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CO_2 decomposition with oxygen-deficient Mn(II) ferrite

MASAHIRO TABATA, YOSHIKAZU NISHIDA, TATSUYA KODAMA,
KEISUKE MIMORI, TAKASHI YOSHIDA, YUTAKA TAMAURA
*Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku,
Tokyo 152, Japan*

An oxygen-deficient Mn(II) ferrite ($Mn_{0.97}Fe_{2.02}O_{3.92}$) was synthesized and its reactivity to reduce CO_2 gas into carbon was studied at 300 °C. The oxygen-deficient Mn(II) ferrite was obtained by flowing H_2 gas through Mn(II) ferrite with a nearly stoichiometric composition of $Mn_{0.97}Fe_{2.02}O_{4.00}$ at 300° C. The lattice constant of the oxygen-deficient Mn(II) ferrite (0.8505 nm) is larger than that of the Mn(II) ferrite with a nearly stoichiometric composition (0.8498 nm). The chemical composition of the Mn(II) ferrite changed from $Mn_{0.97}Fe_{2.02}O_{4.00}$ to $Mn_{0.97}Fe_{2.02}O_{3.92}$ during the H_2 reduction process, indicating that the oxygen is deficient in the spinel structure of the Mn(II) ferrite. This was confirmed by Mössbauer spectroscopy and X-ray diffractometry. The efficiency of CO_2 decomposition into carbon at 300 °C with the oxygen-deficient Mn(II) ferrite was much lower by about 10^5 than that of oxygen-deficient magnetite. This is considered to be due to the difference in electron conductivity between Mn(II) ferrite and magnetite, which determines the reductivity for CO_2 into carbon by donation of an electron at the adsorption site.

1. Introduction

Recently, we have reported that oxygen-deficient magnetite can decompose CO_2 gas into carbon with a high efficiency (nearly 100%) at 300 °C [1]. In this reaction, the inner pressure of the reaction cell becomes a vacuum after completion of the reaction. This is due to the incorporation of the oxygen of the CO_2 gas into the oxygen deficient site of the magnetite during the deposition of carbon. Copperthwaite *et al.* [2] have studied the decomposition reaction of CO_2 on the surface of metals using X-ray photoelectron spectroscopy, but there have been no reports on the complete decomposition of CO_2 with efficiency approaching 100% except our report. We found that no CO_2 was efficiently decomposed below 250 °C with metals such as Mg, Al and Cu, and that only a small amount of CO_2 was decomposed at 290 °C (3% after 6 h of reaction). In the Bosch reaction [3], in which CO_2 and H_2 are reacted with iron metal at 426–726 °C, by-products such as CO and CH_4 are formed, and the decomposition efficiency is around 10–20%. In these reactions with metals, the crystal structures of the metals change to those of the corresponding metal oxides. It is considered that the high decomposition efficiency of CO_2 into C with oxygen-deficient magnetite is due to the fact that its spinel structure is kept during the reaction.

In the present paper, we have studied the CO_2 decomposition reaction with oxygen-deficient Mn(II) ferrite, and discuss its reactivity in comparison with that of oxygen-deficient magnetite.

2. Experimental procedure

Mn(II) ferrite was synthesized by the air oxidation of an aqueous suspension [4]. After passing N_2 gas through distilled water (4.0×10^3 dm^3) for a few hours, $FeSO_4 \cdot 7H_2O$ and $MnSO_4 \cdot 4 \sim 6H_2O$ were added. The pH of the solution was adjusted to 10 by adding 3 mol dm^{-3} NaOH solution. Oxidation was carried out by bubbling air into the solution at 65 °C. The product precipitated was collected by decantation. After washing with acetate buffered solution, distilled water and acetone successively, the product was dried in an N_2 gas stream. The product was identified by X-ray diffractometry with FeK_α-radiation (Rigaku, RAD-2A diffractometer). The chemical composition of the product was determined by chemical analysis combined with atomic absorption spectrometry. The powder of Mn(II) ferrite (2.00 g) was placed in the quartz tube of a reaction cell (ϕ20 mm × 200 mm), and H_2 gas was flowed through the reaction cell at 300 °C for 20 or 40 min. After evacuating the reaction cell, CO_2 gas was introduced into the reaction cell (30% of the CO_2 content). The inner pressure was measured with a pressure gauge. The inner gas species was determined by gas chromatography (Shimadzu GC-8A). The carbon deposited on the solid sample was analysed by an elemental analyser (Perkin-Elmer 2400 CHN analyser). The solid phase was identified by X-ray diffractometry with FeK_α-radiation. All Mössbauer spectra were recorded at room temperature with a ^{57}Co (diffused in Rh) source oscillated in the constant acceleration mode. The Doppler velocity scale was calibrated using a natural iron foil. Each spectrum consisting of 512 data points was analysed by computer-fitting into Lorentzian lines using a non-linear least-squares routine.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of Mn(II) ferrite (pattern (a)) and the H_2 reduced Mn(II) ferrite prepared by passing H_2 gas through Mn(II) ferrites for 40 min (b), and 8 h (c) at 300 °C, respectively. As can be seen in pattern (b), small peaks corresponding to mangano-wüstite appeared at 40 min of H_2 reduction time. These peaks of mangano-wüstite increased with H_2 reduction time as shown by X-ray diffraction pattern (c) (H_2 reduction time = 8 h) in Fig. 1. Thus, the Mn(II) ferrite seems to be decomposed into mangano-wüstite by passing H_2 gas through it. However, in the X-ray diffraction pattern of H_2 reduced Mn(II) ferrite at 20 min, no peaks of mangano-wüstite appeared; the same pattern as that of Fig. 1a was obtained. This suggests that there is a stage where the Mn(II) ferrite is not decomposed into mangano-wüstite but reduced. This was confirmed by Mössbauer spectroscopy (Fig. 2) and by measurement of the lattice constant (Table I). As seen in Fig. 2, the Mössbauer spectrum slightly changed when H_2 gas was passed through the Mn(II) ferrite at 300 °C for 20 min; the internal magnetic field was slightly reduced. This lowering of the internal magnetic field would be due to the reduction of Fe^{3+} ions in the Mn(II) ferrite into Fe^{2+} ions. Thus, there seems to be a stage where we can reduce the Fe^{3+} ions in the spinel structure of Mn(II) ferrite without the formation of mangano-wüstite during flowing the H_2 gas through at 300 °C. This is confirmed by chemical analysis and lattice constant measurement. These results are given in Table I. As can be seen here, the lattice constant increased in 20 min of H_2 reduction time from 0.8498 to 0.8505 nm. This increase in the lattice constant was accompanied by a change in the chemical composition, as shown in the third column in Table I. The chemical composition of Mn(II) ferrite before the reduction was $Mn_{0.97}\,Fe_{2.02}\,O_{4.00}$ but changed to $Mn_{0.97}\,Fe_{2.02}\,O_{3.92}$, indicating that some Fe^{3+}ions in the Mn(II) ferrite are reduced. Thus, the lattice constant change is closely related to the reduction of Fe^{3+}ions in the spinel structure of the Mn(II) ferrite into Fe^{2+}. Thus, it was found that we can prepare H_2 reduced Mn(II) ferrite which possesses the spinel structure, and some of the Fe^{3+}ions are reduced. We shall hereafter refer to this H_2-reduced Mn(II) ferrite obtained at H_2-reduction time = 20 min as "oxygen-deficient Mn(II) ferrite".

As described above, the reduction of Mn(II) ferrite results in the reduction of the Fe^{3+} content, and causes an increase in the lattice constant. However, as seen in Table I, a further reduction over 40 min did

TABLE I The relationship among reduction time, lattice constant and chemical composition of H_2 reduced Mn(II) ferrite

Reduction time (min)	Lattice constant (nm)	Chemical composition
0	0.8498	$Mn_{0.97}Fe_{2.02}O_{4.00}$
20	0.8505	$Mn_{0.97}Fe_{2.02}O_{3.92}$
40	0.8506	$Mn_{0.97}Fe_{2.02}O_{3.91}$[a]
80	0.8506	$Mn_{0.97}Fe_{2.02}O_{3.88}$[a]

[a] MnO–FeO (Mangano-wüstite) was observed.

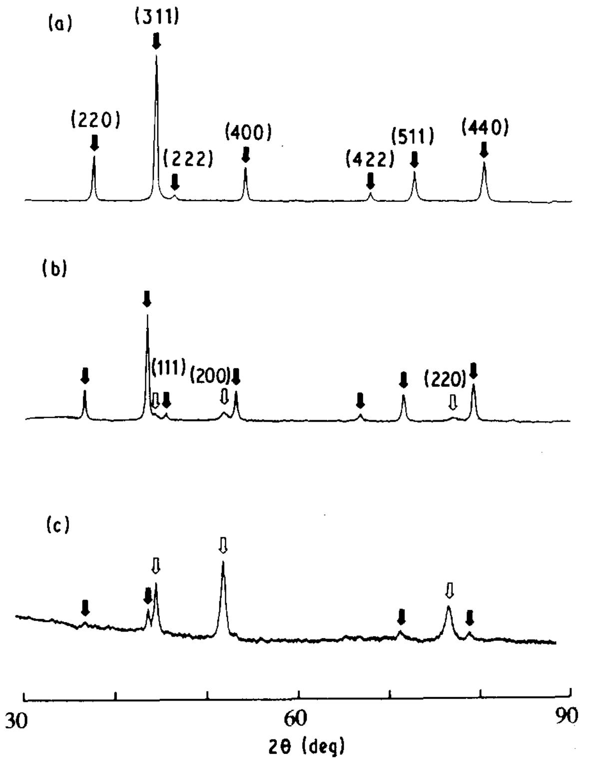

Figure 1 X-ray diffraction patterns (FeK_α) of (a) Mn(II) ferrite, and H_2 reduced Mn(II) ferrite obtained by passing H_2 gas for (b) 40 min and (c) 8h at 300 °C. Solid arrows: Mn(II)ferrite, open arrows: mangano-wüstite (MnO–FeO).

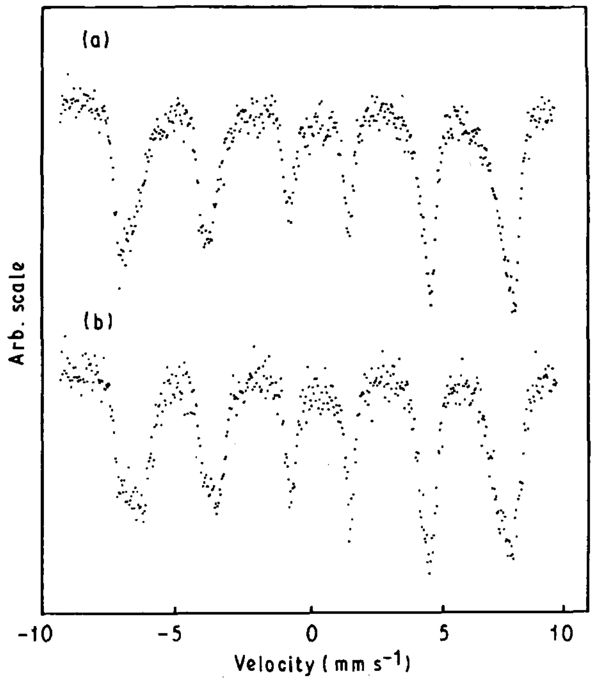

Figure 2 Room-temperature Mössbauer spectra of Mn(II) ferrite (a) before H_2 reduction and (b) after 20 min of H_2 reduction time.

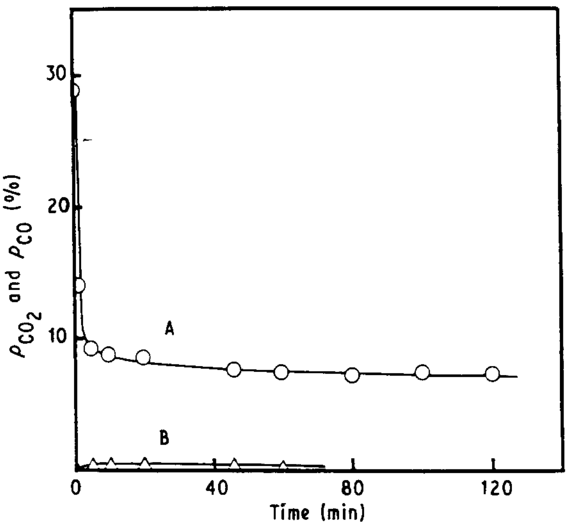

Figure 3 Variations in the inner pressures of (A) CO_2 and (B) CO in the presence of oxygen-deficient Mn(II) ferrite at 300°C.

not give rise to an increase in the lattice constant. As mentioned above, the further H_2 reduction over 40 min gives rise to the decomposition of Mn(II) ferrite into mangano-wüstite. Therefore, the increase in the Fe^{2+} content in the chemical composition of H_2 reduced Mn(II) ferrite having a lattice constant of around 0.8505 nm is considered to cause its decomposition into mangano-wüstite.

Curve A in Fig. 3 shows the time variation of CO_2 content in the reaction cell in the presence of oxygen-deficient Mn(II) ferrite at 300 °C. When the CO_2 gas (30 vol%) was injected into the reaction cell at zero time, the CO_2 gas was rapidly adsorbed and the inner pressure in the reaction cell decreased from about 30 kPa to 10 kPa. This rapid decrease is considered to be a non-specific adsorption of CO_2 to the oxygen-deficient Mn(II) ferrite. We will discuss later this non-specific adsorption. After the rapid decrease in CO_2 content owing to non-specific adsorption, the CO_2 content was lowered gradually, as shown by curve A in Fig. 3. During this lowering in the CO_2 content a small volume of CO gas evolved, as shown by curve B. However, the evolved CO gas eventually disappeared.

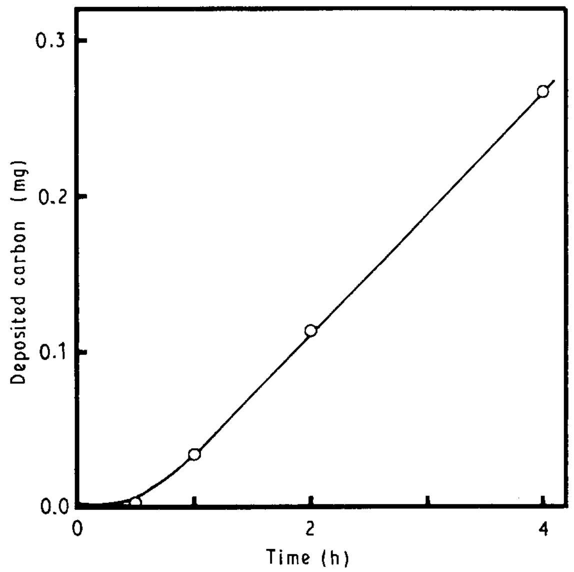

Figure 4 Relationship between reaction time and the amount of carbon deposited on oxygen-deficient Mn(II) ferrite.

Fig. 4 shows the time variation of the amount of carbon deposited on oxygen-deficient Mn(II) ferrite. The amount increases with reaction time. The amount deposited after 4 h of reaction time was about 0.3 mg. The carbon deposition rate observed in the present study using oxygen-deficient Mn(II) ferrite is very low compared with that reported previously for oxygen-deficient magnetite [1].

The rapid adsorption observed in the initial stage was found to be due to non-specific adsorption which does not give rise to CO_2 reduction into carbon. When we studied CO_2 adsorption using Mn(II) ferrite without the reducing treatment, nearly the same amount of adsorption was observed as that of the rapid adsorption by oxygen-deficient Mn(II) ferrite. A similar result was obtained when we carried out the adsorption experiment for oxygen-deficient Mn(II) ferrite at room temperature, where no CO_2 decomposition reaction takes place. From these findings, we have concluded that the rapid adsorption observed for oxygen-deficient Mn(II) ferrite is not associated with CO_2 decomposition reaction into C.

In the case of magnetite, which contains Fe^{2+}ion instead of the Mn^{2+} in Mn(II) ferrite, we could not observe such a non-specific adsorption. The same rapid adsorption is observed in the early stage of the CO_2 decomposition reaction for oxygen-deficient magnetite. However, in the case of oxygen-deficient magnetite this rapid adsorption results in the decomposition of the CO_2 into elementary carbon, which is readily converted into CH_4 by the reaction with H_2 gas [5]. Thus, there is a large difference in the rapid adsorption phenomena between oxygen-deficient Mn(II) ferrite and oxygen-deficient magnetite. This difference is considered to be as follows: the adsorption of CO_2 on a site where an electron is readily donated to the carbon of the CO_2 molecule, and the oxygen of the CO_2 molecule is readily incorporated into a lattice point in the form of O^{2-} (oxygen-deficient site), will facilitate CO_2 decomposition into C or CO. In the case of oxygen-deficient Mn(II) ferrite, the number of such sites is considered to be very small, since the major metal ions are Mn^{2+} and Fe^{3+}ions. These considerations would lead us to conclude that the number of adsorption sites, where CO_2 is readily decomposed into C will be very low for oxygen-deficient Mn(II) ferrite. In contrast, the number of adsorption sites such as Mn^{2+} and Fe^{3+} ions, where no electrons are donated and no oxygen-deficient sites are present, is very high. These sites will work as non-specific adsorption sites for CO_2. However, in the case of oxygen-deficient magnetite, we cannot distinguish between the Fe^{2+} and Fe^{3+} ions, since electrons are hopping between these ions in the spinel-type structure of the magnetite. Therefore, both Fe^{2+} and Fe^{3+} ions can donate electrons. Also the oxygen-deficient site can exist in the neighbourhood of both Fe^{2+} and Fe^{3+} ions. This means that the reactive adsorption sites, where the CO_2 is readily decomposed into C, are distributed over the surface of the oxygen-deficient magnetite. In the case of oxygen-deficient magnetite, the CO_2 decomposition rate (or capacity) is 10^5 times higher than that for oxygen-deficient Mn(II) ferrite. This large difference will arise from the reason discussed above.

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