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β- and β"-Gallate, Gallium Analogues of β- and β"-Alumina, as Catalysts for High Temperature Combustion of Methane

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β- and β"-Gallate, gallium analogues of β- and β"-alumina, were tested for their catalytic activity for methane combustion. In spite of small surface areas, K- and Rb-β"-gallate gave promising results.

The compounds of β- and β"-alumina type structure, well known as solid electrolytes, are also attractive as catalyst materials. Recently it has been reported that some kinds of β-alumina retain large surface areas after calcination at high temperatures.[1,2] It is said that β-alumina structure contributes to improved resistance to sintering. Furthermore, Machida et al. prepared excellent catalysts for high-temperature combustion by introducing transition elements into Al^{3+} sites[3] and cation substitution in the "mirror plane"[4] of β-alumina. They have layered structure which show many variations in detail according to cation species and additives. So these compounds would be good samples for investigating the effects of structural variation on catalytic property. In this study, alkali metal β- and β"-gallate, gallium analogues of β- and β"-alumina, were prepared and characterized

Table 1. Surface areas and combustion activities of β- and β"-gallate

	T_{cal} a) / °C	$T_{10\%}$ b) / °C	$T_{90\%}$ c) / °C	Surface area / $m^2 g^{-1}$
Na-β"-gallate	1200	>800	>800	0.8
K-β"-gallate	1200	570	770	0.8
K-β-gallate	1300	670	795	0.4
Rb-β"-gallate	1200	565	755	0.9
Rb-β-gallate	1300	695	>800	0.3
Cs-β-gallate	1200	765	>800	0.0
Cr_2O_3	-	445	630	2.5
	1200	650	>800	0.9
β-Ga_2O_3	-	445	650	11.2
	1200	650	>800	1.3

a) Final calcination temperature.

b) Temperature giving 10% conversion of CH_4 to CO_2.
Reactant gas N_2:O_2:CH_4=82:16:2, 100 cm^3/min for 1.0 g of sample.

c) Temperature giving 90% conversion of CH_4 to CO_2.

from the standpoint of their application to catalysis. Gallium compounds have found little use as catalysts, and no attempt has been reported to employ β- and β"-gallate for catalysts so far.

Preparation of samples was similar to those reported in earlier works on Na-β and β"-gallate[5,6] and K-β and β"-gallate.[7] A_2CO_3(A=Na,K,Rb,Cs) and β-Ga_2O_3 were mixed in a molar ratio of 1:6 using ethanol as a dispersing reagent. After drying at 90 °C for 2 h, the mixture was heated at 1200 °C for 20 h in a platinum crusible. In order to prepare K- and Rb-β-gallate, the obtained samples were reheated at 1300 °C for 20 h. The products were identified by powder X-ray diffraction. Surface areas of these samples were measured by BET method (Table 1). The prepared samples were tested for catalytic activity by methane combustion, using a conventional flow reactor system. A catalyst sample (1.0 g) was mixed with inert quartz sands (4.0 g), to which gas mixture (N_2:O_2:CH_4=82:16:2) was supplied at flow rate of 100 cm^3/min. Reaction temperature was ranged from 400 to 800 °C. Reaction products were analyzed by gas chromatography. Although activities of some samples were sensitive to pretreatments, steady state activities shown in Table 1 were attained after holding the samples in flowing reactant gas mixture at 800 °C for 30 min. Cr_2O_3 and β-Ga_2O_3, the latter of which has been hardly examined for combustion activity, were also tested in the same manner for the purpose of comparing to the gallate.

Surface areas of β- and β"-gallate were less than one tenth to those of β-alumina. Three samples of β"-gallate had almost the same surface areas. Catalytic activities, however, differed distinctly from each other. Rb-β"-gallate was the most active of all the gallates, while in the case of Na-β"-gallate, combustion activity was extremely low and CH_4 conversion to CO_2 was less than 10% even at 800 °C. β-Ga_2O_3 exhibited high performance, which is comparable to that of Cr_2O_3 known for one of the most active oxide for methane combustion. But activities of these oxides were considerably lowered probably due to the decrease in surface areas after calcination at 1200 °C for 20 h. Lower $T_{10\%}$ value than that of β-Ga_2O_3 after calcination at 1200 °C was attained by K- and Rb-β"-gallate.

In Rb_2O-Ga_2O_3 system, molar ratio of Ga/Rb was varied from 4 to 10. A trace amount of Rb-β-gallate was detected at Ga/Rb=4 by X-ray diffraction measurement. In the range of Ga/Rb=5 to 8, single phase of Rb-β"-gallate was obtained. β-Ga_2O_3 coexisted at Ga/Rb=9 and 10. Surface area and CH_4 conversion to CO_2 at 600 °C were plotted in Fig.1 against Ga/Rb ratio. Surface areas increased in proportion to Ga/Rb ratio. Catalytic ativities, however, remained almost constant in the range of Ga/Rb=5 to 9. At Ga/Rb=9, or under the condition that Rb is insufficient for the formation of a single phase of Rb-β"-gallate, high activity was retained. This fact indicates that the active species in these samples is not residual Rb_2O (or Rb_2CO_3) which was in excess for formation of Rb-β"-gallate. Formation of β"-gallate structure seemed essential to the catalytic activity. In spite of the largest surface area, activity was unexpectedly lowered at Ga/Rb=10.

Although sample preparation includes a calcination process at high temperature and consequently surface areas are very small, some of β"-gallate showed combustion activities for methane. It can be said that these gallates are promising as thermally stable catalysts.

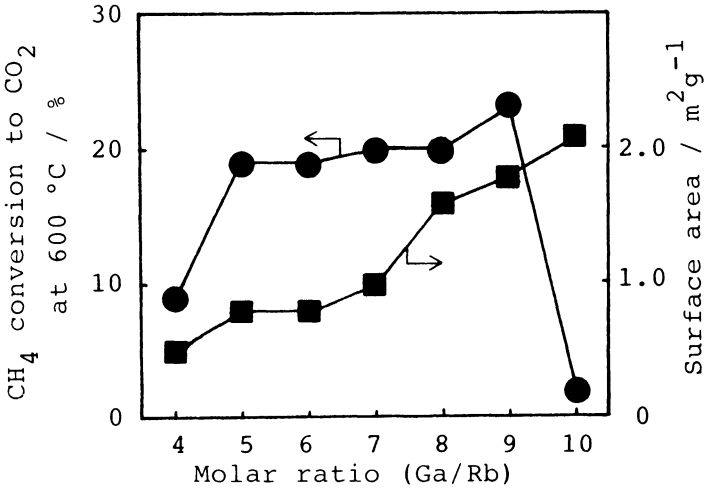

Fig.1. Surface area and activity in Rb_2O-Ga_2O_3 system.
Samples are calcined at 1200 °C for 20 h, reaction conditions are identical to those in Table 1.

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