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Catalytic Reforming of Methane with Carbon Dioxide on $LaBO_3$ (B = Co, Ni, Fe, Cr) Catalysts

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The reforming reactions of CH_4 with CO_2 diluted with He on perovskite structural oxides, $LaBO_3$ (B = Co, Ni, Fe, Cr), were examined. The reaction activity at 1073 K followed the order $LaCoO_3 > LaNiO_3 > LaFeO_3 > LaCrO_3$, and the highest selectivities to CO and H_2 were obtained on a $LaCoO_3$ catalyst. The reaction on the $LaCoO_3$ catalyst under the reaction condition of $CH_4/CO_2 = 1$ showed a H_2/CO ratio of 1; the ratio was less than 1 on other catalysts. In the initial stage of the reactions of CH_4+CO_2 on $LaCoO_3$ and $LaNiO_3$ catalysts, an induction period accompanying the reduction of the catalysts was observed. During the reforming reaction, both the $LaCoO_3$ and $LaNiO_3$ catalysts were decomposed by reduction to Co to Ni metal and La_2O_3. No induction period, however, was observed in the reaction on the $LaFeO_3$ and $LaCrO_3$ catalysts, which were stable during the reaction. The high activity of the decomposed $LaCoO_3$ catalyst is ascribed here —as a result of EPMA, SEM analysis and of comparison with the reaction behaviors of Co catalysts supported on La_2O_3 — to the high concentration of metallic cobalt uniformly dispersed as fine particles on the catalyst surface. The reaction mechanism on the cobalt metal was inferred from the results of the reaction of CH_4 or CO_2 alone on the decomposed $LaCoO_3$ catalyst.

Attention has recently been focused on the possibility that natural gas can be used effectively by reforming the methane in order to manufacture synthetic gases (syngas) consisting of H_2 and CO, as reviewed in the literature.[1—3] Some reactions of concern are, for example, those of methane and oxygen, of methane and water, and of methane and carbon dioxide. Because a reaction between methane and oxygen is liable to occur, it has been the subject of many studies.[1,4—7] The reforming reaction of methane with carbon dioxide was investigated by Fischer and Tropsch,[8] who reported that it proceeds through activation by a metal catalysts, such as Ni or Co; however, there have been few reports on this reaction for a long time.

It has recently been found, however, that carbon dioxide is abundant in low-grade natural gas. Furthermore, the massive release of CO_2 as a result of human activities is thought to contribute to global warming. Studies on the reforming of methane with carbon dioxide have thus been looked at again for clues as to how low-carbon resources can be used more effectively[1,9,10] and these studies are significant in terms of environmental protection.

The reforming reaction of methane with carbon dioxide has feature that allows syngas with a low ratio of H_2/CO (< 1) to be obtained. Since the rate of conversion at equilibrium is low at low temperatures, because the reaction is endothermic, the reforming reaction must usually be carried out at an elevated temperature. In addition, the CH_4+CO_2 reaction is more likely to deposit carbon than reactions using oxygen or water.[9,11,12] For the reaction at high temperature, carbon deposition and sintering of the catalyst are easily achieved.

Although many previous investigations of the CH_4+CO_2 reaction have used transition-metal or noble-metal catalysts supported on oxides, such as silica, alumina, and magnesia,[5,12—21] there have been few reports concerning the use of active perovskite-type catalysts. Hayakawa et al.[6] have reported that the reaction was accelerated when Co^{3+} or Ni^{3+} in catalysts consisting of the perovskite-type compound $Ca_{1-x}Sr_x Ti_{1-y}M_yO_3$ (M = Co,Ni) was reduced to the metallic state by the reaction of methane with air or with carbon dioxide.

With the intention of obtaining highly active catalysts from materials with simpler perovskite structures and of examining the function of metals, we further investigated the CH_4+CO_2 reaction catalyzed by $LaBO_3$ compounds (B = Co, Ni, Fe, Cr), in which the rare-earth metal is combined with a transition metal. We found that a high level of activity was produced when the B-site elements, especially cobalt, were reduced during the CH_4+CO_2 reaction that accompanied the decomposition of the $LaBO_3$ catalysts. We examined the cause of the high level of activity of the decomposed $LaCoO_3$ catalyst in comparison with the Co catalyst supported on La_2O_3 and the function of Co metal in the reaction.

Experimental

Preparation of Catalyst. In preparing $LaCoO_3$ and $LaNiO_3$ catalysts, represented by the general formula ABO_3, we used the acetate compounds of elements A and B (A = La, B = Co or Ni). In preparing $LaCrO_3$, we used lanthanum acetate and chromium trioxide. After a mixed aqueous solution containing A and B components in a 1 : 1 molar ratio was evaporated to dryness the thus-obtained powder was preliminarily calcined at 623 K in air to decompose the acetate. This was followed by calcination at 1123 K for 5 h. In preparing the $LaFeO_3$ catalyst, we made a precursor by coprecipitating the mixed aqueous solution of both iron and lanthanum nitrate by adding aqueous ammonia. The precipitate was washed well with deionized water, dried at 373 K in air, and then calcined at 1123 K for 5 h.

The Co catalyst supported on La_2O_3, for a comparison with the decomposed $LaCoO_3$ catalyst, was prepared by using an aqueous solution of cobalt nitrate to impregnate lanthanum oxide. After the solution was stirred for 4 h at room temperature, it was evaporated to dryness; then, after preliminary calcination at 623 K, the residue was calcined in air at 773 K. This catalyst is hereafter described as Co/La_2O_3. The amount of Co supported on the La_2O_3 was either 10 wt% or 18 wt%. These catalysts were confirmed by XRD to be different from $LaCoO_3$. The Co content of the catalysts was determined by inductively coupled plasma (IPC) emission spectroscopy (Emission Spectro Analyzer, Jobin Yvon-Rigaku 70C), after the catalyst sample was resolved in 6 M (1 M = 1 mol dm^{-3}) HNO_3 and diluted with deionized water.

Reaction of Methane and Carbon Dioxide. This reaction was carried out by using a flow reactor in a fixed-bed system under atmospheric pressure. Two grams of catalyst were filled into a quartz-tube reactor (with a length of 30 cm and inner diameter of 18 mm), and the reaction was carried out at 1073 K by adding He as diluent gas under the specified ratio of CH_4 to CO_2. The effluent gas was immediately cooled with two sets of ice-salt coolers in order to remove the produced water.

The reaction products were analyzed using a gas chromatograph (Shimadzu GC-8A) equipped with columns of active carbon and Porapack Q to separate H_2, CO, CO_2, CH_4, and C_2 compounds (C_2H_4 and C_2H_6). This was done using He as a carrier gas at 353 K. The conversion of CH_4 and CO_2 and the selectivity to CO, H_2, and C_2 compounds were calculated by the following equations:

$$CH_4(CO_2)\ \text{conversion} = [\text{fed amount of } CH_4(CO_2) - (\text{unreacted amout of } CH_4(CO_2))] / \text{fed amunt of } CH_4(CO_2)$$

$$\text{selectivity to CO} = (\text{produced amount of CO}) / (\text{reacted amout of } CH_4{+}CO_2)$$

$$\text{selectivity to } H_2 = (\text{produced amount of } H_2) / 2 \times (\text{reacted amout of } CH_4)$$

$$\text{selectivity to } C_2 \text{ compound} = (\text{produced amount of } C_2 \text{ compound}) / (\text{reacted amout of } CH_4)$$

Here, the "fed amount of $CH_4(CO_2)$−unreacted amount of CH_4 (CO_2)" is equal to the reacted amount of $CH_4(CO_2)$.

In these equations the unit of the amount is mol min^{-1}.

The reacted and produced amounts of CH_4, CO_2, and syngas were calculated from the amount of dry exit gas per minute and the chromatography results.

The activity of the catalyst was defined as the consumed rate of CH_4 or CO_2.

Measurement of Deposited Carbon. After the reaction the reactor-containing catalyst was cooled to 773 K in a He stream; then, H_2 instead of He was fed through it for 1 h at 60 ml min^{-1}. The effluent gas was collected in a Tedlar bag for sampling, and its amount was calculated from a flow-meter measurement.

The amount of CH_4 produced was quantitatively analyzed by gas chromatograph, and the quantity of the deposited carbon was estimated from this amount.[22)]

The catalyst was returned to the original state before the reaction by treating it with H_2 at 773 K for 1 h.

Characterization of Catalysts. Instrumental Analysis: The crystal structure of the catalysts was measured by X-ray powder diffraction (XRD) (Rigaku RAD-C) of Ni-filtered Cu $K\alpha$ radiation. When the samples used in the reaction or after the reduction with H_2 were measured, they were rapidly occluded with liquid paraffin in order to protect them from oxidation by air.

The catalyst surface was analyzed by XPS (ULVAC-PHI Model 558) with Mg $K\alpha$ radiation. The sample of catalyst powder was arranged as a thin disk 1 cm in diameter, and the sample surface was sputtered with Ar for 5 min before the measurement. The binding energy was calibrated by using the C_{1s} level of trace contaminant carbon (284.6 eV) as a reference. The atomic ratio of Co to La on the catalyst surface was estimated from the ratio of the values obtained by the following simple calculation: the peak heights of Co ($2p_{3/2}$) and La ($3d_{5/2}$) obtained by substitution of the background were divided by calibrated sensitivity factors of Co and La.

A TG-DTA analysis (Rigaku PTC-10A) was carried out by heating 20-mg samples from room temperature to 1073 K at 10 K min^{-1} in air. In this case the reduced catalyst by the treatment of H_2 flow of 40 ml min^{-1} for 3 h at 773 K was also used.

The dispersed state of Co on the catalyst was examined by using an electron-probe microanalysis (EPMA), (Shimadzu-EPMA-1600)).

A scanning electron microscope (SEM) (Hitachi S-4100) was also used for examining the state of the catalyst surface before and after the reaction. The elementary analysis by EDS (Energy Dispersive Spectroscopy) was performed in order to confirm what element was deposited on the catalyst surface.

Adsorption: Gas-adsorption measurements were carried out in a conventional Pyrex-glass volumetric hand-made adsorption apparatus.

The number of cobalt atoms exposed on the catalyst surface were evaluated by measuring the H_2 adsorption at room temperature according to a procedure described in the literature.[23,24)]

This procedure was as follows. First, the catalyst was reduced at 773 K for 3 h in a H_2 flow and the pressure was then reduced (at the same temperature) to 10^{-5} Torr (1 Torr = 133.322 Pa). The catalyst was slowly cooled to room temperature in a vacuum, and H_2 adsorption was performed at that temperature. After H_2 adsorption, the vessel containing the catalyst was evacuated again to 10^{-5} Torr and O_2 chemisorption at 723 K was performed to determine the percentage of cobalt reduced to the metallic state. The chemisorption of H_2 and O_2 described above was also performed on La_2O_3. The amount of adsorbed H_2 covering the catalyst surface with a monomolecular layer was obtained by extrapolating to zero the curve relating the amount of H_2 adsorbed to the adsorption equilibrium pressures of H_2. The number of exposed cobalt atoms was calculated by assuming that a hydrogen atom dissociated from H_2 adsorbs on a single cobalt atom.

The specific surface area of the catalyst was evaluated using the BET method from the measured adsorption of N_2 at 77 K.

Results and Discussion

1. CH_4+CO_2 Reactions over $LaBO_3$. Figure 1 and Table 1 show the time-course change and the steady-state results for the CH_4+CO_2 reaction catalyzed by the $LaBO_3$ (B = Co, Ni, Fe, Cr) catalysts at 1073 K. Figure 1 shows the CH_4 conversion on the $LaCoO_3$ and $LaNiO_3$ catalysts gradually increased and reached the steady state after about one hour. That is, an induction period was observed during the initial stage of the reaction. On the other hand, CH_4 conversion on the $LaFeO_3$ catalyst gradually decreased from

Table 1. Results of the Reaction with CH_4+CO_2 [a)]

Catalyst	Activity[d)] (μmol min^{-1} g^{-1})		Selectivity (%)		Molar ratio	C. B.[b)] (%)	S. A.[c)] (m^2 g^{-1})
	CH_4	CO_2	H_2	CO	H_2/CO		
$LaCoO_3$	199(98)	197(97)	80	79	1.02	80	4
$LaNiO_3$	116(57)	152(75)	67	80	0.72	84	5
$LaFeO_3$	57(28)	93(46)	35	97	0.27	99	5
$LaCrO_3$	20(10)	41(20)	30	90	0.22	99	2
18wt%Co/La_2O_3	63(31)	67(33)	84	74	1.14	72	3
10wt%Co/La_2O_3	113(56)	134(66)	80	76	0.97	86	2

a) Reaction temperature: 1073 K, $CH_4/CO_2/He=10:10:60$ (ml min^{-1}). Catalyst weight: 2 g. b) C. B.: Carbon balance. c) S. A.: surface area. d) The numbers of the parenthesis indicate conversion (%).

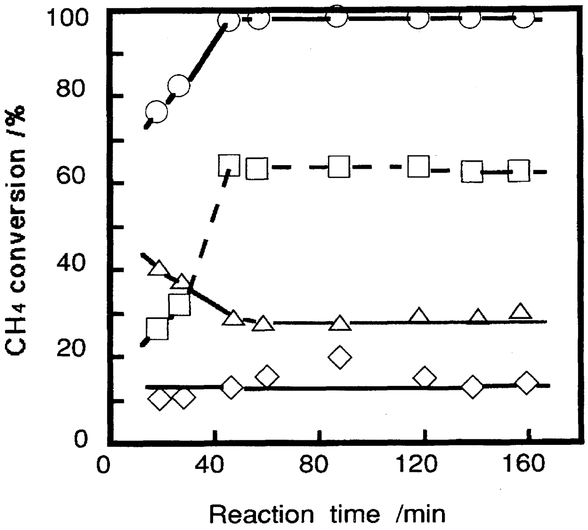

Fig. 1. Time course of the reactions over $LaBO_3$ (B=Co, Ni, Fe, Cr) catalysts at 1073 K. Catalyst weight: 2 g. Gas flow rate: $CH_4/CO_2/He=10:10:60$ (ml min^{-1}). ○ $LaCoO_3$, □ $LaNiO_3$, △ $LaFeO_3$, ◇ $LaCrO_3$.

the start of the reaction and reached the steady state after one hour. The $LaCrO_3$ catalyst yielded a nearly constant rate of CH_4 conversion from the start of the reaction, though the rate was very low.

The activity calculated from the rate of CH_4 or CO_2 consumption per unit time and per unit catalyst weight is also listed in Table 1. Since the specific surface areas of all the catalysts used in the reaction were less than 5 m^2 g^{-1}, we do not consider the values of the surface area to be completely reliable, because there is a large error due to the small amount of adsorbed N_2 used to estimate the surface area.[25)] Consequently, the activity is evaluated here in terms of the CH_4 consumption rate per unit catalyst weight under the assumption that the four catalysts have a similar surface area. The activity or conversion and H_2 selectivity in the steady state were found to decrease in the order $LaCoO_3 > LaNiO_3 > LaFeO_3 > LaCrO_3$ (see Fig. 1). Although the effect of mass transfer in the reaction, especially on the $LaCoO_3$ catalyst, can not be completely ignored, a comparison of the activity of the four catalysts is possible from the conversion data. In the reaction on the $LaCoO_3$ catalyst, the conversion of CH_4 and CO_2 was 98 and 97% respectively, and the molar ratios of the amounts of H_2 and CO formed were about 1 (see Table 1). From this, we consider the main reaction to be reaction (1) (see below). However, it is known that reaction (1) is influenced by the simultaneous occurrence of the reverse water-gas shift reaction[26)] (reaction 2), resulting in H_2/CO ratios of less than 1. Contrary to this supposition, the experimental results showed ratios of nearly 1. Since the carbon deposition is most remarkable in the reaction on the $LaCoO_3$ catalyst, as indicated by the carbon balance given in Table 1, the carbon deposition caused by the decomposition of CO, such as reaction (3), except that of CH_4, can be considered. Reaction (3) will be divided into the following two reactions (4) and (5), respectively. Considering that the dissociation of CO by reaction (4) is rapid on a Ni catalyst,[26—28)] reaction (3) also easily occurs on the $LaCoO_3$ catalyst. By combining reactions (1), (2), and (3), reaction (6) can be obtained. This reaction leads to a H_2/CO ratio of 1. We also considered that the water produced from reaction (2) may contribute to the hydrogen formation by reaction (7).

However, this contribution may be small, because a large amount of water could not be produced in the CH_4+CO_2 reaction.

$$CH_4 + CO_2 \rightleftarrows 2CO + 2H_2 \tag{1}$$

$$CO_2 + H_2 \rightleftarrows CO + H_2O \tag{2}$$

$$2CO \rightleftarrows C + CO_2 \tag{3}$$

$$CO \rightleftarrows C + O \tag{4}$$

$$CO + O \rightleftarrows CO_2 \tag{5}$$

$$CH_4 + CO_2 \rightleftarrows CO + H_2 + H_2O + C \tag{6}$$

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \tag{7}$$

$$CH_4 + 2CO_2 \rightleftarrows 3CO + H_2 + H_2O \tag{8}$$

$$C + H_2 \rightleftarrows CH_4 \tag{9}$$

When the reverse water-gas reaction (2) has a greater influence than reaction (3), reaction (8) can be obtained by combining reactions (1) and (2). Reaction (8) will result in a H_2/CO ratio of less than 1 and a greater conversion of CO_2 than of CH_4. This corresponds to the case of the $LaNiO_3$, $LaFeO_3$, and $LaCrO_3$ catalysts. Other reactions apart from

(1) to (8) are also likely to occur; i.e., reaction (9). In the reaction with the $LaCoO_3$ and $LaNiO_3$ catalysts, however, we can infer that the formation of methane by reaction (9) scarcely occurs, because of the high conversion of CH_4.

Assuming reaction (1) to be the main reaction on the $LaCoO_3$ catalyst, we can calculate the equilibrium constant at 1073 K to be 138.7. Under the reaction conditions indicated in Fig. 1, this value yields a CH_4 conversion of about 97%. Consequently, it can be considered that both the CH_4 and CO_2 conversions given in Table 1 proceed nearly to the equilibrium state.

The decline of CH_4 conversion up to the steady state on the $LaFeO_3$ catalyst, shown in Fig. 1, is considered to be a process of CH_4 with the oxygen adsorbed on the catalyst surface.[29] On the $LaCrO_3$ catalyst steady CH_4 conversion may be seen from the initial stage, probably because of the very small amount of oxygen adsorbed.

The carbon balance, calculated from the difference between the amounts of the reactants and products, was over 99% with the $LaFeO_3$ and $LaCrO_3$ catalysts, but on the $LaCoO_3$ and $LaNiO_3$ catalysts it was as low as 80 and 86%, respectively, at the steady state (see Table 1). The reason that these values differ is thought to be that scarcely any carbon was deposited on the catalysts containing Fe or Cr, whereas significant amounts of carbon were deposited on catalysts containing Co or Ni, as described later.

Takayasu et al.[14] reported that metal elements in noble metals and nickel catalysts supported on silica acted as the active site catalyzing the CH_4+CO_2 reaction. It can therefore be considered that the redox property of the B site in perovskite-type catalysts, described by the general formula ABO_3, may be related to the reaction activity. Consequently, the redox potential between B^{3+} and B^0 of the B-site[30] was related to the activity in the steady state, as shown in Fig. 2. The results indicate that Co and Ni in $LaCoO_3$ and $LaNiO_3$, are liable to reduction to Co^0 and Ni^0, which leads to high activity. Therefore, the zero valent metal can be supposed to be the active site.

We further examined the reaction behaviors on the $LaCoO_3$ catalyst, which exhibited the highest activity, by using different CH_4/CO_2 ratios. The CH_4 conversion gradually increased from the start of the reaction when these ratios were 1/1 and 1/3, and induction periods of about 1 and 2 h, respectively, were observed at these ratios. The high ratio of CH_4/CO_2, in contrast, resulted in a disappearance of the induction period. Thus, the induction period was clearly dependent on the ratio of CH_4 to CO_2. After the reaction the perovskite structure of catalyst was broken by the reduction in the reaction atmosphere, which was detected by a XRD-measurement, as described later. Accordingly, it can be considered that the induction period corresponds to a process in which the catalyst is reduced, probably by H_2 produced from the decomposition of CH_4 and/or by CH_4.

The selectivity of H_2 when $CH_4/CO_2=1/3$ was much lower than the selectivity under the other reaction conditions. This may have been due to the formation of water by the reverse water gas reaction (2) when there was a large amount of CO_2 present. When $CH_4/CO_2=3/1$, the molar ratio of H_2/CO increased to 2.17, whereas the carbon balance was decreased, indicating that the decomposition of CH_4 might have prevailed.

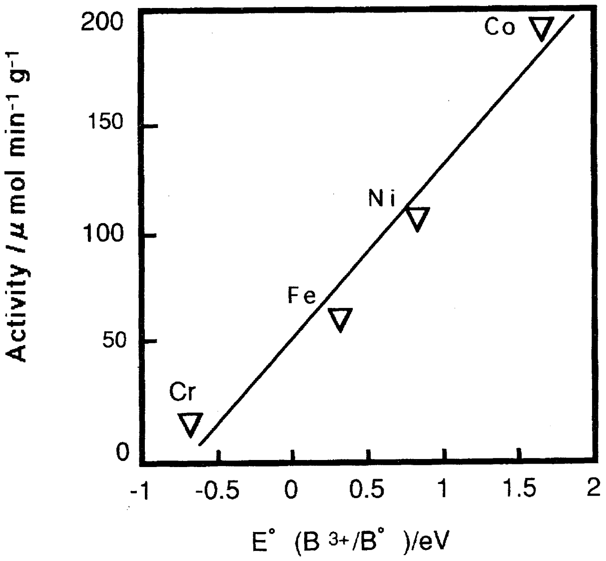

Fig. 2. Relationship between activity and redox potential of the B-site element of $LaBO_3$ (B=Co, Ni, Fe, Cr) catalysts.

2. Structural Change of Catalyst and Reaction Activity. The catalyst used in the reaction were examined by XRD and TG-DTA, the of which results are shown in Fig. 3. Figure 3a is an XRD-diagram of $LaCoO_3$ before the reaction, and is included as a reference to confirm the formation of $LaCoO_3$ as a perovskite structure. The structure of the other catalysts was similarly confirmed (not shown).

For both the $LaCoO_3$ and $LaNiO_3$ catalysts used in the reaction — Fig. 3b and Fig. 3c — the perovskite structure was no longer evident, and the most prominent peaks were those of La_2O_3, including Co; Ni was detected as small peaks. These observations indicate that the reduction of Co and Ni in $LaCoO_3$ and $LaNiO_3$ led to the destruction of the perovskite structure. As can be seen in Figs. 3d and 3e, however, the stable perovskite structure still persisted in both the $LaFeO_3$ and $LaCrO_3$ catalysts used in the reaction.

We suspected that the $LaCoO_3$ catalyst, which decomposed by reduction in the CH_4+CO_2 atmosphere during the reaction, is similar to the Co catalyst supported on La_2O_3. To compare the decomposed catalysts, we prepared both supported Co catalysts by weight of 18 wt% and 10 wt%, respectively on La_2O_3 (hereafter abbreviated as $18Co/La_2O_3$ and $10Co/La_2O_3$ respectively). The surface areas of both these catalysts were also so small (2 and 3 $m^2\,g^{-1}$) that they were comparable to the surface area of the $LaCoO_3$ catalyst. Their catalytic properties were examined under the same reaction conditions as in the case of the $LaCoO_3$ catalyst; the results are listed in Table 1. Although each of the catalysts had nearly the same selectivity to CO and H_2, the decomposed $LaCoO_3$ was 1.7—3 times more active than the supported catalysts. The similar selectivity of the three catalysts indicates that the nature of the active site is the same

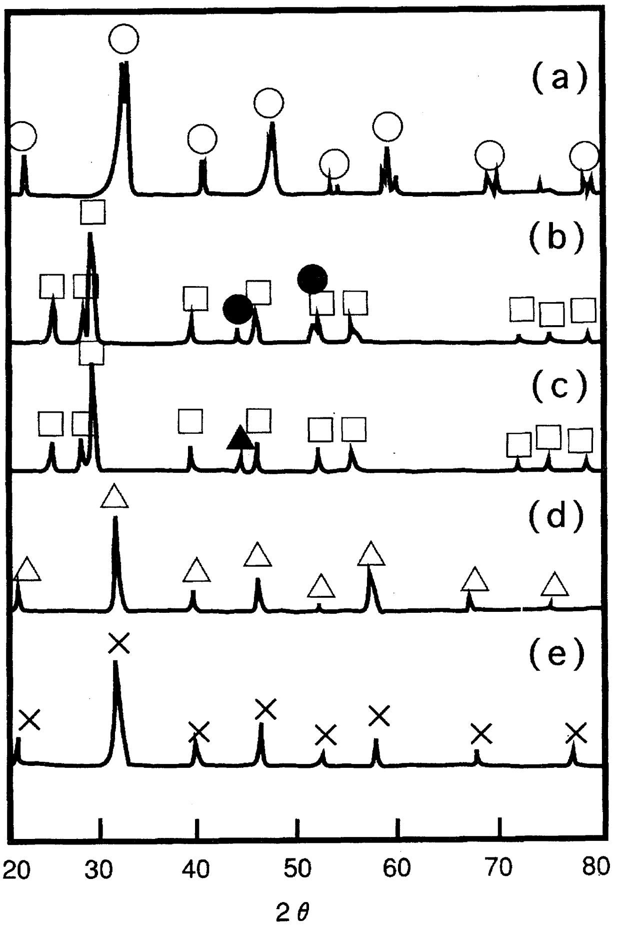

Fig. 3. X-Ray diffraction patterns of $LaBO_3$ (B=Co, Ni, Fe, Cr) catalysts. (a) $LaCoO_3$ before reaction. (b) $LaCoO_3$ used in the reaction. (c) $LaNiO_3$ used in the reaction. (d) $LaFeO_3$ used in the reaction. (e) $LaCrO_3$ used in the reaction. ○ $LaCoO_3$, △ $LaFeO_3$, × $LaCrO_3$, □ La_2O_3, ● Co, ▲ Ni.

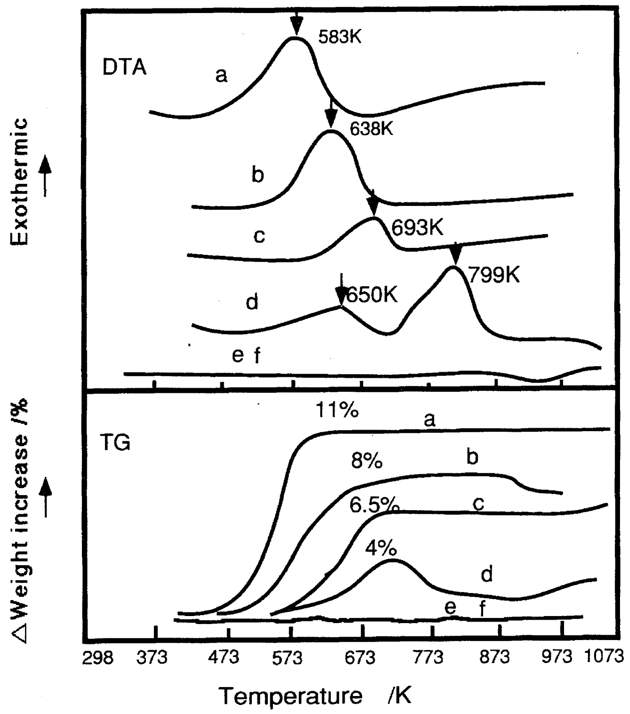

Fig. 4. TG-DTA curves of $LaBO_3$ (B=Co, Ni, Fe, Cr) and 18wt% Co/La_2O_3 catalysts. Temperature was raised with the rate of 10 $K\,min^{-1}$ in air. (a) $LaCoO_3$ after reduction with H_2. (b) $LaCoO_3$ used in the reaction. (c) $LaNiO_3$ used in the reaction. (d) 18wt% Co/La_2O_3 used in the reaction. (e) $LaFeO_3$ used in the reaction. (f) $LaCrO_3$ used in the reaction.

for all the catalysts. The activity of the $18Co/La_2O_3$ catalyst was lower than that of the $10Co/La_2O_3$ catalyst in spite of the larger Co content, and the carbon balance was also low. This might have been due to the poor dispersion of Co in the $18Co/La_2O_3$ catalyst and to the large amount of carbon deposited. The rather large H_2/CO ratio on the $18Co/La_2O_3$ catalyst may have been due to a marked deposition of carbon by the decomposition of CH_4, which can be suspected from the low carbon balance (see Table 1).

The results of TG-DTA of the different catalysts are shown in Fig. 4. To avoid the effect of the deposited carbon, the $LaCoO_3$ catalyst reduced with H_2 was used in this set of experiments. The $LaCoO_3$ catalyst reduced with hydrogen and both the $LaCoO_3$ and $LaNiO_3$ used in the reaction revealed exothermic peaks at 583, 638, and 693 K respectively, and weight increases that might be attributed to the oxidation of metallic Co or Ni. Comparing Fig. 4b with Fig. 4c, we can see that Co is oxidized more easily than Ni.

The TG-DTA analysis of $18Co/La_2O_3$ catalyst used in the reaction revealed two exothermic peaks at 650 K and at 799 K (see Fig. 4d). The maximum increase of weight was observed at around 700 K, and might be ascribed to the oxidation of Co. The weight decrease in the right region after 700 K in TG of Fig. 4d may have been the caused by the combustion of the deposited carbon on the catalyst surface, since the exothermic peak can be seen at around 799 K. The fact that a remarkable exothermic peak at around 800 K, like that in Fig. 4d, is not evident in the TG-DTA curve for the decomposed $LaCoO_3$ catalyst in the reaction, may be due to the gradual oxidation of carbon deposited during the reaction or to the simultaneous oxidation of Co and combustion of carbon. The same reasons might also apply in the case of the $LaNiO_3$ catalyst.

Since carbon was deposited on the catalyst surface or on the wall of the reactor, though the amount seemed to be small, from the results of TG alone, one cannot accurately estimate the amount of carbon deposited. Consequently, it is better to estimate the amount of the deposited carbon from the amount of CH_4 produced by the reaction with H_2 at 773 K[22] introduced on the catalyst bed after the reaction. The amount of the deposited carbon on the $LaCoO_3$ catalyst used in a reaction of 4 h at 1073 K was 2.2 mg, which was less than expected. Due to such a small amount of carbon, a decline in the reaction activity could not be detected and, also, the steady state would be maintained. Neither an exothermic peak nor an increase in weight was observed for either the $LaFeO_3$ or $LaCrO_3$ catalyst used in the reaction (Figs. 4e and 4f). This indicates that the Fe or Cr in these catalysts was not reduced during the reaction, and that either carbon was not deposited or the amount of carbon deposited was so small that it could not be detected.

The surface of the $LaCoO_3$ catalyst before and after the reaction was analyzed by XPS (see Fig. 5). On the $LaCoO_3$ catalyst peak at 779.9 eV assigned to Co^{3+} could be clearly detected, but on the catalyst used in the reaction the peak of Co^{3+} disappeared and peaks at 778.0 and 780.3 eV, which could be assigned to Co^{2+} and Co^0 respectively, were newly detected. The Co^{2+} may have been formed in the measurement process, because the catalyst sample should be exposed in air before the measurement, or it may actually have been present after the reaction, even though Co^{2+} in $LaCoO_3$ was not detected by XRD. Consequently, the reduction degree of the cobalt in the used $LaCoO_3$ catalyst could not be determined from XPS. The atomic ratios of Co/La on the surface of the catalyst before and after the reaction, however, could be obtained as 0.89 and 1.87, respectively. This indicates that cobalt is concentrated on the catalyst surface used in the reaction.

Crespin and Hall[31] reported that at temperatures of around 723 K the cobalt in $LaCoO_3$ was reduced by hydrogen to form Co^0 and Co^{2+}, and that at 773 K Co^{2+} was further reduced to Co^0. They concluded that, at the stage of the reduction, $LaCoO_3$ was decomposed to La_2O_3 and Co through La_2CoO_4. The $LaCoO_3$ catalyst used in this study would also be reduced according to a path similar to that reported by Crespin and Hall, although the reduction condition in Crespin's study differed from that using CH_4+CO_2 in the present study.

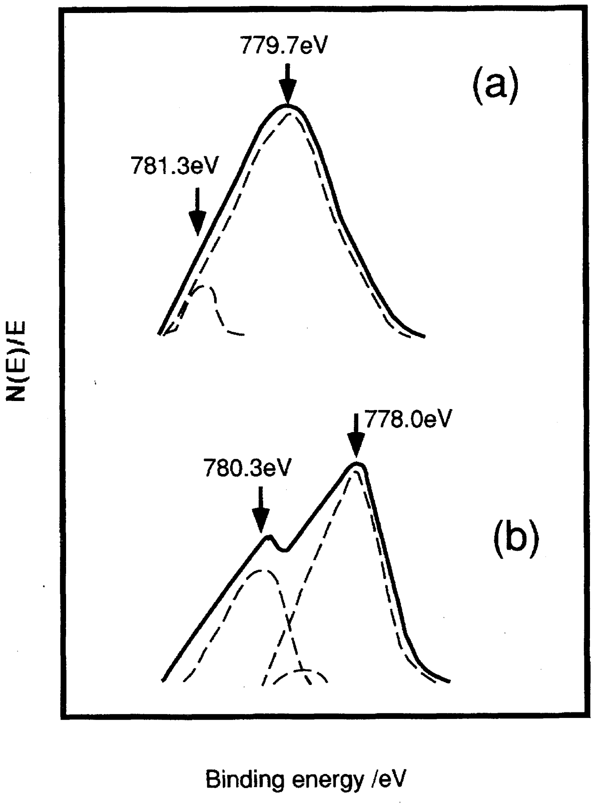

Fig. 5. XPS spectra in $Co(2p_{3/2})$ region of $LaCoO_3$ (a) and of $LaCoO_3$ after reaction (b).

The decomposed $LaCoO_3$ catalyst contained a larger amount of cobalt than did either of the Co/La_2O_3 catalysts (10 wt% or 18 wt%). Nevertheless, the greater activity of the $LaCoO_3$ catalyst can be ascribed to the wide dispersion of Co in fine particles. This confirmed by using an electron probe micro-analyzer (EPMA) on the catalysts used in the reaction at 1073 K. The EPMA results show the distribution of Co particles with different sizes on the catalyst surface. The zigzag curve in Fig. 6a indicates the distribution of Co particles in the region from 0 to 100 μm on the sample surface. The surface of the decomposed $LaCoO_3$ catalyst reveals a rather uniform distribution of fine Co particles, whereas the surface of the $18Co/La_2O_3$ catalyst has a non-uniform distribution of Co particles and a higher density of Co. The smallest particle size of the cobalt in the decomposed $LaCoO_3$ catalyst and in the $18Co/La_2O_3$ catalyst can be estimated from the EPMA photos as being ca. 0.25 and 0.50 μm, respectively. Note that the scale of the abscissa in Fig. 6(a) and Fig. 6(b) is different.

From the XRD results of shown in Fig. 3, although the particle size of Co can also be obtained, we did not estimate the size, because the value obtained from only one peak of Co is not accurate. The number of Co atoms exposed on the surface of the decomposed $LaCoO_3$ catalyst and on that of the $18Co/La_2O_3$ catalyst, which were both reduced with H_2

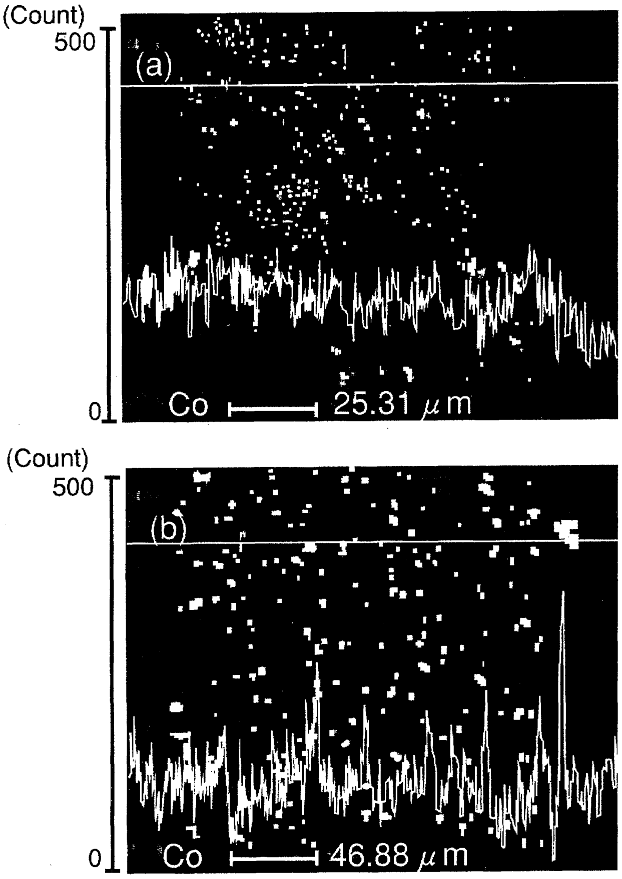

Fig. 6. EPMA images of $LaCoO_3$ and 18wt% Co/La_2O_3 catalysts, respectively, used in the reaction at 1073 K. (a) $LaCoO_3$, (b) 18wt% Co/La_2O_3.

at 773 K for 3 h, is given in Table 2. On the surface of the decomposed $LaCoO_3$ catalyst the chemisorbed uptake of H_2 was lighter than that on the $18Co/La_2O_3$ catalyst. This was probably because the majority of cobalt in the former catalyst was present in the bulk, which may limit the uptake of H_2. On the other hand, the relatively larger amount of cobalt in the latter catalyst would have been dispersed on the surface, allowing for a larger uptake of H_2. The dispersion of Co atoms on both catalysts was estimated, as shown in the last column of Table 2, on the basis of the number of Co atoms from the uptake of O_2 and under the assumption that a hydrogen atom adsorbs on a cobalt atom. There was less dispersion and less chemisorbed uptake of H_2 on both catalysts than was expected, probably due to a strong interaction between cobalt and La_2O_3, i.e., the strong metal support interaction effect like the phenomena seen in the Ni catalyst supported on TiO_2.[32)] Barrault et al. have already suggested that the H_2 uptake is significantly decreased by the addition of La or Ce in a cobalt catalyst,[33)] and that a strong interaction may also exist in this catalyst system.

Under the assumption that the state of the catalyst reduced with H_2 at 773 K was the same as that reduced in the reaction atmosphere of CH_4+CO_2 at 1073 K, we estimated the TOF (turnover frequency) of CH_4 on the basis of both the number of Co atoms exposed on the catalyst surface and the reacted amount of CH_4 per minute per gram of catalyst, as shown in Table 2. From these results, it is clear that the decomposed $LaCoO_3$ catalyst was still more active than the $18Co/La_2O_3$ catalyst.

We can thus conclude that the decomposed $LaCoO_3$ catalyst during the reaction or due to reduction with H_2 contains a large concentrated amount of fine Co particles with a homogeneous size and these particles are uniformly dispersed on the catalyst surface, and that this may be the reason for the high activity of this catalyst.

During the adsorption of O_2 carried out to measure the amount of Co atoms, no uptake of O_2 at 723 K was detected on the La_2O_3 pretreated with H_2 at 773 K for 3 h. Thus, O_2 was consumed to oxidize only the Co metal. The O_2 adsorption allowed the decomposed $LaCoO_3$ catalyst to return to its initial state of $LaCoO_3$ and did the $18Co/La_2O_3$ catalyst to convert to $LaCoO_3$ and La_2CoO_4, as detected by XRD. From these results, it appears that the following oxidation occurs on both catalysts:

$$La_2O_3 + 2Co + 3/2O_2 \rightarrow 2LaCoO_3, \tag{10}$$

$$2La_2O_3 + 3Co + 2O_2 \rightarrow La_2CoO_4 + 2LaCoO_3. \tag{11}$$

Reaction (10) would occur on the decomposed $LaCoO_3$ catalyst and reaction (11) would occur on the $18Co/La_2O_3$ catalyst. From the uptake of O_2 and reaction (10) we can calculate that the amount of cobalt was 4107 μmol/g-cat, which nearly agrees with the value 4060 μmol/g-cat obtained by our analysis (see Table 2). This indicates that the cobalt in the decomposed $LaCoO_3$ catalyst is almost completely oxidized in the O_2 adsorption, including the cobalt in the bulk. On the other hand, we can similarly calculate that the amount of cobalt in the $18Co/La_2O_3$ catalyst was 2475 μmol/g-cat from reaction (11), which does not agree with the content of Co in the catalyst. Consequently, it appears that the Co in the $18Co/La_2O_3$ catalyst is not completely reduced by a H_2 treatment at 773 K, indicating that the cobalt on La_2O_3 is more difficult to reduce than with the decomposed $LaCoO_3$ catalyst. The reducibility of Co in the $18Co/La_2O_3$ catalyst was estimated to be 76% from the uptake of O_2 and the Co content in the catalyst, as shown in Table 2. We can also consider that the difference of this reducibility of Co in both catalysts would be related to the activity difference.

Scanning electron microscopy (SEM) photos of the $LaCoO_3$ catalyst and $18Co/La_2O_3$ catalyst before and after the reaction are shown in Fig. 7. The $LaCoO_3$ catalyst used in the reaction was broken into small particles (compare Fig. 7a and Fig. 7b), while a fiber-like material, which was confirmed to be a deposited carbon by the elementary analysis with EDS, was observed on the $18Co/La_2O_3$ catalyst used in the reaction compare (Fig. 7c and Fig. 7d). Since the fiber-like material disappeared when the catalyst was calcined in air, it seems to have been carbon. The fiber-like carbon seems to be similar to the whisker-like carbon seen in the Ni/SiO_2 catalyst.[34)] However, the fiber-like material was not observed on the decomposed $LaCoO_3$ catalyst. Thus, the rather large amount of carbon deposited on the $18Co/La_2O_3$ catalyst could also be detected in the SEM photos. The deposited amount of carbon estimated from the CH_4 formation reaction was 7.9 mg, which was about four-times grater that the amount of carbon deposited on the decomposed $LaCoO_3$ catalyst.

3. Reaction Mechanism on the Surface of the $LaCoO_3$ Catalyst. Although catalytic reaction of CH_4+CO_2 was previously studied,[1,8,14,18,19)] how the CH_4+CO_2 reaction is affected by the Co released from the $LaCoO_3$ catalyst during the reaction is still not clear. The present study therefore explored the reaction mechanism on the decomposed $LaCoO_3$ catalyst by investigating the reaction of CO_2 alone and the mutual reactions of CH_4 and CO_2.

Table 2. Numbers of Cobalt Atoms and Activities on the Two Kinds of Catalysts

Catalyst	$\frac{\mu\text{mol Co}^{a)}}{\text{g-cat}}$	$\frac{\mu\text{mol } H_{2\ \text{ads}}}{\text{g-cat}}$	$\frac{\mu\text{mol } O_{2\ \text{ads}}}{\text{g-cat}}$	$\frac{\mu\text{mol Co}_{\text{surf}}{}^{b)}}{\text{g-cat}}$	$R\%$[c)]	TOF[d)] ·(min^{-1})		$D\%$[e)]
						CH_4	CO_2	
$LaCoO_3$	4060	7.6	3080	15.2	100	13.2	13.0	0.37
$18wt\%Co/La_2O_3$	3260	8.8	1650	17.6	76	3.6	3.9	0.54

a) Calculated from wt%. b) Amount of Co atoms exposed on the catalyst surface. c) R; Reduction degree. d) TOF_{CH4}=activity/μmol $Co_{suf/g-cat}$. e) D; dispersion of Co atoms on the Co particles.

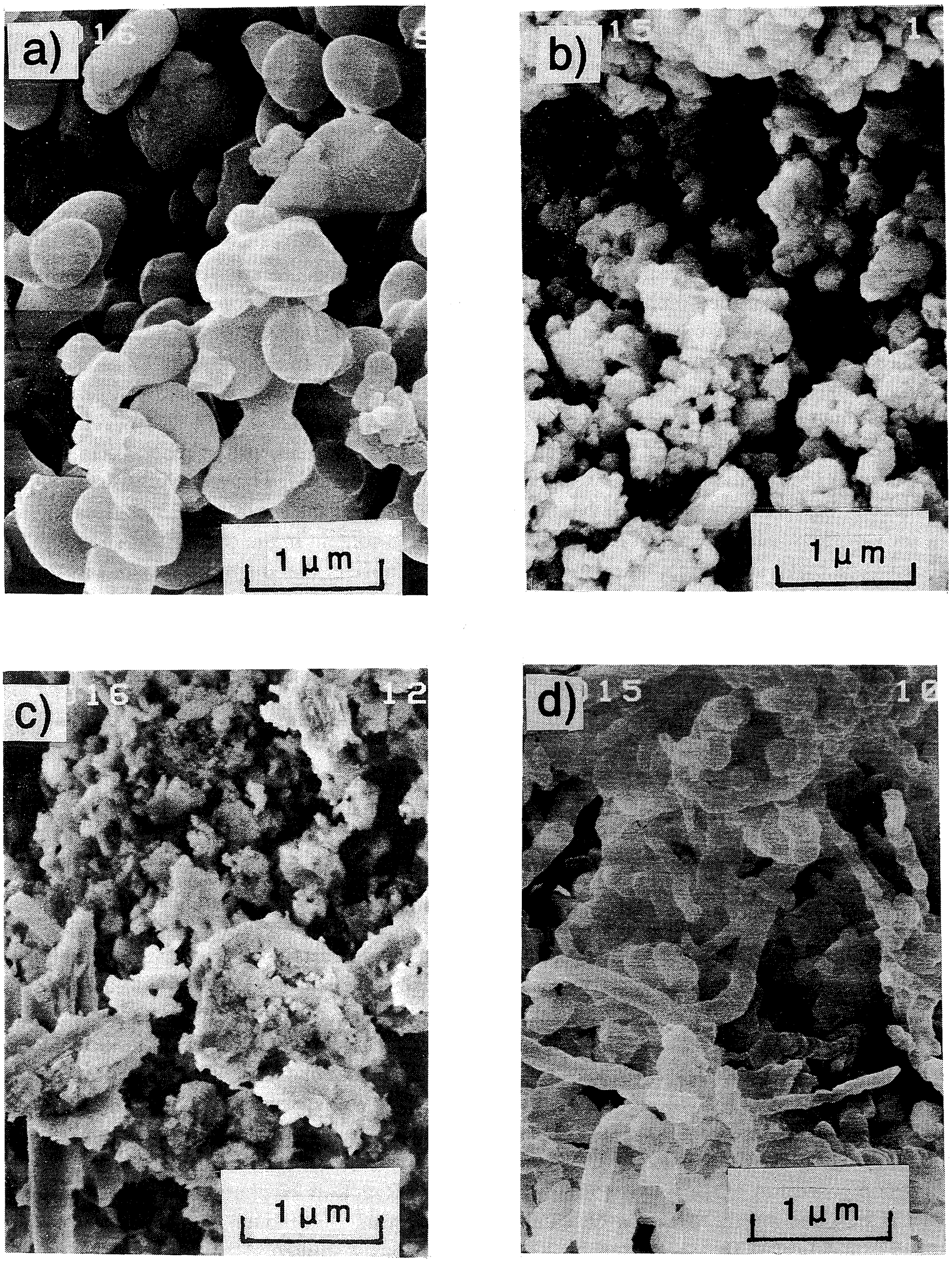

Fig. 7. SEM photographs of $LaCoO_3$ and 18wt% Co/La_2O_3 catalysts. (a) $LaCoO_3$ before reaction. (b) $LaCoO_3$ used in the reaction. (c) 18wt% Co/La_2O_3 before reaction. (d) 18wt% Co/La_2O_3 used in the reaction.

3.1 Reaction of CO_2 Alone: The reaction of CO_2 alone was evaluated at 1073 K both with and without $LaCoO_3$. No reaction occurred in either case unless the $LaCoO_3$ catalyst was reduced by hydrogen. On the decomposed $LaCoO_3$ catalyst by reduction, the formation of CO was observed; however, CO_2 conversion and CO formation gradually decreased (Fig. 8). The results of the XRD measurement of the catalyst before and after a reaction for 180 min are shown in Fig. 9. As mentioned earlier, the $LaCoO_3$ catalyst decomposed with H_2 consists of Co and La_2O_3. After the reaction of CO_2 alone, however, the metal Co was re-oxidized to Co^{2+}, which would be detected as La_2CoO_4.

It thus seems that an active oxygen is formed by the reaction $CO_2 \rightleftarrows CO+O_a$ (where O_a indicates the oxygen atom adsorbed on Co^0 and CoO is formed) and that CoO combines with La_2O_3 to form La_2CoO_4.

3.2 Mutual Reactions of CH_4 and CO_2: Table 3 lists the results of the mutual reactions of CH_4 and CO_2 at 1073 K. In the reaction of CH_4 alone, the CH_4 conversion increased with the reaction time, reached a maximum after 40 or 50 min, and then gradually decreased. Although the formation of CO_2 was detected during the initial stage of the reaction, it suddenly decreased, and the formation of CO and H_2 increased. The formation of a small amount of C_2

Table 3. Results of Reaction with CH_4 or CO_2 at 1073 K

a)	t (min)	Activity (μmol min^{-1} g^{-1})	Selectivity (%)				C. B. (%)
		CH_4	CO_2	CO	C_2[c)]	H_2	
	10	47	50	5	0.2	30	89
	20	58	30	10	0	56	89
	40	131	2	60	0	76	50
	50	128	0	9	0	80	41
	60	121	0	8	0	84	45
	70	113	0	<1	0	99	46
	90	111	0	0	0	99	46

b)	t (min)	Activity (μmol min^{-1} g^{-1})	Formation rate of CO (μmol min^{-1} g^{-1})	C. B. (%)
	30	81	136	168
	60	77	97	127
	180	4	4	100

Catalyst weight: 2 g. Gas flow rate: $CH_4/He=10/70$ ml min^{-1}, $CO_2/He=10/70$ ml min^{-1}.
a) Reaction with CH_4. b) Reaction with CO_2 after (a). c) C_2 indicates C_2H_4 and C_2H_6.

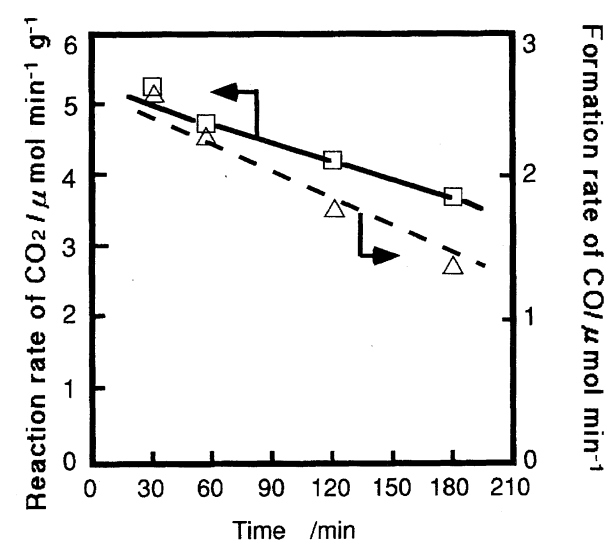

Fig. 8. Results of CO_2 reaction over decomposed $LaCoO_3$ catalyst at 1073 K. Catalyst weight: 2 g. Gas flow rate: $CO_2/He=10:70$ (ml min^{-1}). □ CO_2 conversion, △ produced amount of CO.

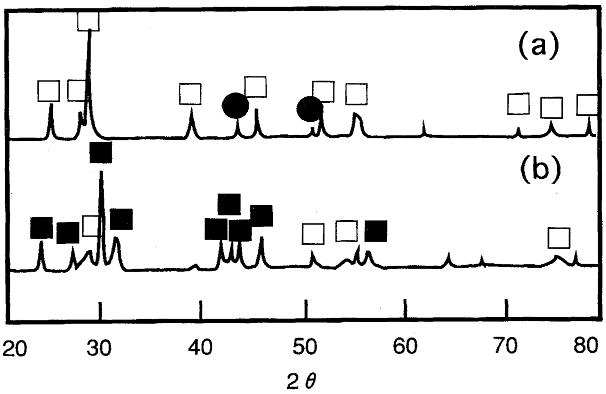

Fig. 9. X-Ray diffraction patterns of $LaCoO_3$ catalysts. (a) $LaCoO_3$ after reduction with H_2. (b) $LaCoO_3$ used in the reaction by CO_2. □ La_2O_3, ● Co, ■ La_2CoO_4.

compounds (C_2H_4, C_2H_6) was observed in the initial stage, but soon stopped. Consequently, it is considered that the oxygen (perhaps from air) adsorbed on $LaCoO_3$ formed both CO_2 and a small amount of C_2 by a reaction with CH_4, and that when this oxygen was consumed, CO was formed by a reaction with lattice oxygen. This formation of CO was accompanied by the formation of both hydrogen and carbon and by the decomposition of $LaCoO_3$ due to reduction.

Even in the decreasing region of the activity after the maximum (about 50—60 min of reaction time) in the reaction of CH_4 alone, the fact that the selectivity to hydrogen continuously increased (see Table 3) indicates that the decomposition of CH_4 preferentially occurred on the decomposed $LaCoO_3$ catalyst (by dehydrogenation).

With the progress of the reaction, the carbon balance decreased remarkably, probably because of carbon deposit. After the reaction of CH_4 alone for 90 min, the CH_4 was replaced by a He flow for 2 h at the same temperature; then, CO_2 was introduced again (Table 3b). The rate of CO_2 consumption decreased remarkably with time, from 5.7×10^{-5} mol min^{-1} g^{-1} in the initial stage of the reaction. This indicates that the decomposed $LaCoO_3$ catalyst would catalyze the reverse reaction of (3), i.e., $CO_2+C\rightleftarrows 2CO$. The carbon balances in the initial stage listed in Table 3b greatly exceeded 100% because of the reaction of CO_2 with the carbon deposited on the catalyst surface during the reaction of CH_4 alone. Also, because the formation of hydrogen was not detected, it is supposed that CH_4 was not strongly adsorbed on the catalyst. From the results shown in Figs. 8 and 9 and listed in Table 3, in combination with the mechanism reported in the literature, the following reaction mechanism can be conjectured:

$$CO_2+Co^0 \rightleftarrows Co\cdots O_a+CO \qquad \text{(I)}$$

$$Co\cdots O_a+CH_4 \rightleftarrows Co^0+CO+CH_{xa}+(4-x)H_a, \quad \text{or } H_2O \qquad \text{(II)}$$

$$Co\cdots O_a+CH_{xa} \rightleftarrows CO+xH_a+Co \qquad \text{(III)}$$

$$2H_a \rightleftarrows H_2 \qquad \text{(IV)}$$

$$Co\cdots O_a + 2H_a \rightleftarrows Co^0 + H_2O \quad (V)$$

$$2H_a + CO_2 \rightleftarrows CO + H_2O \quad (VI)$$

Reaction (I) proceeds on the Co catalyst formed by decomposition of $LaCoO_3$ (by reduction during the reaction) and produces the atomic oxygen species adsorbed on Co metal: $Co\cdots O_a$. This reaction, i.e., the dissociation of CO_2, is also the rate-determining step.[11)]

Once $Co\cdots O_a$ in formed, the reactions from (II) to (VI) proceed one after another and produce CO and a partially decomposed species of CH_4, (CH_{xa}) and hydrogen (H_a) adsorbed on the catalyst, respectively. Sodesawa[34)] indicates that the value of x in CH_x is almost 2 from the results on the CH_4+D_2 reaction. A similar reaction mechanism, with Ni instead of Co, can be conjectured when the catalyst is $LaNiO_3$.

Although for neither the $LaFeO_3$ catalyst nor the $LaCrO_3$ catalyst the decomposition by reduction during the reaction could be detected by XRD, very small amounts of Fe and Cr may be produced on the catalyst surface and participate in this reaction by a mechanism similar to that occurring on $LaCoO_3$.

Conclusion

In this study, exploring the possibility of producing synthetic gas from the CH_4+CO_2 reaction catalyzed by perovskite-type oxide, the following conclusions can be drawn:

1) The $LaCoO_3$ catalyst is more active than the $LaNiO_3$ catalyst, which is more active than the $LaFeO_3$ catalyst, which is in turn more active than the $LaCrO_3$ catalyst. This agrees with the order of the redox potential of the B-site element (Co, Ni, Fe, Cr) in each of the catalysts.

2) When $CH_4/CO_2=1$ the main reaction on the $LaCoO_3$ catalyst can be supposed as $CH_4+CO_2 \rightleftarrows CO+H_2+H_2O+C$, but when the CO_2 ratio increases the reaction $CH_4+3CO_2 \rightleftarrows 4CO+2H_2O$ also occurs.

3) The $LaCoO_3$ catalyst is destroyed by reduction during the reaction of CH_4+CO_2 and the resultant highly dispersed, concentrated, and uniform state of fine Co particles on the catalyst surface is related to the high activity of this catalyst.

4) The reaction-mechanism described in 3.3.2 can be conjectured from the results of the reaction of CH_4 or CO_2 alone.

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References

1) K. Takehira, T. Hayakawa, J. Nakamura, and T. Uchijima, *Petrotech (Tokyo)*, **17**, 838 (1994).

2) M. Hashimoto, *Shokubai (Catalyst)*, **36**, 594 (1994).

3) J. R. Rostrup-Nielsen, *Stud. Surf. Sci. Catal.*, **36**, 73 (1988).

4) A. T. Ashcroft, A. K. Cheetham, J. S. Foord, M. L. H. Green, C. P. Grey, A. J. Murrell, and P. D. F. Vernon, *Nature*, **344**, 319 (1990).

5) J. Nakamura, S. Umeda, K. Kubushiro, K. Kunimori, and T. Uchijima, *Sekiyu Gakkaishi (J. Petroleum Society Jpn.)*, **36**, 97 (1993).

6) T. Hayakawa, A. G. Andersen, M. Shimizu, K. Suzuki, and K. Takehira, *Catal. Lett.*, **22**, 307 (1993).

7) J. Nakamura, K. Sato, K. Aikawa, K. Kunimori, and T. Uchijima, *Shokubai (Catalyst)*, **35**, 84 (1993).

8) F. Fischer and H. Tropsch, *Brennst. Chem.*, **3**, 39 (1928).

9) J. Nakamura and T. Uchijima, *Shokubai (Catalyst)*, **35**, 478 (1993).

10) T. A. Chubb, *Sol. Energy*, **24**, 341 (1980).

11) F. Solymosi, Gy. Kutsan, and A. Erdohelyi, *Catal. Lett.*, **11**, 149 (1991).

12) A. Takano, T. Tagawa, and S. Goto, *Sekiyu Gakkaishi*, **39**, 144 (1996).

13) A. T. Ashcroft, A. K. Cheetham, M. L. H. Green, and P. D. F. Vernon, *Nature*, **352**, 225 (1991).

14) O. Takayasu, M. Yoshida, N. Matsuda, N. Hongo, and I. Matsuura, *Shokubai (Catalyst)*, **34**, 348 (1992).

15) O. Takayasu, I. Matsuura, K. Nitta, and Y. Yoshida, "New Frontiers in Catalysis," p. 1951 (1992).

16) N. R. Udengaard, J.-H. Bak Hansen, D. C. Hanson, and J. H. Stal, *Oil Gas J.*, **90**, 62 (1992).

17) J. R. Rostrup-Nielsen and J-H. Bak Hansen, *J. Catal.*, **144**, 38 (1993).

18) Z. I. Yu, K. Choi, M. P. Rosynek, and J. H. Lunsford, *React. Kinet. Catal. Lett.*, **51**, 143 (1993).

19) T. Ishihara, T. Fujita, Y. Miyashita, and T. Takita, *Shokubai (Catalyst)*, **35**, 324 (1993).

20) V. R. Choudhary, A. M. Rajput, and B. Prabhakar, *Angew. Chem., Int. Ed. Engl.*, **33**, 2104 (1994).

21) T. Osaki, H. Masuda, and T. Mori, *Catal. Lett.*, **29**, 33 (1994).

22) M. Yoneda, S. Komai, T. Yoshida, A. Satsuma, and T. Hattori, "The 78th Annual Meeting of Catalysis Society of Japan, (A)," p. 331 (1996).

23) R. B. Pannell, K. S. Chung, and C. H. Bartholomev, *J. Catal.*, **46**, 340 (1977).

24) C. H. Bartholomev and R. B. Pannell, *J. Catal.*, **65**, 390 (1980).

25) T. Keii, "Kyuchaku=Adsorption," Kyoritsu Shuppan Co., Ltd., p. 107 (1965).

26) M. C. J. Brandford and M. A. Vannice, *Appl. Catal., A: General*, **142**, 97 (1996).

27) C. Astaldi, A. Santoni, F. Della Vell, and R. Rosei, *Surf. Sci.*, **220**, 322 (1989).

28) R. Rosei, F. Ciccacci, R. Memeo, C. Mariani, and L. S. Caputi, *J. Catal.*, **83**, 19 (1983).

29) Y. Y. Wu, O. Kawaguchi, K. Sugiyama, and T. Matsuda, *Nippon Kagaku Kaisi (J. Chem. Soc. Jpn.)*, **4**, 354 (1996)

30) "Chemical Tables," Vol. II, pp. 309 and 473, ed by Japan Chemical Society, Maruzen, Tokyo (1983).

31) M. Crespin and W. K. Hall, *J. Catal.*, **60**, 359 (1981).

32) S. J. Tauster, S. C. Fung, and R. L. Garten, *J. Am. Chem. Soc.*, **100**, 170 (1978).

33) J. Barrault, A. Guilleminot, J. C. Achard, V. Paul-Boncour, and A. Percheron-Guegan, *Appl. Catal.*, **21**, 307 (1986).

34) T. Sodesawa, "The 78th Annual Meeting of Catalysis Society of Japan," Abstr., No. 6J09, p. 335 (1996).