

Surface Areas and Catalytic Activities of Mn-substituted Hexaaluminates with
Various Cation Compositions in the Mirror Plane

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Surface areas and catalytic activities of Mn-substituted hexaaluminates were investigated as a function of cation composition in the mirror plane. After calcination at 1300 °C, the surface areas of $\text{Ba}_{1-x}\text{K}_x\text{MnAl}_{11}\text{O}_{19-\alpha}$ and $\text{Sr}_{1-x}\text{La}_x\text{MnAl}_{11}\text{O}_{19-\alpha}$ increased with x and attained to be above 23 m²/g at the optimum compositions. The methane combustion activities of these oxides were higher than those of 1 wt% Pt/Al₂O₃ and LaCoO₃.

Polycrystalline barium hexaaluminate as well as other "layered" hexaaluminates is known to maintain large surface areas at higher temperatures,¹⁻³⁾ which are quite adequate for catalysts of high temperature combustion.^{4,5)} In particular, the samples prepared by hydrolysis of metal alkoxides retain surface area of more than 10 m²/g after calcination at 1600 °C for 5 h.⁶⁾ As reported previously,^{7,8)} various elements are incorporated in the layered hexaaluminate lattice by partial replacement of Al³⁺ cations in BaAl₁₂O₁₉. When the amount of substituent is small enough not to destroy the large surface area, the manganese-system (BaMnAl₁₁O_{19-α}) was the most active among transition metal substituted hexaaluminates. However, the catalytic activity of BaMnAl₁₁O_{19-α} was not satisfactory to be used as a high temperature combustion catalyst. In this communication, we report the enhancement of the catalytic properties and surface areas of Mn-substituted hexaaluminates ($\text{A}_{1-x}\text{A}'_x\text{MnAl}_{11}\text{O}_{19-\alpha}$) by controlling the cation composition in the mirror plane, x .

Cation-substituted hexaaluminates were prepared by hydrolysis of composite alkoxides as previously described.⁷⁾ Calculated amounts of Ba(OC₃H₇)₂, Sr(OC₃H₇)₂, Ca(OC₃H₇)₂, La(OC₃H₇)₃, and/or Al(OC₃H₇)₃ were dissolved in 2-propanol. An aqueous solution of manganese nitrate and potassium nitrate was added into the 2-propanol solution of alkoxides. The resulting hydrolyzed gel was thermally decomposed at 500 °C and subsequently calcined at 1300 °C in air. Crystal structure and surface area were determined by X-ray diffraction and the BET method, respectively. Catalytic combustion of methane was carried out in a flow system as described elsewhere.³⁾

A series of hexaaluminates are comprised of stacking of close-packed oxygen ion layers (spinel blocks) which are separated each other by a monoatomic layer (mirror plane). The crystal structure of hexaaluminate is β-alumina (AAl₁₁O₁₇) or magnetoplumbite type (AAl₁₂O₁₉), depending on an ionic radius and a valence of the large cation (A-site) in the mirror plane.⁹⁾ β-Alumina structure can be

Table 1. Phases, surface areas, and catalytic activities of Mn-substituted hexaaluminates with various cation compositions in the mirror plane

Composition	r_M a)	Surface area $m^2 g^{-1}$	Catalytic activity $T_{10\%}/^\circ C^b)$	Crystalline phase ^{c)}
BaMnAl ₁₁ O _{19-α}	-	13.7	540	BA ₆
Ba _{0.8} K _{0.2} MnAl ₁₁ O _{19-α}	0.98	23.3	505	BA ₆
Ba _{0.8} La _{0.2} MnAl ₁₁ O _{19-α}	0.84	12.0	550	BA ₆ + α
Ba _{0.6} Sr _{0.2} MnAl ₁₁ O _{19-α}	0.85	15.1	535	BA ₆
SrMnAl ₁₁ O _{19-α}	-	13.4	540	quasi-SA ₆
Sr _{0.8} La _{0.2} MnAl ₁₁ O _{19-α}	0.98	23.8	500	SA ₆
Sr _{0.8} K _{0.2} MnAl ₁₁ O _{19-α}	0.87	12.9	550	quasi-SA ₆
Sr _{0.8} Ca _{0.2} MnAl ₁₁ O _{19-α}	0.86	7.3	550	quasi-SA ₆
CaMnAl ₁₁ O _{19-α}	-	4.0	565	CA ₆ + CA ₂

All samples were calcined at 1300 °C for 5 h.

a) Ratio of ionic radii between A and A' of A_{0.8}A'_{0.2}MnAl₁₁O_{19-α}.

b) Temperature at which conversion level is 10%.

Reaction condition: CH₄ 1 vol%, air 99 vol%, S.V. = 48000 h⁻¹

c) BA₆ = BaAl₁₂O₁₉, SA₆ = SrAl₁₂O₁₉, CA₆ = CaAl₁₂O₁₉, CA₂ = CaAl₄O₇, α = α-Al₂O₃

obtained for the hexaaluminates with alkaline elements and Ba, while magnetoplumbite structure for those with other alkaline earth and some rare earth elements. Crystalline phases, surface areas, and catalytic activities of Mn-substituted hexaaluminates with various compositions of mirror plane cations are investigated as summarized in Table 1. The crystal structure of BaMnAl₁₁O_{19-α} as well as BaAl₁₂O₁₉ was the hexagonal layered hexaaluminate type, whereas that of SrMnAl₁₁O_{19-α} was deteriorated to monoclinic. These two samples, consisting of the single phases, possessed large surface areas (13 m²/g). The CaMnAl₁₁O_{19-α} sample decomposed into CaAl₁₂O₁₉ and CaAl₄O₇ phases. The precipitation of the second phase always results in low surface area.

Substituents A' in A_{0.8}A'_{0.2}MnAl₁₁O_{19-α} are chosen to minimize the deviation of an ionic radius from that of the host cation. Thus, the ratio of ionic radii between A and A' (r_M) is defined as shown in Table 1. Potassium cations occupied the Ba sites without any phase separation after calcination at 1300 °C. Both surface area and catalytic activity were enhanced by substitution of K for Ba. The catalytic activity was also promoted by Sr-substitution for La (Sr_{0.8}La_{0.2}MnAl₁₁O_{19-α}) in which a single hexaaluminate phase attained the surface area of 24 m²/g. Other combinations of mirror plane cations were not effective in improving surface area or catalytic activity. It is noted that the combination of different mirror plane cations enhances the catalyst performance and the surface area of Mn-substituted hexaaluminates, only when the size of substituent is close to that of host cation ($r_M \approx 1$).

Further investigation was focused on the two Mn-substituted hexaaluminates, Ba_{1-x}K_xMnAl₁₁O_{19-α} and Sr_{1-x}La_xMnAl₁₁O_{19-α}, in which large surface area and high catalytic activity are simultaneously attained. Figure 1 shows the surface areas

of the two systems after calcination at 1300 °C as a function of composition, x . The surface area of $\text{Ba}_{1-x}\text{K}_x\text{MnAl}_{11}\text{O}_{19-\alpha}$ increased monotonously with K-substitution up to 26 m^2/g at $x = 1.0$ ($\text{KMnAl}_{11}\text{O}_{19-\alpha}$). The surface area of this system obviously relates to K content in the mirror plane. Sr-substitution for La also gave rise to the maximum surface area at $x = 0.2$ (23 m^2/g). Precise explanation for the effect of substitution on the surface area is unclear at present, but is likely related to the crystalline morphology. Transmission electron microscopic observation indicated that crystal growth along the c axis (normal to the mirror plane) is strongly suppressed in the present system. Substitution of mirror plane cations is expected to modify the interlayer distance of spinel aluminate layers and the stacking rate along the c axis.

Figure 2 shows the catalytic activities for methane combustion over $\text{Ba}_{1-x}\text{K}_x\text{MnAl}_{11}\text{O}_{19-\alpha}$ and $\text{Sr}_{1-x}\text{La}_x\text{MnAl}_{11}\text{O}_{19-\alpha}$. The activities are expressed as ignition temperatures, $T_{10\%}$, at which conversion level attained to be 10%. The ignition temperatures ($T_{10\%}$) of the two systems were lowered with increasing x and maximum activities were obtained at $x = 0.2$. The change in $T_{10\%}$ was very small for $\text{Ba}_{1-x}\text{K}_x\text{MnAl}_{11}\text{O}_{19-\alpha}$ at $x > 0.2$; however, the content of K should be low to avoid its volatilization at high temperatures.

The behavior of catalytic activity corresponds well to that of the surface area in Fig. 1.

The catalytic activities of Mn-substituted hexaaluminates were compared with combustion catalysts so far used popularly, i.e., LaCoO_3 and 1 wt% $\text{Pt}/\text{Al}_2\text{O}_3$ (Fig. 3). After calcination at 1300 °C, combustion activities of the conventional catalysts were significantly lowered because of decreases in surface area. The energy dispersive X-ray analysis of $\text{Pt}/\text{Al}_2\text{O}_3$ revealed that ca. 10% of platinum

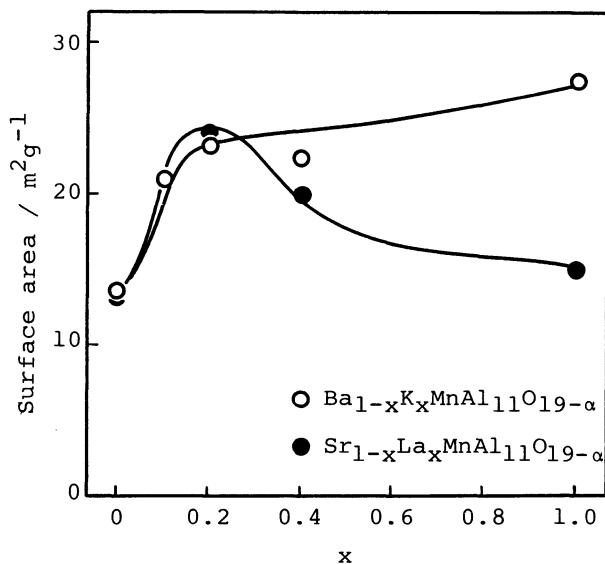


Fig. 1. Surface areas of cation-substituted hexaaluminates after calcination at 1300 °C.

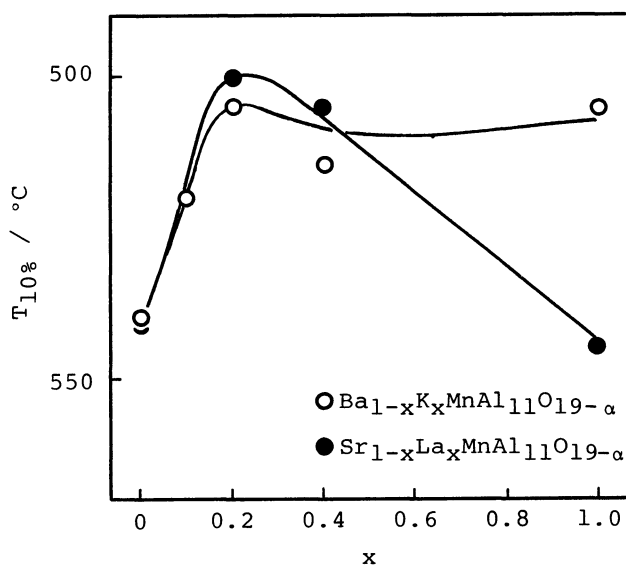


Fig. 2. Methane combustion activities of cation-substituted hexaaluminates after calcination at 1300 °C.

$T_{10\%}$ denotes the temperature at which conversion level of methane is 10%.

Reaction conditions : see Table 1.

loading was eliminated during calcination at 1300 °C for 5 h. In contrast, the large surface area of the cation-substituted hexaaluminates leads to high combustion activity even at low Mn content. The catalytic activities of two cation substituted hexaaluminate samples were the same as or higher than those of LaCoO_3 and $\text{Pt}/\text{Al}_2\text{O}_3$ in the whole temperature range. Since the activities per unit surface area of LaCoO_3 and $\text{Pt}/\text{Al}_2\text{O}_3$ are expected to be higher than those of the cation-substituted hexaaluminates, the large surface area of the latter samples are effective in attaining high combustion activities, especially under high flow rate conditions ($\text{S.V.} > 10^5 \text{ h}^{-1}$) as in a gas turbine combustor. Thus, the characteristic feature of hexaaluminate catalysts is the high resistances against thermal deactivation and sintering, which result from 1) high heat resistance of hexaaluminate matrix, 2) the catalytic activity of Mn species, and 3) the mirror plane cations which stabilize large surface area.

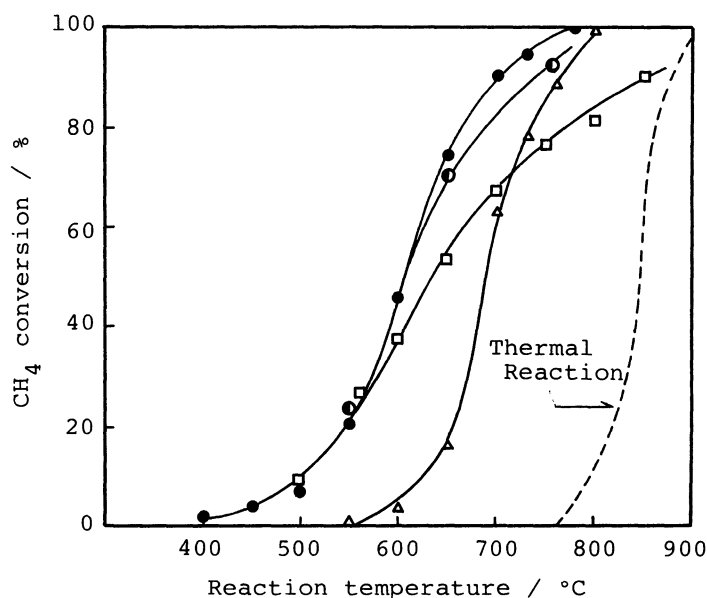


Fig. 3. Catalytic combustion over various catalysts after calcination at 1300 °C.

Catalyst	Surface area/m ² g ⁻¹
● $\text{Sr}_{0.8}\text{La}_{0.2}\text{MnAl}_{11}\text{O}_{19-\alpha}$	23.8
● $\text{Ba}_{0.8}\text{K}_{0.2}\text{MnAl}_{11}\text{O}_{19-\alpha}$	23.3
□ LaCoO_3	0.3
△ 1wt%Pt/Al ₂ O ₃	1.5

Reaction conditions : see Table 1.

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