CHEMISTRY LETTERS, pp. 1993-1996, 1986.

Preparation of Heat Resistant Ceramic Support with Large Surface Area from Composite Alkoxides

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The surface area of $BaO \cdot 6Al_2O_3$ was greatly enhanced by the preparation from alkoxide compared with that prepared from $BaCO_3/\gamma-Al_2O_3$ mixture, and the maximum value attained after calcination at 1600 °C was 11.0 m^2/g. The preparation from alkoxides reduces the temperature for the formation of $BaO \cdot 6Al_2O_3$ because of uniform mixing of the components. The large surface area of support brings about high catalytic activity for combustion of methane.

Recently, there arise much interests in high temperature catalytic combustion for gas turbines, boilers, and jet engines.1,2) Catalyst materials used for this purpose should have a high heat resistance so that the large surface area might be maintained above 1400 °C. Some oxides which are known as refractories have a high heat resistance but their surface area is generally too small to be used as catalyst support. To suppress sintering of oxide by additives is one of the possible way to design a support material with a large surface area. Matsuda et. al.3) reported that the addition of La_2O_3 is effective in maintaining the surface area of alumina. Although the addition of BaO to Al_2O_3 also greatly stabilizes the surface area above 1200 °C,4) the level of the surface area is not satisfactory to use for high temperature combustion. In this communication, we report the marked improvement of surface area of BaO added alumina by applying the preparation from metal alkoxides. It has become evident that the formation of binary compounds has the key role to suppress sintering of alumina-based oxides.

Barium hexaaluminate, $BaO \cdot 6Al_2O_3$, was prepared from hydrolysis of alkoxides. Calculated amounts of Ba metal and $Al(i\text{-}OPr)_3$ were stirred in 2-propanol until the whole solid is dissolved. The solution was refluxed at 80 °C for 5 h in an N_2 atmosphere before hydrolysis reaction. With an addition of water to the alcoholic solution, fine precipitates were formed. After several hours of aging, the resulting suspension was evaporated to dryness in vacuo and the powder was calcined at elevated temperatures. $BaO \cdot 6Al_2O_3$ was also prepared by calcination of $BaCO_3/\gamma-Al_2O_3$ mixture for comparison. Crystal structures of calcined samples were determined by X-ray diffraction (Rigaku Denki, 4011). Specific surface areas of calcined samples were measured by the BET method. The support oxides calcined at 1450 °C were suspended in a cobalt acetate solution, followed by evaporation to dryness. Dried samples were calcined at 1300 °C prior to use for catalytic combustion. Catalytic combustion of methane was carried out in a flow system. A gaseous mixture of methane (1 vol%) and air (99 vol%) was fed to the catalyst bed at S.V.=

48000 h^{-1}. Conversion of methane to CO_2 was analyzed by gas chromatography.

Two kinds of precursors with composition of $(BaO)_{0.14}(Al_2O_3)_{0.86}$, which were a powder mixture of $BaCO_3$ /γ-Al_2O_3 and hydrolyzed alkoxides, underwent calcination at elevated temperatures for 5 h. The surface areas of alumina-based oxides are plotted as a function of calcination temperature in Fig. 1. The surface area of γ-Al_2O_3 most steeply decreased with heating at 1000-1200 °C. Phase transition to α-phase, which occurs at about 1200 °C, is believed to facilitate sintering.$^{5)}$ On the contrary, $(BaO)_{0.14}(Al_2O_3)_{0.86}$ from $BaCO_3$/ γ-Al_2O_3 mixture maintained the surface area which is 4 or 5 times larger than that of Al_2O_3 above 1300 °C. According to the previous report, this effect of BaO is attributed to the formation of $BaO\cdot6Al_2O_3$, which is formed from $BaCO_3$/γ-Al_2O_3 mixture above 1200 °C. It was found that the surface area of $BaO\cdot6Al_2O_3$ is greatly enhanced by preparation from alkoxides. After heating at 1300 °C, the surface area of sample was 2 or 3 times larger than that prepared from $BaCO_3$/γ-Al_2O_3 mixture. Matsuda et al.$^{3)}$ reported the addition of La_2O_3 to Al_2O_3, which leads to the formation of La·β-alumina, is effective in maintaining the surface area of alumina. They attained a maximum surface area of 37 m^2/g after heating at 1200 °C. The surface area of $BaO\cdot6Al_2O_3$ prepared from alkoxides in this study is superior to that attained by La·β-alumina. The surface area of more than 10 m^2/g after calcination at 1600 °C has not been attained by any support materials so far reported.

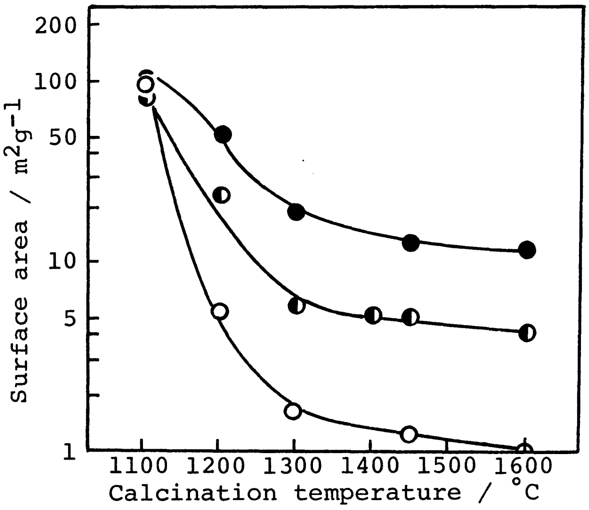


Fig. 1. Temperature dependence of surface areas of $(BaO)_{0.14}(Al_2O_3)_{0.86}$ and Al_2O_3.
● $(BaO)_{0.14}(Al_2O_3)_{0.86}$ (alkoxide)
◐ $(BaO)_{0.14}(Al_2O_3)_{0.86}$ ($BaCO_3/Al_2O_3$)
○ Al_2O_3

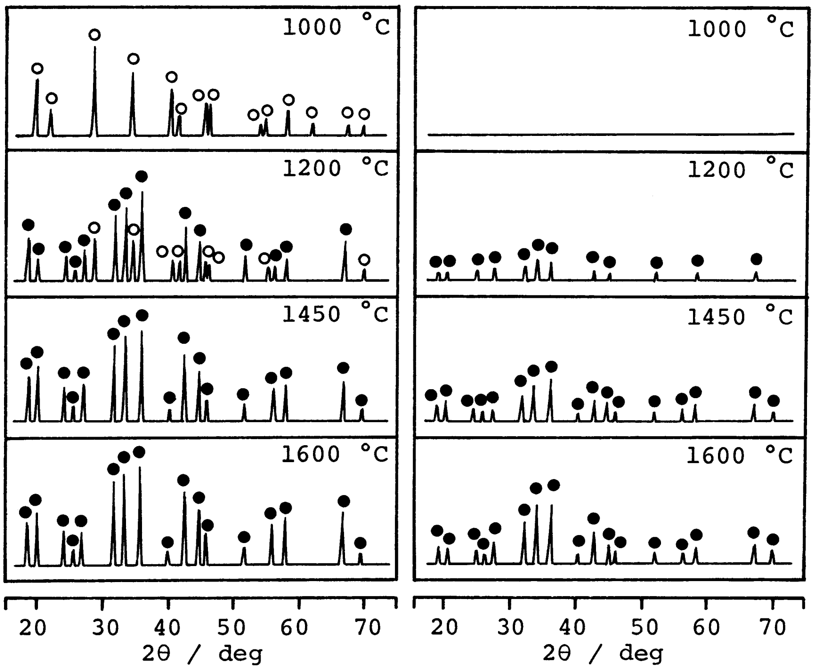
Table 1. Effects of preparation conditions on the surface area of $BaO\cdot6Al_2O_3$

$R(H_2O/MOPr)^{a)}$	Aging period / h	pH of water$^{b)}$	Surface area/m^2g^{-1} 1300°C	1450°C
10	0.5	7.0	10.8	8.8
10	1.0	7.0	12.5	10.2
10	1.0	2.0(HCl)	11.8	-
10	2.0	7.0	16.4	11.2
10	12.0	7.0	18.5	12.5
10	12.0	1.0(HNO_3)	13.6	-
10	12.0	10.0(NH_3)	13.4	-
10	24.0	7.0	18.3	13.4
2	12.0	7.0	15.5	-
1	12.0	7.0	16.2	13.2
0.75	12.0	7.0	17.9	13.7
0.5	12.0	7.0	20.2	12.7
0.3	12.0	7.0	8.8	-

a) The ratio of added water to alkoxide.
b) pH value of the water used for hydrolysis of alkoxides.

Effects of preparation conditions on the surface area of $BaO\cdot6Al_2O_3$ are summarized in Table 1. It is noted that the surface area of $BaO\cdot6Al_2O_3$ increases with the period of aging of hydrolyzed alkoxide solution and becomes almost constant over 12 h. After calcination at 1300 °C, the sample with 12 h of aging maintains the surface area of 18.5 m^2/g which is two times larger than that with 30 min of aging. Amounts of water for the hydrolysis also influences the surface area of $BaO\cdot6Al_2O_3$ calcined at 1300 °C. This parameter is expressed as ratio of the amount of water to that of metal isopropoxyl group ($R(H_2O/MOPr)$) in Table 1. The maximum surface area of 20.2 m^2/g was attained at $R(H_2O/MOPr)=0.5$, but it decreased either by an increase or by a decrease in the amount of water. The optimum condition lies strictly on the stoichiometric ratio for the hydrolysis of alkoxide, i.e., $R(H_2O/MOPr)=0.5$. After calcination at 1450 °C, however, this effect of water amount is not obvious due to sintering of $BaO\cdot6Al_2O_3$. A small amount of acidic or basic reagent such as HCl, HNO_3, and NH_4OH was added to the water used for hydrolysis, but no improvement was achieved by controlling pH of the solution. The origins of above mentioned effects of preparation are not apparent at present, however, they appear to be associated both with size and agglomeration of primary particles produced by hydrolysis of alkoxides.

X-Ray diffraction patterns of $(BaO)_{0.14}(Al_2O_3)_{0.86}$ during the course of calcination is shown in Fig. 2. In the case of preparation from $BaCO_3/\gamma\text{-}Al_2O_3$ mixture, the phase appearing at the first stage of calcination is not the equilibrium phase but the equimolar compound ($BaO\cdot Al_2O_3$) is formed. $BaO\cdot Al_2O_3$ does not contribute to the stabilization of surface area.[4] The solid state reaction between $BaO\cdot Al_2O_3$ and Al_2O_3 is completed at 1450 °C. On the other hand, there are no diffraction peaks from $BaO\cdot Al_2O_3$ phase in the case of hydrolyzed alkoxides. Thus, the alkoxide precursor permits the direct formation of $BaO\cdot6Al_2O_3$ at low temperature. This is very effective in enhancing the surface area of $BaO\cdot6Al_2O_3$ at higher temperatures. The preparation from alkoxide enables homogeneous mixing of Ba and Al atoms at a molecular level. It appears to be attained both by formation of mixed alkoxide of constituent atoms and the condensation of alkoxide molecules occurring at the hydrolysis reaction.[6—8]



(a) $BaCO_3/Al_2O_3$ (b) Alkoxide

Fig. 2. X-Ray diffraction patterns of $(BaO)_{0.14}$-$(Al_2O_3)_{0.86}$ after calcination at various temperatures.

● $BaO\cdot6Al_2O_3$ ○ $BaO\cdot Al_2O_3$

In comparison with the hydrolysis of mixed alkoxide, the suspensions of hydroxide sol of barium and aluminium were mixed after hydrolysis of each alkoxide in 2 propanol solution and evaporated to dryness. The phases appearing after calcination at 1200 °C is not only the $BaO \cdot 6Al_2O_3$ but $BaO \cdot Al_2O_3$. This indicates that the mixing of the component at a particle level does not contribute to the low temperature formation of $BaO \cdot 6Al_2O_3$. Consequently, it is likely that fine particles of $BaO \cdot 6Al_2O_3$ caused by such direct formation at low temperature enables the support with a large surface area. The difference in particle size of $BaO \cdot 6Al_2O_3$ obtained by the two preparation procedures was confirmed by using SEM.

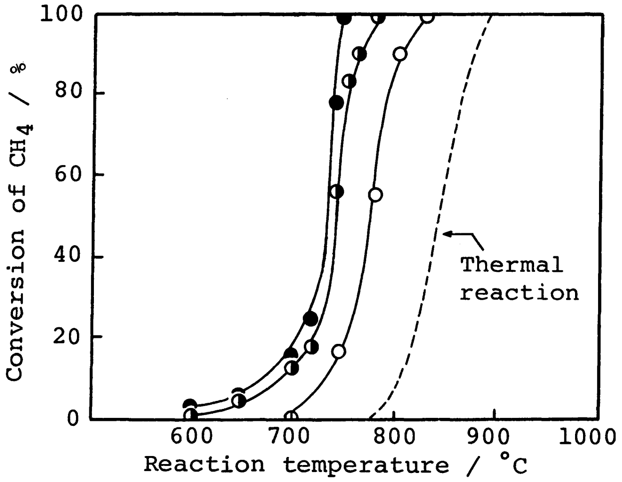


Fig. 3. Dependence of CH_4 combustion over supported CoO catalysts on reaction temperature.

Support oxide Surface area/m^2g^{-1}
● $BaO \cdot 6Al_2O_3$ (alkoxide) 11.2
◑ $BaO \cdot 6Al_2O_3$ ($BaCO_3/Al_2O_3$) 6.0
○ Al_2O_3 1.4

The alumina-based supports loaded with Co oxide were used as catalysts for combustion of CH_4. The activities of catalysts increased with a rise in temperature and depended on the kind of support and its preparation method as shown in Fig. 3. As evidently shown in the temperature dependence, the activity of catalyst is regulated by the surface area of support oxide. The Co oxide catalyst on $BaO \cdot 6Al_2O_3$, especially, which prepared from alkoxides, showed the highest activity for CH_4 combustion. The high activity of $BaO \cdot 6Al_2O_3$ from alkoxide indicates the importance of a large surface area support for the combustion catalyst.

References

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(Received August 28, 1986)