JOURNAL OF MATERIALS SCIENCE 29 (1994) 5481–5484

Methanation reactivity of carbon deposited directly from CO_2 on to the oxygen-deficient magnetite

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The methanation reactivity of surface carbon deposited from CO_2 on the oxygen-deficient magnetite was studied by the isothermal methanation reaction and the temperature programmed surface reaction (TPSR). In the methanation reaction with H_2 gas, in a closed system at 150–200 °C, active carbon, which was not observed by the TPSR measurements, was found. About 20% out of the deposited carbon was in the form of atomic carbon and readily converted into CH_4 (5 min) above 150 °C with H_2, and about 80% at 300 °C. At 350 °C these atomic carbons were transformed into polymerized carbons, which was less reactive for methanation.

1. Introduction

Properties of solid surfaces are markedly different from those of the bulk solid because the surface atoms are unsaturated. The unsaturated bonds present at the surface provide sites for the adsorption of gas molecules [1–3]. Oxygen-deficient oxides prepared by reduction can be assumed to be more unsaturated than the stoichiometric oxides. Hence, the interaction of gas with the surface of the oxygen-deficient oxide will be stronger than that with the stoichiometric oxides.

Tamaura and Tabata [4] described the direct decomposition of CO_2 to carbon over the oxygen-deficient magnetite prepared by H_2 reduction. In this process, two oxygen ions in CO_2 were incorporated into the vacant lattice sites and carbon formed a weak chemical bond with iron on the oxygen-deficient magnetite [5]. The chemisorption of CO_2 on the oxygen-deficient magnetite is expressed by the Langmuir isotherm which can be interpreted by a three-fragment dissociative adsorption model [5]. CO_2 decomposed into a carbon atom and two oxygen ions dissociatively adsorbed at three different sites. Its isosteric adsorption enthalpy was evaluated to be 40 $\mathrm{kJ\,mol^{-1}}$, which is around the CO_2 decomposition energy into three atoms. In the adsorption reaction the reduction step of the surface carbon seemed to be involved; a carbon ion may have been reduced by acceptance of an electron from an oxygen ion to zero-valenced carbon, and the carbon atom would then deposit on the surface of the oxygen-deficient magnetite. Carbon deposition from the disproportionation reaction of CO has been studied extensively as the Boudouard reaction; $2CO \rightleftharpoons C + CO_2$ [6–14]. Carbon deposition from reaction with CO_2 on the oxygen-deficient magnetite is different from the Boudouard reaction [5]. Deposition of carbon by the decomposition reaction of CO_2 on the oxygen-deficient magnetite is a new reaction of carbon deposition.

The carbon species deposited on the surface of metals such as iron or nickel during the disproportionation reaction of CO or hydrogenation of CO have been studied by various techniques, such as FTIR, TPD (temperature programmed desorption), TPSR (temperature programmed surface reaction), TEM, XPS and AES [10–22]. However, the reactivity of the surface carbon deposited on the oxygen-deficient magnetite has not yet been studied.

The objective of the present work was the investigation of the reactivity of the carbon deposited on the surface of the oxygen-deficient magnetite by the decomposition reaction of CO_2 via the conversion rate of the surface carbon into CH_4 with H_2.

2. Experimental procedure

2.1. Preparation of the oxygen-deficient magnetite

Magnetite powder was prepared by the air-oxidation method [23, 24]; Fe^{II} hydroxide suspension (Fe^{II} = 0.048 mol; $FeSO_4 \cdot 7H_2O$) was oxidized in a 3 $\mathrm{dm^3}$ beaker by passing air through the reaction suspension at pH 10 and at a temperature of 65 °C. The black precipitate of the magnetite particles thus synthesized was washed with water and acetone successively and dried *in vacuo* at 50 °C. The BET surface area of the powder magnetite was determined to be 21 $\mathrm{m^2\,g^{-1}}$. The magnetite powder (5 g) was placed in a quartz reaction cell 30 mm in diameter and 150 mm long (illustrated in a previous paper [25]). Heat was supplied indirectly by placing the reaction cell in an electric furnace. The temperature was measured with a chromel–alumel thermocouple in contact with the

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outer surface of the reaction cell, and controlled to within ± 0.3 °C using a regulator (Chino Model DB 1150). Oxygen-deficient magnetite was prepared by flowing H_2 through magnetite powder at 300 °C for 12 h at a flow rate of 10×10^{-3} $dm^3 min^{-1}$.

2.2. Temperature programmed surface reaction (TPSR)

A TPSR experiment was carried out to determine the reaction temperature with H_2. CO_2 gas (5×10^{-4} or 5×10^{-3} $dm^3 g^{-1}$) was injected into the reaction cell to decompose CO_2 over the oxygen-deficient magnetite (1.0 g). A period of 10 min was enough to allow complete decomposition of the CO_2 injected. The system was then evacuated to remove any residual gas and the reaction cell was quenched at 0 °C. The surface density of the carbon deposited on the oxygen-deficient magnetite was estimated to be 0.4 or 2.0 molecules per unit surface area (1 nm^2) (C-density = 0.4 or 2.0). The reaction cell was then heated at a rate of 20 °C min^{-1} up to 700 °C while flowing H_2 gas at a rate of 20×10^{-3} $dm^3 min^{-1}$. The product gases (hydrocarbons and CO) were determined by gas chromatography equipment with an FID detector, and the gas composition was determined by gas chromatography equipment with a TCD detector.

2.3. Methanation reaction in the closed system

The isothermal methanation in the closed system was carried out to determine temperature dependency and reaction rate. Carbons of C-density = 0.4 or 2.0 were deposited on the oxygen-deficient magnetite, as mentioned above. The system was then closed and H_2 gas was injected until the inner pressure of the reaction cell reached ambient pressure. The CH_4 generated was determined by gas chromatography (Shimadzu GC-8A) equipment with a TCD detector.

When a large amount of CO_2 (4.0×10^{-3} $dm^3 g^{-1}$) was injected into the reaction cell, 62.5% of the CO_2 gas injected was adsorbed on the surface of the oxygen-deficient magnetite. The surface density of carbon (C-density) evaluated from the CO_2 gas adsorbed on the surface of the magnetite was 2.0.

3. Results and discussion

3.1. Oxygen-deficient magnetite

The X-ray diffraction pattern and Mössbauer spectroscopy of the oxygen-deficient magnetite showed only the peaks corresponding to those of the spinel-type compound, and no peaks were observed for the metal iron. The lattice constant (a_0) of the oxygen-deficient magnetite was 0.8400 nm, which was larger than that of stoichiometric magnetite (0.8396 nm: JCPDS card No. 19-629). These results corroborated a reduction in the magnetite phase.

3.2. TPSR spectra

Fig. 1a shows the TPSR spectrum of the surface carbon with a lower C-density (0.4). Gas chromatography showed that CH_4 was formed exclusively, other hydrocarbons, CO or CO_2 were not detected during the TPSR measurement. Three peaks of CH_4 appeared, indicating that there were three states in the surface carbon (C-density = 0.4) deposited from CO_2 on the oxygen-deficient magnetite at 300 °C. These carbons are designated α, β and γ-carbon in this study.

Fig. 1b shows the TPSR spectrum of the surface carbons with a higher C-density (2.0). Gas chromatography showed that CH_4 was formed exclusively, other hydrocarbons, CO or CO_2 were not detected. The α-carbon was not observed, but the β- and β′-carbons were formed at higher temperatures. The sample with C-density = 0.4 gave no powder carbon in the dissolution process of the sample with HCl solution, but the sample with C-density = 2.0 gave a visible carbon particle. These results suggested that the β- and β′-carbons were polymerized carbons. The β′-carbons were more polymerized than β-carbons. In the work of McCarty and Wise [15], for carbons deposited on the nickel metal catalyst, two types of carbon were reported in the dispersed (α) and polymerized (β) state forms. These carbons were deposited by exposing CO gas to the nickel metal catalyst. The α-state carbon was considered to represent isolated carbon atoms bonded to nickel and the β-state was taken as amorphous carbon. Bianchi and Gass [19, 20] studied the hydrogenation of carbon deposited on an Fe/Al_2O_3 catalyst, and reported the methanation of the carbonaceous species deposited from the CO

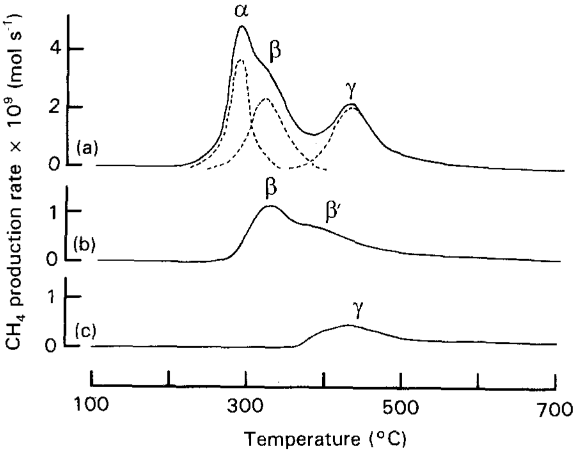

Figure 1 TPSR spectra for the methanation of the surface carbon deposited by the decomposition of CO_2 with (a) oxygen-deficient magnetite (C-density = 0.4); (b) oxygen-deficient magnetite (C-density = 2.0) and (c) α-Fe (C-density = 0.4).

TABLE I CH_4 peak temperature in the TPSR spectra of the surface carbon on the oxygen-deficient magnetite with H_2

State of the carbon	Peak temperature (°C)	Relative intensity of the peaks
α-carbon	278	0.43
β-carbon	314	0.28
γ-carbon	437	0.29

gas. In these studies, it was made clear that elemental carbon was the most readily hydrogenated.

Considering the fact that the sample with a lower C-density (0.4) gave no carbon powder in the dissolution process, the β-peak in the TPSR spectrum of Fig. 1a would have been formed by polymerization of the α-carbon during a temperature increase. The β-carbon was not considered to exist intrinsically in the sample with a lower C-density of 0.4.

Fig. 1c shows the TPSR spectrum for the surface carbon deposited on the metal iron powder. The iron powder with C-density = 0.4 was obtained by the deposition reaction of CO_2 at 300 °C. The metal iron powder was prepared by flowing H_2 gas through the magnetite powder for 12 h at 500 °C. Gas chromatography showed that CH_4 was formed exclusively, other hydrocarbons, CO or CO_2 were not detected in the spectrum. Only one peak of CH_4 appeared, indicating that there was one state in the surface carbon on the metal iron, it may be called γ-carbon. Lee *et al.* [26] showed that carbide phase was formed on the surface of the metal iron during the hydrogenation of CO_2 with H_2 gas on the metal iron catalyst. Also, carbide formation during the CO disproportionation reaction over the metal iron catalyst has been reported by Landes *et al.* [10] and Audier *et al.* [11]. In the work of Bonzel and Krebs [8], for carbons deposited on the nickel metal catalyst, the carbide phase could be converted into CH_4 but was less reactive compared with the atomic (α-) and polymer (β-) carbons. These findings suggested that the third peak in Fig. 1a (437 °C) and a peak in Fig. 1c (430 °C) correspond to the γ-carbon.

As described above, the β- and γ-carbons were not present intrinsically among the surface carbons on the oxygen-deficient magnetite with C-density = 0.4, but were formed during the measurement of the TPSR spectrum. The peaks of the β- and γ-carbons would be less reactive with H_2. If these β- and γ-carbons were intrinsically present among the deposited carbons, 100% of the deposited carbon could not be transformed into CH_4, as shown in the TPSR measurement. The surface carbons with C-density = 0.4 on the oxygen-deficient magnetite were mainly atomic carbons which were considered to be directly in contact with the surface iron ions of the oxygen-deficient magnetite. Therefore, the carbons on the sample would readily transform into polymerized carbon and carbide above 300 °C, which was evidenced by SEM and XRD studies, (details are to be published).

3.3. RT-carbon

Fig. 2a shows the time variation of the conversion ratio of the surface carbon with C-density = 0.4 into CH_4 with H_2 gas under the isothermal conditions in the temperature range of 150–350 °C in the closed system. The surface carbon was converted into CH_4 with a selectivity of nearly 100% without formation of other hydrocarbons. This methanation reaction proceeded above 150 °C, and its conversion ratio and the initial rate reached a maximum at 300 °C. The most reactive carbon, which was converted into CH_4 at 150 °C, was found by this isothermal methanation. Analysis of Fig. 2a showed that CH_4 evolution curves (curves A–D) were composed of the rapid methanation within 5–10 min and slow methanation after 5–10 min. The reactive carbon of the former is called an RT-carbon (rapidly transformed carbon). The amounts of RT-carbon expressed by the conversion ratio are shown in Table II. The amount of RT-carbons converted to CH_4 increased with increasing temperature when the surface carbon was the same in each experiment. If reactivity of the surface carbon was independent of temperature then the conversion ratio should have assumed the same value. The initial rate of CH_4 evolution decreased drastically at 350 °C (curve E in Fig. 2a), since the RT-carbon would be transformed into another carbon less reactive for methanation above 350 °C. Thus, the surface carbon (RT-carbon with C-density = 0.4) was highly reactive for methanation with H_2 gas below 300 °C.

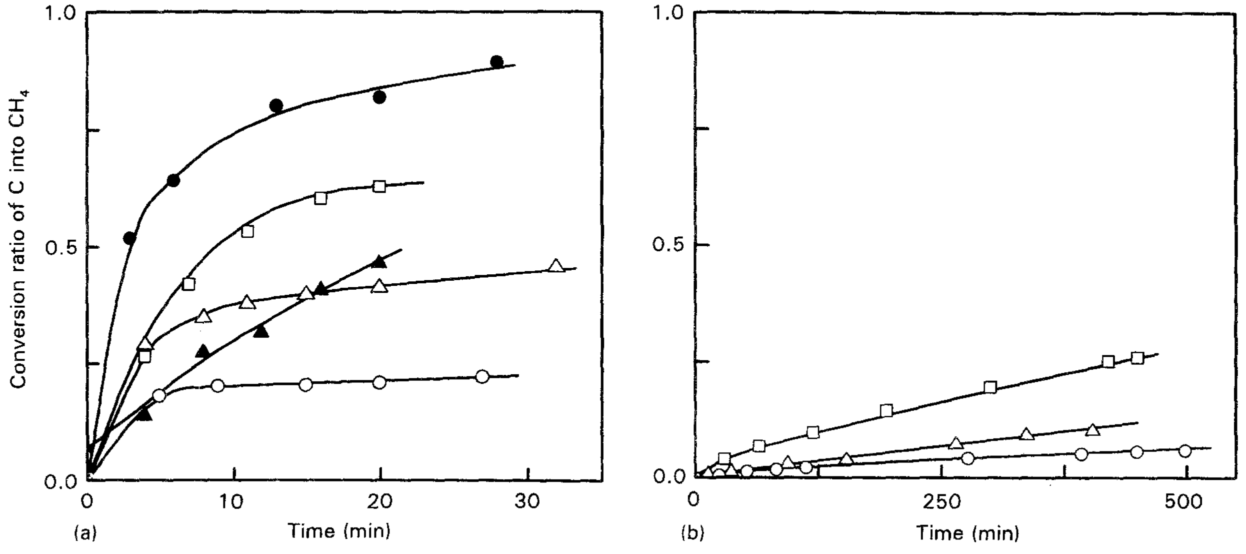

Figure 2 Time variation of the conversion ratio of surface carbon on the oxygen-deficient magnetite into methane. (a) C-density = 0.4; reaction temperature (°C): ○, 150; △, 200; □, 250; ●, 300; ▲, 350. (b) C-density = 2.0; reaction temperature (°C): ○, 400; △, 450; □, 500.

TABLE II The amount of the RT-carbon deposited on the surface of the oxygen-deficient magnetite (C-density = 0.4)

Curves in Fig. 2a	Methanation temp. (°C)	RT-carbon ratio[a]
A	150	0.20
B	200	0.25
C	250	0.45
D	300	0.65

[a] The RT-carbon ratio is expressed by the conversion ratio into CH_4.

TABLE III Activation energy of the surface carbon on the oxygen-deficient magnetite

C-density	Reaction temp. (°C)	Activation energy ($kJ\,mol^{-1}$)
2.0	400–500	90.5
0.4	150–300	17.7

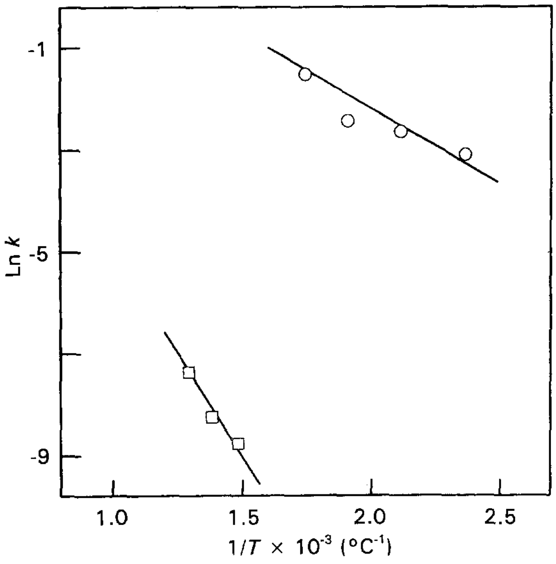

Figure 3 Arrhenius plot of the initial generation rate of methane from the surface carbon on the oxygen-deficient magnetite. ○, C-density = 0.4; □, C-density = 2.0.

Reactivity of the surface carbon also changed with C-density. Fig. 2b shows the time variation of the conversion ratio of the surface carbon with C-density = 2.0 into CH_4 with H_2 under isothermal conditions in the temperature range of 400–500 °C in the closed system. This carbon was not transformed to CH_4 with H_2 gas below 400 °C. The surface carbon was converted into CH_4 with a selectivity of nearly 100% without formation of other hydrocarbons. The surface carbons with C-density = 2.0 were less reactive compared with those of C-density = 0.4. The decrease in reactivity would be due to the polymerized carbon at a high density. The difference in reactivity between the RT-carbon and C-density = 2.0 can be expressed by the activation energy. The activation energy changed from 17.7 (C-density = 0.4) to 90.5 $kJ\,mol^{-1}$ (C-density = 2.0) (Table III), which were calculated on a basis of the Arrhenius plot (Fig. 3).

Acknowledgement

The present work was partially supported by a Grant-in-Aid for Science Research No. 03203216 from the Ministry of Education, Science and Culture.

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Received 20 November 1993
and accepted 21 March 1994