Oxidative Coupling of Methane over Various Barium Salts Mixed with CaO: The Relation with Their Surface Basicities

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Oxidative coupling of methane to ethane and ethylene was carried out over barium salts mixed with CaO catalysts prepared by a wet-mixing method. The mixing effect of the barium salts on the C_2 yield at 800 °C was remarkable in the following order: $BaBr_2 > BaCl_2 \gg BaI_2$, $Ba(OH)_2$, $BaF_2 > BaC_2O_4$, $Ba(NO_3)_2 > BaCO_3$, $BaSO_4 > Ba_3(PO_4)_2 (> CaO)$. The high C_2 yield of the $BaCl_2$/CaO catalysts was kept relatively long, and was nearly constant (19—20%) over a range of 5 to 30 mol% $BaCl_2$. Measurements of the temperature-programmed desorption of the used barium salt/CaO catalysts showed that a catalyst with the high C_2 selectivity and high C_2 yield tended to have large CO_2 desorption peaks at higher temperatures; they were also well-dispersed with barium ions. In the case of $BaCl_2$/CaO catalysts (2.5—40 mol% $BaCl_2$), a large desorption peak of CO_2 was observed at around 730 °C, that was associated with their high C_2 yields. The role of basic sites resulting from the desorption of CO_2 is discussed.

Although natural gas is abundantly available in many areas of the world, its use as an industrial chemical source has been very limited because of its inactivity. Since Keller and Bhasin[1)] studied the oxidative coupling of methane into ethane and ethylene for utilizing natural gas (mainly methane), many authors[2—15)] have reported a number of effective catalysts which can be used for methane coupling. Some of these containe alkali components, such as Li_2CO_3/MgO[4)] and NaCl/Mn oxide,[15)] and show high C_2 yields of 15—30% in spite of a low C_2 STY (space time yield) and a short catalyst life at high reaction temperatures.[16)] Recent efforts regarding this type system have been made in order to prolong the catalyst life.[17)] Other catalysts belonging a group of lanthanoid oxides[3,5,18)] were characterized by their high C_2 STYs; nevertheless, their C_2 yields were generally low. We have already reported that BaO/CaO catalysts[9,19)] yield high C_2 hydrocarbons with a relatively long life, even at a higher temperature of 800 °C in the oxidative coupling of methane. In addition, the addition of chlorides to some oxide catalysts, or in a reactant stream, has been found to enhance the selectivity to C_2 hydrocarbons, particularly to ethylene.[11,20—24)]

This paper describes the mixing effect of barium salts on the catalytic activity for the oxidative coupling of methane. As previously described, a number of effective catalysts for the coupling reaction have been found; the mechanism has also been discussed. Nevertheless, little is known about the surface property or active sites on many of these catalysts. Particularly, in spite of the excellent addition effect of bases on C_2 formation,[13)] information concerning the surface basicity is insufficient.[25)] Hence, our attention in this study was directed on the relation between the catalytic performance over various barium salt/CaO catalysts and their surface basicities. For measuring the basicity, a temperature-programmed desorption (TPD) technique was adopted.

Experimental

Catalyst Preparation. Barium salt/CaO catalysts were prepared by kneading powders of barium salt and calcium hydroxide used as a precursor of the CaO support with an incipient wetness, followed by drying and calcinating at 500 °C over night, and then at 800 °C for 3 h. The reagents used in this study were commercially obtained. All catalysts were pressed into disks, and then crushed into 16—32 mesh grains.

Catalytic Experiments. The coupling reaction was carried out in a fixed-bed continuous-flow reactor under atmospheric pressure. The reactor comprised a quartz tube connecting one tube (10 mm o.d., 8 mm i.d., 300 mm long) with another tube (8 mm o.d., 6 mm i.d., 200 mm long). A thin quartz tube(3.5 mm o.d.) was inserted inside of the wide tube in order to monitor the reaction temperature using a thermocouple. Most of the experiments described in this paper were carried out at a flow of 41 $cm^3 min^{-1}$ and methane, air, and helium of 14.8, 37.1, and 49.4 kPa, respectively (in the feed) using 250 mg of a catalyst. The reaction products were analyzed by gas chromatography with two 2 m-Molecular Sieve 13X-S and 2 m-Porapak Q columns. The yield and selectivity for C_2 hydrocarbons were indicated on the basis of the percentage of methane converted into each product.

Catalyst Characterization. The specific surface areas were measured by the BET method using nitrogen adsorption at liquid-nitrogen temperature (−196 °C). X-Ray powder diffraction (XRD) was carried out with an X-ray diffractometer (Nihon Denshi model DX-1) using Cu $K\alpha$ radiation. TPD measurements were carried out as follows; first, a sample was rapidly cooled as a pretreatment from 800 °C to room temperature in a flow of the reactant gas with the same concentration as described in the section concerning catalytic experiments; it was then weighed(50 mg) and quickly transformed into a TPD system; the TPD system comprised a quartz U-tube (8 mm o.d., 6 mm i.d.) connected to a thermal conductive detector. The sample 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}).

Results and Discussion

Mixing Effect of Various Barium Salts. The mixing effect of barium salts was investigated using catalysts prepared by a wet mixing method. The products were ethane, ethylene, CO_2, CO, H_2O, and small amounts of H_2 and propane. The results using a constant weight of the catalyst (250 mg) are summarized in Table 1. Although barium halides, except for BaF_2, greatly enhanced the C_2 yield and C_2 selectivity, both the BaI_2/CaO and $BaBr_2$/CaO catalysts were deactivated rapidly. Barium chloride showed the most suitable mixing effect among these barium salts, while insoluble barium salts, such as $BaSO_4$ and $Ba_3(PO_4)_2$, also showed a slight mixing effect on C_2 formation. That of the other barium salts was intermediate.

On the other hand, the C_2 yields obtained by $BaCl_2$ and BaO catalysts were lower than those of the mixed ones, because their very low methane conversions, despite the high C_2 selectivity. In addition, physically mixed $BaCO_3$/CaO and $BaSO_4$/CaO catalysts showed almost similar catalytic performance to that of CaO. These facts suggest that a key to the enhancement of the C_2 yields is to disperse the barium salt on a CaO support; dispersion was brought about by the wet-mixing method.

Figure 1 shows the correlation between the C_2 yield of various barium salt/CaO catalysts and the solubility of the corresponding barium salt in water. The solubility is indicated by the barium-ion concentration (mol dm^{-3}), calculated on the basis of the table of solubility products[26] or usual solubility in water at 25 °C. It was found that there was a good correlation between the C_2 yield and the solubility, except for some salts (solid symbols), such as BaC_2O_4, $Ba(NO_3)_2$, and $Ba(OH)_2$, which decomposed under the reaction temperature (800 °C). In the case of such above-mentioned barium salts and well-soluble ones, there was little difference in the C_2 yield between the wet mixing method and the physical one.

Effect of $BaCl_2$ Content. Figure 2 shows the conversions of methane and oxygen, C_2 selectivity, and C_2 yield of the $BaCl_2$/CaO catalysts at 800 °C as a function of the $BaCl_2$ content. The C_2 selectivity and C_2 yield both increased rapidly due only to the addition of 2.5 mol% $BaCl_2$ to CaO, and then remained nearly constant over

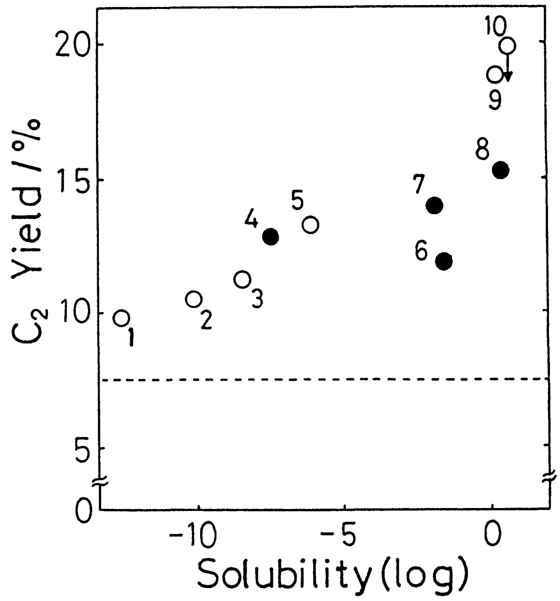

Fig. 1. Relation between the solubility of barium salts and the C_2 yield on the catalyst mixed with them. a) The broken line indicates the level of CaO in C_2 yield. b) The solubility indicates the concentration of barium ions (mol dm^{-3}) calculated on the basis of the table of solubility products. 1; $Ba_3(PO_4)_2$/, 2; $BaSO_4$/, 3; $BaCO_3$/, 4; BaC_2O_4/, 5; BaF_2/, 6; $Ba(NO_3)_2$/, 7; $Ba(OH)_2$/, 8; BaI_2/, 9; $BaCl_2$/, 10; $BaBr_2$/.

Table 1. Effect of Anions in Barium Salt Catalysts Mixed with CaO on Conversions and Selectivities for Oxidative Coupling of Methane[a)]

Catalyst Starting materials[b)]	CH_4 Conv. %	O_2 Conv. %	C_2 Yield %	C_2 Selectivity %
$Ba(OH)_2 \cdot 8H_2O$-$Ca(OH)_2$	43.9	99.8	13.0	29.7
BaF_2-$Ca(OH)_2$	44.2	99.7	13.3	30.1
$BaCl_2 \cdot 2H_2O$-$Ca(OH)_2$	46.5	97.6	18.8	40.5
$BaBr_2$-$Ca(OH)_2$	44.2	98.9	19.5	44.0
BaI_2-$Ca(OH)_2$	44.3	99.0	15.2	34.2
$Ba(NO_3)_2$-$Ca(OH)_2$	40.4	99.9	11.9	29.5
$BaSO_4$-$Ca(OH)_2$	38.1	97.6	10.3	27.1
$BaCO_3$-$Ca(OH)_2$	39.1	95.5	10.3	26.1
$BaC_2O_4 \cdot H_2O$-$Ca(OH)_2$	39.5	99.2	12.8	32.4
$Ba_3(PO_4)_2$-$Ca(OH)_2$	37.5	99.4	9.8	26.1
$Ca(OH)_2$	37.7	99.7	7.6	20.2
$BaCl_2$ (Anhydrous)	10.5	12.2	8.4	79.5
BaO	9.4	32.9	4.3	45.7

a) Conditions: Reaction temperature 800 °C, Catalyst weight 0.25 g, W/F 0.10 g h l^{-1}, $P(CH_4)$ 14.8 kPa, P(air) 37.1 kPa. b) The barium salt loading is 5 wt%.

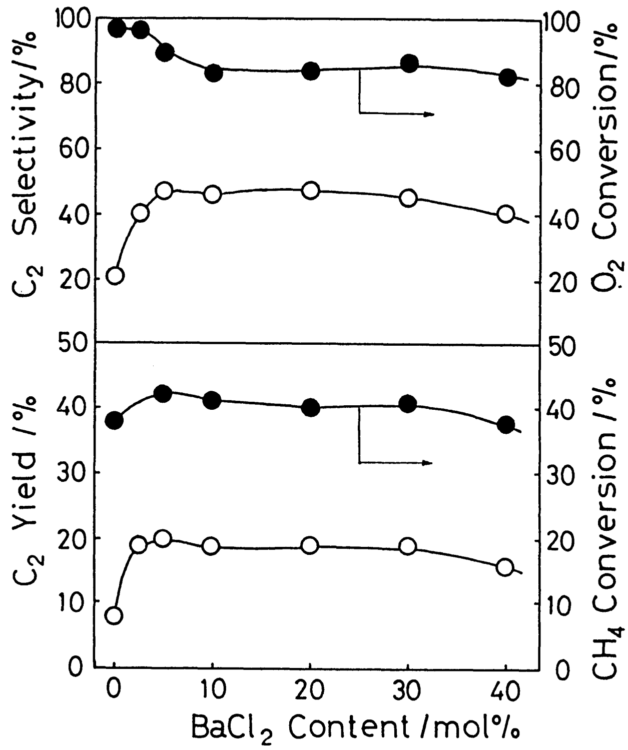

Fig. 2. Effect of the $BaCl_2$ content in $BaCl_2/CaO$ catalysts on the conversions, yield, and selectivity. Conditions: Reaction temperature 800 °C, Catalyst weight 0.25 g, W/F 0.10 g h l^{-1}, $P(CH_4)$ 14.8 kPa, P(air) 37.1 kPa.

Table 2. Sp. Surface Area of $BaCl_2/CaO$ Catalysts

$BaCl_2$ content/mol%	Sp. surface area/m^2 g^{-1}
0	12.0
2.5	6.8
5.0	4.5
10	2.9
20	1.4
30	2.0
40	1.3

the entire range of $BaCl_2$ contents examined. The oxygen conversion, indicating the total activity for methane oxidations, dropped with increasing $BaCl_2$ content up to 20 mol%, remained constant over the range of 20—30 mol%, and again slightly decreased up to 40 mol%.

As shown in Table 2, the surface area of the $BaCl_2$/CaO catalysts appeared to decrease monotonously with increasing $BaCl_2$ content. This variation in the surface areas was similar to that of O_2 conversion, not to that of the C_2 selectivity or C_2 yield. On the basis of the results obtained using alkali-doped MgO catalysts, Iwamatsu et al. suggested that some optimum surface area by sintering is an important factor for the oxidative coupling of methane.[27,28] This suggestion, however, may not be applied in cases regarding $BaCl_2/CaO$ catalysts, since their C_2 selectivities and C_2 yields were nearly constant, while their surface areas decreased with increasing $BaCl_2$ content.

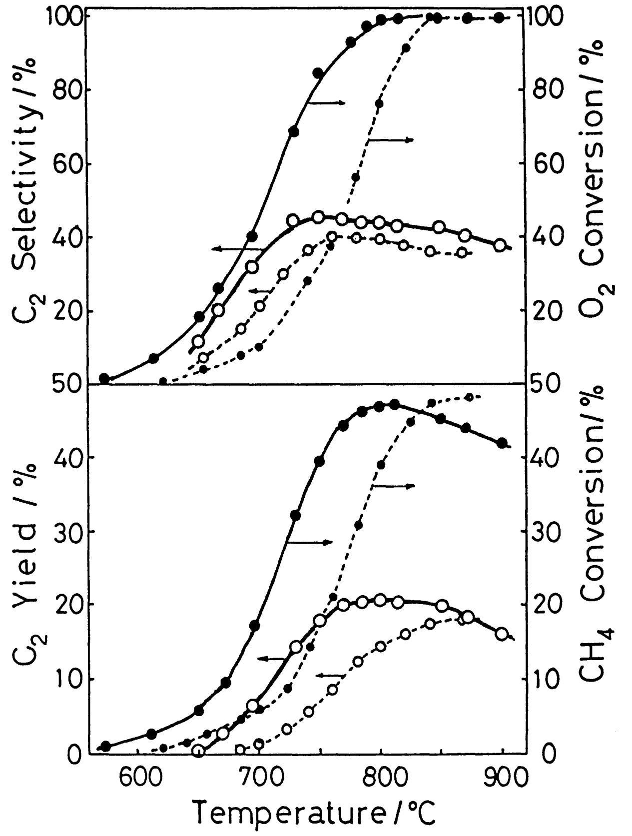

Fig. 3. Conversions, selectivity, and yield as a function of the reaction temperature on $BaCl_2/CaO$ (solid line) and $Ba(OH)_2/CaO$ (dotted line) catalysts. Added $BaCl_2$ and $Ba(OH)_2$ are 2.5 and 8.3 mol% as barium salt, respectively. Conditions: Catalyst weight 0.5 g, W/F 0.21 g h l^{-1}, $P(CH_4)$ 14.8 kPa, P(air) 37.1 kPa.

Effect of the Reaction Temperature. Figure 3 shows the effect of the reaction temperature on the methane and oxygen conversions, C_2 selectivity, and C_2 yield over one of the $BaCl_2/CaO$ catalysts containing 2.5 mol% $BaCl_2$, compared with that of a $Ba(OH)_2/CaO$ catalyst containing 20 wt% (8.7 mol%) BaO. Carbon dioxide, ethane, and ethylene increased remarkably from about 550, 650, and 675 °C, respectively, over the $BaCl_2/CaO$ catalyst. These temperatures were lower by 50—60 °C than those for the $Ba(OH)_2/CaO$ catalyst. In addition, the temperature required to attain the maximum C_2 yield was about 800 °C; it was also lower by about 70 °C than that for the latter catalyst. At around 870 °C, however, the C_2 yields of both catalysts were approximately the same.

Effect of the Contact Time and CH_4/O_2 Ratio. Figures 4 and 5 show the effects of the contact time and CH_4/O_2 ratio, respectively, on the methane and oxygen conversions, the C_2 selectivity, and the C_2 yield. The highest C_2 yield (21.3%) with a C_2 selectivity of 43% was obtained at a contact time of 0.16 g h l^{-1} at 800 °C; the

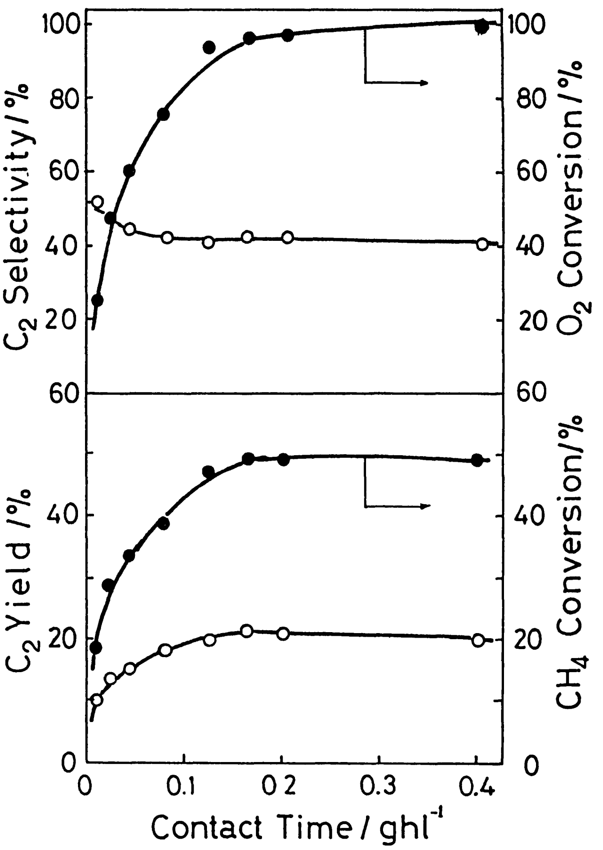

Fig. 4. Effect of the contact time on the conversions, selectivity, and yield on a $BaCl_2/CaO$ catalyst; $BaCl_2$ loading is 20 mol%. Conditions: Reaction temperature 800 °C. Catalyst weight 0.02—1.0 g. Flow rates of CH_4, O_2, N_2, and He gases are 6, 3, 12, and 20 ml min^{-1}, respectively.

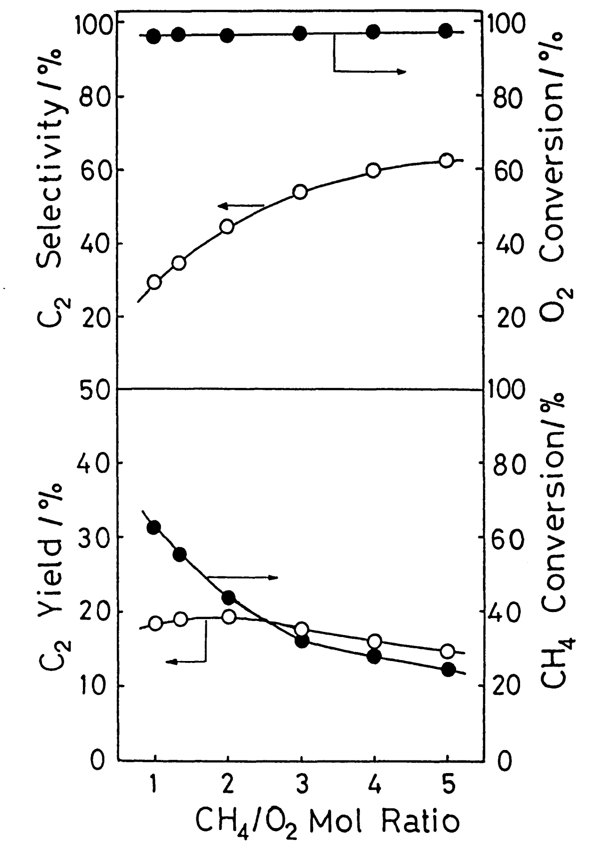

Fig. 5. Effect of the O_2/CH_4 ratio on the conversions, selectivity, and yield. Conditions: Reaction temperature 800 °C, W/F 0.21 g h l^{-1}, $P(CH_4)$ 14.8 kPa.

space-time yield of C_2 hydrocarbons was then estimated to be 4.2 mmol g^{-1} h^{-1}. Increasing the CH_4/O_2 resulted in a monotonous decrease in the methane conversion and in an increase in the C_2 selectivity. Consequently, a maximum C_2 yield was obtained at a CH_4/O_2 ratio of about 2.

Heat-Stability of the Catalyst. Table 3 compares the heat-stabilities of various CaO catalysts mixed with an alkali or alkaline earth metal chloride. About 20% of C_2 yields were obtained after 10 min on stream over all of the catalysts. The catalytic activity, however, was quickly lost, except for a $BaCl_2/CaO$ catalyst, over which the C_2 yield was kept for at least two days. The heat-stability of the $BaCl_2/CaO$ catalyst is due to a slight loss of the active species, since barium chloride has a higher melting point than do the other metal chlorides, as is shown in Table 3.

Table 3. Stability of Metal Chloride/CaO Catalysts for C_2 Formation,[a] and the Melting Point of the Corresponding Chloride

Catalyst[b]	C_2 Yield[c]/%		Melting point
	Initial	Later (Time/h)	°C
LiCl/CaO	19.0	17.8 (6.5)	614
NaCl/CaO	20.2	15.8 (1.5)	800
$MgCl_2/CaO$	19.7	17.8 (4.0)	712
$CaCl_2/CaO$	18.1	10.8 (10.0)	772
$SrCl_2/CaO$	19.2	17.9 (6.5)	873
$BaCl_2/CaO$	20.2	20.0 (48.0)	962

a) Conditions: Reaction temperature 800 °C, catalyst weight 0.50 g, W/F 0.41 g h l^{-1}, $P(CH_4)$ 14.8 kPa, P(air) 37.1 kPa. b) Metal chloride loading is 5 mol%. c) Data in the column of "initial" show C_2 yields after 10 min on stream, and those for the "later" at the sampling time shown in parentheses, respectively.

TPD Measurements. The TPD technique using a quenching method in the reactant gases as a pretreatment of the sample was carried out in order to investigate the relation between the catalytic activity for the methane coupling and the surface property of the catalyst.

Figure 6 shows TPD profiles of the catalysts listed in Table 1, except for the heat-unstable ones. These profiles are arranged in the order of the C_2 yield of the corresponding catalyst from high to low, downward. The TPD spectra comprised a strong desorption peak at around 400 °C, as well as several peaks at temperatures higher than 500 °C. They were confirmed to be due to H_2O and CO_2, respectively, by using a mass spectrometer. Osada and co-workers and Korf et al. also carried

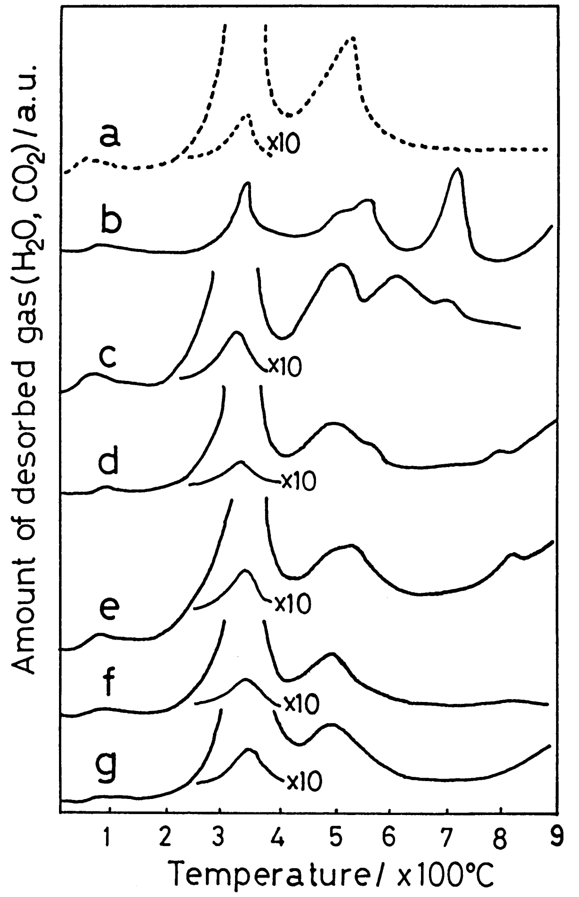

Fig. 6. Profiles of TPD on various Ba salt/CaO catalysts a: CaO, b: $BaCl_2$/CaO, C: $Ba(OH)_2$/, d: BaC_2O_4/, e: $BaCO_3$/, f: $BaSO_4$/, g: $Ba_3(PO_4)_2$/.

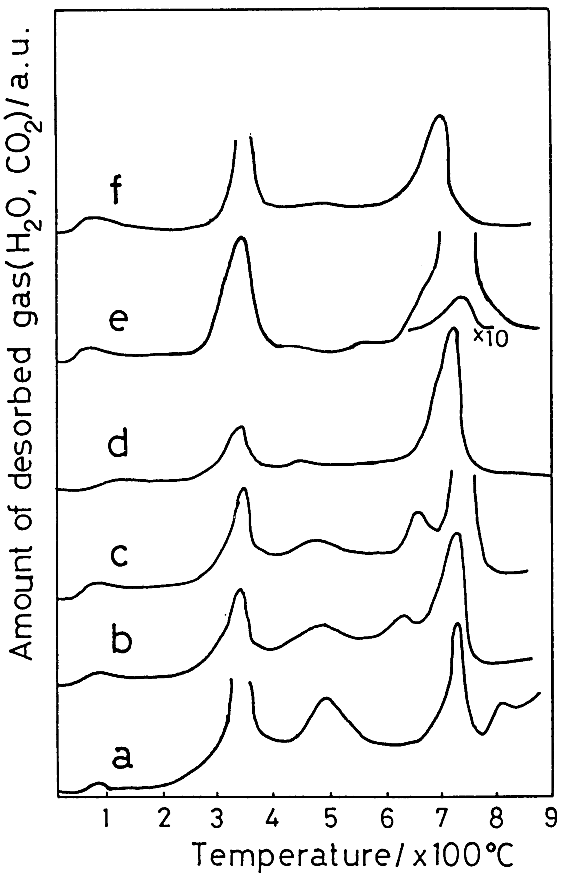

Fig. 7. Effect of the $BaCl_2$ content in $BaCl_2$/CaO catalysts on the TPD profile. a: 2.5 mol%, b: 5 mol%, c: 10 mol%, d: 20 mol%, e: 30 mol%, f: 40 mol%.

out CO_2-TPD measurements on Y_2O_3–CaO[29] and BaO/CaO[30] catalysts, respectively. According to their TPD profiles, only one CO_2 desorption peak was observed in the range of 500 and 850 °C; it is different from our results. The cause of such different profiles is distinctly due to differences in the pretreatment of the sample.

The CaO catalyst gave only one desorption peak of CO_2 at 550 °C (about 0.05 mmol g^{-1}), while $BaCl_2$/CaO and $Ba(OH)_2$/CaO catalysts with high C_2 yields and selectivity gave some additional desorption peaks: the former catalyst at 580 and 730 °C, the latter one at 630 and 730 °C, respectively. The TPD profiles of other catalysts were similar to that of a CaO catalyst in the limited range below 800 °C, though the CO_2 desorption peak had a shoulder at the high-temperature side. The shoulder tended to increase and/or to shift to higher temperatures with increasing the C_2 selectivities and C_2 yields. These facts suggest that the stronger basic sites resulting from CO_2 desorption at higher temperatures may be related to the higher C_2 selectivity and yield.

In the case of catalysts mixed with insoluble barium salts, such as $BaSO_4$ and $BaCO_3$, the wet-mixing method was effective for enhancing the C_2 yields. This method could help disperse their barium salts on the surface of CaO through their dissolution in water. The TPD profiles of the insoluble barium salt/CaO catalysts also support the last fact, since a catalyst mixed with a more soluble barium salt had a lager shoulder peak (which should be due to barium ions) at higher temperatures.

Mixing Effect of $BaCl_2$ on the TPD Profile. The surface property of a mixed catalyst generally depends on the amount of additive. Figure 7 shows the effect of the $BaCl_2$ content on the TPD profiles of $BaCl_2$/CaO catalysts. For a comparison, the results for $Ba(OH)_2$/CaO catalysts are given in Fig. 8. Their CO_2 desorption peaks were grouped into four kinds of peaks, as summarized in Table 4. The first CO_2 desorption peak at around 500 °C was assigned to the desorption of CO_2 from the surface of CaO, though the CO_2 peak in Fig. 6 appeared at 550 °C. The second peak was observed at between 500 and 730 °C for $BaCl_2$/CaO catalysts, and between 500 and 800 °C for $Ba(OH)_2$/CaO catalysts, respectively, at relatively low concentrations of the barium salts. The peak also shifted to the higher temperature side with increasing barium content. Therefore, the second peaks may be due to CO_2 desorption resulting from a mixed system with barium salt and CaO.

The third peak was observed at around 730 °C for all $BaCl_2$/CaO catalysts, and as an appreciably large peak,

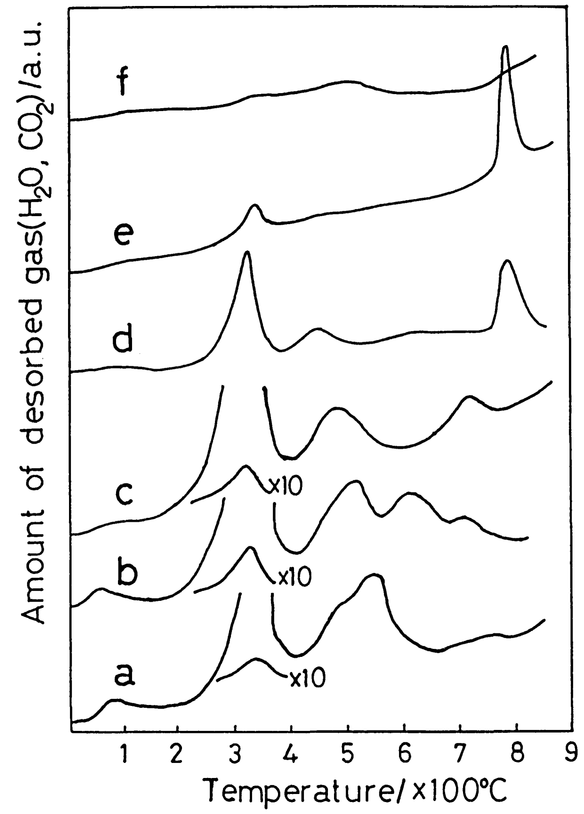

Fig. 8. Effect of the BaO content in $Ba(OH)_2$/CaO catalysts on the TPD profile. a: 2.5 wt%, b: 5 wt%, c: 10 wt%, d: 20 wt%, e: 30 wt%, f: 40 wt%.

Table 4. Summary of the TPD Profiles Given in Figs. 6 and 7

Catalyst content	Temperature of peak/°C				C_2 Yield
	500	500—700	730	800	%
CaO	◎				7.6
$BaCl_2$/CaO					
2.5 mol% $BaCl_2$	○s		○	○	18.8
5	○s	○$_{650}$	◎		19.2
10	○	○$_{670}$	◎		18.4
20			s◎		18.9
30			◎		18.5
40			○		15.5
$Ba(OH)_2$/CaO					
2.5 wt% BaO	◎	○$_{550}$	○		12.9
5	◎	○$_{630}$	○		13.0
10	◎		○		12.7
20	○	○$_{600}$		◎	14.2
30				◎	13.8
40				○	12.8

a) ○: a small peak, ◎: a large peak, s: a shoulder peak.
b) Conditions: Reaction temperature 800 °C, W/F 0.21 g h l^{-1}, $P(CH_4)$ 14.8 kPa, P(air) 37.1 kPa.

even at 2.5 mol% $BaCl_2$. The X-ray powder diffraction patterns of $BaCl_2$ catalysts used at 800 °C indicated that the $BaCl_2$ phase remained, except for a 2.5 mol% $BaCl_2$ catalyst; a long-used one, in which a trace of some phase, except $BaCl_2$ (although not identified), was recognized. However, there was no difference between dryness and wetness in the mixing method. In addition, even when a small amount of $BaCl_2$ (1 wt% for a catalyst) was put on top of a fixed bed of the CaO catalyst, the C_2 yield increased remarkably. These facts suggest that a powder of $BaCl_2$ on stream was easily sublimed, probably due to reaction heat, and was well-dispersed on the surface of the CaO support; the resulting surface was associated with the desorption peak of CO_2 as well as C_2 formation. This is supported by the fact that the desorption peak at around 730 °C was little changed in peak intensity over a wide range of $BaCl_2$ content, as well as the C_2 yield (Fig. 2). On the contrary, both the surface area and the peak intensity of H_2O desorption decreased with increasing $BaCl_2$ content.

On the other hand, a large (fourth) CO_2 peak at about 800 °C was observed for $Ba(OH)_2$/CaO catalysts containing 20 to 30 wt% BaO. They gave the highest C_2 yield among the $Ba(OH)_2$/CaO catalyst (Table 4). XRD measurements have indicated that barium ions were present as a crystallite of $BaCO_3$ in the used $Ba(OH)_2$/CaO catalysts containing more than 10 wt% BaO, and as a composite oxide in that of lower than 10 wt% BaO, respectively. In addition, as shown in Fig. 3, the temperature necessary to attain a maximum C_2 yield over a $Ba(OH)_2$/CaO catalyst containing 20 wt% BaO was higher by about 60 °C than that of the $BaCl_2$/CaO catalyst. The difference between two temperatures is very comparable to the temperature gap (about 70 °C) between the third and fourth CO_2 desorption peaks. Therefore, the active sites of the $Ba(OH)_2$/CaO catalyst for the C_2 formation at 800 °C could be associated with the fourth CO_2 peak, as well as the second one.

Role of Basicity. The results described above can be summarized as follows:

(1) A catalyst with well-dispersed barium ions enhanced both the selectivity and yield of C_2 hydrocarbons.

(2) A catalyst showing a large desorption peak of CO_2 at a higher temperature in the TPD measurement tended to give a higher C_2 selectivity and yield.

We have reported similar results(to the above second paragraph) for BaO-mixed metal oxide catalysts elsewhere.[19] These facts suggest that the surface basicity of a catalyst should play an important role in C_2 formation. Carreiro and Baerns have also emphasized the requirement of surface basicity for the oxidative coupling of methane.[31,32]

The mechanism for this methane coupling has been discussed by many authors in detail, and is believed to be as follows; [12—14,28] first of all, a hydrogen is abstracted from methane to a methyl radical on the surface of a catalyst. The resulting methyl radicals partly couple each other in the gas phase to form first ethane, and then ethylene. They partly react with an oxidized surface and/or a molecular oxygen to form CO or CO_2. However, in spite of the basic materials essentially effective for the oxidative coupling of methane,[13] the role of their basicity has been little discussed regarding the above-mentioned mechanism.

There are two steps for basic sites to participate in this mechanism: before and after the formation of methyl radicals. Regarding the first step, based on kinetic data obtained from a 15 wt% Na/MgO catalyst, Iwamatsu et al. have clamed that the C_2/C_1 selectivity (R_2/R_1) was also affected by the formation rate of methyl radicals (Eq. 5), which was given by the steady-state treatment of reactions(1) to (4): [28,33]

$$O_2 + \text{site} \xrightarrow{2k_1} [\text{oxygen}] \tag{1}$$

$$CH_4 + [\text{oxygen}] \xrightarrow{k_2} \cdot CH_3 + OH(a) + \text{site} \tag{2}$$

$$\cdot CH_3 + xO \xrightarrow{k_3} CO,\ CO_2 \tag{3}$$

$$2 \cdot CH_3 \xrightarrow{k_4} C_2H_6 \tag{4}$$

$$\frac{R_2}{R_1} = \frac{1}{4}\left(\left(1 + \frac{8k_1k_2k_4\, P_{O_2}\, P_{CH_4}}{k_3{}^2 P_{O_2}^{x}(k_1P_{O_2} + k_2P_{CH_4})}\right)^{0.5} - 1\right) \tag{5}$$

According to Aika et al.,[33] if k_1 and k_2 in Eq. 5 are large (the activity is high), R_2/R_1 is thus high because of a difference in the reaction order between C_1 and C_2 productions given by Eqs. 3 and 4, respectively. It could be easily expected to replace the active site in Eq. 1 with a basic site. Furthermore, since the stronger basic sites could adsorb oxygen more strongly, methane would go to more methyl radicals. Too strong basic sites, however, would be inactivated by the irreversible adsorption of CO_2. Actually, BaO_2[34] and Na_2O/CaO[35] catalysts showed high C_2 selectivities, even at low temperatures of 400 and 640 °C, respectively; they were, however, inactivated within a short time. In this sense, $BaCl_2/CaO$ catalysts are considered to have the most suitable basicity, since they have the highest desorption peak of CO_2 around the reaction temperature (about 730 °C) in barium salt/CaO catalysts, as is shown in Fig. 6. It seems reasonable that the active oxygen species in the case of the barium salt/CaO catalysts is O_{2}^{-2}, as it is discussed concerning the BaO/CaO catalyst[30] by Korf et al..

Regarding the second step, we have no evidence that the basic sites play an important role. It is, however, noteworthy that increasing the $BaCl_2$ content decreased the surface area and the amount of H_2O desorption, since these facts could bring about decreases in the reaction rate of Eq. 3 and the surface acidity, respectively.

Our next problem is concerned with active species on the $BaCl_2/CaO$ catalyst, since the above-mentioned basic sites are considered as its active species, but also other radicals as described below. Otsuka and coworkers as well as Anshits et al. have suggested that a chlorine radical generated by the catalyst surface participates in the formation of C_2 hydrocarbons over LiCl-added NiO and MnO_2 catalysts,[15] and over $CaCl_2$-modified CaO[21] catalysts, respectively. This was based on the presence of methyl chloride in the reaction products. As shown in Table 3, however, over the $BaCl_2/CaO$ catalyst a high C_2 yield was maintained for a long time, despite a slight loss of $BaCl_2$, compared with other chlorides.

Recently, Ahmed and Moffat[36] have studied the promotion by tetrachloromethane(TCM) of the oxidative coupling of methane on a BaO/SiO_2 catalyst, and suggested that TCM promoted the coupling reaction by facilitating the hydrogen abstraction step from methane. In addition, they have reported that Mn/SiO_2 catalysts doped with Na and K are remarkably effective for the coupling reaction in the presence of TCM, and suggested that the TCM establishes an additional route for a coupling reaction by modifying the existing sites on the catalyst surface.[37] Although there is evidence that the chlorine-containing additive promotes an activation of methane (as described above), the active species is not sufficiently clear. Our studies concerning the active species on the $BaCl_2/CaO$ catalyst were also made more difficult due to the fact that the $BaCl_2$ on stream was easily sublimed and well dispersed on the CaO support: That is, the $BaCl_2$ catalyst was also essentially a heat-unstable one. Hence, further studies are also require concerning the basic sites of heat-unstable catalysts mixed with $BaBr_2$, NaCl, $CaCl_2$ etc. These are currently in progress in this laboratory.

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