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Oxidative Coupling of Methane over Calcined Coral-Sands: Their Catalytic Property and Comparison with Other Natural Calcium Carbonates

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Coral sands calcined at high temperatures of 800 and 1000 °C were found to be an effective catalyst for the oxidative coupling of methane to C_2 hydrocarbons, especially with high selectivity. The coral-sand catalyst was almost composed of calcium oxide; however, it also contained small amounts of Na, Sr, Mg ions etc., and had a characteristic structure with many small pores of 2—8 μm in diameter, which were formed during calcination. In order to investigate the role of their components in C_2 formation, nine kinds of catalysts were prepared from other natural calcium carbonates, such as turbo shell, short-necked clam shells, and marbles; their catalytic properties were compared with that of the coral-sand catalyst. Consequently, it seemed that the C_2 yield was related to the bulk and surface concentrations of sodium in the catalyst, while the maximum-C_2 selectivity at 700—800 °C was related to those of strontium. The catalysts of corals and coral sands showed the highest maximum-C_2 selectivity as well as the highest strontium-content (about 1.2wt%). It was considered that the strontium ions are well-dispersed in the catalyst and that they enhance the basicity in combination with sodium ions (main active species), leading to the high C_2 selectivity.

The oxidative coupling of methane to ethane and ethylene is one of the most attractive processes for the utilization of natural gas.[1—6] Many effective catalysts for this methane coupling have been reported so far, and almost all of them have been prepared from some chemical reagents. Recently, we have found that coral sands (on sale as a water-cleaning reagent for fish) calcined at high temperatures, such 800 °C, showed a high catalytic activity for the oxidative coupling of methane.[7] According to Terai,[8] fresh and fossil corals comprise calcium carbonate, including small amounts of metal ions, such as Sr^{2+}, Mg^{2+}, and Na^+. As shown in Table 1, the coral sands calcined at 800 °C were essentially calcium oxide containing the above-mentioned alkali and alkaline earth metal ions, which are well-known active components for the oxidative coupling of methane.[9—13] This paper reports on the catalytic activity of the coral sands for the oxidative coupling of methane, as well as the characteristics in their chemical constituents and structure.

Table 1. Chemical Compositions of Coral Sand Catalyst[a)]

Element	Content/wt%	Method[b)]
Ca (as CaO)	94.8	1
Na	0.69	2
K	0.01	2
Mg	0.42	3
Sr	1.22	3
Cl	0.02	4
S (as SO_4^{2-})	0.57	5

a) Calcined at 800 °C for 12 h. The coral sands are unknown about the place of the production. b) Numbers from 1 to 5 indicate titration with EDTA, atomic absorption spectrophotometry, inductively coupled plasma spectrometry (ICP), potentiometric titration, and ion chromatography, respectively.

In addition, in order to obtain further information about the coral-sand catalysts, several catalysts were prepared from other natural calcium carbonates, such as shells, marbles, and corals; their catalytic activities in the oxidative coupling of methane were investigated.

Experimental

Catalyst Preparation. The coral-sand catalyst was prepared as follows: Crude coral sands, which were on sale as a water-cleaning reagent for fish, and a mixture of two coral sands obtained in Taiwan and Philippine (10 to 40 mm in long, 5 to 10 mm in diameter), were purified by removing any foreign substances, such as shells and tiny stones, and washing with distilled water of about 50-fold volumes of the sands for 10 d in order to remove any deposit, such as salt, followed by drying at 120 °C. The resulting coral sands were crushed and sieved into 60—115 mesh grains, and then calcined at 800 °C for 12 h. Other natural calcium carbonate catalysts were also prepared in the same way.

Fe and Mn ion-added and acid-treated coral-sand catalysts were prepared by soaking granular coral sands (60—115 mesh size) with an aqueous solution of ferric nitrate, manganese acetate, and nitric acid, respectively, followed by evaporating at 120 °C and calcining at 800 °C for 12 h. Na and/or Sr ion-promoted CaO catalysts were prepared by mixing powders of calcium hydroxide and carbonates of sodium and strontium with a small amount of water. The catalyst precursors were dried, pelleted, and broken (60—115 mesh), followed by calcining at 800 °C for 12 h.

Catalyst Testing. The catalytic experiments were carried out in a fixed-bed continuous-flow reactor at atmospheric pressure, which is described elsewhere.[14] The catalyst testing was carried out in a stream of reactant gases with or without diluents. The product composition was analyzed using two TCD gas chromatograms fitted with Porapak Q (for CH_4, CO_2, C_2H_6, C_2H_4, and C_3 hydrocarbons) and Molecular Sieve 13X-S (for H_2, O_2, N_2, CH_4, and CO) columns. The yields and selectivities for C_2 and C_3

hydrocarbons (C_{2+}) were indicated on the basis of methane converted into each product.

Catalyst Characterization. Chemical analyses of the catalyst samples were carried out by the following methods: titration with EDTA for Ca,[15)] atomic absorption spectrometry for Na, Sr, and Mg,[16)] potentiometric titration for Cl, ion chromatography for SO_4^{2-}, and fluorescence spectrometry (Shimadzu, Fluorescence Spectrometer Model 7320) for other elements. The surface composition of the catalysts was measured with an X-ray photoelectron spectrometer (Shimadzu, ESCA 750) using Mg $K\alpha$ radiation (8 kV, 30 mA), and was estimated using the photo-ionization cross section as a factor.[17)]

The bulk structure of the catalysts was determined by means of XRD (Nihon Denshi, JDX-50S) using the Cu $K\alpha$ line ($\lambda=1.542$ Å) with a nickel filter. The specific surface areas were measured by the BET method using nitrogen adsorption at liquid-nitrogen temperature (−196 °C). The pore-size distribution was measured using a mercury-porosimeter (Merit, Autopore II 9220). Scanning electron microscope (SEM) pictures were obtained with a Hitachi SEM S-800. The basicity of a catalyst was measured by a temperature-programmed desorption (TPD) method using a sample treated by rapid-cooling from 800 °C to room temperature in a flow of the reactant gas. The detailed method was described in an earlier paper.[14)]

Results and Discussion

Catalytic Activity. The main products of the title reaction without any diluent over coral-sand catalysts were C_2H_6, C_2H_4, CO_2, CO, H_2O, and some C_3 hydrocarbons. Table 2 shows the results of an activity test without any diluent over the coral-sand catalysts and some of the effective catalysts so far reported.[18—20)] According to data obtained at 800 °C after 15 h on-stream, next to $BaCl_2/CaO$, coral sands calcined at 800 or 1000 °C were found to show the highest C_{2+} yield (14.0—14.9%) with high C_{2+} selectivity (68—69%), although oxygen conversions, indicating the catalytic activity, were not so high. As shown in Fig. 1, the C_{2+} yield and selectivity remained kept for a relatively long time, for example, in comparison with those of the Na_2CO_3/CaO catalyst (4 wt% as Na). Although the catalyst, which contained five- or six-times the amounts of sodium ions larger than the coral-sand catalysts, showed a high C_{2+} yield of 13.5% at 750 °C, it began to deactivate soon after starting the reaction at 800 °C, probably due to a loss of the active species. Thus, the coral-sand catalyst seemed to be fairly stable, even at high temperatures.

Figure 2 shows the effect of the reaction temperature on the methane conversion, C_2 yield and C_2 selectivity in a flow of diluted reactant gas, where C_3 production was negligibly small. Ethane and ethylene formed at temperatures higher than about 600 and 650 °C, respectively, and the C_2 yield attained a maximum of 22% at around 775 °C, while the C_2 selectivity passed through a maximum (70% or above) at 700—725 °C and decreased to 58% with an increasing reaction temperature up to 800 °C.

Figure 3 shows the effect of the contact time on the methane conversion, C_2 yield, C_2 selectivity, and methane conversion into each product. The C_2 yield attained nearly a maximum (23%) at a contact time of 2.5 $\mathrm{g\,s\,cm^{-3}}$, although the increase in the methane conversion continued until about 5 $\mathrm{g\,s\,cm^{-3}}$. On the other hand, the C_2 selectivity decreased from 73 to 48% in the range of contact time from 0.7 to 5.0 $\mathrm{g\,s\,cm^{-3}}$. The value of the C_2 selectivity at $W/F=0$ was obtained as ca. 80% by extrapolation. A similar result obtained for the effect of contact time on the selectivity was also found when W/F was adjusted by changing the catalyst weight.

According to several papers, such catalysts as Li/MgO,[21)] BaO/CaO,[21)] $BaCl_2/CaO$,[20)] $Na/NiTiO_3$,[22)] and Sm_2O_3,[23)] showed a nearly constant C_2 selectivity over a wide range of contact times in the oxidative coupling of methane. These facts are very different from that found for the C_2 selectivity of the coral-sand catalyst. Its behavior of the C_2 selectivity is rather close to that over Na^+–ZrO_2–Cl^- prepared via the sol-gel method (methane conversion of 13.8% and total C_2 selectivity of 77%), recently reported by Khan and Ruckenstein.[24)]

Recently, researchers of Japan Petroleum Exploration Co., Ltd.[25)] have found that the C_2 selectivity of the coral-sand catalyst was not very much affected by the O_2/CH_4 ratio in the reactant gas. By considering the reaction conditions shown in Fig. 1 (a very high O_2/CH_4 ratio of 1/5), the calcined coral-sands seemed to be fairly stable as a catalyst, even under severe conditions, and were thus found to have some characteristics for the oxidative coupling of methane.

Characterization of Coral-Sand Catalysts. As shown in Table 1, chemical analyses of the calcined coral sands indicated that the amounts of metal ions, except for calcium ions, were very small, namely even the sum of the ions was at most 3 wt%. This value is considerably small, compared to those of the promoters in the effective catalysts generally used for the oxidative coupling of methane.[6,26)] Chlorine, one of very promotive elements for the title reaction,[27—29)] was also found to be slightly contained in the coral-sand catalyst.

XRD measurements revealed that the coral sands consist of in large part an aragonite phase and in part a Mg-rich calcite phase with an XRD pattern of $Ca_{0.7}(Mg, Mn)_{0.3}CO_3$ (File No. 11-345),[30)] of which the lattice constant is very close to that of calcite. The aragonite phases transformed into calcite phases at around 300 °C.

Figure 4 shows the result of a thermal gravity analysis of the coral sands. Here, the heat treatment was carried out by holding the sample for 1 h at every temperature elevated stepwise by 100 °C from 100 to 1200 °C. The weight decreased by about 1.4 wt% at between 200 and 500 °C. At around 500 °C, the coral sands were darkened by carbon-deposits, possibly due

Table 2. Catalytic Activity for the Oxidative Coupling of Methane

Catalyst	Reaction temperature$^{b)}$/°C									Reference
	700			750			800			
	O_2 Conv.	C_{2+} Yield	(Select.)	O_2 Conv.	C_{2+} Yield	(Select.)	O_2 Conv.	C_{2+} Yield	(Select.)	
	%	%	%	%	%	%	%	%	%	
Coral Sand										
800 °C$^{c)}$	17	2.4	(60)	46	9.5	(74)	80	14.0	(69)	
1000 °C$^{c)}$	14	2.0	(61)	46	9.3	(73)	91	14.9	(68)	
7 wt% Li^+/MgO	12	1.3	(64)	31	5.3	(70)	51	9.4	(72)	18$^{e)}$
10 wt% NaOH/CaO	35	5.1	(57)	71	10.8	(66)	96	13.8	(67)	19
5 mol% $BaCl_2/CaO$	40	4.8	(57)	91	14.4	(66)	98	15.1	(67)	20
No Catalyst	—	—	(—)	4	0.4	(47)	11	1.6	(59)	

a) Reaction Conditions: Catalyst weight 0.5 g, W/F 0.625 g s cm^{-3}, Partial pressures of CH_4 and O_2 84.4 and 16.9 kPa, respectively. b) Reaction temperature was initially kept at 750 °C for 3 h, next at 800 °C for 12 h, finally at 700 °C for 6 h. The table shows final data obtained at each reaction temperature. c) Calcination temperature. e) References for the preparation of the catalyst.

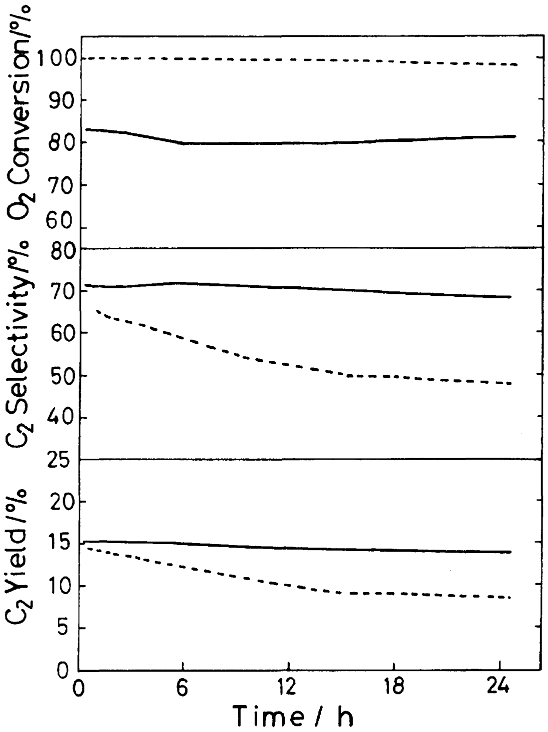

Fig. 1. Time courses of O_2 conversion, C_2 yield, and C_2 selctivity at 800 °C over the coral-sand (——) and 4 wt% Na^+/CaO (- - -) catalysts. Reaction conditions; refer to Table 2.

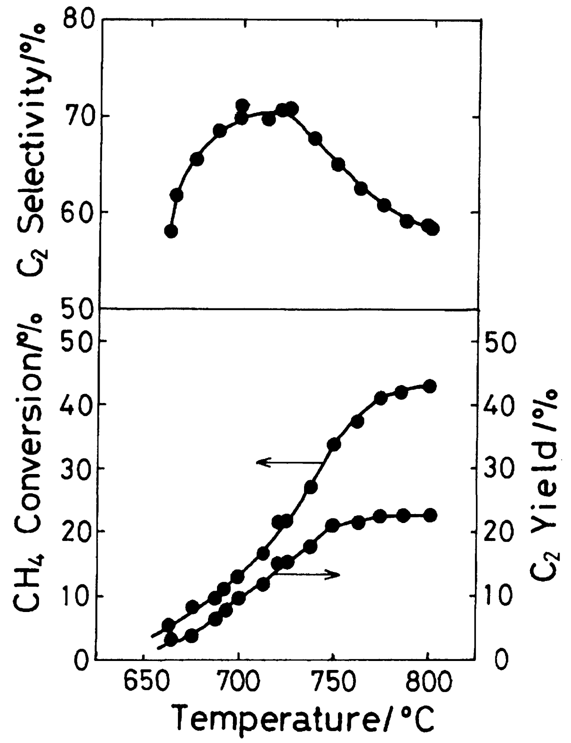

Fig. 2. Effect of reaction temperature on CH_4 conversion, C_2 yield, and C_2 selectivity over coral sands calcined at 800 °C. Reaction Conditions: Catalyst weight, 1.0 g; W/F, 1.67 g s cm^{-3}; Partial pressures of CH_4 and O_2, 16.9 and 8.4 kPa, respectively.

to a thermal decomposition of the organic substances contained in the sands. In further calcination at temperatures higher than 600 °C, the calcium carbonate of calcite was decomposed into calcium oxide. In this calcination process, the carbons which were burnt up and the mixed-oxide phase disappeared. If all of the residue after calcination at 1000 °C or above was assumed to be only CaO, the coral sands may comprise 98.5 wt% of calcium carbonate and 1.5 wt% of others. This value (1.5 wt%) almost coincided with the weight loss (1.4 wt%) up to 500 °C. This fact supports that the weight loss is due to decomposition of some organic substances as mentioned above.

Figure 5 shows SEM pictures of the coral-sand catalyst calcined at 800 °C. A grain of the catalyst comprised an interpenetrating porous structure (Fig. 5a), and had specific pores of μm size (Fig. 5b). Measurements of the pore-size distribution revealed that the pores were formed during calcination and ranged in diameter from 2 to 8 μm. The surface area of the catalyst

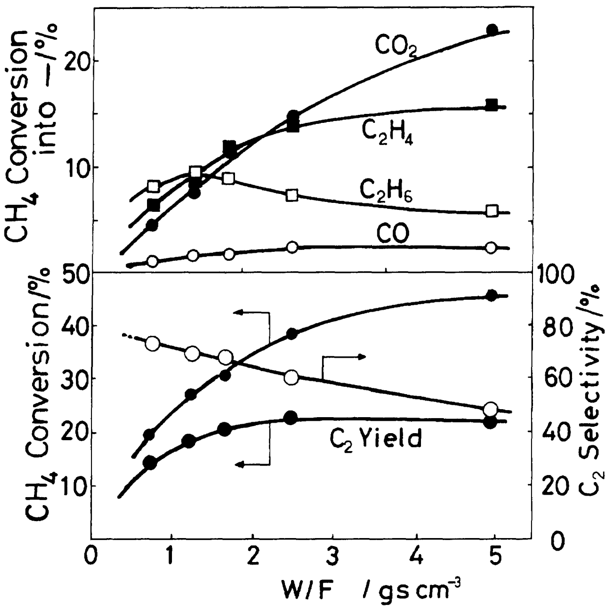

Fig. 3. Effect of contact time on CH_4 conversion, C_2 yield, C_2 selectivity, and CH_4 conversion into each product over the coral-sand catalyst calcined at 800 °C. Catalyst weight, 1.0 g; Reaction Temperature, 750 °C; Partial pressures of CH_4 and O_2, 16.9 and 8.4 kPa, respectively.

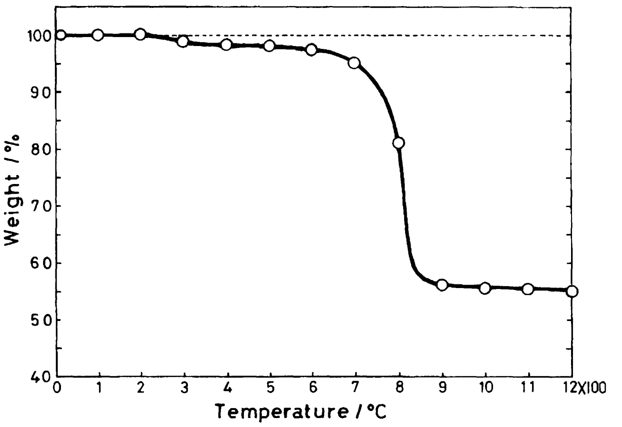

Fig. 4. Thermal gravity analysis of coral sands.

was too small to measure, while that after use was about 0.7 $m^2 g^{-1}$.

Comparison with Other Natural Calcium Carbonate Catalysts. In the previous sections we have described that the calcined coral-sands show unique catalytic performance for the oxidative coupling of methane and have specific pore-structures. In this section, in order to further investigate the specific behavior of the coral-sand catalyst, the behavior is compared with those of nine kinds of catalysts prepared from other natural calcium carbonates, such as shells and marbles (Table 3).

The catalytic behavior for the oxidative coupling of methane is summarized in Table 4, showing the maximum C_2 yields and selectivities at reaction temperatures of 650—800 °C. Catalysts prepared from short-necked clam shells (hereinafter indicated by Clam), turbo shell (Turbo), and corals (Corals) gave high C_2 yields, being equal to or higher than that of the coral-sand catalyst (Coral Sand). Among them, Clam showed the highest C_2 yield of 24.0% with a C_2 selectivity of 56%.

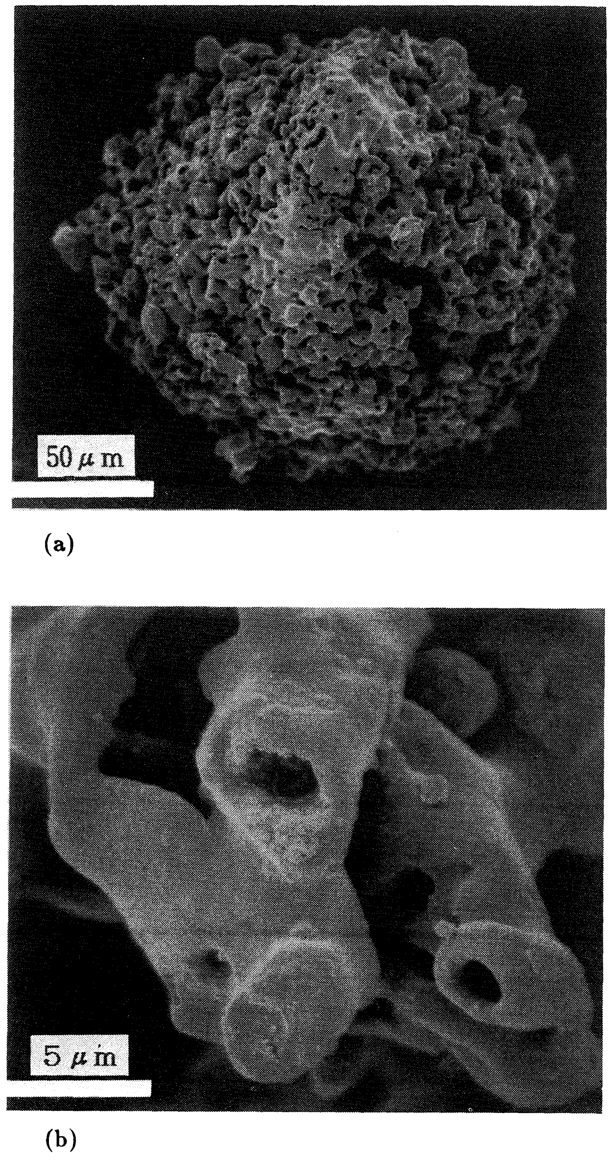

Fig. 5. SEM pictures of the coral-sand catalyst; a) 500 magnifications, b) 5000 magnifications.

Regarding the selectivity, two Corals and Coral Sand showed the highest maximum-C_2 selectivity above 70%, and Turbo and Clam showed the second highest selectivity. The order of the maximum C_2 selectivity for other catalysts was as follows:

Scallop > Oyster > Ikechou > Egg > Marble.

This order was the same as that observed for the maximum C_2 yield.

Table 3. Various Natural Calcium Carbonates Used in This Experiment

Starting Material	Main crystal form[a)]	References
1. Coral A	A	"Hanagasa"-like
2. Coral B	A	Honeycomb-like
3. Coral sands	A	In the text
4. Turbo shell	A	In the market
5. Short-necked clam shells	A	From Akkeshi in Hokkaido
6. Scallop shells	C	In the market
7. Oyster shells	C	In the market
8. Ikechou shells	A	From Kasumi Sea
9. Egg shell	C	In the market
10. Marble	C	From Hitachi

a) Symbols of A and C indicate the crystal forms of aragonite and calcite, respectively.

Table 4. Oxidative Coupling of Methane over Various Natural Calcium Carbonate Catalysts[a)]

Catalyst	Max. C_2 Yield %	Max. C_2 Select. %
Coral A	21.7 (800)[b)]	80 (725)[b)]
Coral B	23.3 (800)	75 (725)
Coral Sand	22.3 (800)	70 (710)
Turbo	22.8 (775)	66 (700)
Clam	24.0 (800)	65 (730)
Scallop	21.8 (800)	54 (710)
Oyster	20.9 (800)	50 (800)
Ikechou	18.7 (800)	46 (800)
Egg	13.2 (800)	36 (800)
Marble	1.3 (725)	8 (625)

a) Reaction Conditions: Catalyst weight, 1.0 g; Reaction temperature, 650 to 800 °C; W/F, 1.46 g s cm^{-3}; Partial pressures of CH_4 and O_2, 14.8 and 7.4 kPa, respectively. b) The value in parentheses shows the temperature (°C) giving the maximum C_2 yield and selectivity.

Table 5 shows the bulk and surface compositions of Na, Sr, Mg, etc., in natural calcium carbonate catalysts calcined at 800 °C. Except for Marble and Egg, which were at a very low level in the maximum C_2 yield and selectivity as well as in the Na content, all of the catalysts were found to range in bulk concentration of Na from 0.3 to 0.9 wt%. The Na concentration corresponded to two or three ions of Na per one hundred ions of Ca, since the catalysts contained 94—97 wt% of CaO. On the other hand, the surface concentrations of Na in catalysts showing C_2 yields of 19—23% were estimated to be about thirty ions of Na per one hundred ions of Ca. Clam, which gave the highest C_2 yield (24.0%), showed a still higher surface concentration of Na (about sixty ions of Na per one hundred ions of Ca). These facts suggest that the Na ions in the catalyst are considerably concentrated in the surface, and that the catalysts showing high C_2 yields secure a high Na concentration in the surface. However, the concentrations of Na in the bulk and surface were not always correlated with the maximum C_2 selectivity.

In contrast, there was a large difference in the bulk concentration of Sr between various catalysts, and a good correlation was found between the Sr concentration and the maximum C_2 selectivity. The two Corals and Coral Sand showing a C_2 selectivity higher than 70% contain about 1 wt% of Sr, while Clam with that of 65% contains a few amounts (0.1 wt%) of Sr, and Egg with that of 36% only 0.02 wt%. A similar good correlation was observed between their C_2 selectivities and the surface concentrations. However, the latter was not so distinct as the former. On the other hand, no correlation was found between the composition of Mg or Cl and the C_2 yield or selectivity. From these results, the high C_2 selectivity on Corals and Coral Sand was suggested to be associated with Sr ions as well as Na ions in the surface.

It is now generally accepted that the generation of methyl radicals from methane by the reactive oxide is a significant step in the oxidative coupling of methane.[5,6)] In addition, evidence that the high-C_2 selectivity catalysts have strong basic sites has been found by some experiments on CO_2-TPD[20,24,31)] and CO_2-chemisorption,[32)] although the mechanism is not well known.[4)]

In order to determine the basicity of the natural calcium carbonate catalysts, TPD measurements were carried out. In these measurements, a pretreatment of the sample was made by rapid-cooling in a flow of the reactant from the reaction temperature (800 °C) to room temperature. As shown in Fig. 6, the TPD curves had a desorption peak of H_2O at around 350 °C and a series of desorption peaks of CO_2 above 400 °C. There appeared to be the following tendency between the desorption peaks and the maximum C_2 selectivity: The high-C_2 selectivity catalyst exhibited large amounts of CO_2 desorptions at around 680 and 780 °C, while the low-C_2 selectivity catalyst exhibited large amounts of H_2O desorption and CO_2 desorption at around 500 °C. Desorption of CO_2 above 850 °C would not be associated with C_2 formation at 800 °C.

For Corals and Coral Sand, showing a maximum-C_2 selectivity higher than those of other natural calcium carbonate catalysts, the CO_2 desorption occurred

Table 5. Compositions of Bulk and Surface in the Natural Calcium Carbonate Catalysts[a)]

Catalyst	Bulk				Surface				
	CaO	Na	Sr	Mg	Na	Sr	Mg	Cl	Reference[b)]
	wt%				(Atomic Ratio to Ca) ×100				
Coral A	95.4	0.80	1.28	0.12	33	10	26	9	
Coral B	94.3	0.72	1.27	0.14	33	11	34	13	
Coral Sand	94.8	0.55	1.08	0.96	26	18	44	17	
Turbo	96.4	0.71	0.14	0.28	35	10	31	12	
Clam	96.2	0.85	0.18	0.03	62	7	27	15	
Scallop	94.6	0.48	0.08	0.07	26	4	18	3	Fe ca. 0.1%
Oyster	89.0	0.88	0.05	0.50	35	4	14	34	Fe ca. 0.1%, Zn 0.05%
Ikechou	96.0	0.35	0.01	0.01	35	5	7	6	
Egg	97.0	0.16	0.02	0.63	12	3	42	8	
Marble	95.3	0.01	0.01	0.10	3	2	6	9	Fe ca. 0.3%

a) After calcination at 800 °C for 12 h. b) Other elements detected by fluorescence spectrometry.

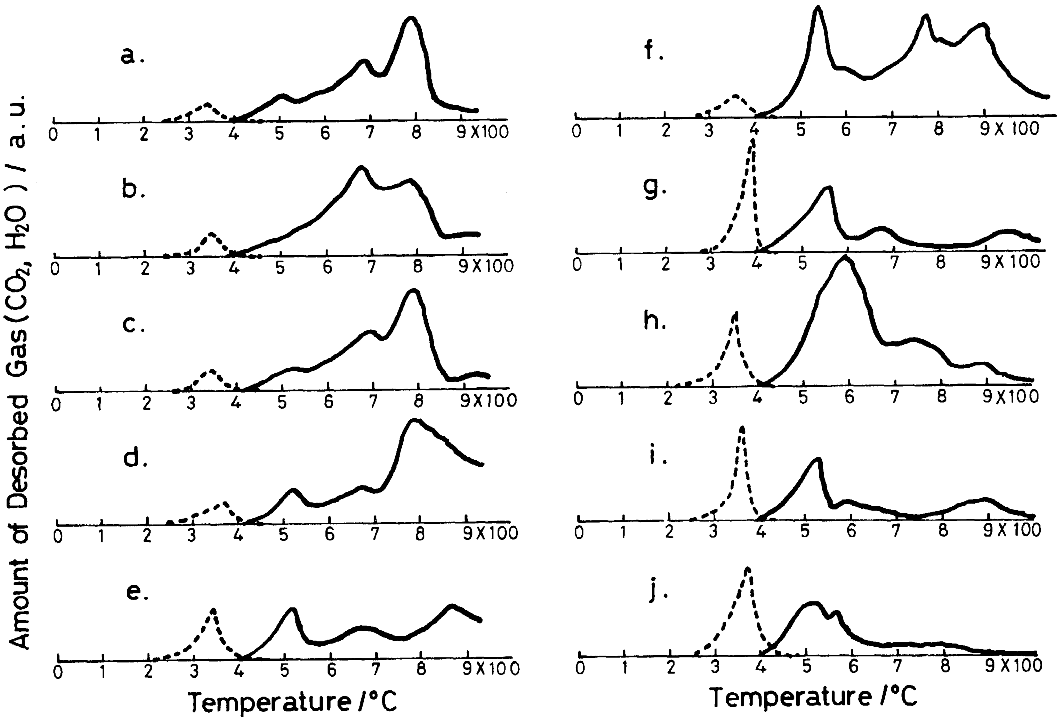

Fig. 6. TPD spectra of various natural calcium carbonate catalysts: CO_2-desorption curve(—) and H_2O-desorption curve(- - -); Sample weight, 50 mg; a. Coral A, b. Coral B, c. Coral Sand, d. Turbo, e. Clam, f. Scallop, g. Oyster, h. Ikechou, i. Egg, j. Marble.

exclusively around 780 and 680 °C. For assignment, TPD profiles of a reference sample and three catalysts prepared from chemical reagents are shown in Fig. 7, Curves a—e. A pure CaO catalyst showed H_2O desorption at 350 °C and CO_2 desorption at 500 °C with a shoulder peak at 570 °C. For the Na_2CO_3/CaO catalyst (1 wt% as Na) very broad CO_2 desorption peaks were observed at around 580 and 680 °C. When the Na content was increased up to 4 wt%, the CO_2-desorption peak increased and shifted to 630 °C, and another CO_2 desorption, probably due to the decomposition of Na_2CO_3, occurred above 850 °C. Hence, CO_2 desorptions ranging from 550 to 700 °C could be attributed to basic sites enhanced by Na ions. The $SrCO_3$/CaO catalyst (2 wt% as Sr) had CO_2 desorption peaks at around 500, 770, and 820 °C. The first peak was considered to be due to basic sites of CaO, and the second and third peaks due to the basic site of mixed oxides of Sr and Ca, and to the decomposition of a small amount of $SrCO_3$, respectively. This TPD profile suggested that mixing in the system of $SrCO_3$–CaO was somewhat difficult. In any case, these facts concluded that the CO_2 desorptions at around 680 and 780 °C in Coral Sand were caused by Na and Sr ions, respectively.

On the other hand, the addition effects of Fe and Mn ions, which were contained in Scallop, Marble, Ikechou, etc. (Table 5), and of acid (nitric acid) on the TPD profiles, are shown in Fig. 7, Curves f—h. Although the

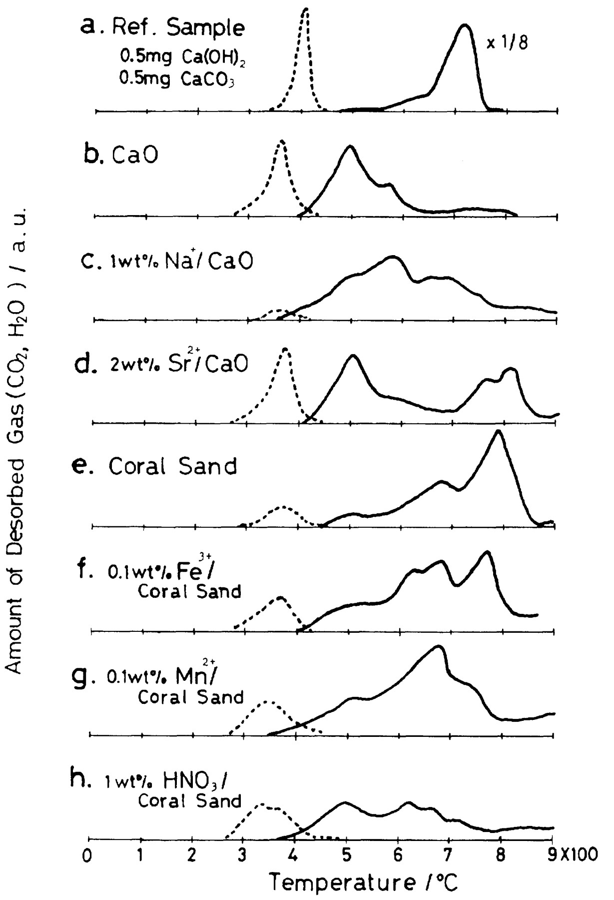

Fig. 7. TPD spectra of the catalysts prepared from chemical reagents and Coral Sands promoted with metal ions and acid: CO_2-desorption curve(——) and H_2O-desorption curve(- - -); Sample weights, 10 and 50 mg for TPD spectra of b—d and e—h, respectively.

addition amount was small and carried out before calcination, it remarkably diminished the CO_2 desorption at around 780 °C, while it increased the H_2O desorption and CO_2 desorption at around 500 °C. At the same time, as expected, the maximum C_2 selectivities were lower than that of the original Coral Sand (70%); those of Fe^{3+}-, Mn^{2+}-, and HNO_3-added catalysts were 66, 64, and 60%, respectively.

However, the addition of Sr ions (0.2 wt%) did not always enhance the maximum C_2 selectivity (69%), while that of Na ions (0.2 wt%), on the contrary, enhanced it (76%). This fact indicates that the main reactive site in the oxidative coupling of methane on Corals is associated with not Sr, but Na species. The high maximum-C_2 selectivity is, therefore, considered to be caused by the strong basic site due to Sr ions in combination with the Na ions. Such a combination effect of basic ions on C_2 formation has been observed for the Li^+–Ba^{2+}–CaO catalyst.[26] Since the strong basic sites (due to Sr^{2+} or Ba^{2+}) naturally have strong affinity to CO_2 of a by-product, they probably slow the rate of CO_2 desorption from the surface, that is, of CO_2 formation from methane. In addition to this effect, when the basic sites adsorb CO_2, they may no longer react with oxygen to deep-oxidize methyl radicals until the release of the adsorbed CO_2. However, since the main active sites (Na^+ or Li^+ species) are only little affected, even in the above-mentioned process, the C_2 formation rate may remain unchanged, and then relatively increased. This is an explanation for the high C_2 selectivity on the catalyst having two kinds of strong basic sites, such as Corals.

Role of Strontium Ion in Corals. The experimental data suggested another role of Sr ions in Corals: Although the Na_2CO_3/CaO catalyst was deactivated soon after starting the reaction at 800 °C as shown in Fig. 1, the addition of a small amount of strontium carbonate (2 wt% as Sr) to the catalyst reduced the deactivation; the C_2 yield and selectivity after 24 h on-stream were improved from 8.4 to 11.7% and from 47.9 to 58.9%, respectively. However, they did not attain to those of Coral Sand (13.9 and 69%, respectively). Further, Clam containing a smaller Sr content than Coral Sand was deactivated sooner than was the latter catalyst. These facts suggest that the Sr ions in Corals play an important role in maintaining their high C_2 yield and selectivity. How are such Sr ions in corals?

It is known that shells and corals are composed of calcite and/or aragonite crystals.[33] As shown in Table 3, precursors of Coral Sand, Turbo, Clam, etc. containing relatively large amounts of Sr were of the aragonite-type, in which Ca ions are surrounded by nine oxygen ions and can be replaced with larger ions, such as Pb^{2+}, Sr^{2+}, Ba^{2+}, etc. than Ca^{2+}. Such a structure of aragonite leads to the Sr-richness in corals etc.

Strontium ions in aragonite are considered to be well-dispersed at the atomic level; also, the dispersion state may be maintained after calcination. Such a good dispersion must be effective for the stability of the catalyst as well as the formation of the strong basicity in Coral Sand.

In this study, although we tried to obtain a similar catalyst to Coral Sand with chemical reagents, our trials went wrong, as mentioned previously. For the good dispersion of a promoter, a man-made catalyst often requires nearly equal metal-ion radii of the materials, such as the Li/MgO catalyst (Li^+ 0.68 Å, Mg^{2+} 0.66 Å). The reason for our failure may be due to the difficulty of dispersion of the Sr ion into a CaO support, because of a difference in the ionic radius; that is, Sr^{2+} 1.13 Å, Ca^{2+} 0.99 Å. On the other hand, Corals introduce Sr ions into the aragonite structure through a biochemical process. Regarding this point, exaggeratedly speaking, Coral and Coral Sand are considered to be catalysts due to the biofunction.

In conclusion, there seems to be another reason for the extremly high C_2 selectivity on Corals. The catalyst has a small surface area compared to that of the man-made catalyst (1—5 $m^2\,g^{-1}$). According to Iwamatsu et al., the small surface area is an important factor in obtaining high C_2 selectivity.[34] It is also known that the morphology of the catalyst is an important factor in controlling C_2 formation.[14,35,36] Therefore, the Coral Sand catalyst should be further investigated regarding this point as well as the participation of its characteristic pores in the reactivity. We will report on this problem elsewhere.

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