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High Temperature Catalytic Combustion over Cation-substituted Barium Hexaaluminates

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The combustion activities of various oxide catalysts were investigated using $BaO\cdot 6Al_2O_3$ as support. Conventional impregnation of oxide catalysts only lead to a decrease in surface area of the support. Cation-substituted barium hexaaluminates generally retained the large surface area. In particular, $BaMnAl_{11}O_{19-\alpha}$, showed the excellent activity and the large surface area of 13.7 m^2/g after calcination at 1300 °C.

Recently,[1,2] much interest has arisen in new application of catalytic combustion to gas turbines which are operated at above 1300 °C. One of the main subjects for this purpose is how to fabricate a heat-resistant catalyst. Noble metal catalysts, such as Pt or Pd, which are mainly used for combustion below 1000 °C should be excluded due to high volatility of their oxides above 1300 °C. Some perovskite-type oxides are known as very active oxidation catalyst.[3] However, the sintering of them at high temperatures accompanies the serious decrease in surface area.[4] Dispersion of active metal oxides on support materials is necessary to obtain a large reaction surface but the use of support sometimes leads to a solid state reaction between components at high temperatures. We have previously reported that barium hexaaluminate, $BaO\cdot 6Al_2O_3$, derived from mixed alkoxide retains a large surface area above 1200 °C[5] and is suitable for use as a heat-resistant support. In this study, we developed a new type of combustion catalyst with high catalytic activity and large surface area, in which the active cations are doped into the lattice of support.

A series of cation-substituted as well as unsubstituted barium hexaaluminates, $BaMAl_{11}O_{19-\alpha}$ (M = Al, Cr, Mn, Fe, Co, and Ni) were prepared from hydrolysis of alkoxides. An aqueous solution of acetate or nitrate salt of transition metal was added to the alcoholic solution of $Ba(i\text{-}OPr)_2$ and $Al(i\text{-}OPr)_3$. The precipitate formed with gelation was evaporated to dryness. $La_{0.6}Sr_{0.4}MnO_3$ was supported on $BaO\cdot 6Al_2O_3$, which was prepared from a mixture of $BaCO_3$ and $\gamma\text{-}Al_2O_3$, by a conventional impregnation method using metal acetates. All the samples were calcined at 1300 °C prior to use them for catalytic reaction. The method for the measurement of catalytic combustion of methane have been described elsewhere.[5]

Cation-substituted perovskite type oxide, $La_{0.6}Sr_{0.4}MnO_3$, which is known as one of the most active oxide catalysts for combustion,[4] was impregnated onto $BaO\cdot 6Al_2O_3$. The surface area and activity for methane combustion over supported perovskite-type oxide are listed in Table 1. The activity is expressed as temperatures, $T_{10\%}$ and $T_{90\%}$, at which conversion levels are attained to be 10% and 90%, respectively. It is preferable for combustion catalysts that both ignition($T_{10\%}$) and complete combustion temperatures ($T_{90\%}$) are lowered to avoid misfire and not to exhaust unreacted fuels. The surface area of the unloaded support was largest. The impregnation of $La_{0.6}Sr_{0.4}MnO_3$ lead to a decrease in surface area, due to precipitation of oxide particles in the pores of the support. The initiation temperature of oxidation was obviously reduced with an increase in loading amount of $La_{0.6}Sr_{0.4}MnO_3$, whereas the activity at the high conversion level was significantly lowered. The large surface area is responsible for the catalytic activity at high conversion level as was suggested previously.[5] Thus, the large surface area and enough loading of active component can not be achieved simultaneously by the direct impregnation method. Loading of oxide on support and subsequent calcination at high temperatures also induced deactivation through partial solid state reaction between oxides.

Table 1. Surface areas and methane combustion activities of $La_{0.6}Sr_{0.4}MnO_3$ supported on $BaO\cdot 6Al_2O_3$

Loading wt%	Surface area a) m^2g^{-1}	$T_{10\%}$ °C	$T_{90\%}$ b,c) °C
0	6.0	-	-
10	4.8	695	755
20	4.2	610	740
30	3.4	555	790

a) $BaO\cdot 6Al_2O_3$ was prepared by calcination of a mixture of $BaCO_3$ and γ-Al_2O_3 at 1450 °C. Supported catalysts were calcined at 1300 °C.
b) Temperatures at which conversion levels are 10% and 90%.
c) Reaction condition: CH_4 1 vol%; air 99 vol%; Space velocity 48000 h^{-1}.

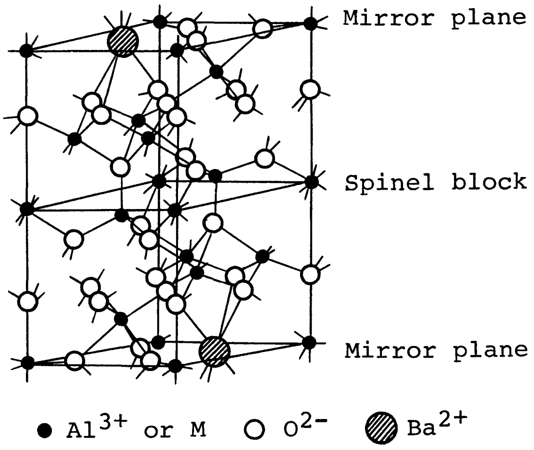

Fig. 1. Magnetoplumbite structure.

To solve these problem in conventional impregnated catalyst, Misono et al.[6] reported a new preparation method for supported perovskite catalyst,in which solid state reaction is prevented by precoating the support with La_2O_3. But, now we propose other type of catalysts for high temperature combustion which consist of the equilibrium phase. The crystal structure of $BaO\cdot 6Al_2O_3$ is basically classified into magnetoplumbite(MP)-type (Fig. 1)[7] but the coordination in the mirror plane slightly deviated from ideal structure. Since the large surface area of $BaO\cdot 6Al_2O_3$ is related with the formation of this MP-like phase as reported previously, we examined the substitution of active metal cations for Al^{3+} without destroying the crystal structure. Some transition metals can be situated at Al^{3+} site in the MP-like lattice[7] and the cation-substituted barium hexaaluminates were used as combustion catalysts. The alkoxide process is effective in reducing the temperature for the formation of cation-substituted $BaO\cdot 6Al_2O_3$ by homogeneous mixing of the components. The X-ray diffraction patterns of substituted samples ($BaMAl_{11}O_{19-\alpha}$) calcined at 1300 °C were assigned to MP-like phase but the unsubstituted single oxides were hardly detected. However, unsubustituted oxide were observed in the sample prepared from the powder mixture. Transition metal ions added in the alkoxide process seem to be dispersed in the layered aluminate structure after calcination at 1300 °C. The substitution of M for Al^{3+} site was confirmed by the shifts of diffraction lines to low angles compared with those of unsubstituted $BaO \cdot 6Al_2O_3$. The surface area of $BaO \cdot 6Al_2O_3$ was lowered by the substitution but they still maintained the large surface areas of 10-15m^2/g after calcination at 1300 °C (Table 2). The high heat resistance of barium hexaaluminate is retained in the cation-substituted samples, because their layered aluminate structure is effective in maintaining the surface area. Combustion activities of the cation-substituted samples are listed in Table 2. $BaCoAl_{11}O_{19-\alpha}$ attained complete combustion at the lowest temperature, but its $T_{10\%}$ value was not satisfactorily low. On the contrary, the activity of Fe-substituted compounds was not high at a high conversion level. The lowest $T_{10\%}$ value was attained by $BaMnAl_{11}O_{19-\alpha}$, which also showed relatively high activity at a high conversion level. The activity of $BaMnAl_{11}O_{19-\alpha}$ exceeded to those of supported oxide catalysts mentioned above, and is comparable to those of Pt/Al_2O_3 and of $LaCoO_3$. Although methane combustion initiated at the lowest temperature over $LaCoO_3$ of the oxide catalysts, the conversion increased only gradually with increasing temperature due to its low surface area. It is noted that only the low concentration of Mn dispersed in the structure can attain the high activity. Thus, Mn-substituted barium hexaaluminate is quite adequate to high temperature combustion because of the high heat-resistance and high catalytic activity.

Table 2. Surface areas and methane combustion activities of $BaMAl_{11}O_{19-\alpha}$

M	Surface area$^{a)}$ / m^{2}g^{-1}	$T_{10\%}$ / °C	$T_{90\%}$$^{b,c)}$ / °C
Al	15.3	710	730
Cr	15.7	700	770
Mn	13.7	540	740
Fe	11.1	560	780
Co	15.2	690	720
Ni	11.1	710	770
$LaCoO_3$	0.3	500	830
1wt%Pt/Al_2O_3	1.5	630	760

a) After calcination at 1300 °C.
b,c) See Table 1.

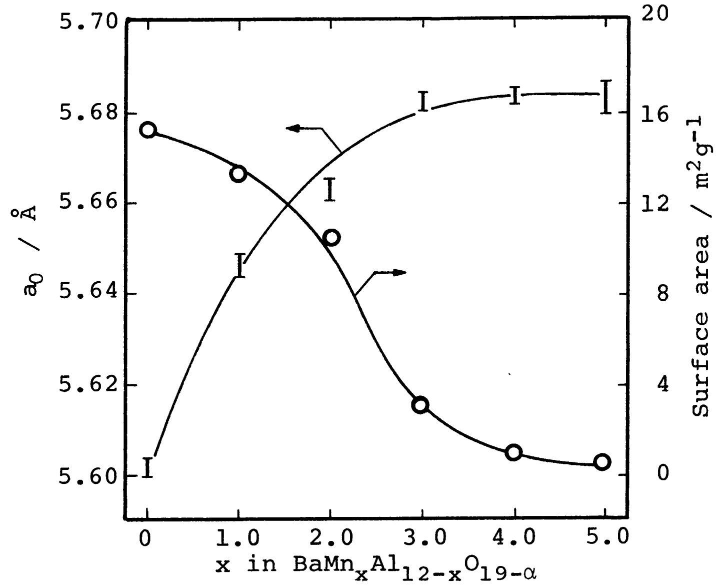

Fig. 2. The lattice constants of magnetoplumbite-like phase and surface areas for the $BaMn_xAl_{12-x}O_{19-\alpha}$ system calcined at 1300 °C.

The crystal structure of Mn-substituted system was investigated by X-ray diffraction as a function of the atomic fraction of Mn in $BaMn_xAl_{12-x}O_{19-\alpha}$ (Fig.2). The lattice constant of MP-like phase increased with substitution of Mn ions, which are rather larger than Al^{3+}, for Al^{3+} sites at $x < 3.0$. However, further addition of Mn at $x > 3.0$ unchanged the lattice constant. The second phase i.e., $BaO \cdot Al_2O_3$ was detected at $x > 3.0$ by X-ray diffraction. This indicates that the samples at $x < 3.0$ are a homogeneous solid solution of MP-like aluminate and the samples at $x > 3.0$ are a mixture of MP-like phase and $BaO \cdot Al_2O_3$. Moreover, homogeneous mixing of the components cannot be attained by the hydrolysis of alkoxide at low content of Al(i-OPr)$_3$. Figure 2 also shows the change in surface areas of BaMn$_x$Al$_{12-x}$O$_{19-\alpha}$ calcined at 1300 °C. Although the surface area decreased monotonously with the substitution of Mn, the decrease was only gradual at $x < 3.0$. At this composition, the sample consisted of the layered aluminate phase. In contrast, the surface area steeply reduced as the second phase of BaO·Al$_2$O$_3$ precipitated. Although the MP-like structure is effective in retaining the large surface area, BaO·Al$_2$O$_3$ does not contribute to this effect.[5)]

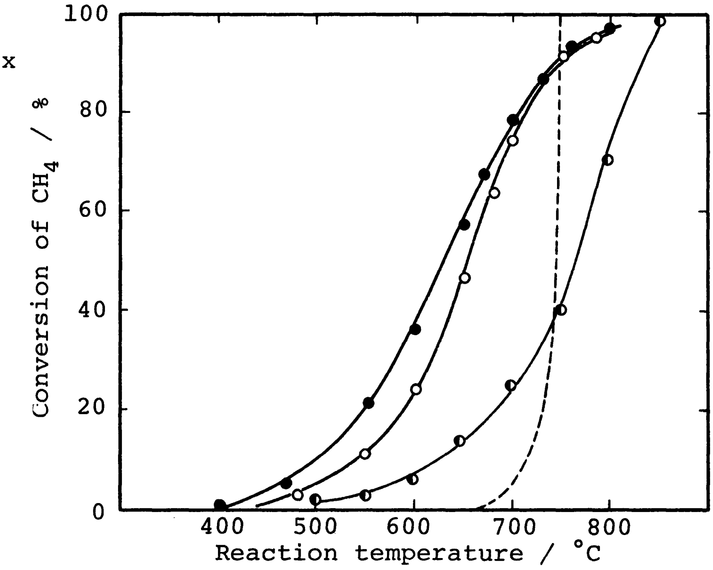

Fig. 3. Dependence of CH$_4$ combustion over BaMn$_x$Al$_{12-x}$O$_{19-\alpha}$ on reaction temperature.

Symbol	x	surface area/m^{2}g^{-1} a)
--------	0	15.3
○	1.0	13.7
●	2.0	10.4
◐	4.0	0.9

a) After calcination at 1300 °C

The catalytic activity for methane combustion over BaMn$_x$Al$_{12-x}$O$_{19-\alpha}$ was tested as a function of the oxide composition in Fig. 3. For comparison, only BaO·6Al$_2$O$_3$ powders are placed in the reactor and temperature dependence of combustion was obtained(broken line). Combustion,in this case, appears to be initiated by the radical formation at the BaO·6Al$_2$O$_3$ surface and progressed through chain reaction in the gas phase, as can be characterized by the high initiation temperature and steep rise in activity. The initiation temperature of reaction was significantly reduced with the partial substitution of Mn up to $x = 2.0$. However, the catalyst became inactive, especially at the high conversion level, with a further substitution at $2.0 < x < 4.0$ due to the decrease in surface area. The catalyst with optimum composition,BaMn$_2$Al$_{10}$O$_{19-\alpha}$, exhibited no significant decrease in surface area or catalytic activity during the course of calcination at 1300 °C for 5h. It is suggested from the discovery of Mn-substituted barium hexaaluminate that the dope of active component to heat resistant support matrix is one of the promising approach to design active catalysts for high temperature combustion, because the system consisted of thermally stable phase and atomic dispersion of active components is attained.

References

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