the reaction must be fast migration of oxide ions in the oxide. The fast migration of oxide ions of the β, γ, and δ peaks was confirmed by the TPD and the mass spectrometry. That is, even after a labeling procedure of the β, γ, and δ peak oxygens with ^{18}O, only a few percent to the whole desorbed oxygens was found to be $^{18}O^{16}O$ and $^{18}O_2$ in the each oxygen peaks. The amount of the lattice oxide ions reacted with carbon monoxide after 6h corresponded to about 4% of the lattice oxide ions of the oxide, so that the amount of $C^{18}O^{16}O$ formed was much less than that of $C^{16}O^{16}O$.

In conclusion, CO was catalytically oxidized with the surface lattice oxide ions of Pr_6O_{11}, probably a part of the lattice oxygen, which was continuously supplied from the bulk. The incorporated oxygen into the praseodymium oxide from the gaseous phase imediately migrated into the bulk.

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