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Methanation of CO_2 on H_2-reduced Ni(II)- or Co(II)-bearing ferrites at 200 °C

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The methanation of CO_2 gas at 200 °C was investigated in Co(II) or Ni(II)-bearing ferrites with substitution of up to 0.262 and 0.143, respectively. The metal substitution in the ferrite facilitated the methanation of the deposited carbon from CO_2 gas in the H_2-reduced M(II)-bearing ferrite in comparison with the reactivity of the H_2-reduced magnetite with the same spinel structure. The effect on the reactivity of methanation was found to be much larger in Ni(II)-substitution. The degree of the effect increased with increases in the Ni(II)-substitution, while it remained about the same with increases in the Co(II)-substitution. The maximum methanation (86.9%) of CO_2 was attained in the Ni(II)-bearing ferrite activated by H_2 gas for 3.0 h.

1. Introduction

The decomposition of CO_2 at 300 °C has been reported with magnetite, active wustite, rhodium-bearing magnetite and Mn(II)-bearing ferrite activated by H_2 reduction in recent publications by some of the present authors and others [1–5]. X-ray diffraction (XRD) and Mössbauer studies coupled with chemical analyses for carbon have revealed that these materials decomposed CO_2 to carbon and that they were simultaneously oxidized while the crystal structure was retained. Recent investigations showed that activation of Ni(II)-bearing ferrite by H_2 gas improved the rate of CO_2 decomposition by thirty times (in comparison with a H_2-reduced magnetite) [6]. Analysis of the CO_2 adsorption isotherm for the H_2-reduced magnetite showed that the isosteric adsorption was endothermic and the enthalpy change of the adsorption was estimated to be $+40\,\mathrm{kJ\,mol^{-1}}$. CO_2 was adsorbed on the surface of the H_2-reduced magnetite, and this was associated with the decomposition into elementary carbon and two oxygen ions. This was confirmed from the fact that the adsorption isotherm could be fitted to the three-atom-dissociation model [7]. That is, the adsorbed CO_2 was directly decomposed into an elementary carbon atom and two oxygen atoms on the H_2-reduced magnetite or on the M(II)-bearing ferrite.

The carbon deposited on the H_2-reduced magnetite was selectively transformed to CH_4 gas at 300 °C, and the conversion to CH_4 was attained to about 90% [8]. The temperature of methanation was lowered to 150 °C on the H_2-reduced magnetite [9]. A much lower conversion of CO_2 to CH_4 on catalysts (for example Ru, Fe or Co–SiO_2) has been reported, this was only 0.1 at more favourable conditions at 1.1 MPa [10]. The reaction products were mostly CO gas, and the transformation to CH_4 requires additional chemical processes [11–13].

The present paper will describe the direct methanation of CO_2 on Co(II)- and Ni(II)-bearing ferrites at 200 °C.

2. Experimental procedures

2.1. Preparation of magnetite and Co(II)- or Ni(II)-bearing ferrites

Magnetite and Co(II)- or Ni(II)-bearing ferrites were synthesized by air oxidation of hydroxide suspensions of Fe(II) with or without $NiSO_4$ or $CoSO_4$ according to the wet method reported previously in [14–16]. The requisite portions of $FeSO_4 \cdot 7H_2O$ (typically 312 g) and $NiSO_4 \cdot 6H_2O$ (0–88.5 g) or $CoSO_4 \cdot 7H_2O$ (0–94.3 g) were dissolved in oxygen- and CO_2-free water which was prepared by passing N_2 gas through deionized and distilled water for a few hours. The pH of the mixed solution was raised to 10 by adding $3.0\,\mathrm{mol\,dm^{-3}}$ of a NaOH solution to form a hydroxide suspension. Then, air was passed through the alkaline suspension for 24 h at 65 °C while the pH value was kept constant at 10 by adding the $3.0\,\mathrm{mol\,dm^{-3}}$ NaOH solution. The product was washed by successive decantation with an acetate buffer solution, distilled water and acetone. It was dried in a nitrogen stream at the ambient temperature. The product was identified by XRD with Fe$K\alpha$ radiation (Model RAD-2A diffractometer, Rigaku). The chemical composition of the products was determined by atomic absorption spectroscopy for the total content of Ni(II), Co(II) and Fe_{total} and by colorimetry with a

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TABLE I The chemical compositions of magnetite and M(II)-bearing ferrites

Sample	R_M[a]	M(II)/Fe_{total}[b]	Fe(II)/Fe_{total}[c]	Chemical composition
Magnetite	0.00	–	0.251	$Fe^{2+}_{0.730}Fe^{3+}_{2.18}O_{4.00}$
Ni(II)-bearing ferrite	0.05	0.050	0.159	$Ni^{2+}_{0.135}Fe^{2+}_{0.433}Fe^{3+}_{2.29}O_{4.00}$
	0.15	0.143	0.190	$Ni^{2+}_{0.369}Fe^{2+}_{0.491}Fe^{3+}_{2.09}O_{4.00}$
Co(II)-bearing ferrite	0.05	0.045	0.183	$Co^{2+}_{0.124}Fe^{2+}_{0.503}Fe^{3+}_{2.25}O_{4.00}$
	0.15	0.132	0.121	$Co^{2+}_{0.336}Fe^{2+}_{0.308}Fe^{3+}_{2.24}O_{4.00}$
	0.30	0.262	0.077	$Co^{2+}_{0.609}Fe^{2+}_{0.178}Fe^{3+}_{2.14}O_{4.00}$

[a] The M(II)/Fe_{total} molar ratio in the reaction suspensions.

[b] The M(II)/Fe_{total} molar ratio in the product.

[c] The Fe(II)/Fe_{total} molar ratio in the product.

Hitachi spectrophotometer (model 124) using 2,2′-dipyridyl for the speciation of Fe(II) and Fe(III). The Ni(II)- or Co(II)-bearing ferrite was determined after the Ni(II) or the Co(II) and Fe(II) were separated from the Fe(III) using a Dowex IX8 anion exchange resin column (1 cm inner diameter, 12 cm long) [17].

2.2. Methanation of CO_2 with H_2-reduced magnetite and Ni(II)- or Co(II)-bearing ferrite

The magnetite or the M(II)-bearing ferrite (3.0 g) was placed in a quartz tube reaction cell (the reaction cell had an inner diameter of 12 mm and it was 300 mm long) and heated in an electric furnace to 300 °C while the tube was evacuated. Then H_2 gas was passed through the reaction cell at a flow rate of 50 cm^3 min^{-1} to activate the material at 300 °C. For the XRD studies, the H_2-reduced sample was quenched by quickly placing the reaction cell into a mixed refrigerant of ice/NaCl while nitrogen gas was passed through the reaction cell and taken out in a nitrogen atmosphere.

After the H_2-reduction step, the reaction cell was evacuated and then 1.0 cm^3 of CO_2 gas was injected using a gas-tight syringe into the reaction cell for deposition of carbon on the magnetite. After allowing the reaction cell to stand for 10 min, it was evacuated for 10 min, and the temperature was lowered to 200 °C. Then H_2 gas was introduced into the reaction cell to attain an internal pressure of 1 atm. The time was regarded as the starting time of reaction when the internal presure attained 1 atm. The gas species in the reaction cell were determined as a function of the reaction time by gas chromatography (Shimadzu GC-8A).

3. Results and discussion

3.1. Magnetite and Ni(II)- or Co(II)-bearing ferrites

The XRD pattern of the magnetite and the Ni(II)- or the Co(II)-bearing ferrites corroborated that the synthesized products were a single phase of spinel-type compounds; there were no peaks indicating α-Fe_2O_3 or iron oxide hydroxide such as α-FeO(OH). The chemical composition of the magnetite was determined as $Fe_{2.91}O_4$. It can be represented by 0.67(Fe_3O_4)–0.33(γ-Fe_2O_3); that is as the solid solution of two components of Fe_3O_4 and γ-Fe_2O_3. The deviation of the chemical composition from the stoichiometry is due to the oxidation of Fe(II) to Fe(III). The molar ratios of M(II) to Fe_{total} in the M(II)-bearing ferrites were nearly equal to those of the starting materials (Table I). This result indicates that most of the Ni(II) or Co(II) which was used was quantitatively incorporated into the ferrites during the oxidation of the Fe(II) hydroxide suspension. These materials showed ^{57}Fe-absorption Mössbauer spectra consisting of two sixtets. The profiles were characteristic of ferrite compounds with a crystal structure of the spinel type [18].

3.2. The methanation of CO_2

CO_2 gas was deposited on the activated magnetite and M(II)-bearing ferrites with conversions of greater than 80% (Table II). In particular H_2-activated Ni(II)-bearing ferrite showed a decomposition of CO_2 of nearly 100%. The deposited carbon was then methanated as described above.

Fig. 1 shows the relationship between the reaction time and the conversion of the deposited carbon to CH_4 with the H_2-reduced Co(II)-bearing ferrite at 200 °C. Higher conversions were obtained on the H_2-reduced Co(II)-bearing ferrite with any content of Co^{2+} than were obtained on the H_2-reduced magnetite. The conversion was doubled to give 53% at the reaction time of 60 min. Thus, the formation of CH_4 was facilitated by the substitution of cobalt in the ferrite with a spinel structure. The transformation of CO_2 to CH_4 was not very dependent on the concentration of Co(II) in the ferrite. A small maximum in the

TABLE II CO_2 conversion to carbon on the activated magnetite and M(II)-bearing ferrites

Sample	M(II)/Fe_{total}	CO_2 conversion (%)
Activated magnetite	–	86.4
Activated Ni(II)-bearing ferrite	0.050	97.7
	0.143	98.8
Activated Co(II)-bearing ferrite	0.045	86.8
	0.132	81.1
	0.262	96.9

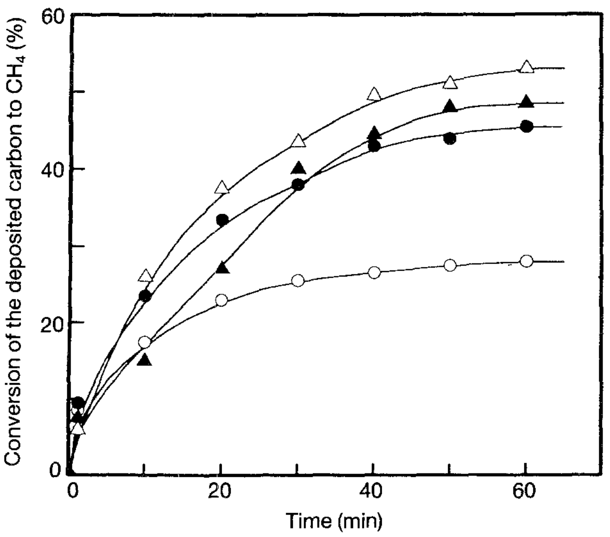

Figure 1 The conversion rate of the deposited carbon to CH_4 on H_2-reduced Co(II)-bearing ferrite at 200 °C: (○) magnetite (for comparison); and Co(II) content of the Co(II)-bearing ferrite of: (●) 0.045, (△) 0.132, and (▲) 0.262.

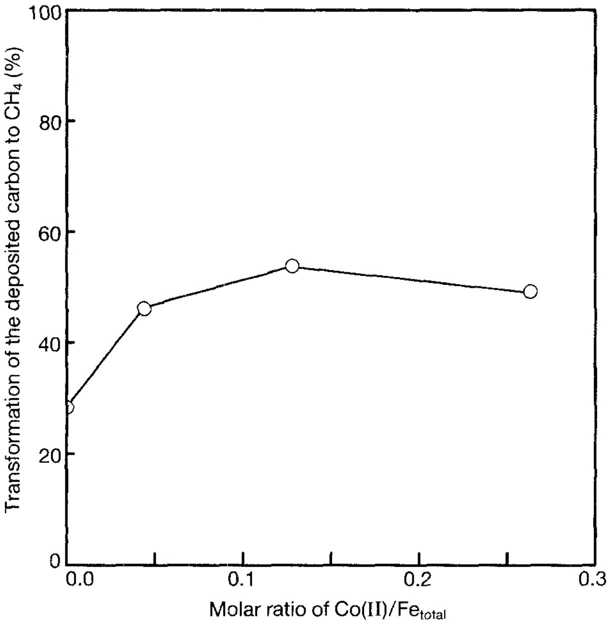

Figure 2 The effect of the Co(II)/Fe_{total} molar ratio on the conversion of the deposited carbon to CH_4 at 200 °C.

conversion was found at a cobalt content of 0.132 (Fig. 2).

Fig. 3 shows a marked increase in the conversion of the deposited carbon to CH_4 within a short period of the reaction of the H_2-reduced Ni(II)-bearing ferrite at 200 °C. Sixty per cent of the adsorbed CO_2 was converted to CH_4 on the H_2-reduced Ni(II)-bearing ferrite with a molar ratio of Ni(II)/Fe_{total} of 0.050 after 40 min of the reaction at 200 °C (curve B). The transformation of the adsorbed CO_2 to CH_4 rapidly increased in the initial stage of the reaction (within 40 min), and then it became nearly constant. The H_2-reduced magnetite showed only a 27% conversion of the adsorbed CO_2 to CH_4 at 200 °C (curve A). The high conversion of 85% after 40 min of the reaction was attained on the H_2-reduced Ni(II)-bearing ferrite with a higher molar ratio of Ni(II)/Fe_{total} of 0.143 (curve C). The conversion of the deposited carbon to CH_4 increased with an increase in the molar ratio of Ni(II)/Fe_{total}. The profile for the change of conversion with the Ni(II) content is presented in Fig. 4. The effect of Ni(II) content should be studied in more detail. The methanation was carried out at 150 °C using the H_2-reduced Ni(II)-bearing ferrite with a molar ratio of Ni(II)/Fe_{total} of 0.143. However, the transformation of the deposited carbon remained at 40%. It is much higher level of transformation to CH_4. Thus, the formation of CH_4 was enhanced by the presence of the nickel in the H_2-reduced ferrite at 200 °C.

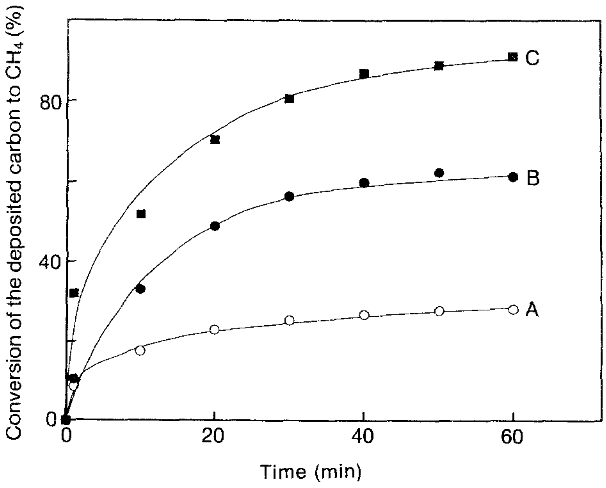

Figure 3 The conversion rate of the deposited carbon to CH_4 at 200 °C: (A) H_2-activated magnetite; and H_2-activated Ni(II)-bearing ferrites with molar ratios of (B) 0.050 and (C) 0.143.

The conversion of deposited carbon on M(II)-bearing ferrites is known to depend on the deficiency of oxygen, which can be determined by the time of the H_2-reduction. Table III shows the relationship between the H_2-reduction time at 300 °C and the transformation of the adsorbed CO_2 or carbon to CH_4 at

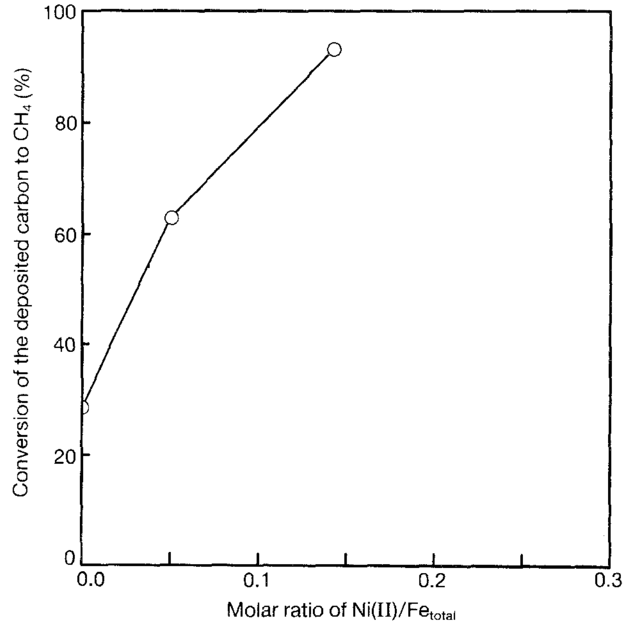

Figure 4 The effect of the Ni(II)/Fe_{total} molar ratio on the conversion of the deposited carbon to CH_4 at 200 °C.

TABLE III The conversion of the deposited carbon to CH_4 on an activated Ni(II)-bearing ferrite (Ni(II)/Fe_{total} molar ratio of 0.143)

H_2 reduction time (h)	Conversion (%)
0.75	45.5
1.5	59.3
3.0	86.9

200 °C at a reaction time of 40 min on the H_2-reduced Ni(II)-bearing ferrite with a molar ratio of Ni(II)/Fe_{total} of 0.143. The transformation increased with an increase in the H_2-reduction time of the Ni(II)-bearing ferrite. A high transformation (85%) was obtained for a H_2 reduction time of 3 h.

These results show that the H_2-reduced Ni(II)-bearing ferrite has a much higher reactivity for the methanation reaction of CO_2 than those of the H_2-reduced magnetite and of the Co(II)-bearing ferrite. This high reactivity is a result of the dissociative adsorption of H_2 to $2H_{ads}$ on the surface of the Ni^0. This H_{ads} will readily react with the elementary carbon deposited on the oxygen-deficient Ni(II)-bearing ferrite, and the methanation reaction of the elementary carbon will be enhanced by the Ni^0.

The methanation of CO gases with various transition metal catalysts has been studied by many investigators. It has been widely accepted that the methanation proceeds by adsorption of carbon species on the metallic nickel of catalysts. The adsorbed carbon is believed to be isolated on the surface as carbon atoms bonded to the nickel [19]. The elementary carbon deposited on the surface of the H_2-reduced magnetite was readily converted into CH_4, and the amorphous polymerized carbon was not so easily transformed to CH_4. The high conversion of adsorbed carbon to CH_4 with the H_2-reduced Co(II)-bearing ferrite is also a result of the high reactivity of the elementary carbon deposited on the surfaces.

4. Conclusion

Substitution of Co(II) and Ni(II) in the ferrite facilitated the methanation of the deposited carbon from CO_2 gas on H_2-reduced ferrite in comparison with the reactivity of H_2-reduced magnetite. The effect on the reactivity of the methanation was found to be larger for Ni(II)-substitution.

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