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EFFECT OF ADDITIVES ON THE SURFACE AREA OF OXIDE SUPPORTS FOR CATALYTIC COMBUSTION

Masato MACHIDA, Koichi EGUCHI, and Hiromichi ARAI
Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Kasugakoen, Kasuga-shi, Fukuoka 816

Effect of additives on the surface area of oxide supports was investigated to use them for combustion catalysts above 1000 °C. An addition of BaO to Al_2O_3 was found to suppress the decrease of its surface area at elevated temperatures. The maximum surface area, 6.0 m^2/g, was obtained for $(BaO)_{0.14}(Al_2O_3)_{0.86}$ after calcination at 1450 °C. The effect of BaO on the surface area of alumina is attributed to the formation of $BaO \cdot 6Al_2O_3$.

Catalytic combustion of hydrocarbons has been extensively investigated by many researchers.$^{1,2)}$ Recently, new applications of combustion catalysts to gas turbines or boilers are drawing research interests on catalysts for high temperature combustion. Although alumina is widely used as an oxide support, its surface area significantly decreases accompanied by the transition from metastable phase into α phase.$^{3)}$ How to suppress the sintering of support oxides is one of the important problems in improving combustion catalysts. The effect of additives such as BaO and SiO_2 on the surface area of alumina was briefly mentioned,$^{4)}$ whereas the details on the effect of additive are not studied extensively from the view point of high temperature combustion. Recently Matsuda et al.$^{5)}$ reported that the mixing of lanthanum oxide with alumina, leading to the formation of β-alumina structure, has an effect to maintain the surface area at elevated temperatures. In the present communication, we report the effect of barium oxide on the surface area of alumina above 1000 °C.

Support oxides were prepared by calcination of oxide mixtures at 1450 °C for 5 h except for the case of Ba-containing samples. Barium carbonate was used as the starting material for Ba-containing samples. Gamma alumina was used for preparation of alumina-based support oxides. Crystal structures of calcined samples were determined by X-ray diffraction (Rigaku Denki, 4011). Specific surface areas of oxides were measured by the BET method. Cobalt oxide was supported on these oxides by a conventional impregnation method. The oxide powders were suspended in a cobalt nitrate solution followed by evaporation to dryness. Dried samples were calcined at 1300 °C for 10 h prior to use for oxidation reaction. Catalytic oxidation of methane was carried out in a flow system. A gaseous mixture of methane (1 mol%) and air (balance) was fed to the catalyst bed at $W/F = 48000\ h^{-1}$. Conversion of methane to CO_2 was analyzed by gas chromatography.

Surface areas of alumina-, zirconia-, and magnesia-based oxides were measured after calcination at 1450 °C to use them as support materials for high temperature combustion (Table 1). Most of the support oxides showed surface area less than 1.5 m^2/g. Effects of additives are scarcely observed on the surface areas of magnesia- and zirconia-based oxides. Of the catalysts examined, BaO-added alumina showed the largest surface area. Oxidation of methane over cobalt oxide catalysts was carried out using various oxide supports thus prepared (Table 1). The catalytic activity is expressed as the temperature at which conversion level is attained to be 90%. Most of catalysts reached this conversion level above 800 °C. Cobalt oxide supported on $(BaO)_{0.1}(Al_2O_3)_{0.9}$ with the largest surface area showed the highest activity for methane combustion. Thus the large surface are should be quite effective to enhance the activity of catalysts. Further study was focused on the $BaO-Al_2O_3$ oxide system to know the origin of its large surface area.

Table 1. Surface areas of oxide supports and catalytic activities of supported cobalt oxide catalysts for methane combustion

Support	Surface area a) m^2/g	$T_{90\%}$ b) c) °C
Al_2O_3	1.4	-
$(BaO)_{0.1}(Al_2O_3)_{0.9}$	4.5	790
$(MgO)_{0.1}(Al_2O_3)_{0.9}$	1.2	820
$(ZrO_2)_{0.1}(Al_2O_3)_{0.9}$	1.0	810
ZrO_2	0.8	-
$(MgO)_{0.1}(ZrO_2)_{0.9}$	0.3	860
$(CaO)_{0.1}(ZrO_2)_{0.9}$	0.9	820
$(Al_2O_3)_{0.1}(ZrO_2)_{0.9}$	0.5	845
$(Al_2O_3)_{0.1}(MgO)_{0.9}$	1.0	820
$(SiO_2)_{0.1}(MgO)_{0.9}$	1.3	840
$(Cr_2O_3)_{0.1}(MgO)_{0.9}$	1.5	825

a) Calcined at 1450 °C.
b) Temperature at which conversion level is 90%.
c) Loading of CoO , 10 wt%
Reaction condition
CH_4 1 vol.% ; air 99 vol.%
Space velocity 48000 h^{-1}

The crystal structure of $BaO-Al_2O_3$ system was investigated by X-ray diffraction. Hereafter, the composition of binary oxide is expressed by the molar fraction of BaO as $(BaO)_x(Al_2O_3)_{1-x}$. Alpha phase is known as the equilibrium phase of pure alumina. In the phase diagram of $BaO-Al_2O_3$ system,⁶⁾ two binary compounds, i.e., $BaO\cdot 6Al_2O_3$ (x = 0.14) and $BaO\cdot Al_2O_3$ (x = 0.5), are known at the composition range between x = 0 and 0.5. Crystal structure of $BaO\cdot 6Al_2O_3$ is disordered β-alumina type with a layered structure.⁷⁾ The structure of equimolar compound, $BaO\cdot Al_2O_3$, is called as stuffed tridimite type.⁸⁾ Figure 1 shows the X-ray diffraction patterns of $(BaO)_x(Al_2O_3)_{1-x}$ with various composition ratios. Pure alumina showed diffraction peaks ascribable to α-phase after calcination at 1450 °C. The diffraction patterns of oxides at x = 0.14 and at x =0.5 consisted of single phases of $BaO\cdot 6Al_2O_3$ and $BaO\cdot Al_2O_3$, respectively. Samples between these composition are mixtures of two compounds, i.e., samples are mixtures of α-Al_2O_3 and $BaO\cdot 6Al_2O_3$ at $0 < x < 0.14$ and of $BaO\cdot 6Al_2O_3$ and $BaO\cdot Al_2O_3$ at $0.14 < x < 1$. Thus, the X-ray diffraction result confirms that samples consisted of equilibrium phases after calcination at 1450 °C.

The surface area of the $(BaO)_x(Al_2O_3)_{1-x}$ system is plotted as a function of the oxide composition in Fig. 2. The surface area increased with the addition of a small amount of BaO. Then the curve showed a maximum at $x = 0.14$ where the surface area reaches 6.0 m^2/g. The composition at the maximum agreed with that of the $BaO \cdot 6Al_2O_3$ suggesting that the formation of this binary compound suppressed the sintering of alumina. The structure of $BaO \cdot 6Al_2O_3$ is almost similar to that of La β-alumina. The formation of La β-alumina is reported to be also effective to maintain the surface area at elevated temperatures.$^{5)}$

Effect of calcination temperature is investigated using the sample at $x = 0.14$. Figure 3 shows the X-ray diffraction patterns of $(BaO)_{0.14}(Al_2O_3)_{0.86}$ calcined at various temperatures. It was evident that the sample calcined below 1100 °C exhibited only diffraction lines from $BaO \cdot Al_2O_3$ instead of those from $BaO \cdot 6Al_2O_3$. The $BaO \cdot 6Al_2O_3$ phase appeared at 1200 °C and became dominant with increasing temperature. Finally, the sample consisted of a single $BaO \cdot 6Al_2O_3$ phase above 1450 °C. This result indicates that, at the first stage, the $BaO \cdot Al_2O_3$ is produced by solid state reaction at low temperatures. The sample below 1100 °C appears to be a mixture of $BaO \cdot Al_2O_3$ and γ-Al_2O_3, whereas the diffraction lines from the latter phase is too weak to be observed due to its poor crystallinity. The $BaO \cdot 6Al_2O_3$ is produced by a solid state reaction between γ-Al_2O_3 and $BaO \cdot Al_2O_3$ above 1200 °C. Such a solid state reaction appears to be facilitated by the phase transition of alumina into α phase, which occurs significantly at the same temperature range. X-Ray diffraction measurement indicated that every sample at $0 < x \leqq 0.5$ also consisted of only $BaO \cdot Al_2O_3$ and/or single oxide phase after calcination below 1100 °C. Further increase in calcination temperature leads to the formation of the equilibrium phases. Change of surface area with calcination temperature was

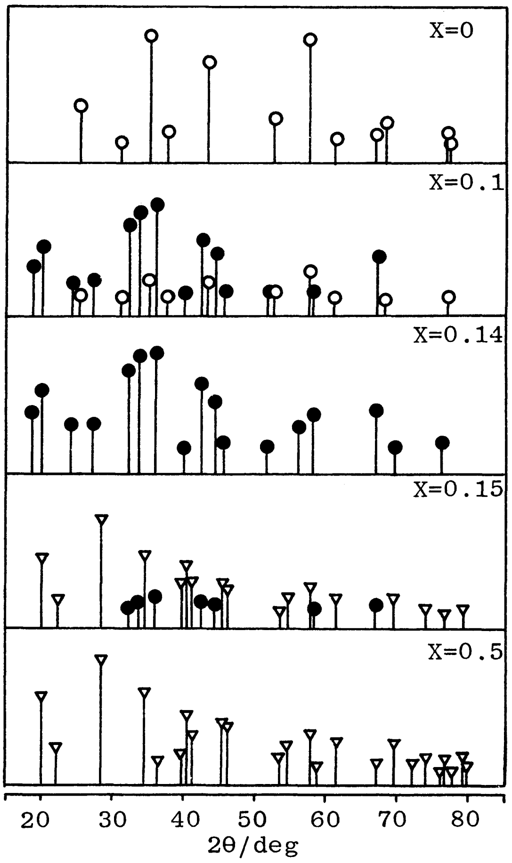

Fig. 1. X-Ray diffraction patterns of $(BaO)_x(Al_2O_3)_{1-x}$ system calcined at 1450 °C.

○ α-Al_2O_3, ● $BaO \cdot 6Al_2O_3$, ▽ $BaO \cdot Al_2O_3$

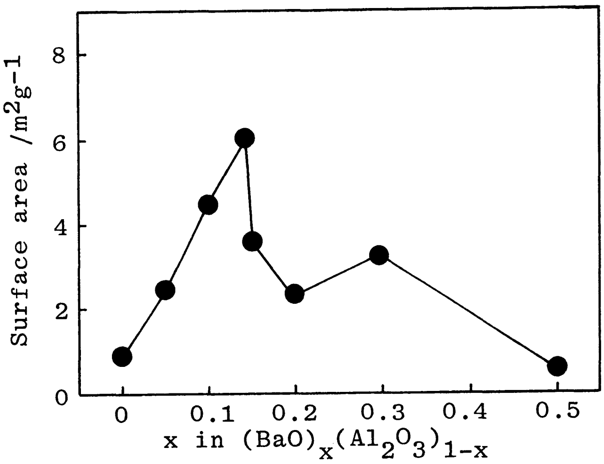

Fig. 2. Change in surface areas of $(BaO)_x(Al_2O_3)_{1-x}$ with the composition.
Calcination temperature=1450 °C.

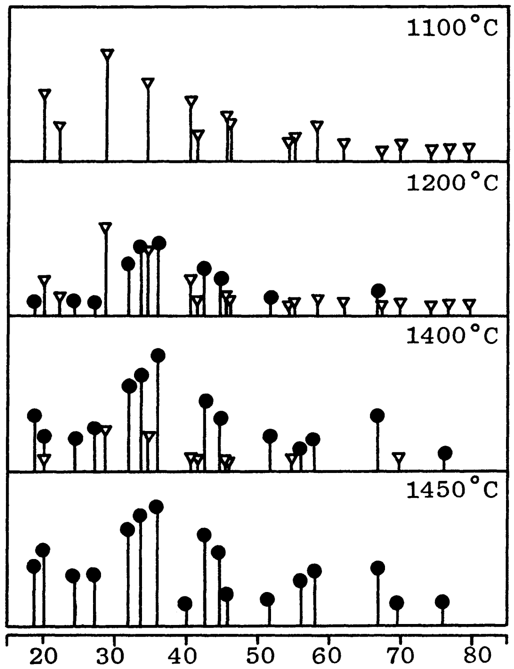

Fig. 3. X-Ray diffraction patterns of $(BaO)_{0.14}(Al_2O_3)_{0.86}$ calcined at various temperatures.
● $BaO\cdot 6Al_2O_3$, ▽ $BaO\cdot Al_2O_3$

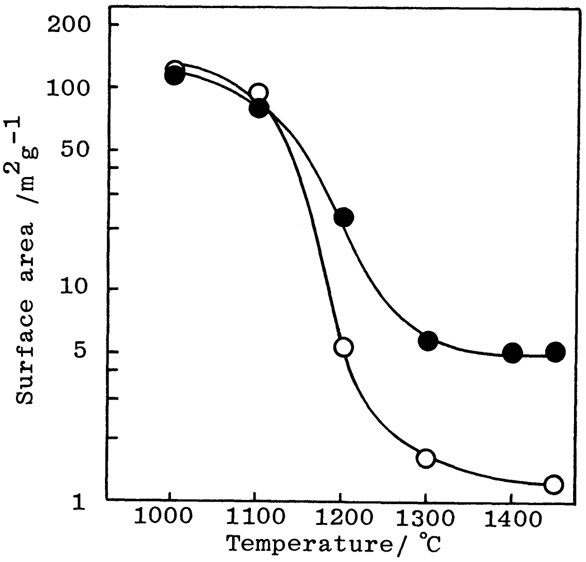

Fig. 4. Temperature dependence of surface areas of $(BaO)_{0.14}(Al_2O_3)_{0.86}$ and Al_2O_3.
● $(BaO)_{0.14}(Al_2O_3)_{0.86}$, ○ Al_2O_3

investigated in relation to its structure (Fig. 4). The surface area of $(BaO)_{0.14}$-$(Al_2O_3)_{0.86}$ sample is almost the same as that of Al_2O_3 after calcination at 1000 °C. The surface areas of both samples decreased with a rise in calcination temperature. The surface area of Al_2O_3 is steeply decreased at about 1200 °C, accompanied by the phase transition to α-phase. At this temperature, $BaO\cdot 6Al_2O_3$ phase is produced by solid state reaction in the case of $(BaO)_{0.14}(Al_2O_3)_{0.86}$. The surface area is almost constant at 6 m^2/g between 1300 and 1450 °C. The formation of binary compound was shown to be effective in maintaining its surface area. Such an effect of BaO on the surface area of alumina promises to design an active catalyst for high temperature combustion.

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