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Preparation of a Voluminous Composite Oxide of $BaLa_2O_4$ and Its Catalytic Performance for the Oxidative Coupling of Methane

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A voluminous composite oxide of $BaLa_2O_4$ was prepared by kneading powders of $Ba(OH)_2{\cdot}8H_2O$ (**A**) and $La(NO_3)_3{\cdot}6H_2O$ (**B**) with a small amount of water, followed by pyrolysis at 1100 °C. The resulting material (apparent volume of ca. 3 $cm^3\ g^{-1}$) was found to be effective as a catalyst for the oxidative coupling of methane to ethane and ethylene. The preparative conditions of the voluminous $BaLa_2O_4$ catalyst and these effects on the C_2 formation were investigated. When reagents A and B were mixed with each other at 33 atom-% Ba and then calcined for 10 min at 1100 °C, the $BaLa_2O_4$ composite oxide was most advantageously produced and a high C_2 yield of ca. 19% was reproducibly obtained over a non-pressed or voluminous catalyst. The high surface basicity and macro-porous structure of the voluminous $BaLa_2O_4$ catalyst, which were responsible for its high C_2 yield, are discussed.

Many authors have paid attention to the promising oxidative coupling of methane into ethane and ethylene for the utilization of natural gas.[1—6] Many studies on this coupling reaction have shown that metal oxides mixed with rare-earth oxides, such as Na_2O/Pr_2O_3,[7] Sr/La_2O_3,[8] $BaCeO_3$,[9] and $LaAlO_3$,[10] are effective for the reaction.

Recently, Yamashita et al.[11] have reported that BaO/La_2O_3 catalysts are most effective for the oxidative coupling of methane among mixed La_2O_3 catalysts prepared by the impregnation method with an alkaline earth metal (Ba, Sr, Ca, Mg) nitrate. They indicated that the surface of BaO/La_2O_3 (15 atom-% Ba) reversibly adsorbs oxygen to form peroxide ions, which are responsible for its high C_2 selectivity and C_2 yield. Zhang et al.[12] suggested that the structural defect sites at the interface of $La_2O_3/BaCO_3$ are associated with the catalytic activity for C_2 formation. In addition, more recently, several studies concerning $BaCO_3/La_2O_n(CO_3)_m$ catalysts have been reported.[13,14]

We have also reported that a voluminous catalyst containing mainly a composite oxide of $BaLa_2O_4$ showed relatively high C_2 selectivity and C_2 yield in the oxidative coupling of methane.[15] In order to obtain further information, this work was carried out concerning the preparative conditions to obtain a voluminous $BaLa_2O_4$ catalyst and its catalytic properties.

It is well known that surface basicity is essential for this type of coupling reaction.[16,17] However, details concerning the function of basic sites for this reaction have not been very clear.[4] It is therefore important to investigate the strength of the basicity of the $BaLa_2O_4$ catalyst. In order to evaluate the surface basicity, a temperature-programmed desorption (TPD) method, that had been used for barium salts/CaO catalysts elsewhere[18] was adopted. In addition, the role of the low apparent density of the voluminous $BaLa_2O_4$ catalyst in this methane coupling is discussed.

Experimental

Catalyst Preparation. The BaO–La_2O_3 catalysts used in this study were prepared by the following three methods. In the first method, powders of lanthanum nitrate hexahydrate (Merck, GR grade) and barium hydroxide octahydrate (Kanto Chemicals, GR grade) were mixed using an auto-kneader for 4 h with the addition of water in order to maintain the viscosity of the mixture. The resulting paste was pyrolyzed at 1100 °C in an electric furnace. The method is called the Pyrolysis Method in this paper. In the second method, samples were prepared by mixing powders of lanthanum hydroxide (Kanto Chemicals, GR grade) and barium hydroxide octahydrate in a manner similar to that mentioned above; the paste was dried at 100 °C, and then calcined at 1000 °C (called the Calcination Method). In the third method, samples were prepared by coprecipitation from an aqueous solution of barium nitrate and lanthanum nitrate with ammonium oxalate and ammonia at 60 °C. After washing with distilled water, the coprecipitate was filtrated and dried at 120 °C. The resulting solid was calcined at 1000 °C for 3 h (called the Coprecipitation Method).

The treated catalysts were pressed into pellets at 240 MPa (Erroneous values were given for the applied pressure in our previous letter.[15] We apologize for this and wish to correct the errors.) and crushed into grains of 0.25—0.5 or 0.5—1.0 mm size before use. A portion of the pyrolyzed catalysts was directly crushed into 0.25—0.5 mm size without pressing.

Catalyst Testing. The reactions were carried out in a fixed-bed flow reactor at atmospheric pressure. The reactor comprised a fused quartz tube connecting one tube (10 mm o.d., 300 mm long) with another tube (8 mm o.d., 200 mm long). A thin fused quartz tube (3.5 mm o.d.) was inserted into the wide tube in order to monitor the reaction temperature using a thermocouple. Methane (Sumitomo Seika, UHP grade >99.95%), air (Hitachi Oxygen), and helium (Johban Helium, Industrial grade >99.99%) were passed through a soda lime tube and then a silica gel tube, and finally supplied to the reactor. Unless otherwise specified, the results con-

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cerning catalyst testing were all obtained with 0.5 g catalyst at a flow rate of 41 $cm^3 min^{-1}$ with partial pressures of CH_4, air, and He of 14.8, 37.1, and 49.4 kPa, respectively. The product composition was analyzed using two TCD gas chromatographies fitted with a Molecular Sieve 13X-S column (for H_2, O_2, N_2, CH_4, and CO) and a Porapak Q column (for CH_4, CO_2, and C_2 hydrocarbons), respectively. The yields and selectivities for C_2 hydrocarbons were indicated by the percentage of methane converted into each product.

Catalyst Characterization. The bulk structure of the catalysts was determined by means of XRD (Nihon Denshi, DX-1) using the Cu $K\alpha$ line ($\lambda=1.542$ Å) with a nickel filter. Measurements of the surface basicity were carried out using the following TPD technique: first, the sample was pretreated by rapid cooling (at a rate of about 200 °C min^{-1} at between 800 and 500 °C) from the reaction temperature (800 °C) to room temperature in a flow of the reactant gas with the same concentration as described in the section concerning catalyst testing. The sample (100 mg) was then taken out and transformed into a TPD system; the TPD system comprised a fused quartz U-tube (6 mm i.d.) connected to a mass spectrometer (Hitachi, M70-S) through a separator for helium. It was heated from room temperature to 900 °C at a constant rate (10 °C min^{-1}) in a stream of helium (40 $cm^3 min^{-1}$). The TPD spectra were auto-recorded using a micro computer (Hitachi, M-003). The specific surface areas were measured by the BET method using nitrogen adsorption at liquid-nitrogen temperature (−196 °C). The apparent volume of the catalysts was measured by weighing a granular sample packed in a measuring cylinder. The total pore volume and median pore diameter were measured by a mercury-porosimeter (Merit, Autopore II 9220). SEM pictures were obtained with a Hitachi SEM S-800.

Results

Preparation of the $BaLa_2O_4$ Catalyst. Figure 1 shows a typical XRD pattern of the catalyst (33 atom-% Ba) prepared by the pyrolysis method. It was found that the catalysts comprised of a small amount of La_2O_3 (ASTM card 5-602) and a large amount of $BaLa_2O_4$ composite oxide, the XRD pattern of which coincided with those obtained by annealing a mixture of La_2O_3 and $BaCO_3$ at above 1300 °C, followed by quenching.[19] The lattice parameters reported by Lapato et al. are an orthorhombic prism: $a=10.075$, $b=12.662$, and $c=3.705$ Å. The other two preparation methods, however, did not results in such a $BaLa_2O_4$ composite oxide at the testing temperatures.

When the precursor of the pyrolyzed catalyst was heated in an electric furnace at 1100 °C, it released water vigorously by vaporization, and then swelled like baked bread with a gas of nitrogen dioxide. The SEM pictures showed the catalyst sample to be very porous (Fig. 2). According to a thermal gravimetric analysis (TGA), the release of nitrogen dioxide occurred twice: from 370 to 450 °C due to decomposition of about one third of the lanthanum nitrate in the precursor and from 500 to 770 °C due to that of the other. In the latter half of the second decomposition, the formation of $BaLa_2O_4$ composite oxide was almost completed. The resulting material hardened with increasing barium content and was available as a catalyst without pressing to pellets.

Comparison of Catalytic Activity. Table 1 shows the results obtained for the oxidative coupling of methane over BaO–La_2O_3 catalysts prepared by the different preparation methods. Among them, the catalysts prepared by the pyrolysis method gave the highest C_2 yield and selectivity at 800 °C, particularly in the case of non-pressed oxide catalysts. The voluminous catalyst showed a high C_2 yield of 19.6% (the maximum C_2 yield was 21.5% at 815 °C and $W/F=0.025$ $g\,h\,dm^{-3}$) with a C_2 selectivity of 43.8%, even when using a catalyst with half the weight of the other catalysts.

Effect of Ba Content. Figure 3 shows the effect of the barium content on the C_2 yield and C_2 selectivity at several reaction temperatures for the pyrolyzed catalysts, which were pelletized under a pressure of 240 MPa and crushed into 0.5—1.0 mm size. Both the C_2 yields and C_2 selectivities increased with increasing barium content up to 33 atom-% at 750 °C and above (especially at 800 °C). However, the C_2 yields decreased with increasing barium content to more than 33 atom-%, whereas the C_2 selectivity remained nearly constant.

Figure 4 shows the effect of the barium content on the XRD intensities of the (101) planes of La_2O_3 and the (320) planes of $BaLa_2O_4$. The amount of La_2O_3 decreased monotonously with increasing barium content, while the $BaLa_2O_4$ phase was observed from 20 atom-% Ba. The XRD intensity of the phase remarkably increased up to 33 atom-% Ba and then decreased. According to the phase diagram of a La_2O_3–BaO system proposed by Lopato et al.,[18] the system comprises La_2O_3 and $BaLa_2O_4$ phases in the range of less than 33 atom-% Ba, while comprising BaO and $BaLa_2O_4$ phases in the range of more than 33 atom-% Ba. Compared to this diagram, it was found that the composition of pyrolyzed catalysts containing over 33 atom-% Ba did not attain equilibrium because of a residual La_2O_3 phase in them. This fact seems to be reasonable, since the calcination temperature was considerably lower than the melting point of the system. Nevertheless, the pyrolysis method was able to form the $BaLa_2O_4$ composite oxide, even at 800 °C, which was fairly lower than the melting point of $BaLa_2O_4$ (1845 °C). As is shown in Figs. 3 and 4, the change in the C_2 yields at 800 °C with increasing barium content corresponds well with that of the XRD intensity of $BaLa_2O_4$. This fact suggests that the high C_2 yield and selectivity of the pyrolyzed catalysts is associated with the presence of the $BaLa_2O_4$ composite oxide.

Effect of Calcination Time. In the earlier stage of this work, no reproducible high C_2 yields were obtained over the $BaLa_2O_4$ catalyst, unlike in the cases over other catalysts. The causes of the poor repro-

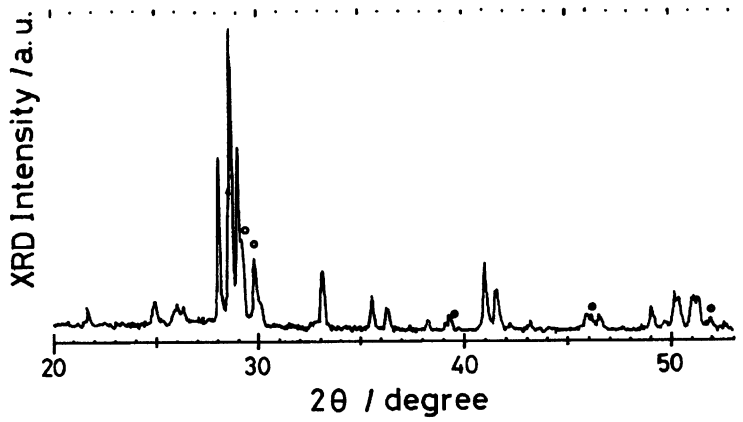
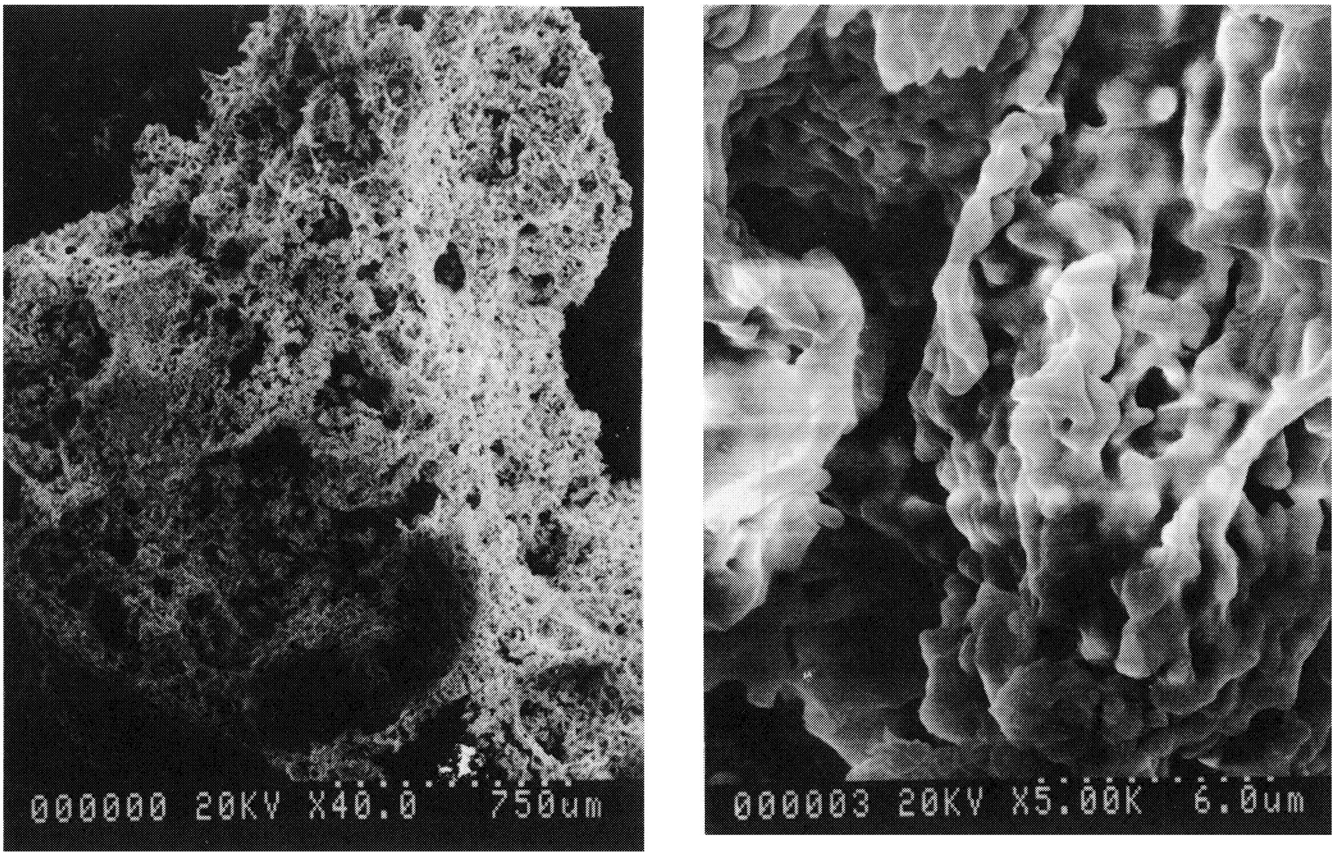


Fig. 1. XRD spectra of the $BaLa_2O_4$ catalyst prepared by the pyrolysis method. The small circles indicate the XRD pattern of La_2O_3.



(a)

(b)

Fig. 2. SEM pictures of the $BaLa_2O_4$ catalyst prepared by the pyrolysis method: a) 40 magnifications, b) 5000 magnifications.

ducibility should arise from a lack of complete information concerning the catalyst preparation and from the ready decomposition of $BaLa_2O_4$ due to moisture and carbon dioxide in the air. Thus, the calcination process was investigated in order to understand how the structure and composition of the catalyst are determined during the process.

Figure 5 shows the effect of the calcination time on the XRD intensities of La_2O_3 and $BaLa_2O_4$ for nonpressed $BaLa_2O_4$ catalysts. Calcination for 10 min was sufficient to complete the formation of the $BaLa_2O_4$ phase. Prolonged calcination slowly decomposed the $BaLa_2O_4$ phase, probably due to attacks of moisture and carbon dioxide, as described above. A decrease in the XRD intensity of La_2O_3 after 10 min may have been due to the progressive reaction of lanthanum oxide with

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

Catalyst Method	Ba content atom-%	CH_4 Conversion %	C_2 Yield %	C_2 Selectivity %
$BaO-La_2O_3$				
Calcination	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
BaO (Merck)	100	10.3	4.6	45.7

a) Catalyst weight, 0.5 g. All the catalysts were pressed at 240 MPa except non-pressed one. Grain size, 0.5—1.0 mm. b) Catalyst weight, 0.25 g. Grain size, 0.5—1.0 mm.

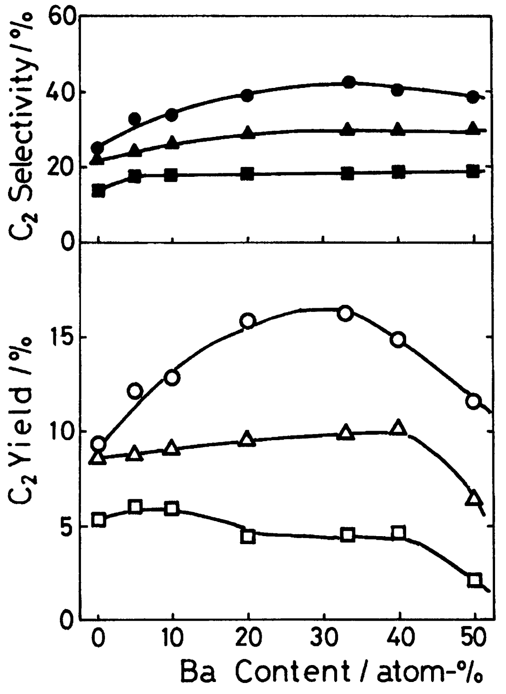


Fig. 3. Effect of the barium content in the pyrolyzed catalysts on the C_2 yield and C_2 selectivity. All catalysts were pressed at 240 MPa and crushed into 0.5—1.0 mm of grains. □, ■: at 700 °C. △, ▲: at 750 °C. ○, ●: at 800 °C.

a barium compound.

As shown in Fig. 6, the C_2 yields of the catalysts varied similarly to the XRD intensity of $BaLa_2O_4$ with the calcination time. The high activity of the $BaLa_2O_4$ catalyst for the oxidative coupling of methane remained for a long time (at least for 50 h). However, once the structure of $BaLa_2O_4$ was destroyed by decreasing the reaction temperature, the high C_2 yield and selectivity were decreased, and never recovered. These facts support the above-mentioned suggestion that the $BaLa_2O_4$ composite oxide was responsible for the high C_2 yield and C_2 selectivity of the pyrolyzed catalysts.

Effect of Applied Pressure. As is shown in Table 1, compressing the voluminous $BaLa_2O_4$ catalyst decreased the C_2 yield from 19.6 to 16.2%. The effect of the compression on the C_2 yields and C_2 selectivity was further investigated. As shown in Fig. 7, the C_2 yield decreased promptly at first, and then gradually with an increase in the applied pressure, as well as the C_2 selectivity (with a few exceptions). The apparent volumes of the catalysts (0.25—0.5 mm grains) were also decreased with an increase in the applied pressure. As a result, it was found that catalysts with a larger apparent volume tended to show higher C_2 yields, especially in the range from 0.55 to 0.83 $cm^3\,g^{-1}$ (Fig. 8). Such a tendency was more remarkable at 700 °C than at 800 °C. In addition, a 0.5—1.0 mm sample with a larger apparent volume (4.4 $cm^3\,g^{-1}$) gave only a slightly higher C_2 yield than those of 0.25—0.5 mm size (3.1 $cm^3\,g^{-1}$).

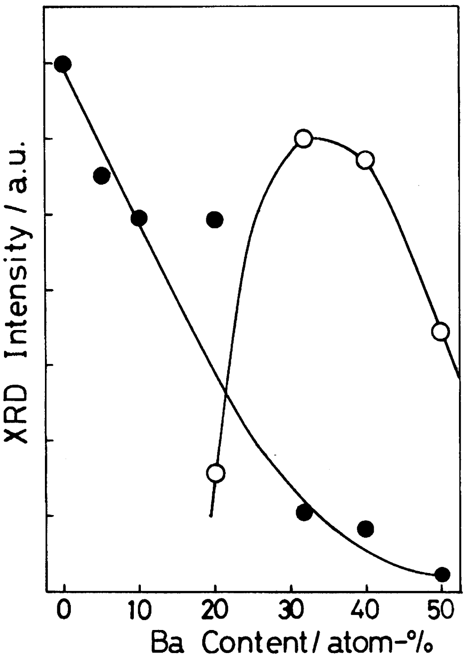


Fig. 4. Effect of the barium content on the XRD intensities of the pyrolyzed catalysts. ○: the (320) planes of $BaLa_2O_4$. ●: the (101) planes of La_2O_3.

In several papers[21,22)] the surface area has been pointed out as being one of the important factors con-

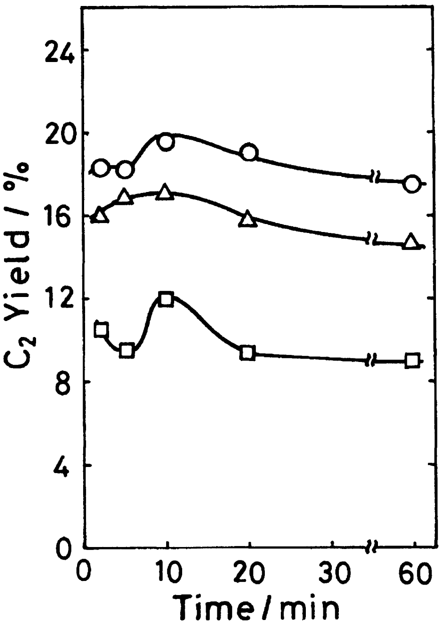


Fig. 5. Effect of the calcination time on the C_2 yield over non-pressed $BaLa_2O_4$ catalysts by the pyrolysis method. □: at 700 °C. △: at 750 °C. ○: at 800 °C.

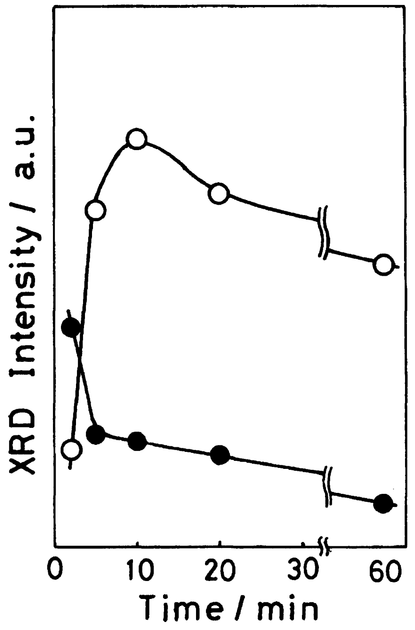


Fig. 6. Effect of the calcination time on the XRD intensities in non-pressed $BaLa_2O_4$ catalysts by the pyrolysis method. ○: the (320) planes of $BaLa_2O_4$. ●: the (101) planes of La_2O_3.

trolling C_2 formation. For the $BaLa_2O_4$ catalysts, there was little difference in the surface area between the non-pressed and pressed catalysts (for both ca. 1 $m^2 g^{-1}$). On the other hand, there were marked differences in the pore volume and median pore diameter between these catalysts; the values of the non-pressed catalyst were 2.1 $cm^3 g^{-1}$ and 17 μm, respectively, while those of the

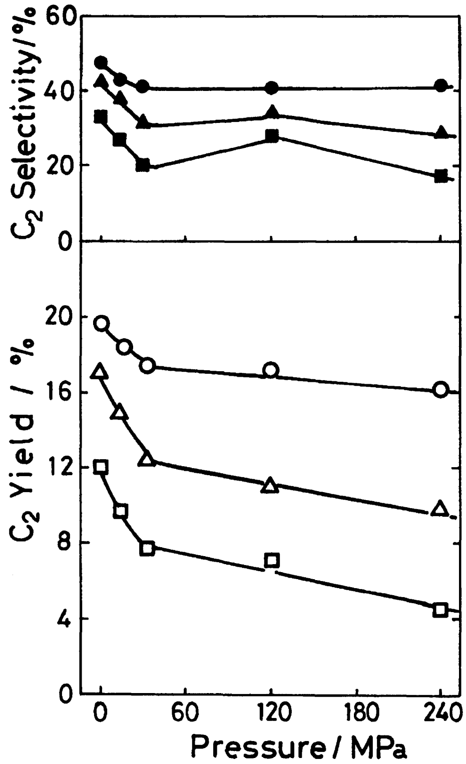


Fig. 7. Effect of the pressure applied on the $BaLa_2O_4$ catalysts by the pyrolysis method on the C_2 yield and C_2 selectivity. □, ■: at 700 °C. △, ▲: at 750 °C. ○, ●: at 800 °C.

catalyst pressed under a pressure of 240 MPa were 0.24 $cm^3 g^{-1}$ and 1.6 μm. It is probable that such differences in the pore volume and pore distribution affect the formation of C_2 hydrocarbons. In addition, in the cases of a reaction at a high temperature, by using a catalyst with small pore size, etc., it is well known that the diffusion speed in pores decreases in a porous catalyst, thus resulting in a lowering of the apparent catalytic activity.[23)]

Discussion

Basicity of the $BaLa_2O_4$ Catalyst. It has been pointed out that the oxidative coupling of methane requires surface basicity. Although the kinetics of the basic sites has not been well clarified,[4)] some TPD measurements have supported the need of basicity.[24—28)] It has recently been reported that catalysts with higher C_2 selectivities and yields tend to show large desorption peaks of CO_2 at higher temperatures on barium salt/CaO catalysts.[18)] Hence, in order to investigate the basicity of $BaLa_2O_4$ catalysts, TPD measurements were carried out.

Figures 9 and 10 show the TPD profiles of three BaO–La_2O_3 catalysts prepared by the different preparation methods as well as the effect of the barium content on the profiles for the pyrolyzed catalysts, respectively. The TPD profiles comprised several desorption peaks

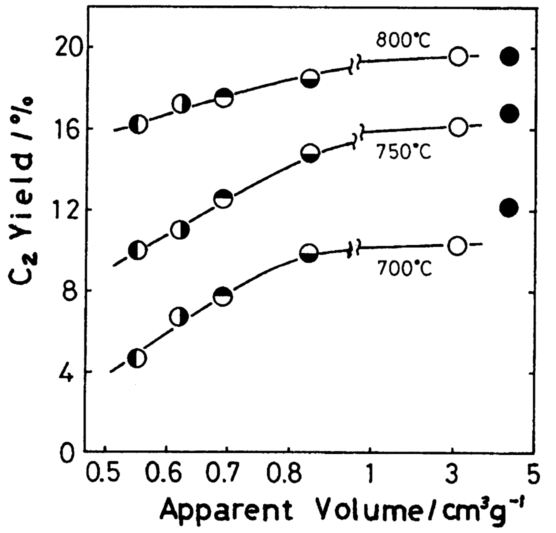


Fig. 8. Relation between the apparent volume of the $BaLa_2O_4$ catalyst by the pyrolysis method and C_2 yields at 700, 750, and 800 °C. a) Symbols ○, ◒, ◓, ◑, and ◐ correspond to the catalysts pressed at 0, 30, 60, 120, and 240 MPa, respectively. b) The symbols ● correspond to a 0.5—1.0 mm catalyst; the others correspond 0.25—0.5 mm catalysts. c) Catalyst weights of non-pressed and pressed catalysts are 0.25 and 0.50 g, respectively.

of H_2O and CO_2. The CO_2 desorption indicating the surface basicity was grouped into three temperature-regions, namely 350—550, 550—750, and higher than 750 °C. The La_2O_3 catalyst showed a large desorption peak in the first region. As a result of more detailed studies,[29] when a sample for TPD measurement was pretreated by slow cooling (30 °C min^{-1}) in a flow of reactant gas, the CO_2 desorption peak shifted from 480 to 650 °C. This shift was considered to arise from the fact that the state of CO_2, once weakly adsorbed on the La_2O_3 catalyst, converted into that adsorbed strongly during a prolonged treatment. However, since this fact has not been fully confirmed, results obtained by the slow-cooling method have been omitted in this paper.

All of the catalysts containing barium showed additional desorption peaks of CO_2 in the second and third temperature-regions. Regarding the second region, the $BaLa_2O_4$ catalyst (33 mol% Ba) showed the largest desorption peak among them. In addition, it is worth noting that no CO_2 desorption was observed in the 350 to 550 °C range for $BaLa_2O_4$-rich catalysts of 33 atom-% Ba and above. The other catalysts, which showed a large XRD pattern of La_2O_3, even if they contained large amounts of barium, gave a broad peak of CO_2 in the first region. Consequently, the CO_2 desorption in the first-region was attributable to the surface of a La_2O_3 phase, the second desorption to that of a $BaLa_2O_4$ phase or a mixed system of Ba–O–La, and the third one to that of barium components, such as BaO and $BaCO_3$. The last surface may not appreciably participate in C_2 formation, since a fairly large amount of CO_2 was adsorbed on it at a reaction temperature of 800 °C. Therefore, as mentioned by several workers,[11—13] the active species of BaO–La_2O_3 mixed oxide catalysts are considered to be well-dispersed BaO on La_2O_3; the $BaLa_2O_4$ composite oxide is one of the ultimate species regarding the degree of dispersion.

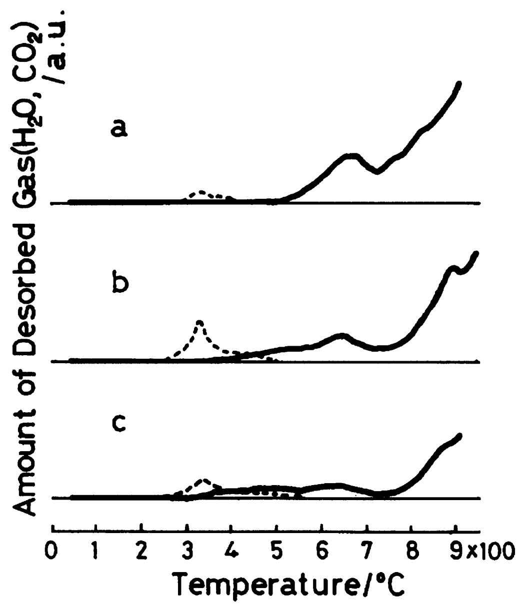


Fig. 9. TPD profiles of catalysts prepared by different methods. The bold and broken lines indicate the TPD spectra of CO_2 and H_2O, respectively. a: Pyrolysis method, b: Coprecipitation method, c: Calcination method.

$BaCl_2$/CaO catalysts with a C_2 yield of ca. 19% for the oxidative coupling of methane at 800 °C showed a large CO_2 desorption peak around 730 °C; BaO/CaO catalysts with the C_2 yield of about 14%, however, showed a large CO_2 peak at around 550 °C and additional small peaks at 730 and 800 °C.[18] The $BaLa_2O_4$ catalysts used in this study showed a C_2 yield of 16.2% and a relatively large desorption peak at around 650 °C. It was considered that the basicity of $BaLa_2O_4$ catalysts is midway between those of BaO/CaO and $BaCl_2$/CaO catalysts. In addition, it was suggested that there is a good correlation between the C_2 yields obtained for these catalysts and their basicities.

The Role of Low Apparent-Density Catalysts in the Coupling Reaction. The voluminous $BaLa_2O_4$ catalyst was effective for the oxidative coupling of methane, as shown in Table 1. In order to investigate whether other voluminous catalysts are similarly effective, a voluminous La_2O_3 catalyst was prepared by calcining a cake-like precipitate of lanthanum oxalate at 800 °C. As shown in Fig. 11, the effect of the applied pressure to the La_2O_3 catalyst on the C_2 yields was analogous to that obtained for $BaLa_2O_4$ catalysts. This confirms that the low apparent density of the catalyst is an important factor in the oxidative coupling of

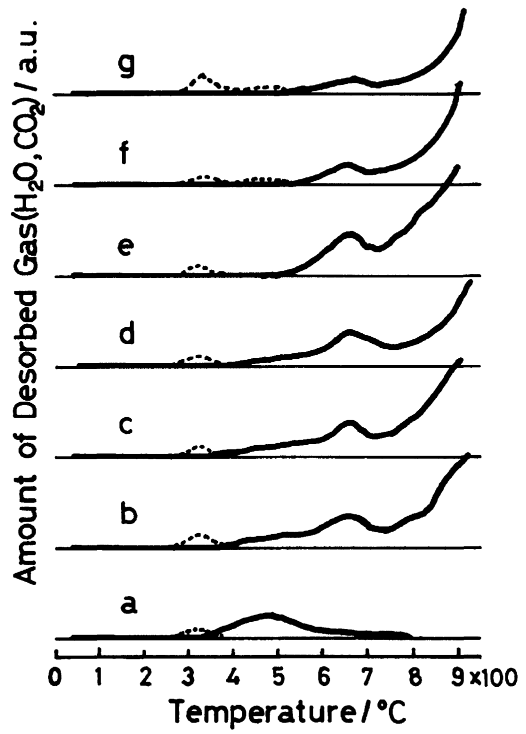


Fig. 10. Effect of the barium content on the TPD profiles for the BaO–La_2O_3 catalysts (pressed at 240 MPa) prepared by the pyrolysis method. Bold and broken lines indicate TPD spectra of CO_2 and H_2O, respectively. a: La_2O_3, b: 5 atom-% Ba, c: 10 atom-% Ba, d: 20 atom-% Ba, e: 33 atom-% Ba, f: 40 atom-% Ba, g: 50 atom-% Ba.

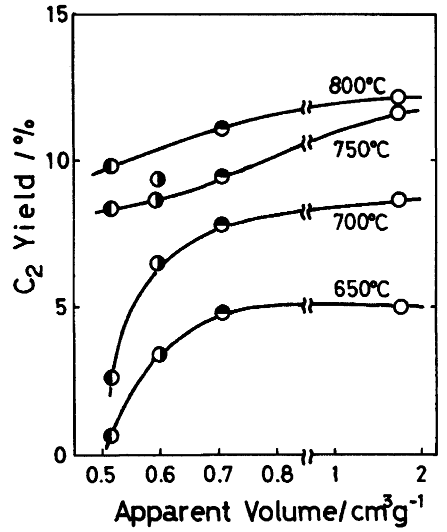


Fig. 11. Relation between the apparent volume and the C_2 yield of La_2O_3 catalysts. a) Symbols ○, ◓, ◑, and ◐ indicate the results obtained for catalysts pressed at 0, 60, 120, and 240 MPa, respectively. b) 0.5 g of 0.25—0.5 mm catalyst was used.

methane.

The oxygen conversions of non-compressed catalysts were significantly high at lower reaction temperatures, such as 650 °C over La_2O_3 and 700 °C over $BaLa_2O_4$, as well as the C_2 yield, compared with those of compressed catalysts. The high catalytic activity of the non-compressed catalysts for C_2 formation could therefore be understood in terms of the large effective diffusion coefficient[30,31] resulting from its structure. However, compressing the catalyst decreased not only the C_2 yields, but also the C_2 selectivity, even at about 100% O_2 conversion, as shown in Fig. 7. Hence, the compressing effect should be discussed concerning the decrease in the C_2 selectivity, rather than the catalytic activity.

So far, the oxidative coupling of methane has been considered to proceed as follows.[6,32—34] At first, on the oxidized surface hydrogen is abstracted from methane, thus producing methyl radicals. The resulting methyl radicals partly combine with each other to form ethane in the gas phase, and partly react with the oxidizing surface and/or molecular oxygen forming CO_x.

Iwamatsu and Aika[34] have investigated the surface-area effect on the production rate and selectivity to C_2 hydrocarbons by changing the specific surface area (S_{sp}) at a constant catalyst weight in a constant volume on the basis of the Redeal-redox mechanism. Although the rate of the CO_x formation occurring on the oxidized surface was almost proportional to S_{sp}, that of C_2 formation gradually approached saturation. The C_2 selectivity thus became higher when S_{sp} was small. Since both pressed and non-pressed $BaLa_2O_4$ catalysts had almost the same surface area, we could not apply their relation between the surface area and the C_2 selectivity in order to explain our compressing effect.

However, if we pay attention to the space around the active sites (where methyl radicals couple with each other) and suppose various catalysts which have the same chemical properties and surface areas, but different volumes in catalysts (that is porosity), the porosity effect on C_2 formation could be similarly discussed in terms of Iwamatsu et al.'s argument: In compressed catalysts the space in which methyl radicals couple with each other decreases, while the chance for the radicals to react with the oxidized surface would relatively increase compared with that of non-compressed catalysts. The large porosity, or low apparent-density catalyst, would result in the high C_2 selectivity. This fact agreed well with the results obtained in this study.

On the other hand, Baerns et al.[35] have reported that the particle size of the catalyst affects the C_2 selectivity in the oxidative coupling of methane over a $NaOH/CaO$ catalyst, and discussed the particle effect in terms of reaction-engineering calculations while taking into account transport phenomena. The results suggest that our catalytic data should also be taken into account concerning transport phenomena under our experimental conditions: the particle size of the catalyst (0.2—1.0 mm), the very high O_2 conversion and so on. In order to argue this problem, further detailed data will be required.

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