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Methanation of CO_2 with H_2-reduced magnetite

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The methanation reaction of CO_2 was studied with H_2-reduced magnetite. A high conversion ratio of about 0.9 (in 30 min of the reaction time) with a selectivity of nearly 100% was obtained at 300 °C and at 0.1 MPa for H_2-reduced magnetite which had been prepared by passing H_2 gas for 1–5 h at 300 °C. From the results of X-ray diffractometry and Mössbauer spectroscopy, and from chemical analysis of the deposited carbon, H_2-reduced magnetite is considered to decompose adsorbed CO_2 into carbon, and to incorporate the oxygen of the CO_2 into the spinel-type structure of the magnetite, associated with oxidation of the Fe^{2+} ion into Fe^{3+} ion in the magnetite. The high conversion ratio in the methanation reaction is considered to come from a higher reactivity of the elementary carbon deposited on the surface of the H_2-reduced magnetite.

1. Introduction

The hydrogenation of CO has been extensively studied by many investigators; however, much less attention has been paid to hydrogenation of CO_2. In the hydrogenation of CO_2 using as catalysts the metals of Ru, Fe and Co–SiO_2, the reaction temperature ranges from 200 to 300 °C and the conversion ratio is around 0.1 [1]. Those studies were carried out under a high reaction pressure of 1.1 MPa. For Fe–SiO_2 catalysts, the selectivity of the conversion into CH_4 is only 40% [1]. There are only a few reports concerning CO_2 hydrogenation with iron as the catalyst, and most of these studies involved differential reaction conditions in which the main product was CO [2–4]. The hydrogenation of CO_2 to hydrocarbons is considered to proceed via two elementary steps: CO_2 first reacts with H_2 to form CO and H_2O, the so-called reverse water–gas shift reaction, followed by the Fischer–Tropsch (F–T) reaction where CO is further hydrogenated to the hydrocarbon [4]. Bianchi and Gass [5, 6] recently reported that in the CO–H_2 reaction on an alumina-supported iron catalyst, CO is hydrogenated via carbonaceous adsorbed species.

In the present paper, we have studied the methanation of CO_2 using H_2-reduced magnetite. A highly efficient conversion of CO_2 into CH_4 at 300 °C and at 0.1 MPa will be reported, and we discuss the methanation process in relation to the carbonaceous adsorbed species.

2. Experimental procedure

2.1. Magnetite powder

Magnetite powder was prepared by the air oxidation method [7, 8]; an Fe(II) hydroxide suspension (Fe(II) = 0.048 mol; $FeSO_4 \cdot 7H_2O$) was oxidized in a 3 dm^3 beaker by passing air through the reaction suspension at pH 10 and at 65 °C. The black precipitate of magnetite particles synthesized was washed with water and acetone successively, and dried *in vacuo* at 50 °C. The BET adsorption surface area of the magnetite powder was estimated to be 21 $m^2 g^{-1}$.

2.2. Apparatus

The preparation of H_2-reduced magnetite and the methanation experiments were conducted in a quartz tube with diameter 30 mm and length 150 mm (the reaction cell) (Fig. 1), where 30 g of the magnetite powder was placed. Hydrogen gas was passed through the magnetite powder in the preparation of H_2-reduced magnetite. In the methanation experiments, however, the reaction was carried out in a batch system as will be seen below. To measure the weight loss due to the release of oxygen from the magnetite powder as H_2O during passage of H_2 gas in the preparation of H_2-reduced magnetite, the reaction cell was removed from the gas flow lines and weighed before and after the H_2 passed through. Heat was indirectly supplied by placing the reaction cell in an electric furnace. The temperature was measured with a Chromel–Alumel thermocouple in contact with the outer surface of the quartz tube of the reaction cell. The temperature was controlled within ± 0.3 °C using a regulator (Chino Model DB1150).

In the methanation experiments, the H_2O formed in the methanation reaction was removed from the reaction cell by condensation in a quartz tube with a small diameter (5 mm), which was placed outside the electric furnace and cooled in iced water (Fig. 1).

2.3. Gases

Research-grade H_2 and CO_2 gases were used. Reactant gases used for the methanation experiments

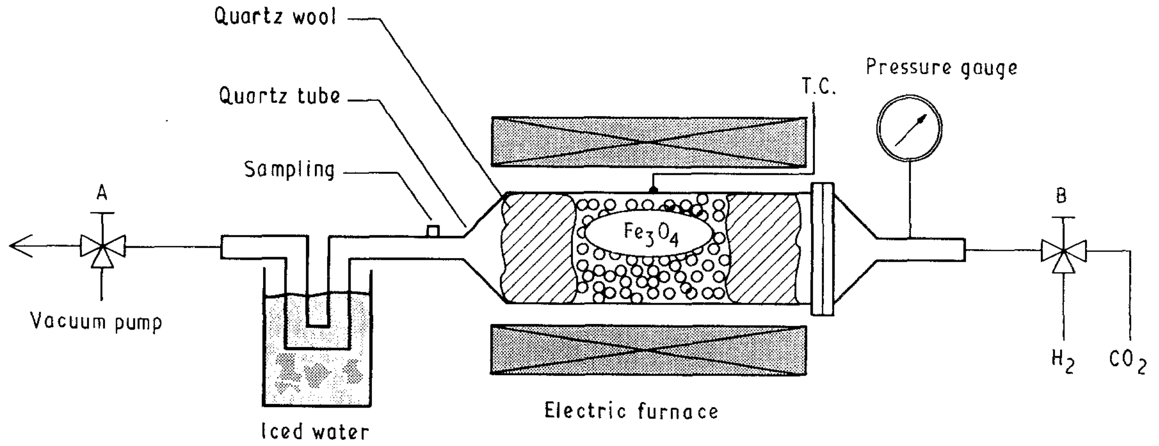

Figure 1 Reaction apparatus used for the preparation of H_2-reduced magnetite and for the methanation reaction. The water trap was kept in an iced water bath while the methanation reaction was carried out.

were admitted to the solid reactant by injecting the gases into the reaction cell. Mass flow controllers (G. L. Science Model NF-2B) were used to adjust the flow rates of the gas streams (H_2 gas: 0.06 dm^3 min^{-1}). Standard gases (CO_2, H_2) for the calibration were purchased from G. L. Science Co.

2.4. Analysis

The gas composition in the reaction cell was analysed by gas chromatography equipment (Shimadzu GC-8A) equipped with Porapak Q or Molecular Sieve 13X columns. The conversion ratio of CO_2 into CH_4 was calculated by dividing the CH_4 volume evolved in the reaction cell by the CO_2 gas volume initially injected into the reaction cell. The carbon deposited on the surface of the solid phase was determined by an elemental analyser (Perkin Elmer 2400) for the carbon powder recovered after dissolving the solid phase in HCl solution (1:1).

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.

The solid phase was identified by X-ray diffractometry with FeK_α (Model RAD-2A diffractometer, Rigaku). The samples for identification of the solid phase of H_2-reduced magnetite were prepared by quenching the powder in a refrigerant (NaCl–ice); the reaction cell was rapidly cooled by keeping it in the refrigerant after the H_2-reduced magnetite preparation process.

2.5. Methanation procedure

The magnetite powder (30 g) placed in the reaction cell was reduced by flowing H_2 gas through it for 0.1–5 h at 300 °C. After closing valve B (Fig. 1), the reaction cell was evacuated by opening valve A and the temperature was fixed at 300 °C. After allowing the reaction cell to stand at the fixed temperature, valve A was closed and the CO_2 and H_2 gases were successively injected using a gas-tight syringe. The concentrations of CO_2, H_2 and CH_4 in the reaction cell were monitored during the methanation reaction.

3. Results and discussion

3.1. Methanation with H_2-reduced magnetite

Table I shows the relationship between the H_2 flow time in the preparation of H_2-reduced magnetite (first column) and the conversion ratio (third column) of CO_2 gas into CH_4 with H_2-reduced magnetite at 300 °C. As can be seen here, the conversion ratio of CO_2 into CH_4 increased with the H_2 flow time. A high conversion ratio (nearly 0.9 in 30 min of reaction time) was obtained for an H_2 flow time of 1–5 h. In the table, the values of the reduction parameter δ (from $FeO_{1.33-\delta}$) are also given in Table I; these were evaluated from the weight loss due to the release of oxygen from magnetite powder as H_2O by reaction with the H_2 gas. The δ value is represented as a deviation from the chemical composition of the stoichiometric magnetite ($Fe_3O_4 = FeO_{1.33}$). Thus δ indicates the degree of reduction and represents how far reduced the H_2-reduced magnetite was from the iron oxide composition of stoichiometric magnetite (Fe_3O_4). Table I suggests that the increase in the conversion ratio is closely related to the degree of reduction. In the X-ray diffraction patterns of H_2-reduced magnetites prepared in H_2 flow times of

TABLE I Relationship between H_2 flow time, conversion ratio of CO_2 into CH_4, selectivity, and the reduction parameter of H_2-reduced magnetite in the methanation reaction at 300 °C (0.1 MPa) using H_2-reduced magnetite (CO_2 volume injected = 15×10^{-3} dm^3)

H_2 flow time (h)	Reduction parameter, δ	Conversion ratio at reaction time = 30 min	Selectivity (%)
0	−0.11	0	–
0.1	−0.033	0.05	98.7
0.2	0.013	0.32	96.7
0.4	0.021	0.64	97.0
1.0	0.051	0.86	99.3
5.0	0.065	0.87	98.3

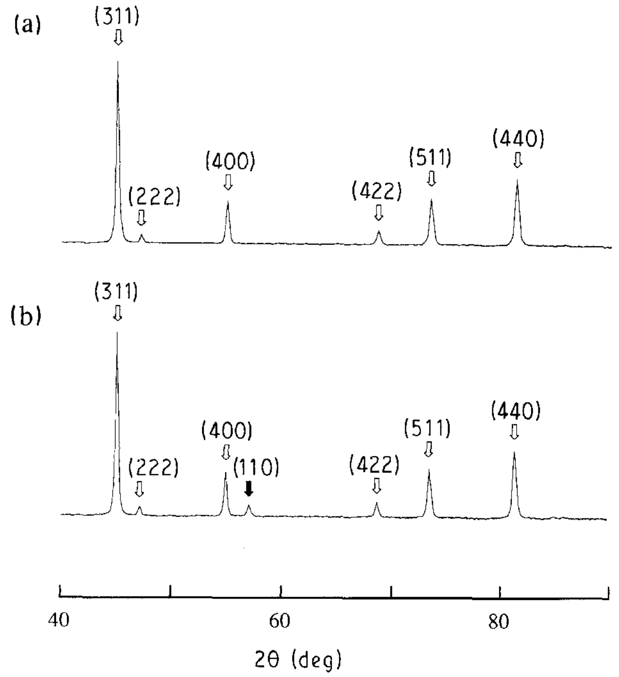

Figure 2 X-ray powder diffraction patterns (FeK_α) of H_2-reduced magnetite before the methanation reaction: H_2 flow time (a) 0.4 h, (b) 5 h. Solid arrows, α-Fe; open arrows, Fe_3O_4.

0.1–1 h the peaks of a spinel-type compound were observed, but for an H_2 flow time of 5 h they were observed along with very small peaks of the metal iron (Fig. 2a and b). The same results were obtained from Mössbauer spectroscopy (Fig. 3a and b). Precise analysis of the peak position in the X-ray diffraction patterns for estimation of the lattice constant showed that the lattice constant increased with an increase in the H_2 flow time. This increase in the lattice constant would come from cation repulsion arising from reduction of the anion of oxygen in the spinel-type structure. Thus, we can obtain magnetite which forms a spinel-type structure but lacks some oxygen ion (oxygen-deficient magnetite). The oxygen-deficient magnetite is a metastable intermediate which is formed in the course of the reduction of Fe_3O_4 to α-Fe at 280–300°C [9]. The appearance of small peaks of the metal iron at the longer H_2 flow time (5 h) suggests that the magnetite phase of the oxygen-deficient spinel-type structure with a higher deficiency concentration will be transformed into the metallic iron phase.

Table II summarizes the results of methanation experiments carried out at 300 °C using H_2-reduced magnetite which had been prepared by flowing H_2 gas through magnetite powder for 5 h at 300 °C. The CO_2 gas was successively injected after each run of the methanation reaction (0.014 dm^3 for each run). During the methanation reaction, the inner pressure of the reaction cell fell owing to reduction of the total volume of the reactant and product gases in the reaction cell. Therefore, we injected H_2 gas during the reaction to keep the inner pressure of the reaction cell at 0.1 MPa. As can be seen in Table II, the injected CO_2 gas was converted into CH_4 by nearly 60–70% in 20 min in each run. In the final run (the fifth run), the conversion ratio measured at 30 min of reaction time was 0.87 (the data on the bottom line of Table II). The selectivity of the methanation was nearly 100% for each injection (Table II); apart from CH_4, no peaks of CO and hydrocarbons such as C_2H_4 and C_2H_2 were observed in the gas chromatograms.

The H_2 gas volumes consumed during the methanation reaction in 20 min reaction time in each run (in the final run, values at both 20 and 30 min) are also listed in Table II. It can be seen that H_2 gas corresponding to about four times the CH_4 gas evolved was consumed in the methanation reaction in each run. It can be concluded that the methanation reaction proceeds according to the reaction $CO_2 + 4H_2 = CH_4 + 2H_2O$ with a high efficiency at 300 °C in the presence of a powder of H_2-reduced magnetite. X-ray diffractometry and Mössbauer spectroscopy showed that there was no change in the X-ray diffraction pattern and the Mössbauer spectra of the H_2-reduced magnetite before and after the methanation reaction. This shows that H_2-reduced magnetite is regenerated successively in the methanation of CO_2 gas at 300 °C.

3.2. Adsorption of CO_2 to H_2-reduced magnetite

Fig. 4 shows the results of CO_2 adsorption experiments* using H_2-reduced magnetite (H_2 flow time = 5 h) (curve A) and non-reduced magnetite (curve B) at 300 °C. The adsorbed CO_2 gas volume was evaluated from the change in the inner pressure of the reaction cell before and after the injection of a constant volume of CO_2. This was −760 mm Hg before the CO_2 injection, which is taken as the origin in the vertical axis in Fig. 4. For H_2-reduced magnetite, no change in the inner pressure was observed in the range of 5–15 $\times 10^{-3}$ dm^3 of CO_2 volume injected (curve A). This indicates that the injected CO_2 gas of 5–15 $\times 10^{-3}$ dm^3 is adsorbed to the H_2-reduced magnetite. However, for the non-reduced magnetite, the inner pressure increases linearly as given by curve B crossing the origin of the figure, indicating that no CO_2 gas was adsorbed on the non-reduced magnetite at 300 °C. The difference in the inner pressure between curves A and B comes from the adsorption of CO_2 to the H_2-reduced magnetite. The CO_2 volume corresponding to this pressure difference is given by curve C in Fig. 4. Since no CO_2 conversion capacity into CH_4 was observed for non-reduced magnetite (H_2 flow time = 0 in Table I), the CO_2 adsorption capacity of the H_2-reduced magnetite seems to be related to the CO_2 conversion capacity into CH_4. In the experiment on CO_2 adsorption of Fig. 4, the change in the inner pressure was measured immediately after the injection of CO_2 gas. However, the CO_2 adsorption profile for H_2-reduced magnetite changed to the profile given by curve A′, where the inner pressure change was measured 1.5 h after CO_2 injection. This suggests that the

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* In the present reaction, the CO_2 adsorbed on H_2-reduced magnetite seems to be decomposed into C, therefore we use the term "adsorption" in the meaning of chemisorption.

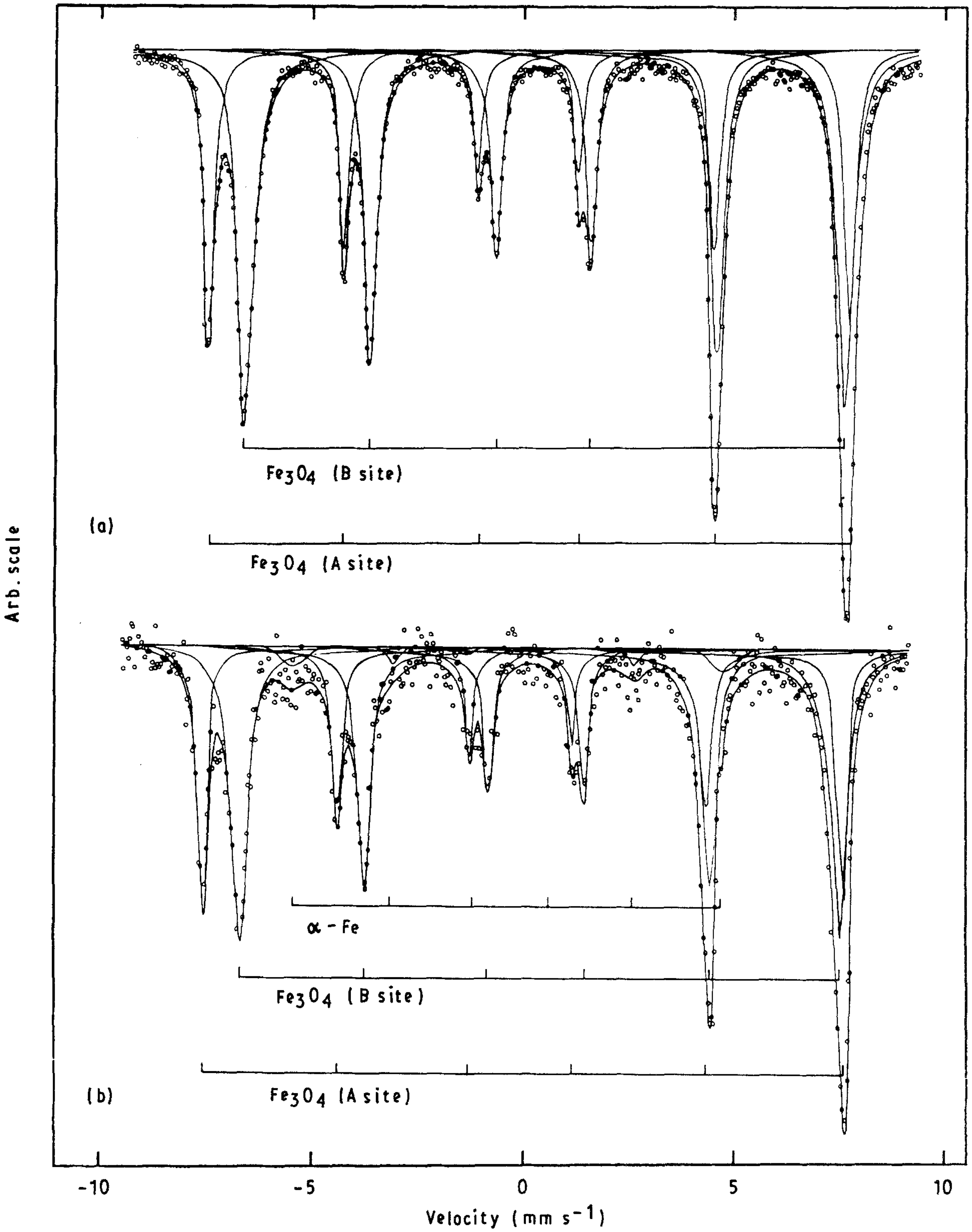

Figure 3 Room-temperature Mössbauer spectra of H_2-reduced magnetites before the methanation reaction: H_2 flow time (a) 0.4 h, (b) 5 h.

CO_2 adsorption reaction proceeds with time. As mentioned below, chemical analysis showed that the adsorbed CO_2 is chemically decomposed into carbon (chemisorption).

Fig. 5 shows the relationship between the conversion ratio of adsorbed CO_2 into CH_4 and the number of the CO_2 molecules adsorbed to unit surface of H_2-reduced magnetite at 300 °C. The CO_2 adsorption step before the methanation step was carried out, as mentioned above for Fig. 4, at 300 °C. The CO_2 volumes adsorbed were varied by changing the reaction time in the CO_2 adsorption step. As can be seen from Fig. 5, a high conversion ratio of around 0.85 (methanation reaction time = 30 min) was maintained at a CO_2 molecule number lower than 0.7 per 1 nm^2 of unit surface area of H_2-reduced magnetite. However, the conversion ratio decreased abruptly at a CO_2 molecule number above 0.7 per unit area, and became below 0.1 at CO_2 molecule numbers above 1.2–1.5. Since the cubic crystal unit cell of the spinel-type structure of the magnetite has a dimension of about 0.8–0.9 nm, we can say that the CO_2 adsorbed

TABLE II Results on the methanation reaction in the successive injection of CO_2 and H_2 gases into the reaction cell at 300 °C (reaction time = 20 min in each run; inner pressure of reaction cell kept to 0.1 MPa by injecting H_2 gas during the methanation reaction)

Run No.	CO_2 injected (10^{-3} dm^3)	CH_4 generated[a] (10^{-3} dm^3)	H_2 consumed (10^{-3} dm^3)
1	14	9.0 (0.64)	36
2	14	9.3 (0.66)	36
3	14	9.0 (0.64)	34
4	14	9.5 (0.72)	40
5	14	8.8 (0.73)	35
		10.5 (0.87)[b]	43[b]

[a] Values in parentheses are conversion ratios.
[b] Reaction time = 30 min.

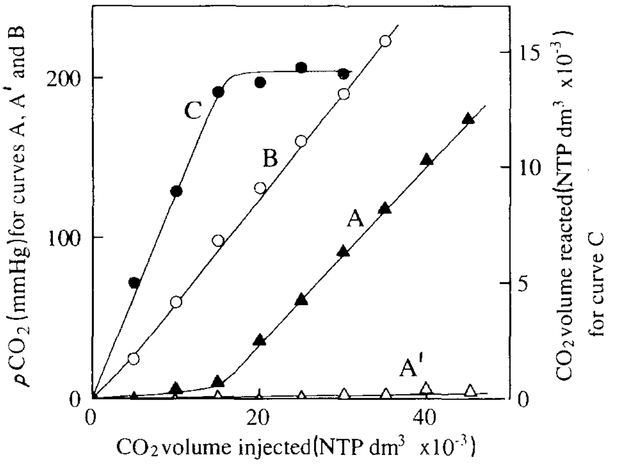

Figure 4 Relationship between CO_2 volume injected into the reaction cell and the increase in the inner pressure due to CO_2 gas not adsorbed to (A) H_2-reduced magnetite and (B) non-reduced magnetite; (C) CO_2 volume adsorbed to H_2-reduced magnetite at 300 °C. Curves A and B were obtained from the inner pressure measured immediately after CO_2 injection. The CO_2 gas was injected into the reaction cell evacuated to − 760 mm Hg; therefore the zero in the vertical axis corresponds to − 760 mm Hg. Curve A′ is the relationship between the CO_2 volume injected into the reaction cell and the inner pressure measured 1.5 h after CO_2 injection at 300 °C.

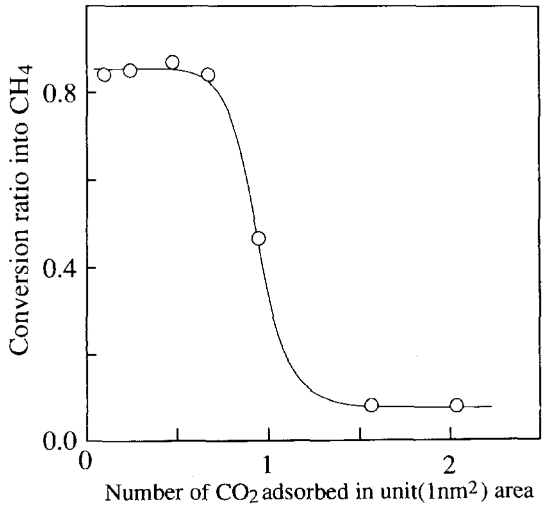

Figure 5 Relationship between the conversion ratio of carbon deposited on H_2-reduced magnetite (H_2 flow time = 5 h) into CH_4 and the number of the CO_2 molecules adsorbed to the unit surface area (1 nm^2) of H_2-reduced magnetite at 300 °C in 30 min of methanation reaction time.

is readily converted into CH_4 under conditions where about one molecule of CO_2 is adsorbed on a face of the unit cell of the spinel-type structure.

3.3. Carbon deposition in the CO_2 adsorption reaction

Carbon analysis showed that carbon was detectable in the powder sample which adsorbed CO_2 gas as given by curve A′ in Fig. 4. This suggests that the CO_2 adsorbed is decomposed into carbon on the surface of H_2-reduced magnetite (chemisorption), and that the CO_2 adsorption reaction proceeds with time (the CO_2 adsorption reaction time). From the relationship between the amount of carbon deposited on H_2 reduced magnetite (H_2 flow time = 5 h) and the CO_2 adsorption reaction time at 300 °C, it was found that the deposited carbon increased with the CO_2 adsorption reaction time, and that 60–70% of the initial CO_2 gas (50×10^{-3} dm^3) injected into the reaction cell was adsorbed and converted into carbon in 1.5 h of CO_2 adsorption reaction time. Thus, the CO_2 gas adsorbed on the surface of H_2-reduced magnetite is converted into carbon, as reported previously [10].

In the X-ray diffraction pattern of the powder sample obtained 1.5 h after the CO_2 adsorption reaction (injected CO_2 gas volume = 5×10^{-3} dm^3), only the peaks corresponding to those of the spinel-type compound appeared, and no peaks for the metal iron were observed, which appeared (but as very small peaks; see Fig. 2b) in the diffraction pattern of the sample before the CO_2 adsorption reaction. Mössbauer spectroscopy showed that the very small absorption lines of the metallic iron phase, which had appeared in the spectrum of the sample before the CO_2 adsorption reaction (Fig. 3b), disappeared and only a typical absorption profile for magnetite appeared. These results suggest that the metallic iron phase in H_2-reduced magnetite reacted with the CO_2 gas during the CO_2 adsorption reaction at 300° C, and that the iron phase transformed into magnetite. Since the carbon was deposited on H_2-reduced magnetite after the CO_2 adsorption reaction, the reaction between the metallic iron phase and CO_2 gas is considered to form carbon as a final product. Also, since only the absorption lines for magnetite appeared in the Mössbauer spectrum, the oxygen of the CO_2 is considered to be eventually incorporated into the lattice points of the magnetite. Moreover, the area ratio of A to B sites in the Mössbauer spectrum was lower than before the CO_2 adsorption reaction, which indicates that the oxygen-deficient magnetite phase in H_2-reduced magnetite also reacted with CO_2 gas and decomposed it into carbon; the oxygen of the CO_2 gas is transferred in the form of O^{2-} ion into the spinel-type structure of the oxygen-deficient magnetite, and the C^{4+} would be reduced to carbon, associated with the oxidation of iron ion (Fe^{2+}).

Thus, the CO_2 adsorption reaction proceeds to incorporate the oxygen of the CO_2 into H_2-reduced magnetite, and eventually into the spinel-type structure of the magnetite. These findings suggest that in the methanation reaction in the present study, the

CO_2 adsorbed on the surface of H_2-reduced magnetite would be decomposed into carbon, associated with the incorporation of the oxygen of the CO_2 in the form of O^{2-} into the spinel-type structure of the magnetite.

In the work of McCarty and Wise [10] on carbon deposited on a nickel metal catalyst, two types of carbon in the dispersed (α) and polymerized (β) forms are reported. These carbons were deposited by exposing CO gas to the nickel metal catalyst. The α-state carbon is considered to represent isolated surface carbon atoms bonded to the nickel, and the β state is taken as amorphous carbon [10]. Bianchi and Gass [5, 6] studied the hydrogenation of carbon deposited on an iron–alumina catalyst, and reported methanation from the carbonaceous adsorbed species which was deposited from the CO gas. From these studies, it was made clear that elementary carbon is most readily converted into CH_4, and that carbide and amorphous polymer carbon are not so readily transformed into CH_4 or hydrogenated [5, 6]. As mentioned in Fig. 5, CO_2 which is adsorbed to H_2-reduced magnetite at about one molecule of CO_2 per 1 nm^2 is readily transformed into CH_4 (conversion ratio = 0.85 in 30 min of reaction time), but the conversion ratio abruptly falls below 0.1 at CO_2 molecule numbers above 1 per 1 nm^2 (Fig. 5). Thus, this lowering of the conversion ratio is accompanied by an increase in the number of CO_2 molecules adsorbed on the surface of the catalyst. This increase in the number of the CO_2 molecules adsorbed would facilitate polymerization of the deposited carbon. In chemical analysis of the deposited carbon we were able to collect carbon powder from powder samples dissolved in HCl solution when the adsorbed CO_2 molecule number was above around one per unit area (1 nm^2). This suggests that at CO_2 molecule numbers below around one per unit area the carbon is deposited as elementary carbon, which is hardly collected as carbon powder in the chemical analysis adopted in the present study. From these findings and the results reported by McCarty and Wise [10] and Bianchi and Gass [5, 6], it would be concluded that the high conversion ratio comes from the higher reactivity of the elementary carbon deposited on the surface of H_2-reduced magnetite, and that the lowering of the conversion ratio at CO_2 molecule numbers above 1 in Fig. 5 comes from the formation of a polymerized form of carbon with a lower reactivity.

When we used metallic iron powder which had been prepared by passing H_2 gas through magnetite powder at 500 °C for 10 h, the conversion ratio became about 1/5 of that obtained as described above, even though the iron powder gave nearly the same CO_2 adsorption characteristic as that of H_2-reduced magnetite. In the X-ray diffraction pattern of metallic iron powder after the CO_2 adsorption reaction, small peaks corresponding to those of carbide (α-Fe_3C) appeared, indicating that CO_2 adsorbed to the iron powder forms carbide. On the other hand, in the case of H_2-reduced magnetite these carbide peaks were not observed. The lower conversion ratio for the metallic iron powder seems to be related to carbide formation from the adsorbed CO_2, as reported by Bianchi and Gass [6, 7]. In the case of H_2-reduced magnetite elementary carbon, which is reactive for the methanation reaction, is formed. Thus, the difference in the conversion ratio between metallic iron powder and H_2-treated magnetite would come from the form of the deposited carbon.

When we used H_2-reduced magnetite which had been prepared by passing H_2 gas through it for 1 h at 300 °C, the same results as those for H_2-reduced magnetite prepared at H_2 flow time = 5 h were obtained. As described above, the H_2-reduced magnetite prepared at H_2 flow time = 1 h is a single phase of oxygen-deficient magnetite, so long as the homogeneity of the solid phase is discussed on the basis of results from X-ray diffractometry and Mössbauer spectroscopy. However, we would not neglect the possibility that a very small amount of metallic iron phase may be present in the H_2-reduced magnetite, even though no peaks or absorption lines were observed in the X-ray diffractometry and Mössbauer spectroscopy. Anyway, however, the metallic iron phase, if present, will be a minor phase. Also in the case of H_2-reduced magnetite prepared at H_2 flow time = 5 h, the iron phase is not a major constituent. The reason why carbide is hardly formed in the CO_2 adsorption reaction for H_2-reduced magnetite would be the fact that the major phase is not the metal iron, but oxygen-deficient magnetite. The principal driving force of the methanation reaction presented here is considered to be the instability of H_2-reduced magnetite, which can be readily transformed into magnetite with CO_2. This instability is considered to produce a high reactivity to reduce the CO_2 gas directly into carbon. However, there seems to be a possibility that the metallic iron phase, if present in H_2-reduced magnetite, has an important role in the higher reactivity for methanation. We may say that the higher reactivity of H_2-reduced magnetite could be due to a unique heterogeneity of the oxygen-deficient magnetite phase with a small amount of the metallic iron phase in H_2-reduced magnetite.

Thus, using H_2-reduced magnetite in which the major phase of oxygen-deficient magnetite may contain a small amount of the metal iron, it is considered that we can deposit elementary carbon from CO_2, and efficiently convert into CH_4 at 300 °C.

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