CO$_2$ absorption properties and characterization of perovskite oxides, (Ba,Ca) (Co,Fe) O$_{3-\delta}$

K. Nomura a,*, Y. Ujihira b, T. Hayakawa c, K. Takehira c

a Graduate School of Engineering, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113, Japan
b Research Center for Advanced Science and Technology, The University of Tokyo, Komaba 4-6-1, Meguro-ku, Tokyo 153, Japan
c National Institute of Materials and Chemical Research, Tsukuba Research Center, Higashi 1-1, Tsukuba, Ibaraki 305, Japan

Received 21 June 1995; revised 13 November 1995; accepted 17 November 1995

Abstract

Perovskite oxides, Ba$_{0.95}$Ca$_{0.05}$Co$_{1-x}$Fe$_x$O$_{3-\delta}$, were found to be useful as materials for CO$_2$ absorption at high temperatures between 900 to 1123 K, and CO$_2$ absorbed perovskite oxides were characterized by Mössbauer spectrometry. Before absorption of CO$_2$, a magnetic sextet with sharp peaks and two paramagnetic doublets due to Fe$^{3+}$ and Fe$^{4+}$ were observed for the cubic oxides with $x > 0.4$. Perovskite oxides with lattice oxygen vacancies, which were produced at high temperature, easily absorbed CO$_2$. After absorption of CO$_2$, the paramagnetic peaks disappeared and magnetic fields were produced due to less interaction of lattice oxygens with iron atoms, where CO$_2$ reacted with lattice oxygen to form CO$_3^-$ ions. Finally only one magnetic sextet with sharp peaks remained. It was considered to be due to α-Fe$_2$O$_3$ with a small magnetic field, dispersed in BaCO$_3$ matrix.

Keywords: Perovskite oxides; (Ba,Ca) (Fe,Co)O$_{3-\delta}$; Oxygen vacancy; CO$_2$ absorption; Mössbauer spectroscopy

1. Introduction

Perovskite oxides, which have both electron and oxide ion conductivity, are promising catalysts for deep oxidation of hydrocarbons. Perovskite oxides based on LaCoO$_3$ or LaMnO$_3$ have been used as catalysts for deep oxidation of hydrocarbons [1]. We have studied the partial oxidation properties of perovskite
oxides containing with iron and cobalt to produce C\textsubscript{2} hydrocarbons. It was found that Ba(Fe,Co)\textsubscript{3-δ} and Sr(Fe,Co)\textsubscript{3-δ} showed high activity for oxidative coupling of methane [2], and these oxides were characterized by Mössbauer spectrometry [3].

We have further investigated the catalytic properties and microstructure of mixed Ba\textsuperscript{2+}/Ca\textsuperscript{2+} ion perovskite oxides to confirm whether the oxygen permeability can be controlled by mixing alkaline earth ions with different ionic radius [4]. It was found that perovskite oxides, Ba\textsubscript{0.95}Ca\textsubscript{0.05}Co\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{3-δ}, show high selectivity for oxidative coupling of methane at 823–1023 K [5]. A large amount of carbon dioxide was produced as a byproduct at 573–823 K. In those experiments, we noticed further that these oxides have high potential in absorbing CO\textsubscript{2} at high temperature. The mixed Ba and Ca perovskite oxides absorbed CO\textsubscript{2} easily, but perovskite oxides excluding either Ba or Ca did not absorb significantly.

It is known that the CO\textsubscript{2} concentration in the atmosphere increases year by year. CO\textsubscript{2} is one of the key materials that increase the temperature of the earth’s surface. That is a green house effect. It is important to reduce the large amounts of CO\textsubscript{2} exhausted into the air. One of the most effective solutions is to consolidate directly the CO\textsubscript{2} gas exhausted from industry.

Perovskite oxides have many crystal structures such as cubic, tetragonal and rhombic systems, depending on the number of oxygen vacancies. Changes in the microstructure of the iron environments are reflected in the \textsuperscript{57}Fe Mössbauer spectra with high sensitivity. In this paper, the absorption properties of CO\textsubscript{2} in perovskite oxides of Ba\textsubscript{0.95}Ca\textsubscript{0.05}Co\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{3-δ} were investigated, and the chemical and magnetic changes of the perovskite oxides before and after absorption of CO\textsubscript{2} were characterized mainly by Mössbauer spectroscopy.

2. Experimental

Oxides of (Ba\textsubscript{0.95}Ca\textsubscript{0.05})(Co\textsubscript{1-x}Fe\textsubscript{x})O\textsubscript{3-δ} were prepared by a citrate method. Citric acid and ethylene glycol were first added to a solution of metal nitrates. The solution was evaporated at 353 K, thermally decomposed at 573–773 K in air and finally calcined at 1123 K for 10 h in air. The thermal gravimetric analysis (TGA) of the perovskite oxides was performed in (CO\textsubscript{2} + N\textsubscript{2}) and (CO\textsubscript{2} + air) atmospheres, respectively, and then the absorption rate of CO\textsubscript{2} was obtained by isothermal gravimetry. The perovskite oxides treated in air and CO\textsubscript{2} atmospheres were analyzed by Mössbauer spectrometry and X-ray powder diffraction. Before the absorption of CO\textsubscript{2}, a cubic phase (\(a = 4.03–4.08 \text{ Å}\)) was observed for the oxides with \(x > 0.4\) as shown in Fig. 1, whereas an orthorhombic structure of BaCoO\textsubscript{2.93} was dominantly observed for oxides with \(x < 0.4\) as shown in Fig. 2. The lattice constants of the cubic phase of these oxides increased with increase of Co content as shown in Fig. 3.
Fig. 1. X-ray diffraction patterns of (Ba$_{0.95}$Ca$_{0.05}$)(Co$_{1-x}$Fe$_x$)$_3$O$_{10-8}$.

Fig. 2. X-ray diffraction pattern of (Ba$_{0.95}$Ca$_{0.05}$)(Co$_{0.9}$Fe$_{0.1}$)$_3$O$_{10-8}$.

Fig. 3. Lattice constant of (Ba$_{0.95}$Ca$_{0.05}$)(Co$_{1-x}$Fe$_x$)$_3$O$_{10-8}$.
Fig. 4. X-ray diffraction patterns of \((\text{Ba}_{0.95}\text{Ca}_{0.05})(\text{Co}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}\) partially absorbed with \(\text{CO}_2\).

After the absorption of \(\text{CO}_2\), the black color of the oxides did not change much. A distorted \(\text{BaCO}_3\) phase was identified by X-ray diffraction as shown in Fig. 4. The trace peaks of (100), (110), and (111) in the cubic structure, observed before absorption of \(\text{CO}_2\), were detectable and the other oxides were not determined precisely. \(^{57}\text{Fe}\) Mössbauer spectra of these oxides treated in some gas atmospheres were measured at room temperature and decomposed into some subspectra by a computer fitting.

3. Results and discussion

3.1. \(\text{CO}_2\) absorption properties of perovskite oxides

Fig. 5 shows absorption curves of \((\text{Ba}_{0.95}\text{Ca}_{0.05})(\text{Co}_{0.1}\text{Fe}_{0.9})\text{O}_{3-\delta}\) in air, (air + 10\%\(\text{CO}_2\)) and \(\text{CO}_2\) atmospheres, obtained by thermal gravimetric analysis. The heating rate was 15 K/min. In air atmosphere, the weight of perovskite oxides decreased gradually with increase of temperature, but in air containing \(\text{CO}_2\), the weight decreased progressively until near 773 K, followed by a rapid increase at about 873 K.

In a \(\text{CO}_2\) atmosphere, the initial weight loss was larger than in air at low temperatures. The weight started to increase rapidly around 823 K, and it decreased at about 1210 K. The initial loss and subsequent gain of weight were clearly caused by evolution of oxygen and absorption of \(\text{CO}_2\), respectively. The second weight loss was mainly due to discharge of \(\text{CO}_2\) absorbed in the oxides. It was confirmed as follows. While a \(\text{CO}_2\) absorbed sample was heated in He
atmosphere, the released gases were analyzed by mass spectrometry coupled with TGA. It was found that a large amount of CO$_2$ and a trace amount of CO and O$_2$ were released together with the weight loss at more than 1050 K in He atmosphere.

Fig. 6 shows absorption curves of CO$_2$ at a constant temperature of 1123 K using perovskite oxides with different contents of Fe and Co in (10%CO$_2$ + air) and (10%CO$_2$ + N$_2$) atmospheres. Perovskite oxides substituted with higher amounts of Co were more active for the absorption of CO$_2$. The rate and amount of CO$_2$ absorption in (CO$_2$ + N$_2$) atmosphere were larger than in (CO$_2$ + air) atmosphere. This suggests that the absorption and desorption of CO$_2$ are
somewhat affected by oxygen gas in air. The competitive reaction of CO₂ and O₂ is considered to occur over the whole temperature range, but CO₂ was absorbed predominantly into the perovskite oxides in the temperature ranges between 973 K and 1150 K than oxygen gas. The CO₂ absorbed oxides were decomposed at more than 1173 K in air, discharging CO₂ to reform perovskite oxides.

BaFeO₃₋₅, CaFeO₃₋₅ and (Ba,Ca)FeO₃₋₅ did not absorb so quickly as (Ba,Ca)(Fe,Co)O₃₋₅, whereas fresh CaO, prepared from decomposition of calcium oxalate, had almost the same potential of CO₂ absorption as (Ba,Ca)(Fe,Co)O₃₋₅. The absorption properties of CaO should be further studied in the future, but even a small amount of Ca and Co doping in perovskite oxides was found to be very effective for a quick absorption of CO₂.

3.2. Characterization of perovskite oxides

Some Mössbauer spectra of perovskite oxides prepared before absorption of CO₂ are shown in Fig. 7, and some Mössbauer parameters analyzed are listed in Table 1. A magnetic sextet with sharp peaks (inner magnetic field \(B_{in}\) = 47.5 T, isomer shift \(\text{IS} = 0.26 \text{ mm/s}\), quadrupole splitting \(\text{QS} = 0.30 \text{ mm/s}\)) and two paramagnetic peaks of Fe³⁺ (\(\text{IS} = 0.35 \text{ mm/s}\), \(\text{QS} = 0.63 \text{ mm/s}\)) and Fe⁴⁺ (\(\text{IS} = 0.06 \text{ mm/s}\), \(\text{QS} = 0.60 \text{ mm/s}\)) were observed for the cubic perovskite oxides with \(x > 0.4\). Since the magnetic iron species with sharp peaks is produced by doping Ca into Ba perovskite oxides, the Ba perovskite oxides doped with Ca are not a simple mixture of Ba perovskite and Ca perovskite oxides. In Ba₁₋ₓCaₓFeO₃₋₅, the same magnetic sextet with sharp peaks (47.5 T) has been observed together with a couple of sextets (51 T and 43 T) in octahedral and tetrahedral sites, in which the magnetic fields come from the ordering of oxygen deficiencies with more than \(\delta = 0.35\) [4]. The magnetic species with 47.5 T was not enough clarified by X-ray diffraction (XRD) although it was considered to be produced due to the A site distortion of Ba and Ca ions with different ionic radius. Mössbauer parameters of the magnetic sextet with sharp peaks in the samples, measured at liquid nitrogen temperature, showed \(B_{in} = 49.1 \text{ T}\), \(\text{QS} = -0.37 \text{ mm/s}\), and \(\text{IS} = 0.21 \text{ mm/s}\). The sign of the QS value changed by cooling the sample. The behavior is similar to that of anti-ferromagnetic hematite, but the magnetic field is less than that of hematite (\(\alpha\)-Fe₂O₃; Morine transition temperature = 260 K [5], and \(B_{in} = 51.8 \text{ T at 296 K}\).

With the increase of Co content, the lattice parameter of the cubic structure increased as shown in Fig. 3. It was considered to be caused by the change of the valence state of B site ions such as from Fe⁴⁺ to Fe³⁺ together with the production of oxygen deficiencies. It was reconfirmed by the fact that the relative intensity of Fe⁴⁺ decreased with the increase of Co content in Mössbauer spectra of cubic phases in Table 1. Two magnetic hyperfine fields (32.3 and 25
T) with broad peaks were observed in addition to a small amount of paramagnetic doublets for oxides with $x = 0.8$, which have a cubic structure. In the case of cubic (Ba, Ca) FeO$_{3-\delta}$ doped without Co, the magnetic fields in the octahedral and tetrahedral sites were 51.0 T and 43.3 T, respectively, and the intensity of both magnetic fields increased with increasing Ca content, i.e. with the increase in oxygen vacancies [4]. The whole structures are similar to that of SrFeO$_{3-\delta}$ ($0 < \delta < 0.5$), for which the most probable vacancy-ordering schemes have been proposed by Takano et al. [7]. In the oxide structure with $\delta = 0.5$, four-coordinated sites coexist with six-coordinated sites. The replacement of a
Table 1

Mössbauer parameters of \((\text{Ba}, \text{Ca})(\text{Co}_{1-x}, \text{Fe}_x)\text{O}_3\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>IS (mm/s)</th>
<th>QS (mm/s)</th>
<th>(B_0) (T)</th>
<th>(I) (mm/s)</th>
<th>Int. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ba}<em>{0.95}\text{Ca}</em>{0.05})</td>
<td>0.26</td>
<td>0.30</td>
<td>47.5</td>
<td>0.33</td>
<td>16.0</td>
</tr>
<tr>
<td>(\text{Fe}<em>x\text{Co}</em>{1-x}\text{O}_3)</td>
<td>0.35</td>
<td>0.63</td>
<td>-</td>
<td>0.53</td>
<td>38.0</td>
</tr>
<tr>
<td>(x = 1)</td>
<td>-0.06</td>
<td>0.60</td>
<td>-</td>
<td>0.53</td>
<td>45.9</td>
</tr>
<tr>
<td></td>
<td>0.29</td>
<td>0.37</td>
<td>47.5</td>
<td>0.33</td>
<td>18.6</td>
</tr>
<tr>
<td>(x = 0.9)</td>
<td>0.36</td>
<td>0.70</td>
<td>-</td>
<td>0.51</td>
<td>47.2</td>
</tr>
<tr>
<td></td>
<td>-0.02</td>
<td>0.60</td>
<td>-</td>
<td>0.51</td>
<td>34.2</td>
</tr>
<tr>
<td></td>
<td>0.29</td>
<td>0.35</td>
<td>47.3</td>
<td>0.30</td>
<td>13.6</td>
</tr>
<tr>
<td>(x = 0.8)</td>
<td>0.46</td>
<td>-0.04</td>
<td>32.3</td>
<td>1.5</td>
<td>49.5</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.3</td>
<td>25.</td>
<td>0.84</td>
<td>12.2</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.82</td>
<td>-</td>
<td>2.0</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>-0.1</td>
<td>1.2</td>
<td>-</td>
<td>2.0</td>
<td>19.8</td>
</tr>
<tr>
<td>(x = 0.2)</td>
<td>0.25</td>
<td>0.79</td>
<td>-</td>
<td>0.69</td>
<td>59.6</td>
</tr>
<tr>
<td></td>
<td>-0.15</td>
<td>0.57</td>
<td>-</td>
<td>0.52</td>
<td>41.0</td>
</tr>
<tr>
<td>(x = 0.1)</td>
<td>0.27</td>
<td>0.58</td>
<td>-</td>
<td>0.51</td>
<td>69.0</td>
</tr>
<tr>
<td></td>
<td>-0.16</td>
<td>0.63</td>
<td>-</td>
<td>0.51</td>
<td>31.0</td>
</tr>
<tr>
<td>(x = 0.9) after partial</td>
<td>0.27</td>
<td>0.31</td>
<td>47.8</td>
<td>0.33</td>
<td>20.0</td>
</tr>
<tr>
<td>(\text{CO}_2) absorp.</td>
<td>0.30</td>
<td>0.09</td>
<td>48.5</td>
<td>0.40</td>
<td>29.0</td>
</tr>
<tr>
<td>4 sextets</td>
<td>0.40</td>
<td>0.04</td>
<td>50.4</td>
<td>0.48</td>
<td>25.5</td>
</tr>
<tr>
<td>(x = 0.9) after full (\text{CO}_2) absorp.</td>
<td>0.45</td>
<td>0.35</td>
<td>41.4</td>
<td>0.48</td>
<td>25.5</td>
</tr>
<tr>
<td></td>
<td>0.23</td>
<td>0.30</td>
<td>47.4</td>
<td>0.31</td>
<td>100</td>
</tr>
</tbody>
</table>

\(^{a}\) \(\text{FeI} = \text{Magnetic component produced by mixing Ba and Ca in perovskite oxides.}\)

neighboring \(\text{Fe}^{3+}\) ion by a diamagnetic \(\text{Co}^{3+}\) ion results in a reduction in the flux density of the supertransferred hyperfine field at \(^{57}\text{Fe}\) nucleus [8].

With a large Co content, magnetically inhomogeneous structures were observed in the Mössbauer spectra of perovskite oxides with \(x < 0.6\) as shown in Fig. 7. These are considered to be caused by the poor ordering of oxygen deficiencies and the local fluctuation of magnetic moments of Co as was observed for \(\text{SrFe}_x\text{Co}_{1-x}\text{O}_3\) [9]. The valences of the iron species in the paramagnetic doublets were \(3^{+}\) and \(4^{+}\). The peak intensity ratio of paramagnetic \(\text{Fe}^{4+}\) to \(\text{Fe}^{3+}\) species was smaller for perovskite oxides with \(x = 0.1\) than with \(0.2\). These results show that the oxygen vacancies increased with increasing cobalt content.

When the perovskite oxides were quenched from 1123 K, magnetic sextets and paramagnetic doublet of almost all \(\text{Fe}^{3+}\) species were produced as shown in Fig. 8. This demonstrates that the oxygen vacancies produced in perovskite oxides at high temperature can be trapped by quenching and suggests that the structure will transform to the brownmillerite structure with \(\delta = 0.5\). However, high temperature X-ray diffraction showed that perovskite oxide with \(x = 0.1\) obtained a cubic structure \((a = 4.132 \text{ Å})\) at temperatures higher than about 1020
K. These results suggest that oxygen vacancies move very quickly between tetrahedral and octahedral sites of the brownmillerite structure at high temperature.

3.3. Characterization of CO$_2$ absorbed perovskite oxides

Mössbauer spectra of perovskite oxides partially saturated with CO$_2$ (about 11 wt.-%) are shown in Fig. 9. The Mössbauer spectrum of Fig. 9b was first decomposed into three sub-spectra based on the appearance of the peaks. However, from the relatively high intensity (49%) and broadened width (0.49 mm/s) of the magnetic component with $B_{in} = 47$ T as well as from the consideration of phase decomposition of perovskite oxides absorbed with CO$_2$, the magnetic component with $B_{in} = 47$ T was further decomposed into two magnetic components. The Mössbauer parameters of four magnetic components decomposed are thus shown in Table 1.

The magnetic hyperfine fields of four magnetic components were 47.8 T, 48.5 T, 50.4 T and 41.4 T. Two magnetic sextets with 50.4 T and 41.4 T were
assigned to ordinary Fe\(^{3+}\) species in octahedral and tetrahedral sites. The other magnetic sextets with 47.8 T and 48.5 T were attributed to Fe\(^{3+}\) species produced by mixing Ba and Ca into perovskite oxides and by absorption of CO\(_2\), respectively. The relative intensity of the new component with \(B_{\text{in}} = 48.5\) T produced by partial absorption of CO\(_2\) (11 wt.-\%) was about 29\%, which corresponded to half the mole amounts of fully absorbed CO\(_2\). BaCO\(_3\) was detected in XRD patterns of CO\(_2\) absorbed oxides. One of six oxygen atoms coordinated around Fe sites is considered to be extracted to form CO\(_3^{2-}\). Although the axis of the electric field gradient (EFG) of the iron nucleus in the octahedral and tetrahedral sites of (Ba\(_{0.95}\)Ca\(_{0.05}\))(Co\(_{1-x}\)Fe\(_x\))O\(_{3-\delta}\) with \(x = 0.9\) is perpendicular and parallel to the direction of the magnetic moment, respectively [6], the axis of the EFG in CO\(_2\) absorbed oxides was found to be parallel to the direction of the magnetic moment from the positive sign of the QS values of
both magnetic components. The difference between the EFG comes from the absence or presence of oxygen atoms in the structures.

After full absorption of CO$_2$, the paramagnetic peaks disappeared and two magnetic fields were produced due to the lower interaction of lattice oxygen with iron sites because CO$_2$ reacted with lattice oxygen to form CO$_3^{2-}$ ions. Finally only one magnetic sextet with sharp peaks remained. It is considered to be due to $\alpha$-Fe$_2$O$_3$, dispersed in a BaCO$_3$ matrix although the magnetic field is smaller than that of $\alpha$-Fe$_2$O$_3$ ($B_{in} = 51.8$ T). The perovskite oxides are considered to be converted finally to the carbonate and oxide compounds by absorption of CO$_2$ as follows:

$$2(\text{Ba,Ca})(\text{Fe,Co})O_{2.5} + 2\text{CO}_2 \rightarrow 2(\text{Ba,Ca})\text{CO}_3 + (\text{Fe,Co})_2\text{O}_3$$

At high temperatures, many vacancies of lattice oxygen are produced and are ordered into strings along a certain direction of the parent perovskite oxides. The absorption rate depends on the number of collisions of CO$_2$ with the oxide surface with oxygen vacancies. The stretching motion along a line of the CO$_2$ structure is considered to become a driving force of absorption because the molecular structure of CO$_2$ is a straight line, which consists of a C atom centered between two O atoms. The conductivity of an oxide ion seems to promote the absorption of CO$_2$ into the bulk lattice.

It is known that the super-conductive perovskite oxides with infinite layers are affected by slow CO$_2$ absorption (for example Ref. [10]). The mechanism may be almost the same as Ca and Ba mixed perovskite oxides absorbed CO$_2$ quickly at high temperature.

4. Conclusion

The properties of perovskite oxides for absorption of CO$_2$ have been improved by doping Ca and Co into BaFeO$_{3-\delta}$ oxides. The deviation of the microstructure in the A site and the electron transfer of mixed valence in the B site of perovskite oxides with oxygen deficiencies are very effective for absorption of CO$_2$ at high temperature. When absorbed CO$_2$ was trapped as CO$_3^{2-}$ in the microstructure of an A site, iron species in the B site became dispersed as $\alpha$-Fe$_2$O$_3$ in the matrix. These perovskite oxides are expected to be promising materials for the direct absorption of CO$_2$ in combustion gas of fuels, exhausted at high temperature, since they have the possibility of controlling the temperature of CO$_2$ absorption by composition control in perovskite oxides.

Acknowledgements

The authors are grateful to Dr. M. Ichiwatari, and Dr. A. Hayashi for measurements of perovskite oxides with a TG-mass spectrometer and high-temperature X-ray diffraction, respectively.
References