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Importance of Apparent Density of $BaLa_2O_4$ Catalysts in Oxidative Coupling of Methane

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A voluminous catalyst composed of mainly a composite oxide of $BaLa_2O_4$ was found to be effective for oxidative coupling of methane to ethane and ethylene. The high C_2 yield is probably due to the low apparent density of the catalyst as well as to its high basicity.

Since an oxidative coupling of methane into ethane and ethylene for the purpose of a utilization of natural gas was studied by Keller and Bhasin,$^{1)}$ many authors$^{2-13)}$ have reported effective catalysts for this coupling reaction. Some catalysts$^{3-7)}$ containing alkaline compounds such as Li-MgO$^{3)}$ and NaCl-Mn oxide$^{5)}$ showed very high C_2 yields of 15-30% although their C_2 STYs(space time yield) were low and the activities were not hold for so long. Other catalysts, including lanthanide oxides,$^{8-10)}$ are characterized by their high-C_2 STYs; nevertheless they show low C_2 yields in general. We have already reported that the BaO-CaO catalysts$^{11)}$ show higher activity with the stability even at a higher temperature such as 800 °C. In addition, it has been pointed out that the surface basicity,$^{2)}$ the surface area,$^{6)}$ the existence of radical centers,$^{3)}$ and the addition of chlorides$^{12)}$ were important functions for the C_2 formation.

In this communication, we propose another factor for the oxidative coupling of methane over a voluminous BaO-La_2O_3 catalyst. The catalyst was prepared by kneading a mixture of lanthanium nitride hexahydrate (Merk) and barium hydroxide octahydrate (Kanto Chemical Comp.) with a small amount of water for 4 hours, followed by pyrolyzing at 1100 °C. The resulting material was very voluminous. It hardened with increasing the barium content and became usable as a catalyst without compression, as described later.

For comparison of the catalytic activity, some catalysts were prepared by mixing powders of $La(OH)_3$ and $Ba(OH)_2$ with a small amount of water or by coprecipitating an aqueous solution of $La(NO_3)_3$ and $Ba(NO_3)_2$ with an ammonium oxalate, followed by heat-treatment at 1000 °C. All of the powdery catalysts except for ones prepared by the pyrolysis method were compressed under a pressure of about 20 MPa before crushing. All catalysts were crushed into grains of 16-32 or 32-60 mesh size.

The coupling reactions were carried out in a conventional flow reactor at an atmospheric pressure. The reaction conditions were as follows; the weight of catalyst= 0.25 or 0.5 g, T= 700-800 °C, flow rate= 2.46 l h^{-1}, $P(CH_4)$= 14.8 kPa, P(air)= 37.1 kPa, P(He)= 49.4 kPa. All of the reaction products were analyzed by gas chromatography. The yield and the selectivity of C_2 formation were expressed by methane conversion to each product.

Table 1 shows the effect of the different preparations on the activity for the C_2 formation at 800 °C. The voluminous catalyst prepared by the pyrolysis method showed a high C_2 yield of 19.6% (maximum yield; 21.5%, 815 °C, W/F= 0.025 g h l^{-1})[13] even by using a half weight of the other catalysts. Recently, Machida et al.[14] reported that high C_2 yields of 18% were obtained over BaO/La_2O_3 catalysts by the impregnation method using $Ba(NO_3)_2$ and La_2O_3 for the oxidative coupling of methane at 750 °C. So, these results suggest that the preparation method of $BaO-La_2O_3$ catalysts greatly affects the catalytic activity for the C_2 formation.

For the pyrolysis method, the highest C_2 yield was obtained when a molecular ratio of BaO/La_2O_3 is 1.0 (Ba content is 33 atomic%). The XRD

Table 1. Catalytic Activity for Oxidative Coupling of Methane at 800 °C[a)]

Catalyst Method	Ba Content atomic%	CH_4 Conversion %	C_2 Yield %	C_2 Selectivity %
$BaO-La_2O_3$				
Mixing	10	36.9	11.8	32.0
Coprecipitation	33	39.1	13.7	35.0
Pyrolysis	33	38.3	16.2	42.5
non-pressed[b)]	33	44.7	19.6	43.8
La_2O_3	0	37.6	9.3	24.8
$BaO-CaO$	8	38.8	14.1	36.4

a) Reaction conditions; catalyst weight 0.50 g, grain size 16-32 mesh, contact time 0.20 g h l^{-1}, $P(CH_4)$= 14.8 kPa, P(air) 37.1 kPa.

b) Catalyst weight 0.25 g. The contact time is 0.10 g h l^{-1}.

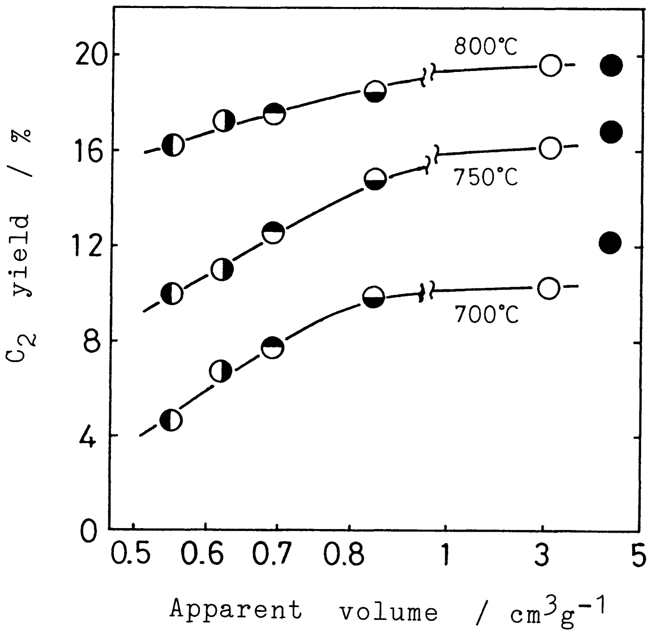

Fig. 1. Relation between apparent volume and C_2 yield at 700, 750, and 800 °C. a) Symbols of ◐, ◑, ◓, and ◒ show results at pressures of 2.5, 5, 10, and 20 MPa, respectively. b) Symbols of ● and ○ show results of non-compressed catalysts of 16-32 and 32-60 mesh sizes, respectively. c) The catalyst weight are 0.25 and 0.50 g in the case of non-compression and compression methods, respectively.

measurement showed that the voluminous catalyst was mainly composed of a composite oxide, $BaLa_2O_4$,[15] and a trace of La_2O_3. It is well known that the oxidative coupling of methane requires surface basicity.[17] Thus, the high C_2 yield obtained in this study may be due to this basic species of $BaLa_2O_4$.

However, when the voluminous $BaLa_2O_4$ catalyst was compressed in the same manner as the other catalysts, the C_2 yield decreased to 16.2%. In order to examine this point, the effect of the applied compression on the C_2 yield and apparent volume, which was determined by weighing a granular sample packed in a measuring cylinder, was investigated.

As is shown in Fig. 1, the C_2 yield was found to be correlated with apparent volume, especially for the catalysts having apparent volume ranging from 0.55 to 0.83 $cm^3\ g^{-1}$. In addition, the 16-32 mesh sample with a larger apparent volume (4.4 $cm^3\ g^{-1}$) gave higher C_2 yields than the sample of 32-60 mesh size (3.1 $cm^3\ g^{-1}$). Such a tendency was remarkable at a lower reaction temperature.

Specific surface area has been pointed out in several papers[6,18-20] as one of factors controlling C_2 hydrocarbon production. However, there was little difference in the specific surface areas between the compressed $BaLa_2O_4$ catalysts and non-compressed ones(for both ca. 1 m^2 g^{-1}). Therefore, it was suggested that low apparent density resulting from large amounts of macro-pore produced by the pyrolysis method plays an important role in the oxidative coupling of methane.

This methane coupling reaction is considered to take place by abstraction of a hydrogen atom from methane on the surface of the catalyst giving a methyl radical.3,18,20) The resulting methyl radicals combine each other forming ethane in the gas phase, and also react with the oxidizing surface and in part with molecular oxgen forming CO_x. If we consider that the catalysts have the same surface areas but different volumes of the space around active sites, it can be presumed that the C_2 formation in the gas phase is more favorable for larger spaces, compared with the CO_x formation. This presumption may support the importance of low apparent density of the catalyst in the methane coupling, and is not conflict with the results obtained by Iwamatsu et al.18) and Agarwal et al.20)

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