Effect of Additives on the Surface Area of Oxide Supports for Catalytic Combustion

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The effect of additives on the surface area of oxide supports was investigated to use them for high-temperature catalytic combustion. When the addition of oxide to alumina led to the formation of layered aluminate structure, the sintering of oxides is significantly suppressed. The mixing of BaO with Al_2O_3 exhibited the most outstanding effect in maintaining the large surface area above 1200°C. The surface area is maximum at the oxide composition of $(BaO)_{0.14}(Al_2O_3)_{0.86}$. The effect of BaO on the surface area of alumina is attributed to the formation of barium hexaaluminate (BaO · $6Al_2O_3$). The surface area of BaO · $6Al_2O_3$ was further improved by preparation from corresponding alkoxides. Barium hexaaluminate prepared by hydrolysis of composite alkoxides maintained its surface area above 10 m^2 g^{-1} even after calcination at 1600°C. The activities of cobalt oxide supported on these oxides greatly depended on the surface area of the support. The cobalt oxide supported on barium hexaalumiante, especially prepared from alkoxides, showed the highest activity for methane combustion. © 1987 Academic Press, Inc.

INTRODUCTION

Catalytic combustion has been used for clean-up systems of car exhaust, odor removal, and flame-less heaters and most of them are operated below 1000°C. Recently, much interest has arisen in high-temperature catalytic combustion for gas turbines, boilers, and jet engines. Catalytic combustion has many advantages over conventional noncatalytic combustion. Emission of NO_x is greatly diminished by low operating temperatures and high efficiency can be attained by stable combustion (*1, 2*).

In the past several years, high-temperature catalytic combustion has been studied in both combustion systems and the design of catalysts to be replaced with the conventional combustion systems. From the viewpoint of catalyst research, it should be considered first that the combustion catalysts for such purposes must retain their activities above 1200°C. These applications require the design of new catalysts because supported noble metals used so far are deactivated due to sintering of both the active metal and the support oxide (*2*). Maintain-

ing the surface area of the catalyst is one of the most important problems for the industrial application of high-temperature catalytic combustion. Most of hydrocarbon molecules are almost completely oxidized for such purposes but complete combustion of residual hydrocarbons at a high conversion level is strongly affected by the mass transfer of reactants to the active surface from gas phase rather than activity of each active site (*1*). The activity at the high-conversion region is almost determined by the area of the reaction surface.

Although alumina is widely used as an oxide support, its surface area significantly decreases simultaneously with the transition from the metastable phases into α-phase (*3*). Some attempts have been made to design oxide supports, but few materials satisfy both high heat resistance and large surface area at the temperature of interest. The effect of additives such as BaO and SiO_2 on the surface area of alumina was briefly reported by Amato *et al.* (*4*). They found that these additives are effective in suppressing the enlargement of micropores and in maintaining the large surface area

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below 1250°C, but the details were not studied as to use them for support materials for high-temperature combustion. Recently, Matsuda *et al.* (5) reported that the mixing of lanthanum oxide with alumina brought about a large surface area at elevated temperatures. The oxide with the composition of $La_2O_3 \cdot 11Al_2O_3$ maintains its surface area of 37 m^2 g^{-1} even after heating at 1200°C and the effect of La_2O_3 on the surface area is ascribed to the formation of La β-alumina structure. In this paper, we have investigated the effect of additives on the surface area of Al_2O_3-, ZrO_2-, and MgO-based oxides in use of them as supports for combustion catalysts. Since the barium oxide–alumina system was revealed to have high surface area in the catalyst screening, its crystal structure and the effects of preparation conditions on surface area were investigated as a function of the oxide composition. The supports thus prepared were finally evaluated using them for combustion of methane.

EXPERIMENTAL

Preparation of sample. Metal oxide and carbonate ($CaCO_3$, $SrCO_3$, $BaCO_3$) powders were used as starting materials for oxide supports. γ-alumina was used for preparation of alumina-based support oxides. The powder mixtures of oxides and/or carbonates were calcined at 1450°C for 5 h in air. Barium hexaaluminate, $BaO \cdot 6Al_2O_3$, which showed the largest surface area among the oxide supports, was also prepared from the corresponding alkoxides. Barium isopropoxide ($Ba(i-OPr)_2$) was obtained by the reaction between Ba metal (99.9% Kishida Chemical) and 2-propanol in a nitrogen stream. Calculated amounts of $Ba(i-OPr)_2$ and $Al(i-OPr)_3$ (99.9%, Kishida Chemical) were dissolved in 2-propanol and kept at 80°C for 5 h. As water was added dropwise to the solution, a fine precipitate was obtained. After several hours of aging, the resulting suspension was evaporated to dryness *in vacuo* and the powders were calcined at elevated temperatures.

Cobalt oxide was selected as an active component for combustion of methane and was supported by a conventional impregnation method. Support oxides were suspended in a cobalt nitrate solution followed by evaporation to dryness. Dried samples were calcined at 1300°C prior to use in the oxidation reaction. The loading amount of CoO was 10 wt% for every catalyst.

The crystal structures of calcined samples were determined by X-ray diffraction (Rigaku Denki, 4011) with CuKα radiation. The specific surface areas of calcined samples were measured by the BET method using nitrogen as the adsorption gas.

Catalytic combustion of methane. Catalytic activities were measured in a conventional flow system at atmospheric pressure. Catalysts were fixed in a quartz reactor by packing alumina beads at both ends of the catalyst bed. A gaseous mixture of methane (1 vol%) and air (99 vol%) was fed to the catalyst bed at a flow rate of 48,000 cm^3 h^{-1} (space velocity = 48,000 h^{-1}). The methane conversion in the effluent gas was analyzed by on-line gas chromatography with a molecular sieve and a silica gel column. The activities of catalysts were generally evaluated in terms of the temperature at which conversion level attains 90% and denoted as $T_{90\%}$. Thus, the small value of $T_{90\%}$ indicates correspondingly high catalytic activity. The values were estimated from the temperature dependence of the conversion.

RESULTS AND DISCUSSION

Surface Area of Oxide Support and the Effect of Additives

Some oxides, which are known as refractories, have high heat resistances but the surface areas of them are generally too small to be used as catalyst supports. The effect of additives on the surface area of oxide support has been scarcely understood so far. Surface areas of alumina-, zirconia-, and magnesia-based oxides containing 10 mol% of additives were measured after calcination at 1450°C and were used as

TABLE 1

Surface Areas of Oxide Supports and Catalytic
Activities of Supported Cobalt Oxide Catalysts for
Methane Combustion

Support	Surface area[a] $(m^2 g^{-1})$	$T_{90\%}$[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 conditions: CH_4 1 vol%; air 99 vol%; space velocity 48,000 h^{-1}.

support materials for high-temperature combustion (Table 1). Most of the support oxides showed surface areas less than 1.5 $m^2 g^{-1}$. The effect of additives was barely observed or was observed as a slight decrease in surface area for magnesia- and zirconia-based oxides. Although the surface area of pure alumina is less than 1.5 $m^2 g^{-1}$ after calcination at 1450°C, that of BaO-added alumina, i.e., $(BaO)_{0.1}(Al_2O_3)_{0.9}$, was three times larger. It seems that the addition of barium oxide suppresses the sintering of alumina and retains its surface area at high temperatures.

Oxidation of methane over cobalt oxide catalysts was carried out using the oxide supports thus prepared. The catalytic activities of supported cobalt oxide catalysts are summarized in Table 1. It is noted that activities, which are expressed by $T_{90\%}$, roughly depend on the surface area of support materials. Most of the catalysts attained 90% of conversion level only above 800°C. In this temperature region, methane is oxidized by homogeneous gas phase reaction by passing through the alumina bead

bed. However, cobalt oxide supported on $(BaO)_{0.1}(Al_2O_3)_{0.9}$ with the largest surface area showed relatively high activity.

A series of alkaline earth metal oxides were also mixed with alumina and the effect on surface area was investigated (Table 2). The addition of strontia and calcia to alumina also brought about high surface area at high temperatures. However, their effect was not so large as that observed by the addition of barium oxide. Although the three alkaline-earth metal oxides, i.e., CaO, SrO, and BaO, improved the surface area of alumina as mentioned, the addition of magnesia slightly decreased the surface area. The difference in the additive effect appears to be related to the crystal structures of oxides, as is discussed later. The methane oxidation activity indicated that the catalysts supported on calcia- and strontia-added alumina were more active than that supported on pure alumina, and the catalyst supported on MgO–Al_2O_3 showed relatively low activity. Thus, the large surface area should be quite effective in enhancing the activity of catalyst. Further study was focused on the BaO–Al_2O_3 system to find the origin of its large surface area.

Phase Diagram and Crystal Structure of $(BaO)_x(Al_2O_3)_{1-x}$

The barium oxide–alumina system exhibits the greatest surface area and is most

TABLE 2

Surface Areas of Alkaline Earth Metal Aluminates
and Catalytic Activities of Supported Cobalt Oxide
Catalysts for Methane Combustion

Support	Surface area[a] $(m^2 g^{-1})$	$T_{90\%}$[b] (°C)	Phase[a,c]
Al_2O_3	1.4	—	α
$(BaO)_{0.14}(Al_2O_3)_{0.86}$	6.0	760	Pseudo-MP
$(SrO)_{0.14}(Al_2O_3)_{0.86}$	4.2	765	MP
$(CaO)_{0.14}(Al_2O_3)_{0.86}$	5.0	755	MP
$(MgO)_{0.10}(Al_2O_3)_{0.90}$	1.2	820	α+ spinel

[a] Calcined at 1450°C.

[b] Temperature at which conversion level is 90%.

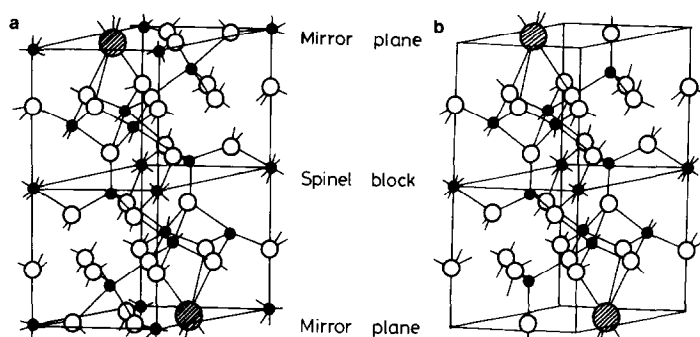[c] α, α-Al_2O_3; MP, magnetoplumbite type.

FIG. 1. Crystal structures of (a) magnetoplumbite and (b) β-alumina. ●, Al^{3+}; ○, O^{2-}; ⊘, Ba^{2+}.

promising for support material for high-temperature combustion. In this section the reported phase diagram and the crystal structures of this system are briefly described for the later discussion. The molar fraction of BaO in binary oxides is expressed by x in $(BaO)_x(Al_2O_3)_{1-x}$. Equilibrium phases appeared in the phase diagram of the $BaO-Al_2O_3$ system were reported by Purt et al. (6). α-phase is the equilibrium phase of pure alumina. Two binary compounds, i.e., $BaO \cdot 6Al_2O_3$ ($x = 0.14$) and $BaO \cdot Al_2O_3$ ($x = 0.5$), are known in the composition range from $x = 0$ to $x = 0.5$. The oxides except for these two compositions are the mixtures of $BaO \cdot 6Al_2O_3$ and $BaO \cdot Al_2O_3$.

Crystallographic analysis indicated that barium hexaaluminate, $BaO \cdot 6Al_2O_3$, is a layered aluminate structure. Crystal structure of two types of related aluminate are shown in Fig. 1. The structure of $BaO \cdot 6Al_2O_3$ is an intermediate of these two structures (7). The unit cell of magnetoplumbite structure consists of two spinel blocks which are separated by a plane containing a Ba^{2+} cation, an Al^{3+} cation, and three oxygen ions. But there are a Ba^{2+} cation and an oxygen ion on the corresponding crystal plane for the β-alumina structure. It was also reported that the barium hexaaluminate is a mixture of these two types of crystallines (8).

The structure of equimolar compound, $BaO \cdot Al_2O_3$, is called a stuffed trydimite type. The atomic arrangement in this structure is represented by completely replacing the Si^{4+} site in trydimite lattice with Al^{3+} ions. Because of the charge neutrality requirement, barium ions are placed at the large holes in the framework of AlO_4 tetrahedra (9, 10).

Phase and Surface Area of $(BaO)_x(Al_2O_3)_{1-x}$

The X-ray diffraction patterns and the surface area of the barium oxide–alumina system with various composition ratios were measured after heating at 1450°C. Figure 2 shows the X-ray diffraction patterns of $(BaO)_x(Al_2O_3)_{1-x}$. All of the diffraction peaks from pure alumina are ascribable to the α phase. The diffraction patterns of oxides at $x = 0.14$ and 0.5 consisted of single phases of $BaO \cdot 6Al_2O_3$ and $BaO \cdot Al_2O_3$, respectively. Samples between these compositions 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 $0.14 < x < 0.5$. Thus, the X-ray diffraction results confirm that samples consisted of the equilibrium phases after calcination at 1450°C.

The surface area of $(BaO)_x(Al_2O_3)_{1-x}$ after heating at 1450°C is plotted as a function of x in Fig. 3. It is clearly shown that the surface area increased with the addition of barium oxide to alumina up to the maximum value of 6.0 m^2 g^{-1} at $x = 0.14$. Then, it decreased gradually with a further increase

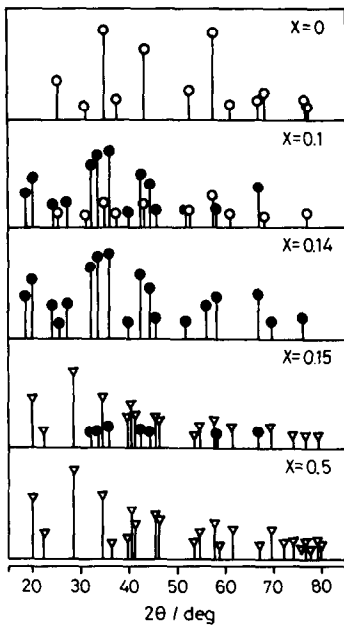FIG. 2. X-ray diffraction patterns of (BaO)$_x$ (Al$_2$O$_3$)$_{1-x}$ system calcined at 1450°C. O, α-Al$_2$O$_3$; ●, BaO · 6Al$_2$O$_3$; ∇, BaO · Al$_2$O$_3$.

FIG. 3. Change in surface areas of (BaO)$_x$(Al$_2$O$_3$)$_{1-x}$ with composition. Calcined temperature = 1450°C.

in barium oxide content at $0.14 < x < 0.5$. The composition at the maximum surface area agreed closely with that of barium hexaaluminate, indicating that the formation of this binary compound suppressed the decrease in surface area during the heating process.

Effect of Calcination Temperature on the Formation and Surface Area of Barium Hexaaluminate

Detailed investigations were focused on the sample at $x = 0.14$, which showed the largest surface area in the BaO–Al$_2$O$_3$ system. Figure 4 shows the X-ray diffraction patterns of (BaO)$_{0.14}$(Al$_2$O$_3$)$_{0.86}$ during the course of heating. It is noted that the binary compound produced at the first stage of the solid state reaction is not the equilibrium phase but BaO · Al$_2$O$_3$ is produced from γ-alumina and barium carbonate. The sample below 1100°C should be the mixture of BaO · Al$_2$O$_3$ and alumina phases, whereas the diffraction lines from the latter phase

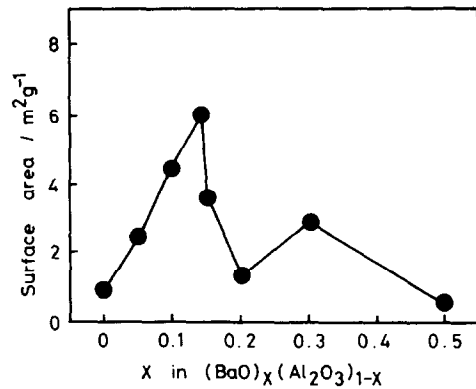are too weak to be observed due to its poor crystallinity. The equilibrium phase, i.e., BaO · 6Al$_2$O$_3$, appeared only after heating above 1200°C. This means that barium hexaaluminate is produced by a reaction between alumina and BaO · Al$_2$O$_3$ at the second stage. The sample finally consisted of a single BaO · 6Al$_2$O$_3$ phase above 1450°C with the completion of the solid state reaction. The formation of barium hexaaluminate is expected to be facilitated by the
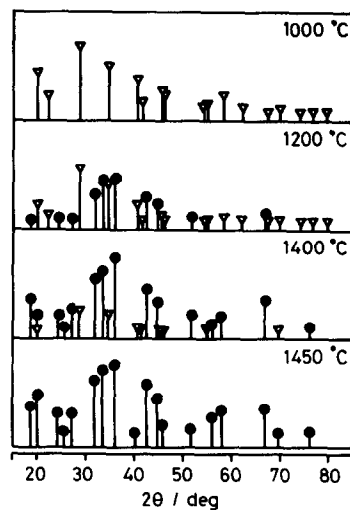

FIG. 4. X-ray diffraction patterns of (BaO)$_{0.14}$ (Al$_2$O$_3$)$_{0.86}$ calcined at various temperatures. ●, BaO · 6Al$_2$O$_3$; ∇, BaO · Al$_2$O$_3$.
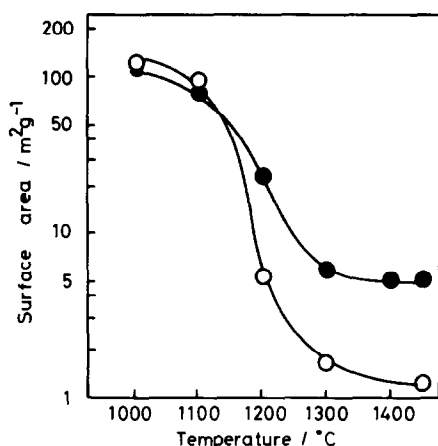
FIG. 5. Temperature dependence of surface area of $(BaO)_{0.14}(Al_2O_3)_{0.86}$. ●, $(BaO)_{0.14}(Al_2O_3)_{0.86}$; ○, Al_2O_3.

phase transition of alumina to α-phase, which occurs significantly at about 1200°C.

The change in surface area of $(BaO)_{0.14}(Al_2O_3)_{0.86}$ in the heating process is shown in Fig. 5 with reference to pure alumina. Although both samples had almost the same amount of surface area after calcination at 1000°C, significant decreases follow a rise in calcination temperature. It is noted that the decrease was more steep for Al_2O_3 than for $(BaO)_{0.14}(Al_2O_3)_{0.86}$. The steep decrease in surface area of alumina is accompanied by the phase transition of alumina to α-phase. In the case of $(BaO)_{0.14}(Al_2O_3)_{0.86}$, however, the barium hexaaluminate phase is produced in this temperature region. The barium hexaaluminate is quite effective in maintaining the surface area as mentioned before.

Effect of Additives on the Surface Area of Alumina

As mentioned, the large surface area of $BaO-Al_2O_3$ system appears to originate from the formation of barium hexaaluminate. Calcia and strontia also maintained the large surface area of alumina at high temperatures, whereas the additive effect is not so strong as that of barium oxide as shown in Table 2. Phase diagrams and crys-

tal structures of alumina–alkaline-earth metal oxide systems were reported (6, 11– 13). X-ray diffraction patterns of $(CaO)_{0.14}(Al_2O_3)_{0.86}$ and $(SrO)_{0.14}(Al_2O_3)_{0.86}$ indicated that these samples have the magnetoplumbite structure, in agreement with the reported phase diagram. Although three alkaline earth oxides, i.e., CaO, SrO, and BaO, are more or less effectively enhanced in surface area at elevated temperatures, addition of magnesia to alumina leads to a decrease in the surface area. A spinel phase is known as the equilibrium phase for the magnesia–alumina system. The magnetoplumbite and other layered aluminate structures are not formed in the magnesia–alumina system because of the small ionic radius of Mg^{2+}.

It was reported by Matsuda et al. (5) that the addition of La_2O_3 to alumina also resulted in the formation of layered aluminate structure. The La β-alumina thus formed also retains its surface area of ca. 30 m^2/g at 1200°C. The La β-alumina is a layered aluminate structure which resembles that of barium hexaaluminate except for a slight difference in the number of coordination cations as mentioned in an earlier section. It seems that such layered aluminates effectively maintain the surface area at elevated temperature. Consequently, the common feature of large surface area supports is that they have a layered aluminate structure of magnetoplumbite or β-alumina. Oxides which crystallize in other structures by mixing with alumina exhibited no effect or a decreasing effect on surface area on heating above 1200°C.

Preparation of Barium Hexaaluminate from Alkoxides

The result mentioned above suggests the barium hexaaluminate is thermally stable and fitted as a support of high-temperature combustion catalyst. The surface area of support sometimes greatly depends on the method of preparation or the calcination procedure. Preparation by the solid state reaction sometimes encounters problems
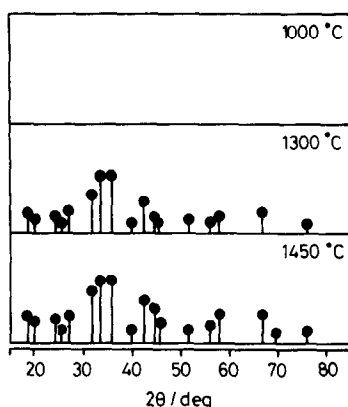
FIG. 6. X-ray diffraction patterns of $(BaO)_{0.14}$ $(Al_2O_3)_{0.86}$ after calcination of the powder prepared by hydrolysis of mixed alkoxides. ●, $BaO \cdot 6Al_2O_3$.

such as contamination, agglomeration of particles, and incomplete reaction. The hydrolysis of alkoxides is one of the excellent methods by which to obtain fine particles of high-purity oxides (14, 15). In addition, this method permits low-temperature processing of complex oxides due to the uniform mixing of component at a molecular level (16). Effects of preparation conditions of the alkoxide process on the surface area of $(BaO)_x(Al_2O_3)_{1-x}$ are summarized in Table 3. Figure 6 shows the X-ray diffraction patterns of hydrolyzed precipitates of $(BaO)_x(Al_2O_3)_{1-x}$ calcined at elevated temperatures. In the case of preparation from the powder mixture, barium hexaaluminate was produced only via $BaO \cdot Al_2O_3$ phase (Fig. 4) and the formation completed only above 1450°C. However, there are no diffraction peaks from the $BaO \cdot Al_2O_3$ phase by the alkoxide process. The alkoxide process enables direct production of barium hexaaluminate above 1200°C. This effect was probably due to homogeneous mixing of Ba and Al atoms. It appears that, in the alcoholic solution, the mixed alkoxide of barium and aluminum is formed, which enables the mixing of each element at a molecular level.

The surface area of barium hexaalumi-

nate prepared from the alkoxides was far larger than that from the mixture of $BaCO_3$ and γ-Al_2O_3. Since the primary particles from the alkoxide process appear to be very fine, the surface areas are two or three times larger than those prepared from the powder mixture. In the case of the alkoxide process, barium hexaaluminate was formed at lower temperatures by the uniform mixing of the component. Further decrease in the surface area at higher temperatures is strongly suppressed by the formation of this phase.

Effect of Preparation Conditions in the Alkoxide Process

In the alkoxide process, the properties of particles are sometimes affected by the addition of acid or base to water used for hydrolysis and aging conditions (17). However, the effect of pH on hydrolysis was not observed in this case. After the addition of water to the alkoxide solution, the suspension was stirred for several hours as a aging step before evaporation. The surface areas of calcined samples depended on the aging period of hydrolyzed alkoxides as shown in Table 3. The surface area increased with an increase in aging period and became constant over 12 h. Barium hexaaluminate with 12 h of aging period maintained the surface area of ca 10 m^2 g^{-1}, even after calcination

TABLE 3

Surface Areas of $BaO \cdot 6Al_2O_3$ Prepared by Hydrolysis of Composite Alkoxides

Aging period[a] (h)	Surface area (m^2 g^{-1})[b]		
	1300°C	1450°C	1600°C
0.5	10.8	8.8	8.6
1.0	12.5	10.2	7.3
2.0	16.4	11.2	8.7
12.0	18.5	12.5	11.0
24.0	18.3	13.4	9.5

[a] Period after addition of water to alkoxide solution.
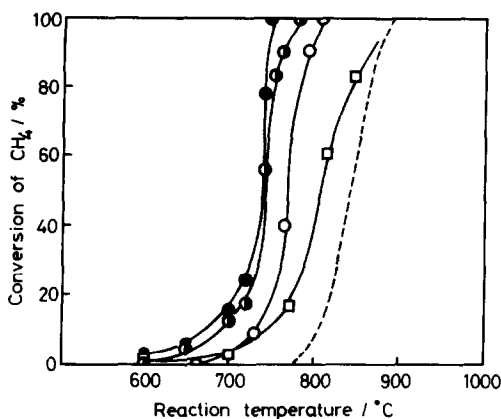
[b] After calcination at each temperature for 5 h.

FIG. 7. Dependence of CH_4 combustion over supported CoO catalysts on reaction temperature.

Symbol	Support oxide	Surface area $(m^2\ g^{-1})$
□	$(BaO)_{0.05}(Al_2O_3)_{0.95}$	2.5
○	$(BaO)_{0.10}(Al_2O_3)_{0.90}$	4.5
◑	$(BaO)_{0.14}(Al_2O_3)_{0.86}$	6.0
●	$(BaO)_{0.14}(Al_2O_3)_{0.86}$[a]	11.7
----	Thermal reaction	

[a] Prepared from alkoxides.

at 1600°C. Barium hexaaluminate prepared from alkoxides satisfies the general requirement for high-temperature combustion catalysts that the supports must maintain a surface area of at least 10 $m^2\ g^{-1}$ above 1400°C.

Catalytic Activity of Cobalt Oxide Supported on $(BaO)_x(Al_2O_3)_{1-x}$

Although noble metal catalysts, for example, Pd/Al_2O_3 and Pt/Al_2O_3, are mainly used for combustion below 1000°C, the use of them for catalytic combustion at high temperatures appears to be limited due to their ease of sintering and oxidation which produces their oxides with high volatility. Therefore, some attempts were made to design active oxide catalysts with high heat resistance. In the present study, cobalt oxide, which is one of the most active single oxides, was supported on $(BaO)_x(Al_2O_3)_{1-x}$ and was used for methane oxidation after calcination at 1300°C. Since the activity of

supported cobalt oxide catalyst was lower than that of 1 wt% Pd catalyst on the same support, further screening are needed to design active oxide catalysts. By X-ray diffraction of the catalyst, single cobalt oxides were not detected. Some cobalt ions seem to react with $BaO–Al_2O_3$ support and are incorporated into its spinel blocks in a divalent state. Figure 7 shows the relation between conversion of CH_4 and temperature of the catalyst bed. The broken line indicates the result of the noncatalytic reaction when only alumina beads are packed in the reactor tube. The oxidation obviously proceeded at low temperature in the presence of the supported Co oxide catalysts. The oxidation activity increased with a rise in reaction temperature. The catalytic activity at low conversion level is determined by the properties and number of each type of active site. However, the activity at high conversion level, e.g., above 90%, is determined mainly by the rate of mass transfer, because reactant molecules reached at the active sites are immediately oxidized and the reaction rate is regulated by the diffusion of reactant to the catalysts surface. Thus, the large reaction surface is effective in this high-conversion level unless complicated pore structures are produced at the catalyst surface. It was noted that the activity of the CoO catalyst was obviously affected by the surface area of the support. The highest activity was obtained at the support composition of barium hexaaluminate ($x = 0.14$). Although it is unclear at present whether radical gas phase reaction is partially involved in the combustion of methane over cobalt oxide catalysts, the high surface area of support oxides plays a primary role in achieving the high oxidation activities. The radical reaction, if involved, is initiated at the surface of the oxide catalyst.

The two barium hexaaluminate samples prepared from the powder mixture and the alkoxide process exhibited different activities. The sample prepared from alkoxides with large surface area was prominent in

the catalytic activities at a high conversion level for methane combustion as shown in Fig. 7 and more active than that prepared from the solid state reaction of barium carbonate and alumina. The differences in catalytic activities of catalysts indicate that the barium hexaaluminate, especially prepared from the alkoxides, is very effective for catalytic combustion and that the surface area of catalyst is of primary importance.

CONCLUSION

The present study indicated that the barium oxide–alumina system, which maintains its large surface area at elevated temperatures, is quite appropriate as a catalyst for high-temperature combustion. When an addition of oxide leads to the formation of a layered aluminate structure, the surface area was always higher than that of pure alumina above 1200°C. The formation of barium hexaaluminate exhibited the most outstanding effect in suppressing the decrease in surface area. Catalytic activity for methane combustion strongly depends on the surface area of the support materials. The large surface area of support always gave rise to enhanced activity and may play a key role in the combustion activity at the high conversion level. The surface area of barium hexaaluminate was greatly increased by employing the hydrolysis of composite alkoxides, which indicates the importance of preparation method to obtain desired support properties. Barium hexaaluminate prepared by the hydrolysis of alkoxides achieved a surface area greater than 10 m^2 g^{-1} at 1600°C and no support reported so far attained such a large value at the same temperature. The choice of support materials is very important for combustion catalysts as was revealed in the present study. The barium hexaaluminate may be the candidate for a heat-resistant support by appropriate combination with the active component.

REFERENCES

1. Trimm, D. L., *Appl. Catal.* **7**, 249 (1983).
2. Prasad, R., Kennedy, L. A., and Ruckenstein, R., *Catal. Rev.* **26**, 1 (1984).
3. Young, D. J., Udaja, P., and Trimm, D. L., "Catalyst Deactivation." p. 331. Elsevier, New York, 1980.
4. Amato, I., Martorama, D., and Silengo, B., in "Sintering and Catalysis" (G. C. Kuczynski, Ed.), p. 187. Plenum Press, New York/London, 1975.
5. Matsuda, S., Kato, A., Mizumoto, M., and Yamashita, H., in "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. 4, p. 879. Dechama, Frankfurt.
6. Levin, E. M., Robbines, C. R., and McMurdie, H. F., "Phase Diagrams for Ceramist," Fig. 206. Amer. Ceramic Soc. Columbus, OH, 1964.
7. Steevels, A. L. N., and Schrama-de Pauw, A. D. M., *J. Electrochem. Soc.* **125**, 691 (1976).
8. Kimura, S., Bannai, E., and Shindo, I., *Mater. Res. Bull.* **17**, 209 (1982).
9. Perrotta, A. J., and Smith, J. V., *Bull. Soc. France Mineral. Crystallogr.* **91**, 85, 1968.
10. Glasser, F. P., and Dent Grasser, L. S., *J. Amer. Ceram. Soc.* **48**, 377 (1963).
11. Levin, E. M., Robbines, C. R., and McMurdie, H. F., "Phase Diagrams for Ceramist," Fig. 231. Amer. Ceramic Soc., Columbus, OH, 1964.
12. Levin, E. M., Robbines, C. R., and McMurdie, H. F., "Phase Diagrams for Ceramist," Fig. 294. Amer. Ceramic Soc., Columbus, OH, 1964.
13. Levin, E. M., Robbines, C. R., and McMurdie, H. F., "Phase Diagrams for Ceramist," Fig. 4331. Amer. Ceramic Soc., Columbus, OH, 1975.
14. Mazdiyasni, K. S., Dolloff, R. T., and Smith, J. S., *J. Amer. Ceram. Soc.* **52**, 523 (1969).
15. Smith, J. S., Dolloff, R. T., and Mazdiyasni, K. S., *J. Amer. Ceram. Soc.* **53**, 91 (1970).
16. Johnson, D. W., Jr., *Amer. Ceram. Soc. Bull.* **64**, 1597 (1985).
17. Gitzen, W. H., "Alumina as a Ceramic Material," p. 13. Amer. Ceramic Soc. Columbus, OH, 1970.