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Methanation of CO_2 with the oxygen-deficient Ni(II)-ferrite under dynamic conditions

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The continuous methanation of CO_2 has been accomplished over hydrogen-reduced Ni(II)-bearing ferrite ($Ni_xFe_{3-x}O_{4-\delta}$; $x = 0.39$, $\delta > 0$) in a mixed gas flow of CO_2 and H_2 at 250–375 °C. The yield and the selectivity for the methanation were larger than 50% and 95%, respectively, at the initial stage of the process. They decreased to 31% and 89%, respectively, after 6 h methanation. The innovative results can be ascribed to the use of the new material; hydrogen-reduced Ni(II)-bearing ferrite. Its formation was evinced by chemical analyses and the increase in the lattice constant; the lattice constant of the Ni(II)-bearing ferrite (a_0 0.8375 nm) was enlarged to 0.8379 nm by hydrogen reduction. The enlarged lattice constant was not changed during the methanation. These findings suggest that the methanation occurs at the oxygen-deficient site of the hydrogen-reduced Ni(II)-bearing ferrite, as well as the formation of water by combination of the incorporated oxygens with hydrogen. The methanation consists of three steps of the elementary reaction. First, the oxygen-deficient sites are formed by hydrogen reduction; second, CO_2 is reduced to elementary carbon and two oxygen ions which are incorporated into the oxygen-deficient sites; and third, the carbon deposited on the surface of the reduced ferrite is selectively hydrogenated to CH_4.

1. Introduction

The reduction of CO_2 emissions is primarily important for the sake of slowing down global warming. One of the clear solutions to the greenhouse effect by CO_2 gas is the *in situ* decomposition of CO_2 to carbon in each stationary source, e.g. power plant, cement plant, etc. It is desirable to do this at as low a temperature as possible, preferably at 200–300 °C of waste heat. Another method must possibly be through low-temperature methanation. These processes could be unified to form a new system with much lower CO_2 emissions, and would contribute to the net reduction of CO_2 emissions.

Methanation of CO_2 has been known to occur over SiO_2-supported transition-metal catalysts such as nickel, ruthenium, iron and Co/SiO_2 [1–6]. The production of CH_4 from CO_2 was lower than CO hydrogenation over the temperature range 500–725 K and the selectivity was low, due to the formation of CO. Recently, a totally different route for the methanation of CO_2 has been reported [7–15]. It involves the decomposition of CO_2 to carbon by the spinel compounds. Much higher selectivity than reported previously by other authors has been attained in a closed system using hydrogen-reduced Ni(II)- or Co(II)-bearing ferrites [7, 8]. CO_2 is decomposed to carbon and two oxygens over these ferrites and the oxygens are incorporated into the oxygen-deficient site of the reduced ferrite. The carbon deposited on the ferrite can be transformed to CH_4. The degree of methanation is higher with ferrites reduced by hydrogen for longer time. The Ni^{2+}-substitution in the magnetite has facilitated the methanation of the carbon deposited from CO_2 gas on the hydrogen-reduced ferrite. Methanation of CO_2 was possible at 200 °C in the batch system. The degree of the effect increased with increase in the level of Ni^{2+}-substitution. The maximum methanation (86.9%) of CO_2 was attained on Ni(II)-bearing ferrite activated by hydrogen gas for 3 h.

The objective of the present work was to investigate the methanation of CO_2 using the hydrogen-reduced Ni(II)-bearing ferrite under dynamic conditions.

2. Experimental procedure

2.1 Preparation of Ni(II)-bearing ferrite

Ni(II)-bearing ferrite was synthesized by air oxidation of a hydroxide suspension of Fe(II) and Ni(II) according to the wet method reported previously [16]. The procedure is briefly described as follows. Portions of $NiSO_4 \cdot 6H_2O$ (44.2 g) and $FeSO_4 \cdot 7H_2O$ (312 g) with the mole ratio Ni:Fe adjusted to 0.15 were dissolved

0022–2461

in water degassed by passing nitrogen gas through distilled water (4.0 dm^3) for a few hours. The pH of the solution was raised to 10 by adding 6.0 $mol\,dm^{-3}$ NaOH solution to form a hydroxide suspension. Air was passed through the alkaline suspension for oxidation for 24 h at 65 °C. The pH was kept constant at 10 by adding the 3.0 $mol\,dm^{-3}$ NaOH solution. The product was collected by decantation. After washing with distilled water and acetone, successively, the product was dried in a nitrogen stream for 30 min at ambient temperature and then for 1 h at 300 °C. The heated product was used in the following experiment. It was identified by X-ray diffractometry (XRD) with CuK_α radiation (Rigaku Rint 1100 XRD diffractometer). The infrared spectrum of the product was recorded by the KBr disc technique (Shimadzu FTIR-8500). The Mössbauer spectrum was recorded at room temperature with a ^{57}Co source diffused in metallic rhodium which was oscillated in a constant acceleration mode. The spectrum was calculated by a curve fitting method to the Lorentzian line shapes. The chemical composition of the product was determined by colorimetry using 2,2′-bipyridyl for the speciation of Fe(II) and Fe_{total} and by inductively coupled plasma (ICP) spectrometry (Seiko Instruments SPS7000) for Ni and Fe_{total}.

2.2. Methanation of CO_2 over hydrogen-reduced Ni(II)-bearing ferrite

The sample (1.0 g) was placed in a quartz tube with a diameter of 8 mm and a length of 330 mm (Fig. 1). Hydrogen gas was passed through at a flow rate of 20 $cm^3\,min^{-1}$ at 300 °C for a given time (1–4 h) to reduce Ni(II)-bearing ferrite. Methanation was then carried out while flowing a mixed gas of H_2 and CO_2 at a constant flow rate of 50 $cm^3\,min^{-1}$. The mole ratio H_2: CO_2 is 4.0, unless otherwise mentioned. The gaseous components formed were determined at the outlet of the reaction cell by gas chromatography (Shimadzu, model GC-8A) equipped with Porapak Q or Molecular Sieve 13X columns. The yields of CH_4 and CO were calculated on a carbon basis. For XRD studies, the hydrogen-reduced materials were quenched by quickly placing the reaction cell in the refrigerant of ice and then taken out of the reaction cell in a nitrogen atmosphere to prevent oxidation. The amount of carbon deposited on the surface of the solid phase was determined by elemental analysis (Perkin–Elmer 2400 CHN Elemental Analyser).

3. Results and discussion

3.1. Preparation of Ni(II)-bearing ferrite and hydrogen reduced form

The XRD pattern of the Ni(II)-bearing ferrite corroborated that the synthesized product was a single phase with the spinel-type structure; any other peaks assigned to α-Fe_2O_3 or iron oxide hydroxides such as α-FeO(OH) were not observed. In the infrared spectrum of the Ni(II)-bearing ferrite, absorption bands were observed at 590 and 360 cm^{-1}, characteristic of ferrite. The infrared spectrum showed no sign of by-products of iron oxide hydroxides such as α-, β-, δ- and γ-FeO(OH); absorption bands at 800–1100 cm^{-1}, characteristic of the iron oxide hydroxides, were not observed. This material showed a ^{57}Fe absorption Mössbauer spectrum at room temperature consisting of two sextets. The profile was characteristic of the ferrite compounds with the crystal structure of the spinel type. The chemical composition of the product was $Ni^{2+}_{0.39}Fe^{2+}_{0.59}Fe^{3+}_{2.01}O_{4.00}$. The mole ratio of Ni(II)/Fe_{total} in the product was nearly the same as that of the starting materials, indicating that most of the Ni(II) used was quantitatively incorporated into the ferrite during the oxidation of the hydroxide suspension. From the XRD studies, the lattice constant, a_0, of the Ni(II)-bearing ferrite was determined to be 0.8375 nm.

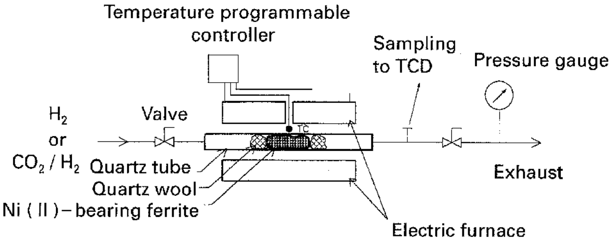

Figure 1 Apparatus for methanation of CO_2 under dynamic conditions. TC = thermocouple

With increase in the reduction time of the Ni(II)-bearing ferrite, there appeared a small and broad reflection assigned to the (1 1 0) reflection of metallic iron or the (1 1 1) reflection of metallic nickel in addition to the reflections of the spinel. The reflection of the metallic phase was not observed after 1 h hydrogen-reduction and appeared with 2 h reduction. The ratio of the reflection intensity of the metallic phase to the (3 1 1) reflection of the ferrite increased to 0.09 for 2 h, 0.12 for 3 h and 0.17 for 4 h. In the following experiment, the sample reduced for 2 h was used. The a_0 of the hydrogen-reduced form was enlarged to 0.8379 nm, irrespective of the duration of hydrogen-reduction. The overall chemical composition of the reduced Ni(II)-bearing ferrite changed to $Ni_{0.39}Fe^{2+}_{1.10}Fe^{3+}_{1.51}O_{3.76}$. The hydrogen-reduced Ni(II)-bearing ferrite thus obtained may be referred to as an oxygen-deficient form and contains oxygen-deficient sites in the spinel-type structure. This oxygen-deficient site was found to be very reactive for the decomposition of CO_2 to carbon [9].

3.2. Continuous methanation of CO_2 over hydrogen-reduced Ni(II)-bearing ferrite

CH_4, C_2H_6 and CO were formed by flowing the mixed gas of H_2 and CO_2 over the hydrogen-reduced Ni(II)-bearing ferrite at 300 °C. The yield for each chemical species was defined by the mole ratio of the species of interest to the sum of all species; CO_2, CO, and CH_4. The selectivity for each reaction was defined by the mole ratio of the species of interest to the other products, CH_4 and CO. The amount of C_2H_6 evolved was about 1/100 of that of the principal product CH_4 and negligible. The yields for CH_4 and CO were plotted as

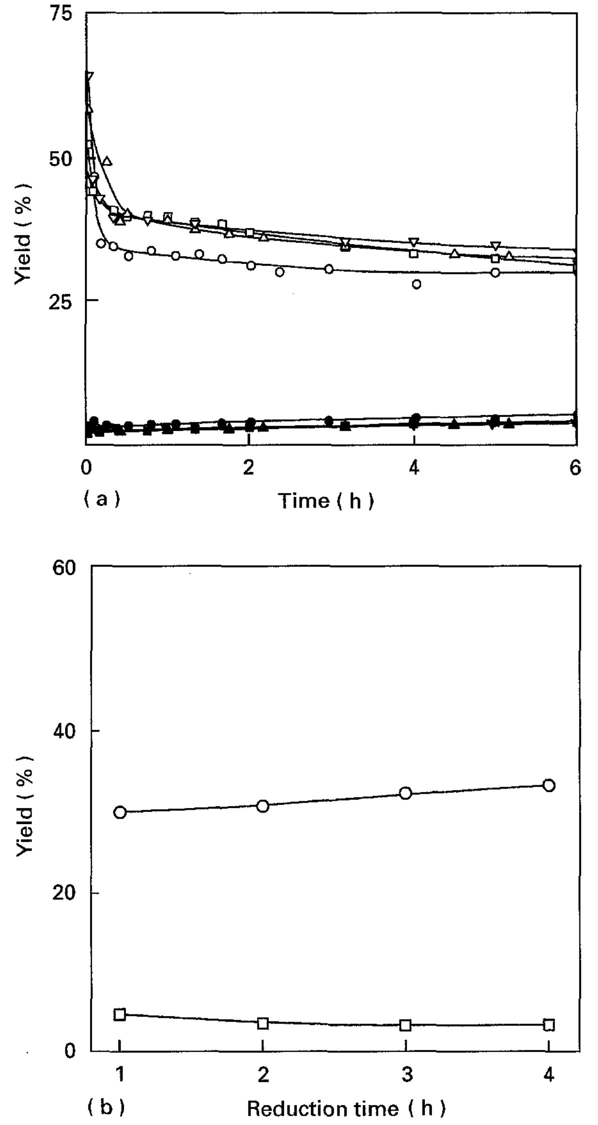

Figure 2 (a) Variation of yields of CH_4 and CO formed by the reaction of a mixed gas stream of H_2 and CO_2 with the hydrogen-reduced Ni(II)-bearing ferrite. (○, □, △, ▽) CH_4, (●, ■, ▲, ▼) CO. Reduction time; (○, ●) 1 h, (□, ■) 2 h, (△, ▲) 3 h, (▽, ▼) 4 h. (b) Yield of (○) CH_4 and (□) CO at 6 h reaction.

a function of reaction time (Fig. 2a). A hydrogen-reduction longer than 1 h has no further effect on the methanation reactivity of the reduced ferrite, because the oxygen-deficient site does not increase even though it was reduced by hydrogen for longer than 1 h; instead the metallic phase increases. The metallic phase does not contribute to the methanation. The yield of CH_4 was 42%–65% in the initial stage and sharply decreased to around 38%. The former may be due to reaction on the surface of the ferrite crystal and the latter may be partly ascribed to a bulk effect. Thereafter, it decreased to a lower value after 6 h (Fig. 2b). The yield of CO was less than 3% throughout the reaction time studied. The yields for both products were not so dependent on the reduction time. The selectivity for CH_4 was more than 85% after reaction for 6 h in this system. Hydrogen-reduced magnetite, under similar conditions, showed less than 3% and 16% for the yield and selectivity of CH_4 formation, respectively. Thus, the high yield and the much larger selectivity for CH_4 have been accomplished over the hydrogen-reduced Ni(II)-bearing ferrite. The amount of deposited carbon was only 0.20 wt % at most, but this was 3.06 wt % on the hydrogen-reduced magnetite. The carbon is apt to polymerize and is not easily transformed to CH_4. This is one of the reasons for these large differences. Such an excellent property for continuous methanation of CO_2 has not been reported previously on conventional catalysts.

TABLE I Change in the lattice constant, a_0, and the chemical composition of hydrogen-reduced Ni(II)-bearing ferrite during the methanation at 300 °C

Sample	Reaction time (h)	a_0 (nm)	Chemical composition
S[a]	—	0.8375	$Ni^{2+}_{0.39}Fe^{2+}_{0.59}Fe^{3+}_{2.01}O_{4.00}$
a[b]	0	0.8379	$Ni^{2+}_{0.39}Fe^{2+}_{1.10}Fe^{3+}_{1.51}O_{3.76}$
b	0.08	0.8378	$Ni^{2+}_{0.39}Fe^{2+}_{1.09}Fe^{3+}_{1.52}O_{3.76}$
c	1	0.8379	–
d	3	0.8379	$Ni^{2+}_{0.39}Fe^{2+}_{1.16}Fe^{3+}_{1.45}O_{3.73}$
e	6	0.8378	$Ni^{2+}_{0.39}Fe^{2+}_{1.04}Fe^{3+}_{1.57}O_{3.79}$

[a] Before hydrogen reduction.
[b] Hydrogen–reduction for 2 h at 300 °C.

The XRD pattern of the hydrogen-reduced Ni(II)-bearing ferrite after 5 min methanation showed only the peaks assigned to the spinel-type compound. A small peak showing metallic iron or nickel disappeared within 5 min methanation. Oxygen for the oxidation may have been supplied from CO_2. During methanation, a_0 and the chemical composition were nearly the same as those of the hydrogen-reduced ferrite prior to use (Table I). The methanation can be assumed to proceed over the reduced ferrite while retaining a single phase. The oxygen-deficient site of the hydrogen-reduced Ni(II)-bearing ferrite will have an important role in the methanation, which will involve at least three elementary reactions: (a) the formation of an oxygen vacancy; (b) decomposition of CO_2 to a carbon and two oxygens, and incorporation of oxygens into the deficient sites; (c) methanation of the carbon deposited on the solid phase. The processes may be represented as follows

$$H_2 + O_O^x + 2Fe_{Fe}^x \rightarrow H_2O + V_O^{\cdot\cdot} + 2Fe_{Fe}' \quad (1)$$

$$CO_2 + 2V_O^{\cdot\cdot} + 4Fe_{Fe}' \rightarrow C_{(a)} + 2O_O^x + 4Fe_{Fe}^x \quad (2)$$

$$C_{(a)} + 2H_2 \rightarrow CH_4 \quad (3)$$

where O_O^x is an oxygen ion in the normal position of the spinel structure, $V_O^{\cdot\cdot}$ is an oxygen vacancy with effective charge of 2 +, Fe_{Fe}^x is an iron ion in the normal position of the spinel structure, Fe_{Fe}' is an iron ion with effective charge of − 1, and $C_{(a)}$ is an adsorbed elementary carbon. The reactions in Equations 1 and 2 are different from the so-called catalytic reaction in which the bulk of the solid phase is not involved. The above reactions are a redox reaction between solid and gas phases in the heterogeneous system.

The following experiments were implemented with a view to finding the optimum conditions for

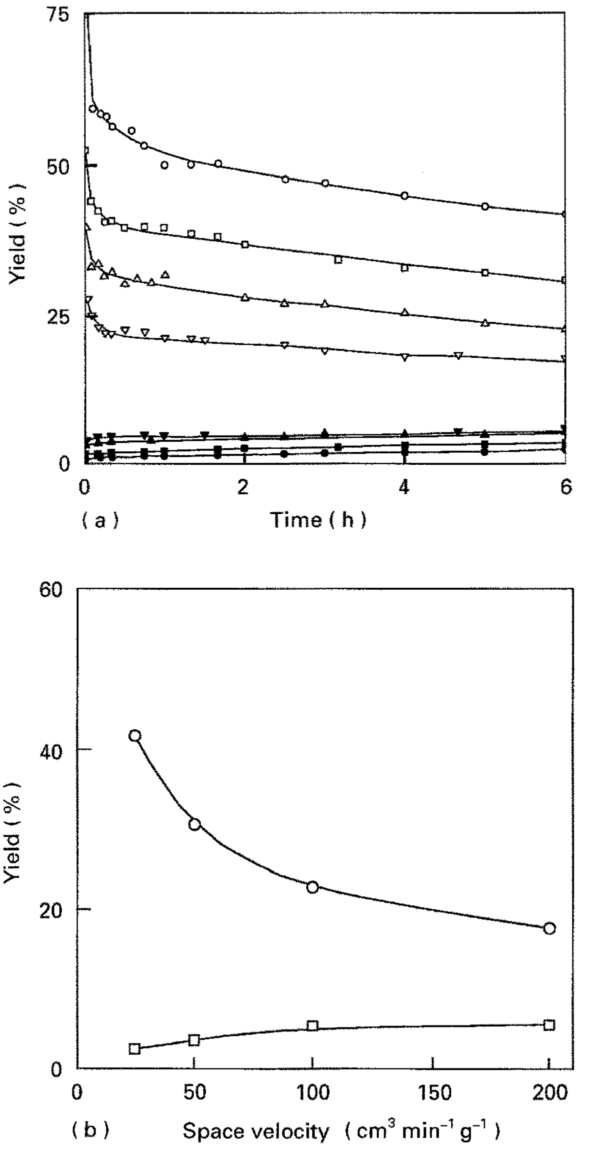

Figure 3 (a) Effect of flow rate on yields of CH_4 and CO at 300 °C. (○, □, △, ▽) CH_4, (●, ■, ▲, ▼) CO. Flow rate ($cm^3 min^{-1}$) : (○) 25, (□) 50, (△) 100, (▽) 200. (b) Plot of space velocity of reactant gas versus yields of (○) CH_4 and (□) CO at 6 h reaction.

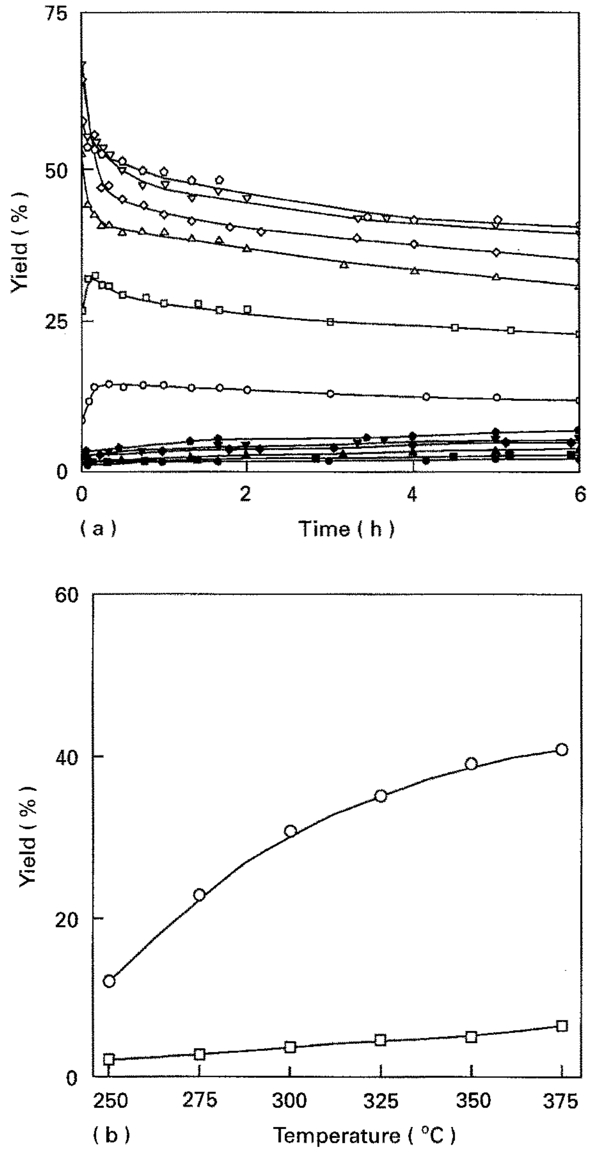

Figure 4 (a) Effect of reaction temperature on yields of CH_4 and CO. Hydrogen-reduction time for Ni(II)-bearing ferrite is 2 h. Mole ratio in reactant gas: 4.0 for H_2 to CO_2. (○, △, ◇, ▽, ⬡) CH_4, (●, ▲, ◆, ▼, ⬢) CO. Reaction temperature (°C) : (○, ●) 250, (□, ■) 275 (△, ▲) 300, (◇, ◆) 325, (▽,▼) 350, (⬡, ⬢) 375. (b) Plot of yields for (○) CH_4 and (□) CO versus reaction temperature.

methanation with respect to the material and the feed gas. Fig. 3a shows the effect of the flow rate of reactant on the yields of CH_4 and CO. The yield decreased with increase in the flow rate, due to the slow rate of the formation reaction. In the initial stage of the process, a very high yield could be obtained, followed by a gradual decrease in the yield. The maximum of 75% has been attained at a flow rate of 25 $cm^3 min^{-1} g^{-1}$. The yields were compared at 6 h reaction with the hydrogen-reduced Ni(II)-bearing ferrite (Fig. 3b). The yield of CH_4 at the flow rate of 200 $cm^3 min^{-1} g^{-1}$ decreased to about half of that in 25 $cm^3 min^{-1} g^{-1}$. The yield of CO was low and slightly dependent on the flow rate. Fig. 4a shows the effect of temperature of methanation on the yields of CH_4 and CO. The yield of CH_4 increased significantly with temperature of methanation, while the yield of CO slightly increased with temperature. The yield of CH_4 increased in the initial stage of reaction below 275 °C. This will be due to the slow rate of reaction and further reduction of Ni(ii)-bearing ferrite by hydrogen in the reactant at those temperatures. Above 300 °C, the yield of CH_4 was high in the initial stage and decreased with reaction time. It was compared using the value at 6 h reaction with the hydrogen-reduced Ni(II)-bearing ferrite (Fig. 4b). The yield increased for both components with increase in the reaction temperature. However, the selectivity for methanation was the highest at 300 °C: 89%. The value is incredibly high compared with the usual catalytic process.

Fig. 5a and b show the effect of the mole ratio of H_2 to CO_2 in the reactant on the yields of CH_4 and CO. The values in Fig. 5b were plotted as a function of mole ratio at 6 h reaction with the hydrogen-reduced Ni(II)-bearing ferrite. The yield of CH_4 increased steeply and that of CO decreased slightly with increase in mole ratio of H_2 to CO_2. It suggests that the equilibrium reactions of Equations 1 and 3 were more shifted to the right-hand side by the increase in the partial pressure of hydrogen.

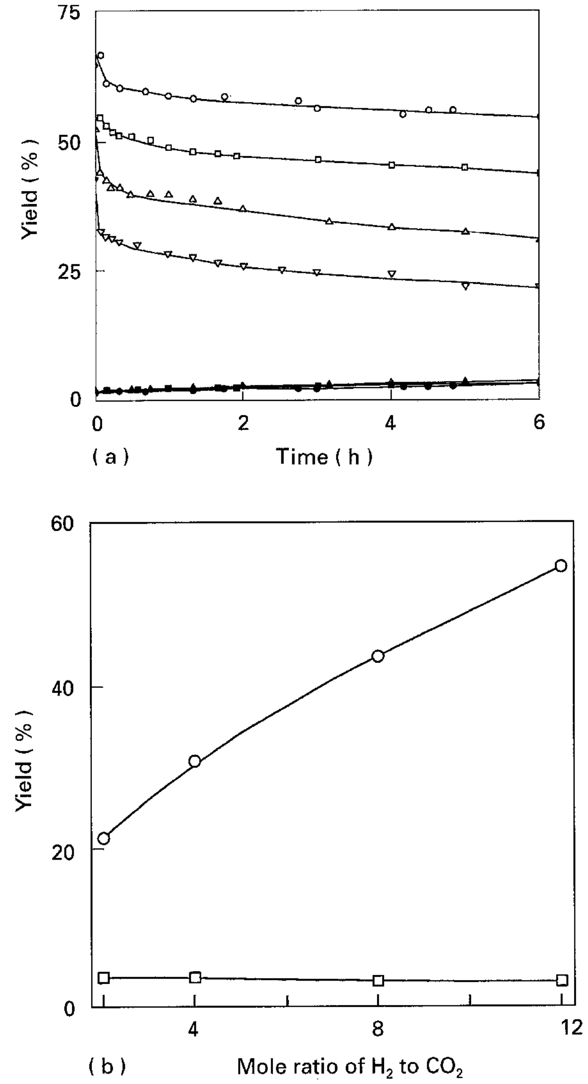

Figure 5 (a) Effect of mole ratio of H_2 to CO_2 on yields of CH_4 and CO. (▽, △, □, ○) CH_4, (▼, ▲, ■, ●) CO. Mole ratio: (▽, ▼) 2.0, (△, ▲) 4.0, (□, ■) 8.0, (○, ●) 12. (b) Plot of yields for (○) CH_4 and (□) CO versus mole ratio of H_2 to CO_2.

4. Conclusion

A continuous methanation of CO_2 has been demonstrated over the hydrogen-reduced Ni(II)-bearing ferrite using a mixed gas of H_2 and CO_2 at a low temperature in the range 250–375 °C. At the initial stage of the reaction, the reduced ferrite was very reactive and changed to the steady state of methanation. The yield of CH_4 at the steady state at 6 h after initiation of methanation increased with temperature of methanation and the mole ratio of H_2 and CO_2; the yield increased from 12% at 250 °C to 40% at 375 °C and from 21% at the mole ratio of 2, to 55% at the mole ratio of 12 at 300 °C. However, the yield was almost independent of the reduction time of the ferrite. The CH_4-producing method will serve an alternative to the traditional process of methanation with respect to energy savings.

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