JOURNAL OF CATALYSIS 76, 61–64 (1982)

The Catalytic Contribution of the Lattice Oxygen Atoms of Praseodymium Oxide to the Oxidation of Carbon Monoxide

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Received September 21, 1981; revised January 21, 1982

Temperature-programmed desorption (TPD) and ^{18}O-tracer techniques have been adopted to examine the contribution of the lattice oxygen atoms (oxide ions) of praseodymium oxide, Pr_6O_{11}, to the oxidation of carbon monoxide. The TPD measurements revealed that some of the lattice oxygen atoms could be removed (reduced) by CO forming CO_2; however, the oxygen vacancies formed by the reduction were continuously filled with oxide ions if oxygen were coexisted in the gaseous phase. Most of the carbon dioxide formed during the reaction of CO with $^{18}O_2$ over Pr_6O_{11} catalyst was composed of $C^{16}O^{16}O$. These results showed that the lattice oxygen atoms of the praseodymium oxide plays an important role in the catalytic oxidation of carbon monoxide.

INTRODUCTION

The lattice oxygen atoms (oxide ions) of bismuth–molybdate catalyst have been shown to participate in the oxidation of propylene by Keulks (*1*), Moro-oka *et al.* (*2*), and other investigators. If the lattice oxygen atoms had particular catalytic properties, it is worthwhile to seek and investigate other oxide catalysts whose lattice oxygen atoms participate in oxidation reactions.

In previous papers (*3, 4*), the authors indicated that a few percent of the lattice oxygen atoms of Pr_6O_{11} could be desorbed by heating it *in vacuo* above ca. 320°C, and the desorbable oxygen atoms could also be removed with nitric oxide at 300°C forming nitrogen dioxide. In the present study, the catalytic behavior of the lattice oxygen atoms of Pr_6O_{11} has been investigated using both TPD and ^{18}O-tracer techniques to the oxidation of carbon monoxide.

EXPERIMENTAL

Materials. The praseodymium oxide (99.9%) was prepared by calcining the oxalate in air at 950°C for 6 hr. This oxide was identified as Pr_6O_{11} by X-ray diffractometry (powder method, Cu$K\alpha$). The surface area was 2.3 $m^2\ g^{-1}$ by the BET method. The oxygen from a commercial cylinder was purified by bulb-to-bulb distillation with liquid nitrogen coolant. Highly pure carbon monoxide (Takachiho Chemical Co.) and $^{18}O_2$ (British Oxygen Co., 99.1%) each in a glass cylinder were used without further purification.

TPD apparatus and reactor. The TPD apparatus was a conventional one (*3*) capable of evacuation to $\sim 10^{-5}$ Torr (1 Torr = 133.3 N m^{-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 (24 cm^3 in volume) through a variable leak valve. The TPD cell also served as the reaction vessel.

RESULTS AND DISCUSSION

1. *TPD Spectra of Oxygen from Praseodymium Oxide*

The typical TPD spectra of oxygen from Pr_6O_{11} ($PrO_{1.83}$) which was pretreated under various conditions were shown in Fig. 1. Spectrum a was obtained by the following procedure: (i) putting 0.0067 g of Pr_6O_{11} in

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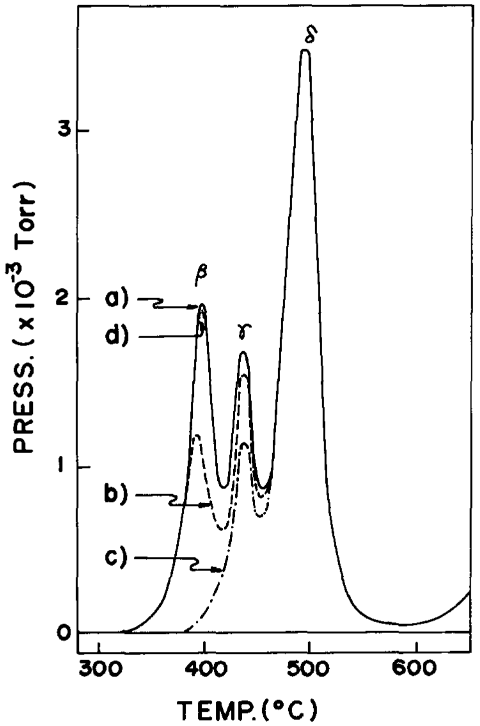

FIG. 1. TPD spectra of oxygen from Pr_6O_{11}. The pretreatments were as follows: (a) Oxygen treatment at 320°C with 10 Torr of O_2 for 1 hr, followed by evacuation at the same temperature [This sample was denoted (A).] The total amount of oxygen desorbed between 320 and 620°C corresponds to 7.5% of the oxygen atoms in the oxide. (b) and (c) Sample (A) was exposed under 2 Torr of CO at 320°C for 30 min and 6 hr, respectively, and then evacuated at the same temperature. (d) Sample (A) was exposed under 2 Torr of CO and 10 Torr of $^{18}O_2$ at 320°C for 6 hr, and then evacuated at the same temperature.

the TPD cell, (ii) heating the cell at 750°C for 1 hr *in vacuo,* (iii) cooling to 320°C, (iv) introducing 10 Torr of oxygen (O_2) into the cell, (v) being allowed to stand for 1 hr, (vi) pumping off the gaseous phase at 320°C, (vii) cooling the cell to 25°C, and (viii) heating the cell at a rate of 20°C min^{-1} during evacuation; the pressure change due to desorption of oxygen from the oxide was recorded. The peaks found in these spectra were termed from the lower temperature β, γ, and δ according to the previous paper (*3*). The total amount of oxygen from these peaks corresponded to 7.5% of the total oxygen atoms in Pr_6O_{11}. The oxide after pretreatment of TPD procedure (vii) was denoted sample (A). Curve a shows the TPD spectrum of this sample. Next sample (A) was exposed to 2 Torr of CO at 320°C, and then evacuated at the gaseous phase at the same temperature after 0.5 hr (spectrum b) or 6 hr (spectrum c). Obviously, β peak oxygen was gradually removed by exposure to carbon monoxide. On the other hand, when a mixture of CO (2 Torr) and O_2 (10 Torr) was introduced into the TPD cell at 320°C after the same pretreatment as for (A), and then evacuated at the gaseous phase at the same temperature after 6 hr (spectrum d), the spectrum gave almost the same features as that of a. While the TPD spectrum feature of d was practically the same as that of a, CO_2 was found to be produced during the exposure to CO and O_2. As previously presented [Ref. (*3*), Fig. 5], the TPD peak oxygens β, γ, and δ were mostly saturated in the presence of more than about 8(β), 3(γ), and 3(δ) Torr of oxygen in the gaseous phase, respectively.

2. Contribution of Lattice Oxygen Atoms of Pr_6O_{11} to the Oxidation of CO

In order to discover the role of the lattice oxygen atoms in Pr_6O_{11}, an ^{18}O-tracer technique was adopted for this system. Figure 2

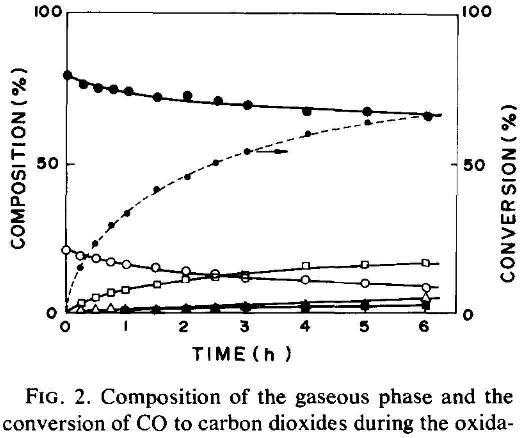

FIG. 2. Composition of the gaseous phase and the conversion of CO to carbon dioxides during the oxidation of CO with $^{18}O_2$ over Pr_6O_{11} at 320°C. P_{CO} = 2 Torr, $P_{^{18}O_2}$ = 10 Torr; ●, $^{18}O_2$; △, O_2; ○, CO; □, $C^{16}O^{16}O$; ■, $C^{18}O^{16}O$; ●, conversion; $P_{CO_2} \times 100/(P_{CO_2} + P_{CO})$.

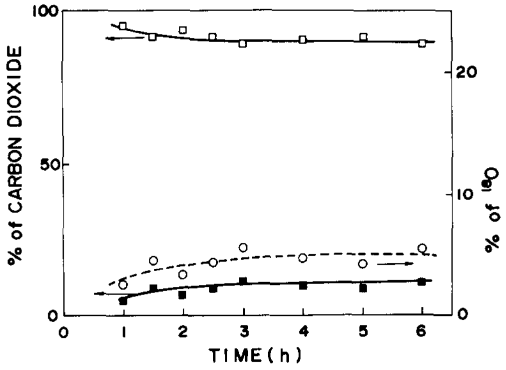

FIG. 3. Composition of carbon dioxides and the percentage of ^{18}O in the total oxygen of carbon dioxides during the oxidation of CO with $^{18}O_2$ at 320°C. P_{CO} = 2 Torr; $P_{^{18}O_2}$ = 10 Torr; □, $C^{16}O^{16}O$; ■; $C^{18}O^{16}O$, percentage of ^{18}O in the total oxygen of carbon dioxides.

shows the composition change of the gaseous phase and the conversion of CO to carbon dioxide in the oxidation of CO (2 Torr) with $^{18}O_2$ (10 Torr) over Pr_6O_{11} catalyst at 320°C. Evidently, most of the carbon dioxide formed was composed of $C^{16}O^{16}O$, with only a little of $C^{18}O^{16}O$. About 70% of CO was oxidized to carbon dioxides after 6 hr, however, an appreciable amount of $C^{18}O^{18}O$ was not detected in the gaseous phase. In Fig. 3, the compositions of the carbon dioxides during the reaction were presented with the percentage of ^{18}O in the total amount of oxygen of carbon dioxides. In the initial stage of the reaction, the percentage of $C^{16}O^{16}O$ was much higher than that of $C^{18}O^{16}O$. This also supports the direct contribution of the lattice oxygen atoms in Pr_6O_{11} to the oxidation reaction. On the basis of the data from X-ray diffractometry, microgravimetry, and TPD measurements shown in the previous paper (*3*), no appreciable amount of readsorbed oxygen must exist, in this case. Moreover, the amount of the oxygen atoms on the top layer of the oxide (0.34 μmol) corresponds to only about 15% of the carbon monoxide introduced (2.3 μmol). The reason why the content of $C^{18}O^{16}O$ was so low during the reaction must be a considerably fast migration of oxygen atoms in the oxide. The fast migration of the lattice oxygen atoms of the β, γ, and δ peaks was confirmed by TPD and mass spectrometry. That is, after the desorption of the β peak oxygen from sample (A) by the TPD procedure (viii), the oxide ($Pr_6O_{10.8}$) was exposed to under 10 Torr of $^{18}O_2$ at 320°C for 1 hr, and then evacuated at the gaseous phase at that temperature. Even after this labeling procedure of the β peak oxygen with ^{18}O, the ^{18}O content in the β peak oxygen was found to be only 3–4%. Moreover, the ^{18}O content in the γ and δ was also found to be 3–4%. The amount of lattice oxygen atoms reacted with carbon monoxide after 6 hr (1.6 μmol) corresponded to about 2% of the lattice oxygen atoms of the oxide catalyst (72 μmol), so that the amount of $C^{18}O^{16}O$ formed was considerably less than that of $C^{16}O^{16}O$. Figure 4 shows the composition change of the gaseous phase and the conversion of CO to carbon dioxides in the oxidation of CO (2 Torr) with $^{18}O_2$ (10 Torr) over $PrO_{1.80}$ ($Pr_6O_{10.8}$, this oxide has no β peak oxygen atoms) (*3*). Since the absorption rate of oxygen into the β peak oxygen vacancy was very fast, most of the β peak oxygen vacancies were replaced with ^{18}O anions in a few minutes after introducing the reactant gases, and residual vacancies were replaced

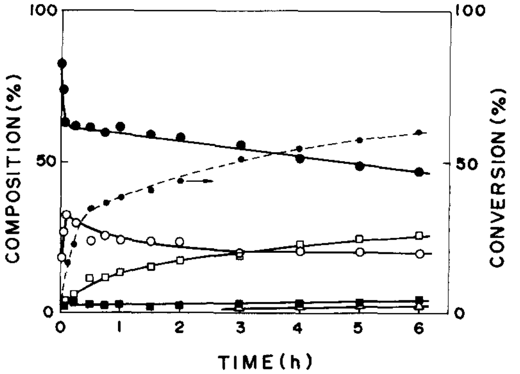

FIG. 4. Composition of the gaseous phase and the conversion of CO to carbon dioxides during the oxidation of CO with $^{18}O_2$ over $Pr_6O_{10.8}$($PrO_{1.80}$) at 320°C. P_{CO} = 2 Torr; $P_{^{18}O_2}$ = 10 Torr; ●, $^{18}O_2$; △, O_2; ○, CO; □, $C^{16}O^{16}O$; ■, $C^{18}O^{16}O$; ●, conversion; $P_{CO_2} \times 100/(P_{CO_2} + P_{CO})$.

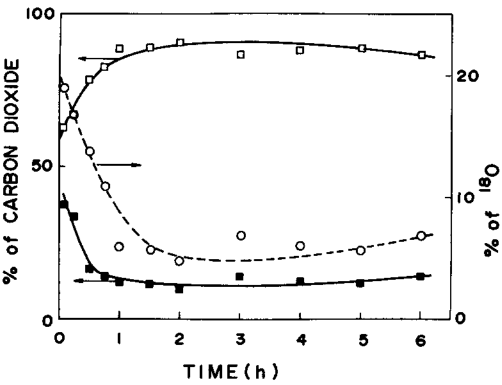

FIG. 5. Composition of carbon dioxides and the percentage of ^{18}O in the total oxygen of carbon dioxides during the oxidation of CO with $^{18}O_2$ at 320°C. P_{CO} = 2 Torr; $P_{^{18}O_2}$ = 10 Torr; □, $C^{16}O^{16}O$; ■, $C^{18}O^{16}O$; ○, percentage of ^{18}O in the total oxygen of carbon dioxides.

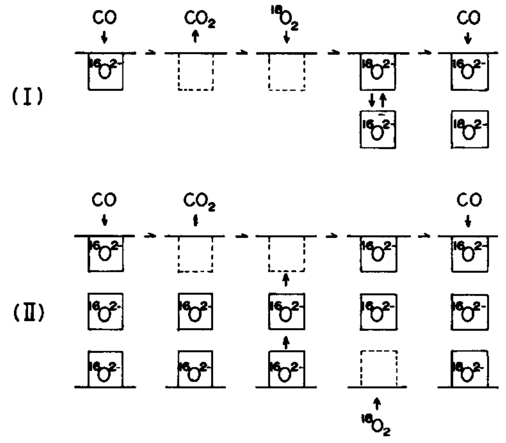

FIG. 6. The models for the process of the removal of the lattice oxygen atom of Pr_6O_{11} by CO and the following incorporation of oxygen ($^{18}O_2$) from the gaseous phase.

with ^{18}O within 1 hr. It must be noted that (i) the conversion rate of CO to carbon dioxides over the $PrO_{1.80}$ catalyst in the initial stage (~1 hr) was higher than that over the Pr_6O_{11} catalyst, (ii) $C^{16}O^{16}O$ was predominantly formed, however the content of $C^{18}O^{16}O$ in the carbon dioxide in the initial stage was comparatively higher than that over the Pr_6O_{11} catalyst. In Fig. 5, the composition of carbon dioxides formed during the reaction is presented with the percentage of ^{18}O in the total oxygen of carbon dioxides. In the initial stage of the reaction, the percentage of $C^{18}O^{16}O$ rapidly decreased with time from 38% at 6 min to 12% at 1 hr. Such a higher content of $C^{18}O^{16}O$ and the higher oxidation rate of CO over Pr_6O_{11} in the initial stage suggest that β peak lattice oxygen atoms directly but catalytically contribute to the oxidation of CO over praseodymium oxide catalyst. Concerning the process for the removal of the lattice oxygen atoms of Pr_6O_{11} by CO and the following incorporation of oxygen from the gaseous phase, two models (*5*, *6*) can be proposed as shown in Fig. 6. The first model (I) assumes that the site from which the oxygen atom is removed to form CO_2 also serves as the site for the incorporation of oxygen from the gaseous phase. Moreover, this model assumes that the migration of the incorporated oxygen into the bulk is very fast. The second model (II) assumes that the site from which the oxygen atom is removed to form CO_2 is not same as the site to which oxygen is incorporated from the gaseous phase, while the diffusion rate of the oxygen atom through the bulk is very fast, as in the case in the first model. In any event, these sites are possibly the β peak oxygen atoms on the surfaces.

In conclusion, CO was catalytically oxidized with the surface lattice oxygen atoms of Pr_6O_{11}, probably β peak lattice oxygen atoms, which was continuously supplied from the bulk. The incorporated oxygen into the anion vacancy of the praseodymium oxide from the gaseous phase immediately migrated into the bulk.

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