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Catalytic and Thermal Behavior of Cerium Oxide Supported on SiO_2 and Al_2O_3 for Methane Combustion

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Synopsis. CeO_2/SiO_2 and CeO_2/Al_2O_3 catalysts oxidized at 1173 K in O_2 stream were employed to investigate the catalytic activity for methane combustion and the behavior of CeO_2 on supports by the oxidation at 1173 K. CeO_2/SiO_2 catalyst gave a poor catalytic activity by comparison with that of CeO_2/Al_2O_3 catalyst. The crystallite size of CeO_2 of the silica catalyst was found to be 1.5 times larger. In addition, Auger Electron Spectroscopy (AES) analysis after the oxidation at 1173 K proved that cerium species existed on and within the silica support. We conclude that the low surface density of CeO_2 might contribute to the poor activity of CeO_2/SiO_2 catalyst for methane combustion.

Recently, the catalytic activity of several rare earth oxides supported on silica and alumina has been extensively reported.[1,2] Among the rare earth oxides, cerium(IV) oxide has been most intensively studied, particularly with regard to the interaction with alumina support and its behavior as an additive in the automotive catalyst.[1—4] Structural analyses on CeO_2/Al_2O_3 catalysts have continued.[4—6] We reported that cerium(IV) oxide interacts strongly with alumina, which results in a reversible structural change between CeO_2 and $CeAlO_3$ with an iterative oxidation and reduction at 1173 K.[5,6] On the other hand, studies on CeO_2/SiO_2 catalysts have been focused on characterizing a precious metal–cerium oxide interface for an activation of adsorbed species. For example, Kiennemann et al.[7] reported that the Rh/SiO_2 catalyst enhanced its ethyl alcohol selectivity for CO hydrogenation reaction by addition of cerium oxide. They explained this as an additive effect of cerium(IV) oxide to Rh for the parallel adsorption of CO on the active sites. There are few studies concerning the interaction and interface between cerium(IV) oxide and silica support, when catalysts were oxidized at high temperature. It is thus of interest to investigate the behavior and catalytic activity of CeO_2 on silica by a high temperature treatment, for comparison with CeO_2 on alumina support.

For this purpose, CeO_2/SiO_2 and CeO_2/Al_2O_3 catalysts oxidized at 1173 K in O_2 stream were employed to study the catalytic activity for methane combustion. The behaviors of CeO_2 on supports before and after oxidation at 1173 K are discussed on the basis of analyses by Auger Electron Spectroscopy (AES), X-ray diffraction (XRD), and pore size distributions derived from nitrogen adsorption isotherms.

Experimental

Silica-supported and alumina-supported cerium(IV) oxide catalysts were prepared by impregnating silica and

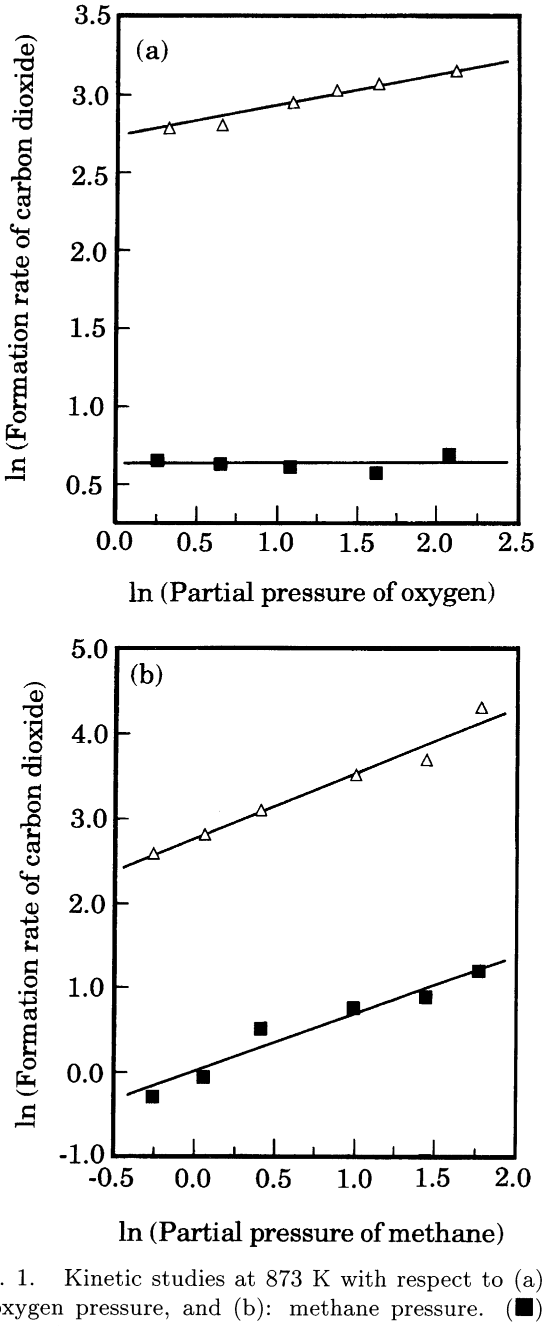

Fig. 1. Kinetic studies at 873 K with respect to (a): oxygen pressure, and (b): methane pressure. (■): CeO_2/SiO_2 catalyst and (△): CeO_2/Al_2O_3 catalyst.

Table 1. Crystallite Size of CeO_2 the BET Surface Area, and the Results of Pore Size Distribution of Alumina-Supported and Silica-Supported Catalysts

Catalysts[a)]	Crystallite size of CeO_2/nm	BET surface area $m^2 g^{-1}$	Mean pore size nm	Pore volume ml g-cat^{-1}
Al_2O_3 (F)	—	120	5.9	0.23
Al_2O_3 (O)	—	98	6.9	0.21
CeO_2/Al_2O_3 (F)	7.1	99	5.0	0.13
CeO_2/Al_2O_3 (O)	10.2	65	6.5	0.13
SiO_2 (F)	—	381	1.9	0.23
SiO_2 (O)	—	226	1.9	0.14
CeO_2/SiO_2 (F)	6.3	207	2.0	0.11
CeO_2/SiO_2 (O)	16.2	115	2.0	0.07

a) "F" and "O" mean "Fresh Catalyst" calcined at 773 K and "Oxidized Catalyst" recalcined at 1173 K, respectively.

γ-type alumina powders, synthesized by hydrolysis of metal alkoxides,[8)] with an aqueous solution of $Ce(NO_3)_3 \cdot 6H_2O$, followed by drying and calcination at 773 K for 4 h (denoted as fresh catalyst). Loadings of cerium oxides, calculated as CeO_2, in the catalysts were 20 wt%. After the catalysts were oxidized at 1173 K for 5 h in flowing O_2 (denoted as oxidized catalyst), a methane combustion was carried out at 873 K in the same manner as described previously.[6)] Structure analyses of cerium oxides were performed by X-ray diffraction (Rigakudenki, Geigerflex) using a Cu tube at 30 kV and 15 mA. A JEOL JUMP-10 was used to obtain the AES spectra. The sample was deposited on a sample holder which was set to 15° of the entrance electron beam to prevent the charge-up phenomenon. Depth profiles were also monitored by sputtering with Ar^+ ions. Nitrogen adsorption isotherms at 77 K were measured volumetrically. Samples were outgassed at 473 K for 2 h. The isotherms were obtained by plotting the amount of adsorbed nitrogen as a function of partial pressure P/P_0. Specific surface areas and pore volumes were calculated in the standard manner. Mean pore radii were derived from the desorption branches of the isotherms from the maxima of pore size distributions calculated on the basis of the Kelvin equation, using a cylindrical pore model.

Results and Discussion

Figure 1(a) and 1(b) show the rate of methane combustion, expressed as the formation rate of carbon dioxide, against the partial pressures of oxygen and methane, respectively. The reactions on both catalysts seem to proceed with similar reaction kinetics. The reaction kinetics, nearly zero order with respect to oxygen pressure and 1st order kinetics for methane pressure, were in good agreement with others.[9)] The CO_2 formation rate was at least 12 times faster for the CeO_2/Al_2O_3 catalyst than for the CeO_2/SiO_2 catalyst. In addition, the oxygen storage capacity (OSC) on CeO_2/SiO_2 catalyst, which is often used as another probe to characterize cerium(IV) oxide, was found to be two-fifths of the fresh CeO_2/SiO_2 catalyst after the oxidation at 1173 K. However, the OSC in CeO_2/Al_2O_3 catalyst were almost the same before and after oxidation.[10)] The results suggest that the conditions of cerium(IV) oxide on the two catalysts, dispersion state and crystallite size, are not identical, although both catalysts were prepared and treated in the same manner.

XRD patterns of four catalysts (fresh and oxidized) showed that the deposited cerium(III) ions were transformed to CeO_2. No other peaks were observed except for the peaks assigned to CeO_2 in all catalysts. In both catalysts, X-ray linewidth analysis summarized in Table 1 indicates the increases of crystallite size after the oxidation at 1173 K. The crystallite sizes of both fresh catalysts were almost the same, but after oxidation the crystallite size of silica catalyst was a factor of 1.5 larger than that of the alumina catalyst. Furthermore, we observed that the surface area of CeO_2/SiO_2 catalyst became one-half of that of its fresh catalyst. It seems that the cerium(IV) oxide on alumina support is stabilized, while some sintering of CeO_2 occurs on the silica support at 1173 K.

The distributions of cerium(IV) oxide on both silica and alumina supports were measured by AES method. Figure 2(a) and 2(b) display the depth profile analyses on both fresh and oxidized catalysts. The atomic ratios (I_{Ce}/I_{Al} and I_{Ce}/I_{Si}) were corrected using relative atomic sensitivity factors. The cerium densities on both fresh catalysts were almost the same and the intensities decreased linearly with Ar^+ bombardment time, especially at the CeO_2/SiO_2 catalyst with an acute slope (Fig. 2(a)). This suggests that cerium species are highly dispersed on the silica surface. Although the I_{Ce}/I_{Al} somewhat decreased after oxidation at 1173 K, CeO_2/Al_2O_3 catalyst showed a similar depth profile to that of the fresh one, indicating that most of the cerium(IV) oxide is still located on the alumina surface. On the other hand, the surface density of CeO_2 on the oxidized silica catalyst was found to be three-fifths of that of the fresh one; this was about 30% lower than that of the oxidized alumina catalyst. In addition, a different depth profile, a parabolic type, was observed on the oxidized CeO_2/SiO_2 catalyst (Fig. 2(b)). This means that cerium(IV) oxide exists not only on the surface but also within the silica support. From XRD and

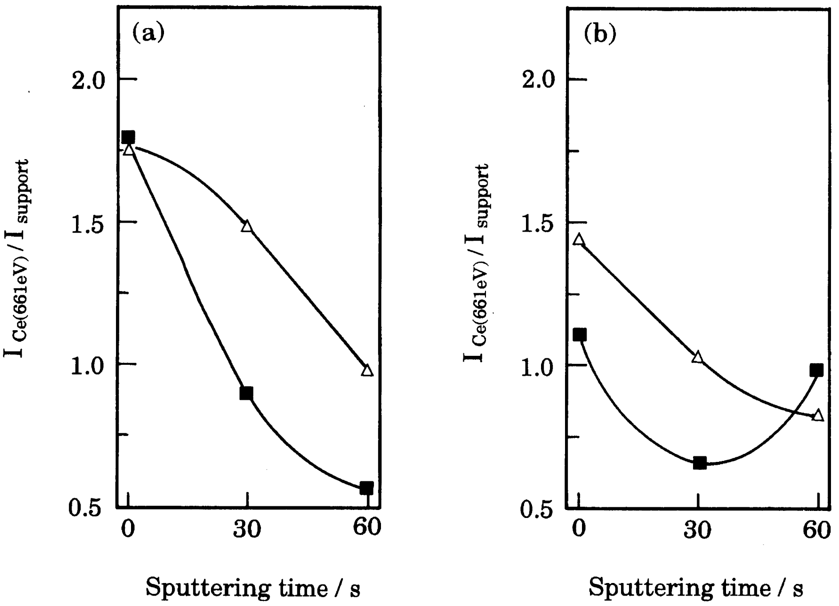

Fig. 2. AES depth profiles showing the Ce/Si and Ce/Al peak intensity ratios corrected using relative atomic sensitivity factors as a function of Ar^+ sputtering time for (a): Fresh catalysts, and (b): Oxidized catalysts. (■): CeO_2/SiO_2 catalysts, and (△): CeO_2/Al_2O_3 catalysts.

AES results, it is clear that the cerium(IV) oxide on the silica support migrates and coagulates at 1173 K.

We now consider the stabilization forces of CeO_2 on supports at 1173 K. It is known that in a reducing atmosphere, CeO_2 reacts easily with Al_2O_3 to form $CeAlO_3$ at 1173 K[5,6] but the formation of $Ce_2Si_2O_7$ needs a higher temperature of 1773 K.[11] The interaction between CeO_2 and supports might be induced around the transformation temperatures and the precursors for $CeAlO_3$ and $Ce_2Si_2O_7$ phases might be formed. Although the catalysts in this experiment are treated under different conditions, the presence of $CeAlO_3$ phase at 1173 K thus seems to be one of the reasons for CeO_2 on alumina surface to be stabilized, whereas the CeO_2 on silica surface can be readily mobile because there is no stable phase at 1173 K.

Pore size distributions of the two catalysts were measured together with that of the supports. The results are summarized in Table 1. The mean pore sizes of CeO_2/Al_2O_3 catalysts slightly changed before and after oxidation and became smaller in the presence of CeO_2. The pore volumes after the oxidation at 1173 K were nearly constant with or without CeO_2. On the other hand, although the mean pore sizes of CeO_2/SiO_2 catalysts did not change before and after oxidation, even with CeO_2, the pore volume of the oxidized catalysts decreased from 0.11 to 0.07 ml g^{-1}. Since cerium(IV) oxide on the oxidized catalyst is present not only on the surface but also within the support, we presume that some of the micropores are covered by the migration of CeO_2 induced at 1173 K and are also covered with the coagulated cerium(IV) oxides. This might lead to a decrease of the number of micropores. Therefore, this reduces the pore volume but the mean pore size is not affected. Consequently, the surface density of CeO_2 is low for the oxidized CeO_2/SiO_2 catalyst. This might then contribute to the poor activity of the oxidized CeO_2/SiO_2 catalyst for the methane combustion.

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