MÖSSBAUER SPECTROMETRIC STUDY OF NONSTOICHIOMETRIC PEROVSKITE, A (Co$_{0.5}$Fe$_{0.2}$)O$_{3-\delta}$(A = Ba, Sr, Ca), FOR OXIDATIVE COUPLING OF METHANE

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Nonstoichiometric perovskites, A(Co$_{0.5}$Fe$_{0.2}$)O$_{3-\delta}$, were prepared by a pyrolysis of mixed metal citrates, and the catalytic property and structure of these perovskites were investigated. The efficiency of an oxidative coupling of methane increases with the order of Ba, Sr, and Ca substituted in A site and decreases with the amounts of deficient oxygens. The mixed valence of B site ions in the disordering of deficient oxygen is considered to contribute mainly to the oxidative coupling of methane.

1. Introduction

The oxygen deficient perovskite, generally formulated as AB$_{03-\delta}$, is one of the most attractive and useful materials/1/. Typical perovskites, Sr$_{1-x}$La$_x$FeO$_3$ and SrFeO$_{3-\delta}$, contain Fe(III) and Fe(IV) by the creation of oxygen vacancies /2/. Cobalt based perovskite shows high ion conductivity and high catalytic activity for the oxidation of propane and methanol /3/. The catalytic activity was correlated to the difference of the interatomic distance from the equilibrium distance /4/. Teraoka et al./5/ reported on the oxygen semipermeability of LaCoO$_3$ based perovskite oxides. The temperature dependence of the rate of oxygen permeation through La$_{1-x}$A'$_x$Co$_{0.5}$Fe$_{0.2}$O$_3$ was measured. Oxygen semipermeability increased with the order of Sr<Ca<Ba. It is considered to result in the difference of ionic radius between substituted alkaline earth metal ions and La$^{3+}$, because the radius of Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, and La$^{3+}$ is 0.099, 0.118, 0.136 and 0.118nm, respectively. Cobalt based perovskite is also a promising catalyst for synthetic C2 hydrocarbon by an oxidative coupling of methane. In order to clarify how much oxidative coupling of methane was affected by the substitution of alkaline earth metal ions, occupied in A site of perovskite structure without the substitution of La, the catalytic property and structure of A(Co$_{0.5}$Fe$_{0.2}$)O$_{3-\delta}$ were investigated.

2. Experimental details

Samples were prepared by a pyrolysis of nitrates and citrate including ethylene glycol. The mixed citrates were first heated at 373K to make paste and secondary heated at 573 K for 5 h, 773 K for 5 h, and 1123 K for 10 h. The samples were pressed to make a pellet at 200 MPa and heated again at 1373 K for 20 h. Before measuring Mössbauer spectra, each sample was preheated at 973 K for 4 h and cooled slowly in a furnace. Ba and Sr perovskites were tetragonal, and Ca perovskite was rhombic crystal. When the samples were heated at 1073 K for 6h and quenched in liquid nitrogen, tetragonal Ba perovskite and rhombic Sr and Ca perovskites were obtained. The crystal structures were dependent on the oxygen deficiency. Oxygen contents were determined by a thermal gravimetry(TG) in hydrogen atmosphere. The catalytic property of these perovskites was measured by a temperature programmed reaction (TPR) analysis, coupled to a gas chromatography.
3. Results and discussion

3.1 Catalytic property of oxidative coupling of methane

CO was released at the temperature higher than 523 K, 573 K, and 773 K in the presence of Ba, Sr, and Ca perovskites, respectively. When Sr perovskite was present, O was released from 623 K to 833 K. Conversion of methane to C2 hydrocarbon (ethane and ethylene) initiated above 823 K in all samples. The conversion ratio at 1073 K were about 74%, 62% and 7% in Ba, Sr, and Ca perovskites, respectively, as shown in Fig.1. MgCoFeO, and CoFeO, which have no perovskite structure, did not show the catalytic activity of the conversion of methane to C2 hydrocarbon. Cations located in A site of perovskite were found to result the selective production of C2 hydrocarbon. From the results of TG analysis of these perovskites in hydrogen atmosphere, the formation of stable intermediate compounds was confirmed because a plateau was recognized at 773 K and 823 K for Ba and Sr perovskite, respectively.

![Fig.1 Selectivity of C2 hydrocarbon produced from CH4 using Ba, Sr, and Ca perovskites.](image)

![Fig.2 Mössbauer spectra of Ba(CoFe)O.](image)

(a) heated at 973 K in air and slowly cooled.
(b) heated at 1073 K in air and quenched in liq. N2.
(c) heated in 5%H gas at 773 K for 7h.

3.2 Ba perovskite

Mössbauer spectra of Ba perovskite annealed at 973 K in air and slowly cooled from 1073 K to liquid nitrogen temperature were shown in a) and b) of Fig.2. The amount of deficient oxygen, δ, was 0.07 and 0.26, respectively. These spectra were decomposed into two doublets. The one was assigned to Fe(IV) species(IS=0.03mm/s, QS=0.5mm/s), and the other to Fe(III) species(IS=0.27mm/s, QS=0.43mm/s). From the peak intensity ratio of Fe(IV) to Fe(III) and the amounts of deficient oxygen, it was estimated that Fe(III): 15%, Fe(IV): 5%, and Co(IV): 80% were included in the annealed Ba perovskite. On the other hand, Fe(III): 14.8%, Fe(IV): 5.2%, Co(III): 37% and Co(IV): 43% were estimated to exist in the quenched Ba perovskite. After Ba perovskite was
heated in a methane atmosphere as high as 973 K, its Mössbauer spectrum showed paramagnetic Fe(III) species ($IS=0.34\text{mm/s}$, $QS=0.63\text{mm/s}$), indicating the remains of disordered oxygen vacancies in perovskite. Even when Ba perovskite was treated in He gas containing 5% $\text{H}_2$ at 773 K for 7 h, any reduced Fe(II) species could not be observed other than two paramagnetic Fe(III) species ($IS=0.33\text{mm/s}$, $QS=0.44\text{mm/s}$; $IS=0.33\text{mm/s}$, $QS=0.84\text{mm/s}$).

![Mössbauer spectra](image)

Fig. 4 Mössbauer spectra of $\text{Ca(Co}_{0.8}\text{Fe}_{0.2})\text{O}_{3-\delta}$
(a) heated at 973 K in air and slowly cooled.
(b) heated at 1073 K in air and quenched in liq. $\text{N}_2$.
(c) heated in $\text{CH}_4$ upto 1073 K.

Fig. 3 Mössbauer spectra of $\text{Sr(Co}_{0.8}\text{Fe}_{0.2})\text{O}_{3-\delta}$
(a) heated at 973 K in air and slowly cooled.
(b) heated at 1073 K in air and quenched in liq. $\text{N}_2$.
(c) heated in $\text{CH}_4$ upto 1073 K.
(d) Sample (c) measured at liq. $\text{N}_2$ temperture.

### 3.3 Sr perovskite

Mössbauer spectra of Sr perovskite annealed at 973K and quenched from 1073K to liquid nitrogen temperature are shown in Fig. 3. The amount of deficient oxygen, $\delta$, was 0.20 and 0.34, respectively. While the annealed Sr perovskite showed two paramagnetic doublets, two sextets were observed besides paramagnetic peaks ($IS=0.22\text{mm/s}$, $QS=0.42\text{mm/s}$) in the spectrum of quenched Sr perovskite. Sextets with the hyperfine fields of 47 T and 41 T were assigned to octahedral Fe(III) ($IS=0.65\text{mm/s}$ and $QS=0.54\text{mm/s}$) and tetrahedral Fe(III) ($IS=0.01\text{mm/s}$, $QS=-0.30\text{mm/s}$) species, respectively. Quadrupole perturbation was recognized in both magnetic hyperfine spectra. The axis of quadrupole
perturbation was perpendicular and parallel to the direction of magnetic moment of octahedral and tetrahedral coordinations, respectively. These sextets are derived from the perovskite structure by ordered arrangement of oxygen vacancies along [101] axis to give an orthorhombic unit cell with layers of iron in tetrahedral coordination, each one separated by two layers of iron in octahedral coordination to oxygen /6/. Paramagnetic peaks included in the spectrum may be attributed to a microdomain texture produced by an intermingling growth of small domains, related to the orthorhombic structure, but randomly oriented along each of three axes. Since all iron atoms were considered to be composed of Fe(III) species in quenched Sr perovskite, Fe(III):20%, Co(III):48% and Co(IV):32% were estimated to locate in B site. The spectrum of a slowly cooled Sr perovskite, treated in a methane atmosphere, was almost the same as that of a rapidly quenched Sr perovskite.

3.4 Ca perovskite
Mössbauer spectra of slowly cooled and rapidly quenched Ca perovskites are shown in Fig.4. A paramagnetic doublet with large QS (=1.54~1.64 mm/s) was observed besides relaxation spectra of hyperfine magnetic splitting of tetrahedral and octahedral coordinated irons. The difference was observed between slowly cooled and rapidly quenched samples in magnitude of two hyperfine fields although the oxygen deficiency, δ, was 0.46 and 0.48, respectively. The spectrum of the former sample was composed of paramagnetic Fe(IV):3.4%, magnetic relaxed Fe(III):16.6%, Co(IV):4.6% and Co(III): 75.4%, while the latter Fe(IV):4%, Fe(III):16%, and Co(III):80%. Fe(IV) species disappeared after the treatment with methane, and all irons became Fe(III) species, which occupied three sites of two magnetic states (octahedral and tetrahedral coordinations) and a paramagnetic state (coordinated by disordered deficient oxygens).

4. Conclusions

The kinds of alkaline earth metal ion affected the amounts of deficient oxygen in the perovskite samples prepared under the same condition. Oxygen deficiency reflected the Mössbauer spectra. Ba and Sr perovskites with random distribution of oxygen vacancies showed a catalytic activity for oxidative coupling of methane remarkably, whereas Ca brownmillerite did not show any significant activity. The treatment of these perovskites in a methane atmosphere transformed Sr and Ca perovskites to brownmillerite structure with oxygen vacancies ordered, although Ba perovskite with randomly distributed oxygens remained. These results show that the disordering of oxygen vacancies in the perovskite lattice plays an important role in an oxidative coupling of methane.

References