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Oxidative coupling of methane over $LaCoO_{3-\delta}$-based mixed oxides

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The catalytic activity of $LaCoO_{3-\delta}$-based mixed oxides for the oxidative coupling of methane has been tested by TPR and cyclic reaction. Characterization has been done by XRD, TGA and Mössbauer spectrometry. It is likely that the perovskite-crystal structure containing hypervalent metal ions has an important role and that unique structural oxygen species in the perovskite contribute to the partial oxidation of methane.

Keywords: Oxidative coupling of methane; perovskites; XRD; Mössbauer; TGA; lattice oxygen; $LaCoO_3$ based catalyst

1. Introduction

Methane is a main constituent of natural gas, often comprising over 90 mol% of the hydrocarbon fraction of the gas. Oxidative coupling of methane is an attractive process for producing C_2 hydrocarbons, and there have been many studies since Keller and Bhasin first demonstrated this possibility [1–3]. It is generally accepted that the initial step in the catalytic oxidative coupling of methane involves the homolytic cleavage of a C–H bond on the catalyst surface to form $CH_3^{\cdot}$ radicals which may undergo coupling to form ethane in the gaseous phase [4]. The $CH_3^{\cdot}$ radicals can undergo deep oxidation to carbon oxides in the presence of molecular oxygen. It has therefore frequently been

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proposed to use a cyclic operation by feeding methane and oxygen alternatively over catalyst interspaced by a short purge of inert gas [3] or to use the membrane reactor in which methane and oxygen are separated by an oxygen-permeable membrane [5]. Methane can be oxidized by oxygen species which are contained in the structure of metal oxide as catalyst, i.e. lattice oxygen in manganese oxide [3], lead oxide and lithium nickel oxide [5].

It is well known that some oxides conduct owing to oxide ion mobility [6], and the oxygen transport can influence the oxidation reaction through oxygen supply from the oxide catalyst. We studied the oxidation of olefins by using an yttria-stabilized zirconia (YSZ) aided system, i.e. Mo–Bi oxide catalyst, Au/YSZ/Ag where YSZ serves as oxygen pump coupled with Au and Ag electrodes [7]. Also, in the study of methane oxidative coupling, similar systems, Bi_2O_3, Ag/YSZ/Ag and $LiNiO_2$, Au/YSZ/Au, have been able to increase the selectivity of C_2 hydrocarbon production [8]. It is likely that the use of a mixed conductor such as perovskite-type oxides which conduct both electrons and oxide ions, is promising in the oxidation of hydrocarbons, because of its strong ability to direct oxygen supply from the bulk oxide to surface-adsorbed species. However, only a few papers [9] have dealt with successful use of perovskites such as $BaCeO_{3-\delta}$, $BaPb_{1-x}Bi_xO_{3-\delta}$ and $CaTiO_{3-\delta}$ in the oxidative coupling of methane, even though many perovskites based on $LaCoO_{3-\delta}$ or $LaMnO_{3-\delta}$ are well known to be active for deep oxidation of hydrocarbons [10]. Here we report the reactivity of structural oxygen in connection with the structure of various mixed oxides obtained by substitution of A(La) site and B(Co) site cations of $LaCoO_{3-\delta}$ with alkaline earth metals (Mg, Ca, Sr and Ba) and transition metals (Fe, Ni and Cu), respectively.

2. Experimental

The mixed oxides were prepared by the citrate method [11] as follows: an aqueous solution of a reagent grade metal nitrate was treated with an equimolar amount of critic acid and ethylene glycol, evaporated at 353–363 K to make a sol of organic metal complex, followed by two-step decomposition by heating at 573 K for 5 h and 773 K for 5 h in air and finally calcining at 1123 K for 10 h. The powder of the mixed oxide thus obtained was compressed into a pellet under a hydrostatic pressure of 200 MPa and sintered in air at 1373 K for 10 h. The pellet was finely powdered and used as the catalyst for temperature-programmed reaction and cyclic reaction of methane oxidation.

The temperature-programmed reaction (TPR) was carried out by using 2.0–3.0 g of the mixed oxide in a conventional fixed-bed quartz tube reactor (10 mm o.d.) under heating rate of 2.5 K/min and flow rate of 1 ℓ/h of methane at atmospheric pressure. The mixed oxide was used after preheating in helium at 373 K for 1 h. The cyclic reaction at 1023 K was carried out by using 2.0 g of mixed oxide in the quartz reactor. Methane and air were alternately fed interspaced by a short purge of helium. Methane and helium (Takachiho Trading Co.) were over 99.99% in purity and used without further purification. The products (C_2H_6, C_2H_4, CO and CO_2) were analysed by gas chromatography at suitable intervals, and selectivities were evaluated on the basis of carbon number.

The powder X-ray diffraction (XRD) diagrams of mixed oxide were recorded by using MXP-18 (MAC Science Co.) with Cu Kα radiation. Mössbauer measurement was done as previously reported [12]. Before measuring Mössbauer spectra, each sample was preheated at 973 K for 4 h and cooled slowly in furnace. The Ba and Sr perovskites were tetragonal but the Ca one was rhombic. Oxygen contents were analyzed by thermogravimetry (TGA) using TGD-7000RH (ULVAC) containing an electrobalance in an hydrogen atmosphere.

3. Results and discussion

3.1. TEMPERATURE-PROGRAMMED REACTION

Catalytic activities of the mixed oxides were tested by the TPR method, a typical curve obtained over $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$ being shown in fig. 1. C_{2t} means a total amount of C_2H_6 and C_2H_4, in which the C_2H_4 content increased with an

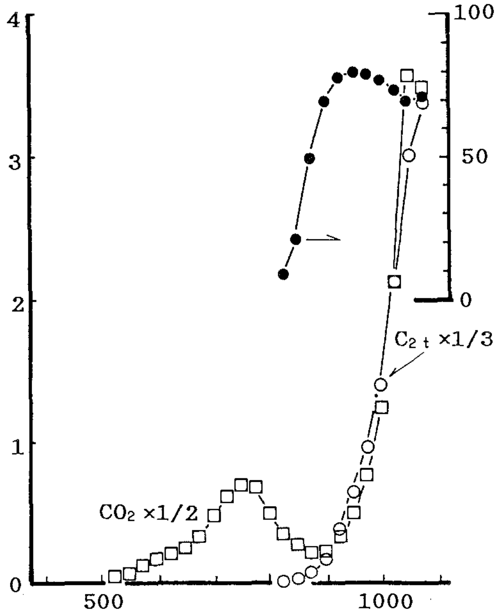

Fig. 1. Temperature-programmed reaction over $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$. Heating rate, 2.5 K min^{-1}; CH_4 flow rate, 1 ℓ h^{-1}; catalyst, 2 g.

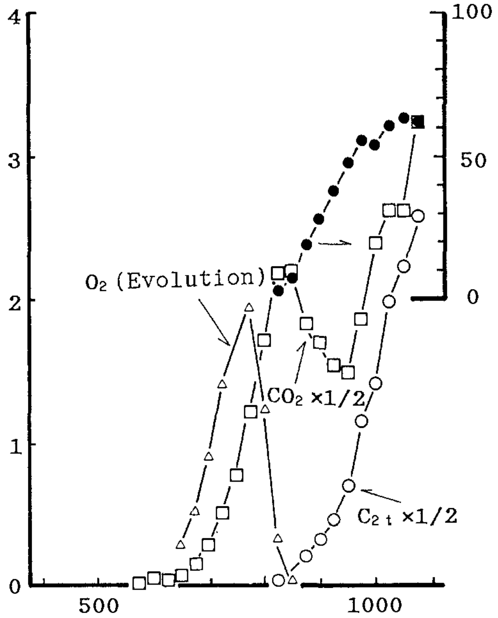

Fig. 2. Temperature-programmed reaction over $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$. Heating rate, 2.5 K min^{-1}; CH_4 flow rate, 1 ℓ h^{-1}; catalyst, 2 g.

increase in the temperature during TPR. The molar ratio of C_2H_4 to C_2H_6 in C_{2t} was 0.05 and 823 K and reached 1.0 at 1073 K. During the TPR experiment, CO_2 began to form at 523 K, while the C_{2t} compounds appeared at 823 K. The rate of CO_2 formation increased, reached a maximum value at 753 K, then decreased and finally again increased at above 923 K, where the rate of C_{2t} formation also largely increased. The former rate did not so substantially increase compared to the latter that the selectivity to C_{2t} kept a relatively high value.

The TPR curve of CO_2 formation obtained over $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (fig. 2) exhibited an almost similar tendency to that over $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$, but the temperature of CO_2 formation and of its maximum value shifted toward higher value by 50 K than those observed over $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$. Interestingly, an evolution of oxygen gas was observed at 673–823 K exclusively over the mixed oxide containing Sr as the A site cation. This result suggests that oxygen species was liberated from $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ without reacting with methane. When Ca was used as the A site cation, the temperature of CO_2 formation largely elevated. The rate of each C_{2t} and CO_2 formation increased simply with increasing in temperature and the selectivity of C_{2t} was very low. The TPR curve obtained over $MgCo_{0.8}Fe_{0.2}O_{3-\delta}$ was almost similar in tendency to that obtained over $CaCo_{0.8}Fe_{0.2}O_{3-\delta}$.

The TPR results thus obtained are summarized in table 1. The maximum rate of C_{2t} formation, $r_{C_{2t}}(\max)$, was observed together with the rate of CO_2 forma-

Table 1
Temperature-programmed reaction over $LaCoO_{3-\delta}$-based mixed oxides.

Mixed oxides	T (K)	$r_{C_{2t}}$(max) (μmol/min)	r_{CO_2} (μmol/min)	$2r_{C_{2t}}$(max)/ [$2r_{C_{2t}}$(max) + r_{CO_2}]
$La_{0.6}Ba_{0.4}Co_{0.8}Fe_{0.2}$	1010	3.48	17.20	0.29
$La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}$	998	0.51	6.28	0.14
$La_{0.6}Sr_{0.4}Co_{0.8}Cu_{0.2}$	998	0.50	12.5	0.07
$La_{0.6}Sr_{0.4}Co_{0.8}Ni_{0.2}$	948	0.24	0.92	0.34
$La_{0.6}Sr_{0.4}Co$	973	0.37	1.80	0.29
$MgCo_{0.8}Fe_{0.2}$	1023	0.16	16.10	0.02
$CaCo_{0.8}Fe_{0.2}$	1048	0.82	20.70	0.07
$SrCo_{0.8}Fe_{0.2}$	1073	5.16	6.46	0.62
$BaCo_{0.8}Fe_{0.2}$	1073	10.14	6.98	0.74
$Co_{0.8}Fe_{0.2}$	948	0	14.15	0

tion, r_{CO_2}, at the temperature T. A selectivity to C_{2t} is here shown as $2r_{C_{2t}}(\max)/[2r_{C_{2t}}(\max)+r_{CO_2}]$. Almost all of these mixed oxides, except of $MgCo_{0.8}Fe_{0.2}O_{3-\delta}$ and $Co_{0.8}Fe_{0.2}O_{3-\delta}$, are considered to have a perovskite-crystal structure and also have a high ability of oxygen permeation as reported by Teraoka et al. [13]; the perovskite-crystal structure was confirmed by X-ray diffraction analyses (vide infra). Among the perovskites in table 1, $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$, $La_{0.6}Ba_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ showed relatively high activities for the C_{2t} compound formation. In all cases over the three mixed oxides, the rates of CO_2 formation and C_{2t} formation reach maximum values at quite different temperatures from each other. A similar phenomenon was observed over $La_{1-x}Sr_xCoO_{3-\delta}$ by the temperature-programmed desorption method by Yamazoe et al. [14], where two types of oxygen desorption were revealed by the appearance of a broad desorption peak at 673–873 K and a sharp one around 1073 K. From XPS, the binding energy of the O 1s level for absorbed oxygen was found to be different from that for structural oxygen and the former desorption can be ascribed to the loss of the absorbed oxygen, while the latter may be the loss of part of the structural oxygen [14]. Likely thus, in the present case, two types of oxygen species exist over the mixed oxides, $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$, $La_{0.6}Ba_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$, and contribute to each of the deep oxidation or the oxidative coupling of methane. The activity for the latter partial oxidation of methane can be attributed to the lattice oxygen species in the perovskite structure.

The best result was obtained over $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$ prepared by the full substitution of the A(La) site with Ba, then followed by $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ and $La_{0.6}Ba_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$. A partial substitution of the B(Co) cation site with Fe or Cu enhanced the CO_2 formation, and use of Ni, i.e. $La_{0.6}Sr_{0.4}Co_{0.8}Ni_{0.2}O_{3-\delta}$, resulted interestingly in an evolution of much hydrogen at high temperature. No C_{2t} formation was observed at any temperature tested during the TPR over non-perovskite $Co_{0.8}Fe_{0.2}O_{3-\delta}$. Most likely the oxidative coupling of methane requires a perovskite-crystal structure of the mixed oxides, where use of Ba or Sr as the A site cation affords a good yield in C_{2t} production. Use of Ca or Mg as the A(La) site cation resulted in a very low activity for the oxidative coupling of methane, while MgO or CaO was frequently reported to be active for this oxidation [15]. When Mg is used as the A(La) site cation in $LaCoO_{3-\delta}$, the perovskite structure cannot be formed because the radius of Mg^{2+} is too small. The radii of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and La^{2+} are 0.065, 0.099, 0.116, 0.136 and 0.118 nm, respectively. $CaCo_{0.8}Fe_{0.2}O_{3-\delta}$ belongs to the rhombic perovskite-type and both $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$ and $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ are of tetragonal perovskite-type as shown in a Mössbauer measurement [12]. All this suggests the importance of the tetragonal perovskite crystal structure in the oxidative coupling of methane. It is thus clearly shown that $LaCoO_{3-\delta}$ which was originally active for the deep oxidation of hydrocarbons [10] revealed a high selectivity for methane oxidative coupling when the cations in A(La) and B(Co) sites were substituted by Ba (or Sr) and Fe, respectively. Use of Sr or Ba as the A site cation in $LaCoO_{3-\delta}$ necessarily results in the formation of tetragonal perovskite structure, which seems to have an important role in the selective oxidation of methane to C_{2t} compounds.

3.2. CYCLIC REACTION

The cyclic reaction over $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$ was carried out to test whether or not the oxide once reduced by methane can be regenerated by air, since the

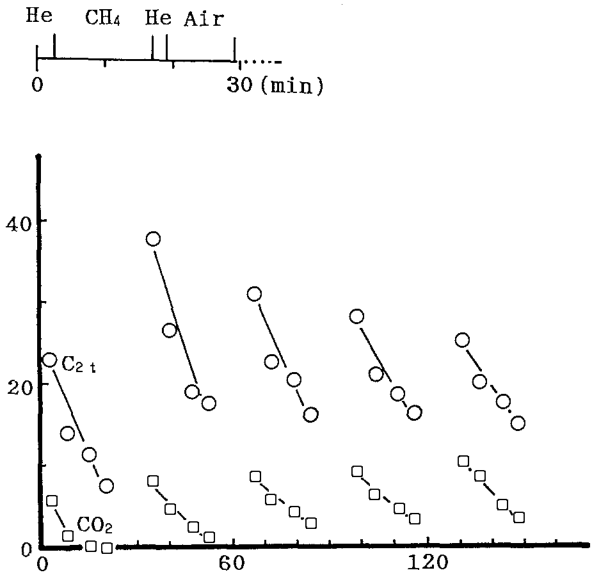

Fig. 3. Result of cyclic reaction over $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$. Temperature, 1023 K; CH_4 flow rate, 1.5 ℓ h^{-1}; catalyst, 2 g.

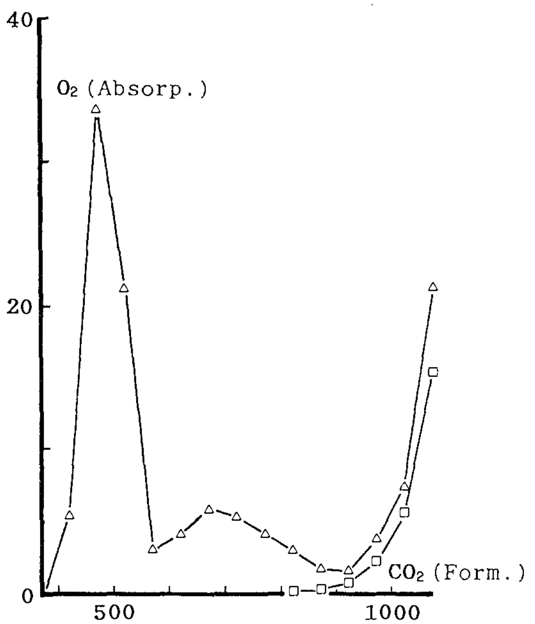

Fig. 4. Absorption rate of oxygen over $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$ reduced in CH_4 flow. Heating rate, 5 K min^{-1}; air flow rate, 1.0 ℓ h^{-1}; catalyst, 1.5 g.

crystal structure of the perovskite can sometimes be irreversibly changed under reducing atmosphere at high temperature. Fig. 3 shows the results of the cyclic reaction together with the feed program of air, helium and methane. The activity for C_{2t} production clearly decreased during one-pass flow of methane, but its high activity was easily recovered after every reoxidation with air and the selectivity of C_{2t} in the effluent gas reached a value around 90% in total. After the TPR experiment under the methane flow upto the temperature of 1073 K, $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$ was immediately quenched by cooling down with cold water still in the methane flow, and then reoxidized in air flow (1 ℓ/h) by increasing the temperature from 373 to 1073 K at heating rate of 5 K/min. Fig. 4 shows the rate of oxygen absorption and the CO_2 formation during heating in this experiment; the absorption rate reached a maximum at 473 K, then followed by a small peak at 673 K, and the reoxidation of the oxide almost finished at 873 K. X-ray diffraction measurements (vide infra) confirmed that the perovskite-crystal structure still remained even in the reduced oxide after the TPR and the original oxide regenerated by absorbing oxygen gas at relatively low temperature around 200°C during the heating in air.

The cyclic reaction over $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (fig. 5) again shows that the activity for C_{2t} production was easily regenerated after every reoxidation with air and the selectivity to C_{2t} compounds in the effluent gas kept a relatively high value above 50%. After the TPR experiment, $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ was treated similarly to the case of $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$, immediately cooled down and then reoxidized

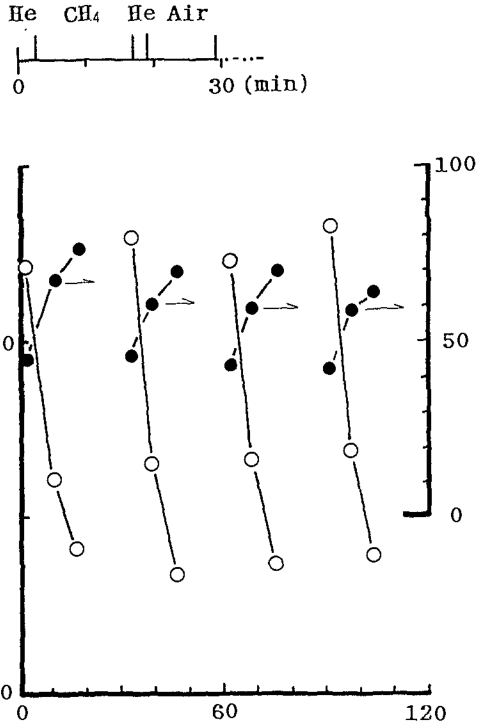

Fig. 5. Result of cyclic reaction over $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$. Temperature, 1023 K; CH_4 flow rate, 1.5 ℓ h^{-1}; catalyst, 2 g.

in air flow (1 ℓ/h) by increasing the temperature from 373 to 1073 K (5 K/min). During the reoxidation (fig. 6), the absorption rate reached a maximum at 473 K, followed by another peak at 673 K and the reoxidation of the oxide almost

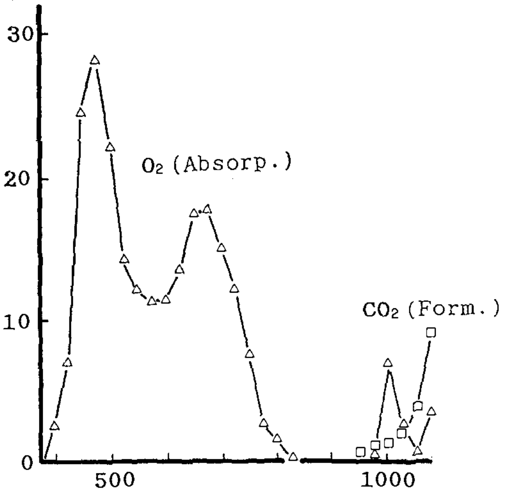

Fig. 6. Absorption rate of oxygen over $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ reduced in CH_4 flow. Heating rate, 2.5 K min^{-1}; air flow rate, 1.0 ℓ h^{-1}; catalyst, 1.5 g.

finished at 823 K. A small peak observed at 973–1073 K may be owing to the oxidation of carbon deposited on the surface of the mixed oxide during the TPR experiment. XRD (vide infra) showed that a redox cycle of $SrC_{0.8}Fe_{0.2}O_{3-\delta}$ was executed between perovskite and brownmillerite structure. It is likely that, in both the cases of $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$ and $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$, the perovskite-structure having oxygen vacancies can be easily regenerated by reoxidation with air after the TPR experiments, since the oxide easily activates and absorbs oxygen at the relatively low temperature of 473 K. Similar phenomena were observed over a perovskite related material composed of La–Co–O, which can easily activate and absorb oxygen at the low temperature of 473–573 K [16].

3.3. THE STRUCTURE OF THE MIXED OXIDES

Fig. 7 shows XRD patterns of $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$ as prepared by the citrate method (a), after the TPR experiment (b) and after the reoxidation (c). In the pattern of fresh $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$ (a), several diffraction peaks assigned to $BaFeO_3$ (JCPDS 14-180) of a perovskite structure and BaO (JCPDS 22-1056) were observed together with some unknown peaks, suggesting that $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$ is a mixture of several phases. When quenched with cold water after the TPR experiment (b), $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$ sample showed a different diffraction pattern from before the TPR, which can still be assigned to perovskite crystal structure. After the reoxidation with air (c), the peaks of $BaCoO_{2.93}$ (JCPDS: 26-144) of another perovskite structure newly appeared

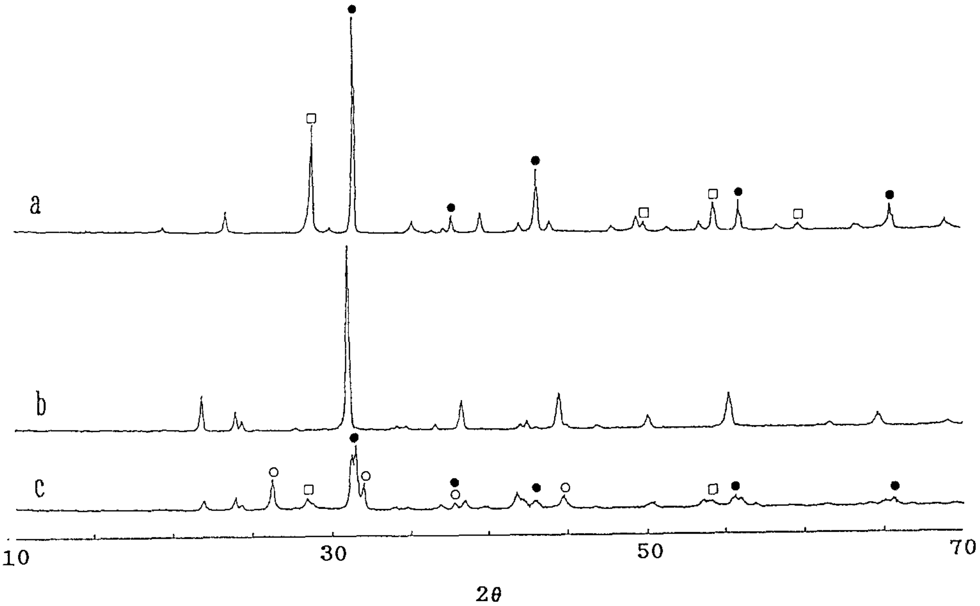

Fig. 7. X-ray diffraction pattern of $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$. (a) Fresh, (b) quenched (after TPR), (c) reoxidized. (●) $BaFeO_3$, (□) BaO, (○) $BaCoO_{2.93}$.

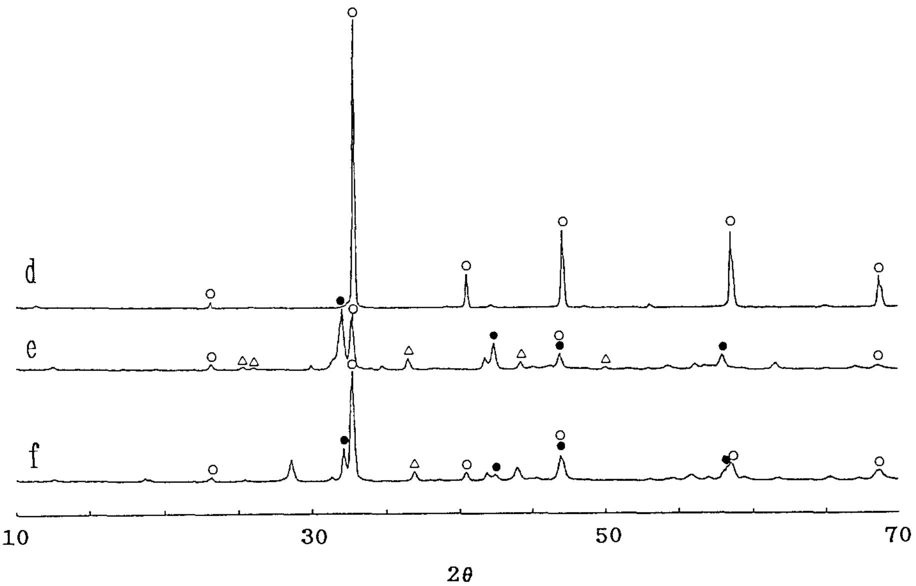

Fig. 8. X-ray diffraction pattern of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$. (d) Fresh, (e) quenched (after TPR), (f) reoxidized. (○) $SrCoO_{2.8}$, (●) $SrCoO_{2.5}$, (△) $SrCO_3$.

together with those of $BaFeO_3$ (JCPDS: 14-180) and BaO (JCPDS: 22-1056). It is thus considered that some perovskite structures can be easily regenerated in $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$, even though some phase transitions occur during the reduction–reoxidation treatment.

In the case of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (fig. 8), the XRD pattern of fresh $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (d) almost coincided with that of $SrCoO_{2.80}$ (JCPDS; 39-1084) of a perovskite structure. The sample quenched with cold water after the TPR (e) showed several new peaks assigned to $SrCoO_{2.5}$ (JCPDS; 34-1475) of a brownmillerite structure together with the weak peaks of $SrCO_3$ (JCPDS; 5-0418). After the reoxidation in air (f), the peaks assigned to the perovskite structure grew up, while those of the brownmillerite structure were weakened. Thus, it was confirmed that the brownmillerite structure as the reduced form of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ can be easily reoxidized by oxygen to its original perovskite structure. It is therefore suggested that the cyclic reaction (fig. 5) can be carried out by a redox cycle of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ which still keeps the perovskite structure or at least by a redox cycle between the perovskite and the brownmillerite structures.

We previously reported a Mössbauer spectrometric study of the perovskite-type oxides, $A(Co_{0.8}Fe_{0.2})O_{3-\delta}$ (A = Ba, Sr and Ca) [12]. The alkaline earth metal ion affected amounts of deficient oxygen in the perovskite samples prepared under the same conditions. Oxygen deficiency reflected the Mössbauer spectra. The Ba and Sr perovskites are of tetragonal system with random distribution of oxygen vacancies and showed a remarkable activity in oxidative coupling of methane in the present study, whereas the Ca perovskite belongs to the rhombic system and showed no catalytic activity. The treatment of these perovskites in methane transformed the Sr and Ca ones to the brownmillerite structure with oxygen vacancies ordered, but the Ba perovskite remained with randomly distributed oxygens. These results showed that disordering of oxygen vacancies in the perovskite structure plays an important role in the oxidative coupling of methane.

3.4. THERMOGRAVIMETRIC ANALYSES OF THE MIXED METAL OXIDES

Fig. 9 shows the TGA curves observed with $A(Co_{0.8}Fe_{0.2})O_{3-\delta}$ (A = Ba, Sr and Ca) in H_2 flow (balances with 5% N_2). Hydrogen gas was used instead of methane as a reducing reagent since use of the latter might lead us to an error in the experimental result owing to carbon deposition on the surface of the oxide. Assuming that the original mixed oxide can be finally reduced by hydrogen gas as follows:

$$ACo_{0.8}Fe_{0.2}O_{3-\delta} + (2-\delta)H_2 \rightarrow AO + 0.8Co + 0.2Fe + (2-\delta)H_2O,$$

the amount of oxygen vacancy, δ, was calculated from the weight loss observed in the TGA curves. The values of δ thus obtained were as follows: 0.07 with Ba, 0.20 with Sr, and 0.46 with Ca as the A site cation, respectively. The value δ obtained with Ba and Sr agreed well with those calculated from the molecular formula of $BaCoO_{2.93}$ and $SrCoO_{2.80}$ mentioned above in the XRD assignment, respectively. The TGA curve of each $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$ and $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ of tetragonal perovskite had a plateau region around 773 and 823 K, respectively, and each temperature coincided well with that observed with a decrease in the rate of CO_2 formation during the TPR experiment as shown in figs. 1 and 2, respectively. It is likely that stable phases formed in the mixed oxides at each

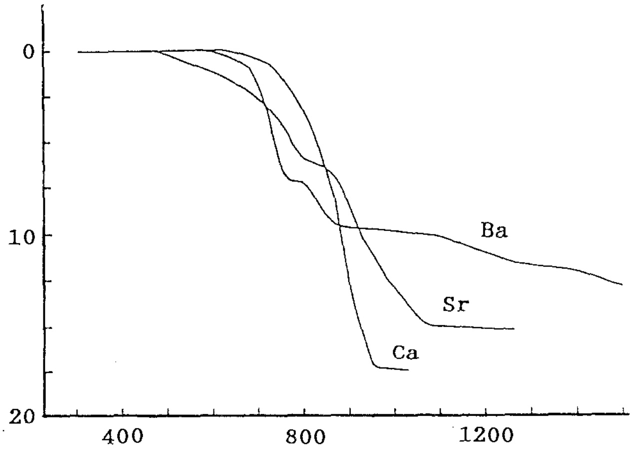

Fig. 9. TGA curve of $ACo_{0.8}Fe_{0.2}O_{3-\delta}$ (A-Ba, Sr or Ca).

temperature region around 773 and 823 K as not produce oxygen species which can react with methane to form CO_2. A very low selectivity in the C_{2t} production and no plateau region in the TGA curve were observed with $CaCo_{0.8}Fe_{0.2}O_{3-\delta}$ (fig. 9), over which the rate of CO_2 formation increased simply with increasing in the temperature upto 973 K. With rhombic perovskite $CaCo_{0.8}Fe_{0.2}O_{3-\delta}$, the CO_2 formation and the weight loss began at higher temperatures than with the two tetragonal perovskites: $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$ and $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$. At high temperature above 873 K, $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$ released oxygen very slowly, followed by a moderate change with $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$, and $CaCo_{0.8}Fe_{0.2}O_{3-\delta}$ rapidly released oxygen. All these mixed oxides were finally changed to the mixture of each reduced transition metal and the oxide of alkaline earth metal. The slow release of oxygen suggests the existence of active oxygen species, which may be contained in the tetragonal perovskite-crystal structure of $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$ and $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ and reflect the disordering of oxygen vacancies in the perovskite.

4. Conclusion

The perovskite-type oxides prepared by substitution of A(La) site and B(Co) site cations of $LaCoO_{3-\delta}$ with Ba (or Sr) and Fe, i.e. $BaCo_{0.8}Fe_{0.2}O_{3-\delta}$, $La_{0.6}Ba_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$, show high activity for the oxidative coupling of methane by the TPR experiment or the cyclic reaction. It is likely that the perovskite-crystal structure accompanied by the formation of hypervalent metal ions such as Co^{4+} and Fe^{4+} has an important role in the activity, and that the disordering of lattice oxygen in this structure plays an important role in the partial oxidation of methane.

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