

Reversible Change in the Structure of Cerium Oxide
in Alumina-Supported Catalyst

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Ceria in the alumina-supported catalyst was found to react with the alumina to produce CeAlO_3 when heated in flowing H_2 and to return reversibly to the original ceria particles when calcined in flowing O_2 at 1173 K, while lanthana was proved to react irreversibly with the alumina to form LaAlO_3 .

Lanthanides have often been used as one of the constituents of catalysts for a control of automobile exhaust and a high temperature combustion reaction.¹⁾ Among the lanthanides ceria and lanthana have extensively studied because of an effective oxygen storage and high resistance for thermal sintering of the catalyst support, respectively.²⁾ Yao et al.³⁾ have studied the oxygen storage of ceria in $\text{CeO}_2/\text{Al}_2\text{O}_3$ catalyst and reported the oxygen storage capacity of the catalyst was attributed to the reversible structural change between CeO_2 and Ce_2O_3 during oxidation and reduction cycles. Matsuda et al.⁴⁾ reported that decrease in the surface area of a supported alumina catalyst when employed for high temperature reactions was significantly improved by addition of a small amount of La_2O_3 to the catalyst. Although the lanthanides have been recognized to play important roles during catalysis, the reactions of lanthanides with the catalyst supports have not been so extensively studied.

In the present work the reaction of ceria particles with the alumina support in $\text{CeO}_2/\text{Al}_2\text{O}_3$ catalyst was studied by means of X-ray diffraction spectroscopy and temperature-programmed reduction (TPR). The results obtained were compared

with those obtained on the reaction of lanthana with alumina in $\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst.

The catalysts used were CeO_2 (20 wt%)/ Al_2O_3 and La_2O_3 (20 wt%)/ Al_2O_3 , prepared by impregnating alumina powder, supplied from Cataler Industrial Co., the surface area of $164 \text{ m}^2 \text{ g}^{-1}$, with the aqueous solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ of an appropriate concentration, followed by drying and calcination at 500°C for 4 h. The surface areas of the catalysts thus prepared were both around $125 \text{ m}^2 \text{ g}^{-1}$. For TPR measurements, 0.5 g of the catalyst powder was placed in a reactor made of quartz tube (8 mm of diameter) equipped with two thermocouples, one was located just at the center of the catalyst bed and connected to a recorder and the other was mounted in a furnace to control the rate of elevating temperature, $10^\circ\text{C min}^{-1}$. The catalyst powder was first treated at 300°C in flowing Ar and then cooled down to room temperature, followed by the introduction of H_2 (10 %)/Ar with a flow rate of 110 ml min^{-1} . The gases were purified by a cold trap (dryice-acetone) packed with molecular sieves 5 A before introduction to the reactor tube. A similar cold trap was also equipped at the outlet of the reactor to eliminate water vapor produced by reduction of the catalyst. The difference in the H_2 concentrations at the inlet and the outlet of the reactor was detected by a thermal conductivity detector. (Shimazu, GC-8A) The typical TPR spectra of fresh and reoxidized $\text{CeO}_2/\text{Al}_2\text{O}_3$ catalysts are depicted in Fig. 1, where the reoxidation was carried out at 900°C in flowing O_2 for 2 h for the samples used for TPR measurement up to 950°C . Three peaks were observed, two small and broad peaks at around 575°C and 800°C and a sharp and strong peak at 910°C , respectively. Yao et al.³⁾ have also reported the similar peaks using $\text{CeO}_2/\text{Al}_2\text{O}_3$ catalyst and concluded that the first two broad peaks are due to the reactions of oxygen atoms located at the surface of and inside the CeO_2 particles and the sharp peak at 910°C will be attributed to the oxygen atoms located at the interface between CeO_2 particles and alumina support. The amount of oxygen reacted during TPR of the fresh catalyst was almost the same as that of the reoxidized one, suggesting the reversible change in the structure of ceria during the oxidation and reduction cycles at 900°C . It is well known that three kinds of crystallographic structures are in cerium oxide; CeO , Ce_2O_3 , and CeO_2 . Among the cerium ions Ce^{3+} and Ce^{4+} are considered to be rather stable, hence the reversible structural change in ceria mentioned above might be attributed to the change between Ce_2O_3

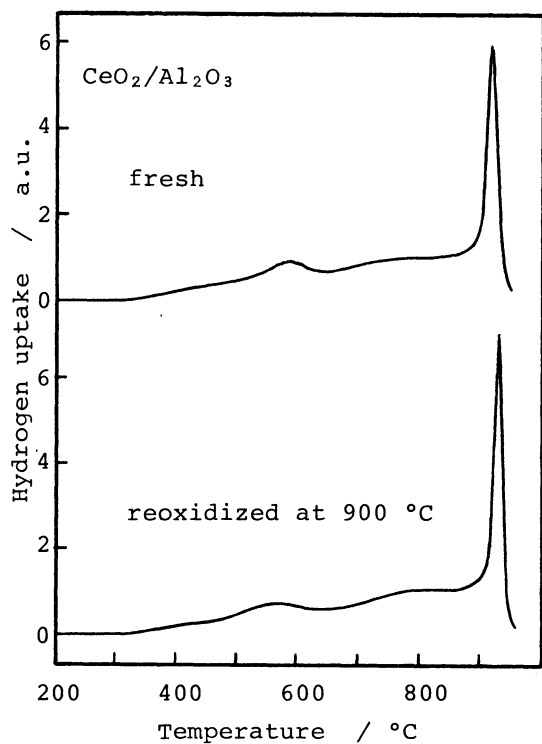


Fig. 1. TPR spectra of fresh and reoxidized $\text{CeO}_2/\text{Al}_2\text{O}_3$ catalysts.

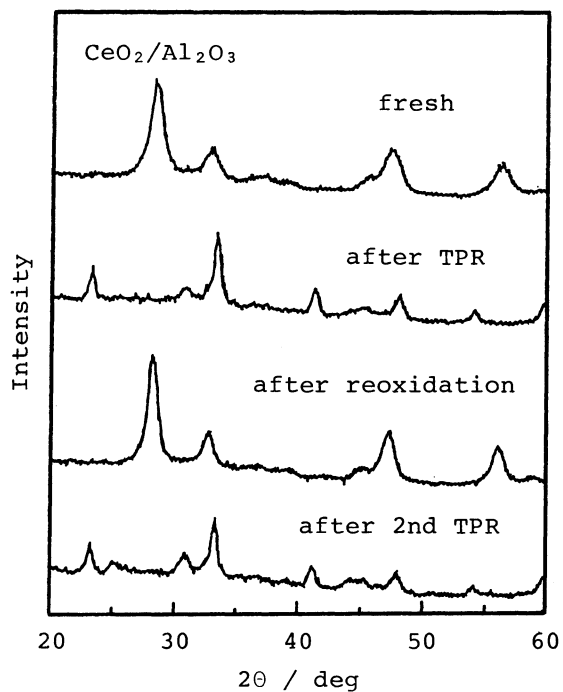


Fig. 2. Change in X-ray diffraction spectra of the $\text{CeO}_2/\text{Al}_2\text{O}_3$ catalyst.

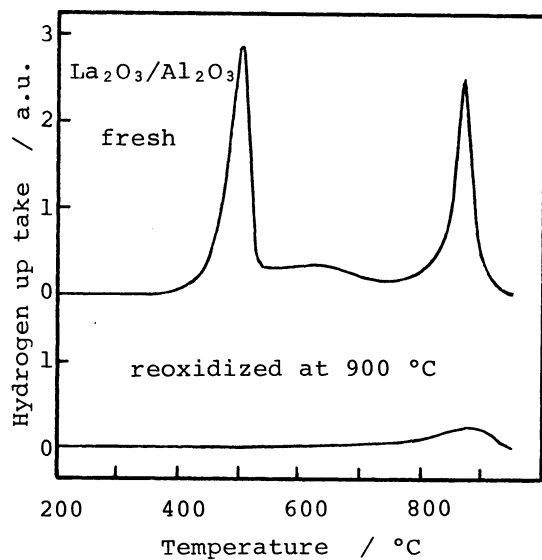


Fig. 3. TPR spectra of fresh and reoxidized $\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts.

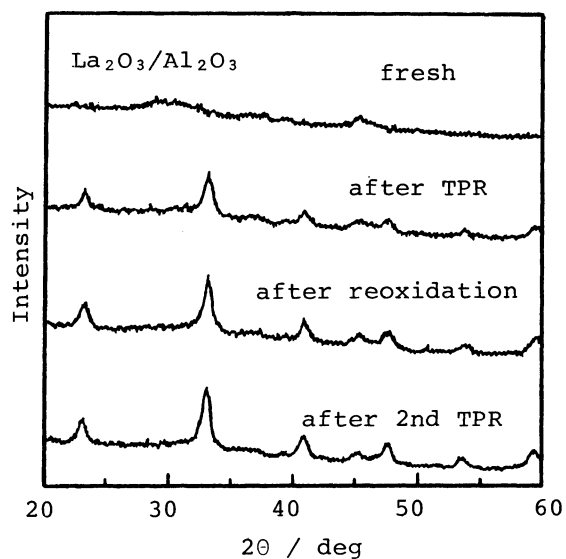


Fig. 4. Change in X-ray diffraction spectra of the $\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst.

and CeO_2 . As could be clearly seen in Fig. 2, however, the X-ray diffraction spectrum of the catalyst after TPR measurements is the same as that of CeAlO_3 and the spectrum of the catalyst reoxidized at 900 °C is the original CeO_2 , though the diffraction peaks are sharpened to some extent. Thus, the reversible change in the structure of ceria in the $\text{CeO}_2/\text{Al}_2\text{O}_3$ catalyst during oxidation and reduction at higher temperatures is ascribed to the change between CeO_2 and CeAlO_3 , but not to the change between CeO_2 and Ce_2O_3 .

For comparison, the reaction of lanthana and alumina support was also studied in the similar manner. Typical TPR spectra of the fresh and reoxidized samples are shown in Fig. 3, where a less amount of oxygen atoms in the reoxidized catalyst was observed to react with H_2 , while two strong peaks at around 500 and 900 °C and a broad peak at 650 °C were observed for the fresh catalyst. Since the reaction of $\text{La}_2\text{O}_3 + \text{Al}_2\text{O}_3 \longrightarrow 2\text{LaAlO}_3$ will not require the presence of H_2 , the peaks shown in Fig. 3 for fresh catalyst may represent the reaction of H_2 with oxygen adsorbed on La_2O_3 and Al_2O_3 particles. The X-ray diffraction spectra (in Fig. 4) show the formation of LaAlO_3 in the catalyst after TPR measurements and that it still remained even when reoxidized at 900 °C. Although both cerium and lanthanide series, reactions of their oxides with alumina are completely different, ceria reacts with alumina reversibly and lanthana irreversibly. This reversible change between CeO_2 and CeAlO_3 might be ascribed to the effective oxygen storage of $\text{CeO}_2/\text{Al}_2\text{O}_3$ catalyst.

References

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(Received November 6, 1987)