NOTES

Catalytic Behavior of Rare Earth Oxides in the Oxidation of Nitrogen Oxide

Several authors have investigated the catalytic activities of the rare-earth oxides to determine if there is any relation between their catalytic activity and their magnetic or crystallographic properties (1–4). In our previous paper (5), the oxidation of nitrogen oxide on SiC-supporting rare-earth oxides was reported. The present study reports the catalytic activity of the series of nonsupported rare-earth oxides in the oxidation of nitrogen oxide and the TPD (temperature-programmed desorption) spectra of the O_2–Pr_6O_{11} system which gave the highest activity in the reaction.

The rare-earth oxides were prepared by decomposition of oxalates (with the exception of ceric chloride) in a stream of an O_2–N_2 mixture (O_2:$N_2 = 1:4$) at 800°C for 4 hr. Each oxide powder was formed into a pellet at a pressure of 25 kg/cm², and was cut into cubes with sides about 1 mm long. The surface area was measured by the BET method using nitrogen adsorption. The catalytic reactor used was a conventional flow system having a 10 mm$^\phi$ reaction tube. The mixture (1 ml) of the catalyst (0.85 g) and SiC (9–20 mesh) was set in the center of the reaction tube. The catalyst bed was held with silica wool and a sheath of a thermocouple. Temperature was measured by an ac thermocouple which was inserted into the middle of the catalyst bed. The flow rate of the reactant gas (NO:500 ppm; O_2:5%; N_2:balance; total 1 atm) was 1000 ml/min. The quanti-

tative analysis of NO and total NO_x was carried out by means of the Saltzman method and nitrate-selective electrode method respectively. The TPD spectra were obtained by following the pressure of gases desorbed from samples by a high-sensitivity Pirani gauge (Dan Kagaku, Ltd., Pirani gauge, Model PS-12). The TPD apparatus was a conventional one capable of evacuation to 10^{-5} Torr by a diffusion pump. The outline of the cell is drawn in Fig. 1. Pretreatment of samples (ca. 100 mesh) was carried out by repeating five times ignition under 100 Torr of O_2 and
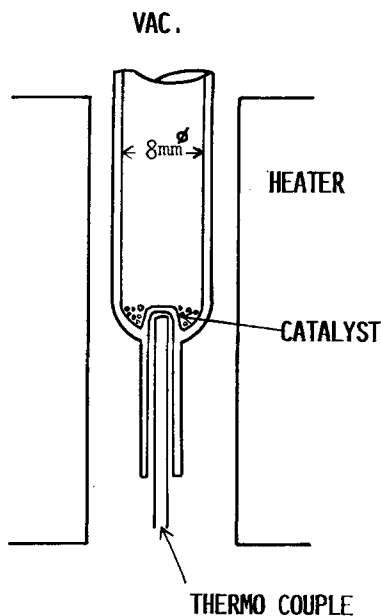

FIG. 1. The cell of the TPD apparatus.

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evacuation at 750°C. For the TPD experiments, high-purity nitrogen oxide in a glass cylinder from the Takachiho Co. was used without further purification. The oxygen from a commercial cylinder was purified by bulb-to-bulb distillation with liquid nitrogen coolant. Thermal microgravimetry was carried out by using a Glubransen-type microbalance set in a high-vacuum apparatus.

Figure 2 shows the specific activities, Rs, of the series of rare-earth oxides at various temperatures, as a function of the atomic number of the element. Rs signifies the rate of formation of nitrogen dioxide at a steady state on a unit surface area of the catalyst per minute. In this figure, it is noteworthy that only the oxides which should make nonstoichiometric oxide (CeO_2, Pr_6O_{11}, Nd_2O_3, and Tb_4O_7) (6, 7) have catalytic activity. Minachev (8) observed a catalytic

FIG. 3. TPD spectra of O_2–Pr_6O_{11} system. *Catalyst:* nonsupported Pr_6O_{11}, ca. 100 mesh, 0.05 g, *Rate of temperature increase:* 40°C/Rin. *Pretreatment:* (a) evacuation at 750°C, introduction of 30 Torr of O_2, gradual cooling to 25°C for 2 hr, and evacuation at 25°C; (b) evacuation at 750°C, introduction of 30 Torr of O_2 gradual cooling to 300°C, and evacuation at 300°C; (c) same treatment as in b, introduction of 100 Torr of NO at 300°C, and evacuation at that temperature for 30 min; (d) evacuation at 750°C, introduction of 30 Torr of O_2, gradual cooling to 350°C, evacuation at 350°C; (e) same treatment as in d, introduction of 100 Torr of NO at 350°C, and evacuation at that temperature for 30 min.
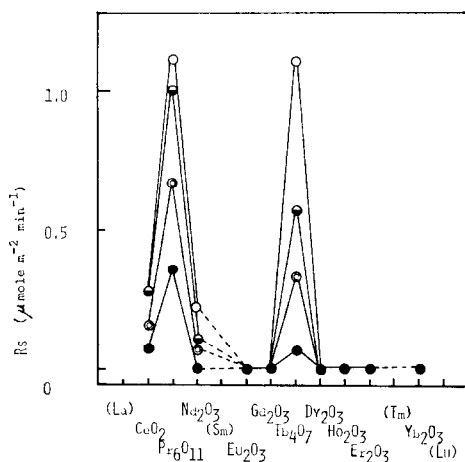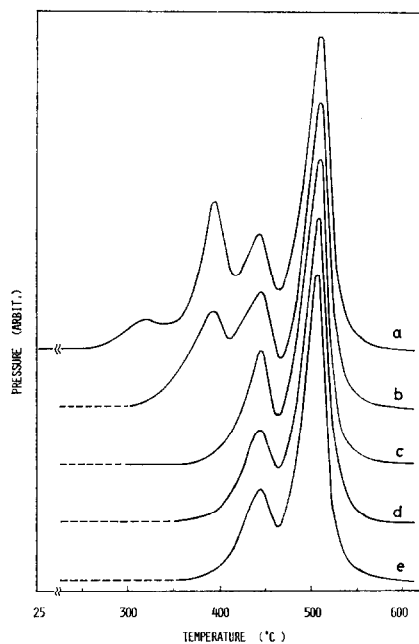

FIG. 2. Specific activities of the rare-earth oxides in the oxidation of nitrogen oxide. *Catalyst:* nonsupported oxide pellet ($1 \times 1 \times 1$ mm), ca. 0.85 g; surface area (m^2/g): CeO_2(5.2), Pr_6O_{11}(3.7), Nd_2O_3-(10.9), Eu_2O_3(6.5), Gd_2O_3(3.0), Tb_4O_7(3.2), Dy_2O_3-(3.5), Ho_2O_3(6.2), Er_2O_3(5.9), Yb_2O_3(2.2). *Catalyst bed:* mixture of the catalyst and SiC(9–20 mesh), 1 ml. *Pretreatment:* gas mixture (O_2:N_2 = 1:4) was allowed to flow at 500°C for 3 hr at a rate of 200 ml/min. *Reactants:* No (500 ppm), O_2 (5%), and N_2 (balance); total, 1 atm. *Flow rate:* 1000 ml/min. *Temperature:* (●) 300, (◎) 350, (◖) 400, and (○) 450°C.

activity pattern similar to our findings in the initial rate of oxygen isotope exchange between oxygen in the oxide and molecular oxygen. He also found the behavior to be directly connected with the mobility of oxygen and concluded that the high mobility of oxygen in the oxide must be due to the defective structure.

To clarify the role of oxygen from the oxide in the oxidation of nitrogen oxide, TPD analysis was carried out for the oxides. After pretreatment of the sample as described above, 30 Torr of oxygen was introduced at 750°C into the cell, which was
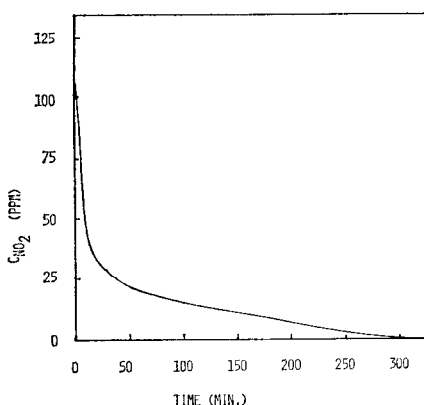
FIG. 4. Formation of NO_2 in the reaction of NO with Pr_6O_{11}. *Catalyst and catalyst bed:* same as described in Fig. 2, except for catalyst weight, 0.82 g. *Pretreatment:* gas mixture ($O_2:N_2 = 1:4$) was allowed to flow at 500°C for 3 hr and at 300°C for 3 hr, at a rate of 200 ml/min. *Reactants:* NO (500 ppm), N_2 (balance); total, 1 atm. *Flow rate:* 1000 ml/min. *Reaction temperature:* 300°C

then cooled gradually to 25°C for 2 hr and was evacuated to a pressure of 10^{-5} Torr. The temperature was then raised linearly at a rate of 40°C/min, evacuating through the diffusion pump. In this experiment, only the oxides (CeO_2, Pr_6O_{11}, Nd_2O_3, and Tb_4O_7) which had some catalytic activity in the reaction gave TPD peaks. However, the features of the TPD spectrum for each oxide were quite different. Figure 3 shows the TPD spectra of O_2 on Pr_6O_{11}, which had the highest activity in Fig. 2. The spectrum of the specimen prepared by the operation described above is denoted a. The spectrum had four peaks, α, β, γ, and δ, between 25 and 600°C. Above 650°C, a very large peak was found; however, only the peaks under 620°C are shown in this figure. These spectra were quite reproducible. X-ray diffractometry showed that the specimen heated *in vacuo* below 300°C was $Pr_6O_{10.9}$ (i.e., lattice constant: $a_{fcc} = 5.474$ Å), and the specimen evacuated at 600°C was $Pr_6O_{10.3}$ ($a_{fcc} = 5.510$ Å) (7). That is, oxygen from the oxide was able to be desorbed by evacuation, even under 600°C. Through an experiment using thermo-

microgravimetry, the amount of oxygen evacuated by this treatment was 0.62 atom per 6 atoms of praseodymium. This finding almost corresponded to the data from X-ray diffractometry. Spectrum b was obtained by the following operation: introduction of 30 Torr of oxygen at 750°C, cooling to 300°C, evacuation at that temperature, and TPD analysis. Through this preparation, peak α disappeared, and peak β became somewhat smaller. After the same preparation as for b, 100 Torr of NO was introduced into the cell at 300°C which was evacuated for 30 min at this temperature, and then TPD analysis was carried out. The spectrum obtained following this procedure is denoted c. Obviously, peak β disappeared following treatment. This was confirmed by an experiment using thermomicrogravimetry. Spectra d and e were obtained by the same operation as used for b and c, respectively, except that the evacuation temperature of the introduced gas, O_2 or NO, was 350°C in these cases. The shapes of spectra d and e were almost the same; therefore, the oxygen causing peaks γ and δ cannot be reduced any further by NO. The peak area reduced by NO at 300°C consisted almost entirely of peak β and was estimated to correspond to 0.15 O atom per 6 praseodymium atoms. Since the surface area of Pr_6O_{11} was 3.7 m²/g, the amount of the oxygen reduced corresponds to ca. 2.0 monolayers of the Pr_6O_{11}. What kind of product had been formed by the oxygen reduced by NO? The oxygen corresponding to peak β should be assigned to be the lattice oxygen of the oxide. Figure 4 should answer the question. This figure shows the content of nitrogen dioxide in the product gas when a reactant gas composed of only NO and N_2 (NO: 500 ppm; N_2: balance; total 1.0 atm; 1000 ml/min) was fed. In the product gas, only NO_2, NO, and N_2 were found; NO and N_2 must be the unreacted reactants. The rate of formation of NO_2 rapidly decreased in the earlier stages of the reaction, i.e., for ca. 10 min,

and then gradually decreased in the later stages. The amount of oxygen reacted with NO, calculated from these data, corresponded to 0.22 atom per six praseodymium atoms. This corresponds to about 2.9 atomic layers of oxygen on Pr_6O_{11}, a somewhat larger number of atoms than was estimated from the TPD spectra. This discrepancy must be due to the difference between the flow method (Fig. 4) and the vacuum method (Fig. 3). As shown in Figs. 3 and 4, the oxygen which corresponds to peak β was very reactive and was able to form NO_2 with NO at 300°C; however, the oxygen which was in the inner layer probably needed a longer time to react with NO because it had to diffuse through the oxide layers.

However, the relation between the oxygen of peaks α, β, γ, and δ and the crystallographic structure is now under consideration.

ACKNOWLEDGMENT

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YOSHIO TAKASU
SUGURU NISHIBE
YOSHIHARU MATSUDA

Faculty of Engineering
Yamaguchi University
Ube, Yamaguchi, Japan