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Methanation of carbon deposited directly from CO_2 on rhodium-bearing activated magnetite

K. NISHIZAWA, H. KATO, K. MIMORI, T. YOSHIDA, N. HASEGAWA, M. TSUJI, Y. TAMAURA
Department of Chemistry, Research Centre for Carbon Recycling and Utilization, Tokyo Institute of Technology, Ookayama, Meguro-Ku, Tokyo 152, Japan

Methanation reactivity was studied for the surface carbon deposited from CO_2 on the surface of Rh-bearing activated magnetite. The most active material (Rh = 0.83 wt %) for methanation was prepared by the impregnation method at 60 °C and showed 98% conversion at 300 °C. The surface carbon was composed of elemental carbon (α-carbon) and polymerized carbon (β-carbon), the proportion being dependent on the density of carbon deposited. In temperature-programmed surface reaction, the extent of conversion of the α- and β-carbon to CH_4 was 0.34 (α-carbon) and 0.53 (β-carbon), respectively,, and the total conversion was 0.87. This result indicates that not only elemental carbon but polymerized carbon (β-carbon) could be converted to CH_4 on the Rh-bearing activated (α-carbon)magnetite, whereas β-carbon is not hydrogenated on activated magnetite.

1. Introduction

CO_2 has been decomposed to carbon with a high efficiency (nearly 100%) at 300 °C on magnetite activated by passing H_2 gas through magnetite [1]. In this reaction, the oxygens of the CO_2 gas incorporated into the oxygen-deficient sites of activated magnetite during the deposition of carbon on the surface of the activated magnetite, while keeping the spinel-type structure. The chemisorption of CO_2 can be expressed by the Langmuir dissociative isotherm for three fragments: one carbon atom and two oxygen ions, and its isosteric heat of adsorption was evaluated to be 40 kJ mol^{-1}, which is around the energy for decomposition of CO_2 to three atoms [2]. Thus, in the adsorption reaction, there seems to be involved a reduction step of the surface carbon; carbon (4 +) may be reduced to zero-valenced carbon, and the carbon atoms will deposit on the surface of the activated magnetite. The X-ray photoelectron spectroscopy (XPS) spectrum showed that carbon was deposited as amorphous or graphite species on the surface of the activated magnetite [3]. The carbon powder could be recovered in visible amounts by the dissolution process into 5.8 N HCl solution.

CO_2 decomposition to carbon with Rh-bearing activated magnetite (Rh-AM) has also been studied in comparison with activated magnetite (AM) [4]. The Rh-AM or AM were prepared by passing H_2 gas through Rh-bearing magnetite (Rh-M) or magnetite (M), respectively, at 300 °C. The activation rate from Rh-M to Rh-AM was about three times faster than that from M to AM at 300 °C. The reactivity for CO_2 decomposition to carbon with Rh-AM (70% of CO_2 was decomposed in 40 min) was higher than with AM (30% in 40 min) at 300 °C.

The methanation reactivity of the surface carbon with H_2 has been studied by isothermal methanation and temperature-programmed surface reaction (TPSR) measurement and is described as follows [5]. The reactivity of the surface carbon obtained by the CO_2 decomposition reaction depends on the C-density (number of carbon atom per unit surface area (1 nm^2)). The extent of conversion of the surface carbon to CH_4 was 0.89 at 300 °C when the surface density was low. The carbon became less reactive for the methanation reaction above 350 °C since the carbon was polymerized.

In the present work, the reactivity was studied by measuring the conversion rate of the surface carbon to CH_4 with H_2 for surface carbon deposited on the surface of Rh-AM by the direct decomposition of CO_2.

2. Experimental procedure

2.1. Preparation of magnetite and Rh-bearing magnetite

Magnetite powder was prepared by the air oxidation method; the Fe(II) hydroxide suspension (Fe(II) = 4.8 × 10^{-2} mol; $FeSO_4$) was oxidized in a 3 dm^3 beaker by passing air through at pH 10 and at 65 °C [6, 7]. The black precipitate of magnetite particles thus synthesized was washed with water and acetone successively, and dried *in vacuo* at 50 °C. The BET specific surface area of the magnetite powder was determined to be 21 m^2 g^{-1}.

Magnetite powder (2.0 g) was suspended in an aqueous solution of $RhCl_3 \cdot 3H_2O$ (1.5×10^{-1} mol dm^{-3}). The pH of the $RhCl_3$ solution was adjusted to 5.0 with 0.1 mol dm^{-3} NaOH before adding magnetite powder, to prevent the dissolution of magnetite in the

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strongly acidic solution. The pH of the suspension (preparation pH) was adjusted to 10.0 with 0.1 mol dm^{-3} NaOH solution. This impregnation process was performed at room temperature and at 60 °C. The precipitates were collected by decantation and dried in air at 120 °C for 15 h. The samples thus obtained were subjected to X-ray diffractometry with FeK_α (model RAD-2A diffractometer, Rigaku) to identify the solid phase. The chemical composition of the sample was determined by colorimetry using 2,2′-bipyridine complex and inductively coupled plasma (ICP) spectroscopy (Seiko SPS7000 plasma spectrometer).

2.2. Carbon deposition and methanation reaction

The CO_2 to C decomposition reaction with Rh-AM or AM was studied using a reaction cell in a closed system. The M or Rh-M (1.0 g) was placed in a quartz tube with a diameter of 8 mm and a length of 330 mm (the reaction cell). It was set up in an electric furnace and heated to the desired temperature. The temperature was measured with a Chromel–Alumel thermocouple in contact with the outer surface of the quartz tube of the reaction cell, and controlled within ± 0.3 °C using a regulator (Chino Model DB1150). After evacuation of the reaction cell, H_2 gas was passed through the Rh-M or M for 2 h (flow rate 10 cm^3 min^{-1}) to obtain Rh-AM or AM. After evacuating residual gases from the reaction cell again, the inlet and the outlet gas valves were closed and CO_2 gas (0.5 cm^3) was injected into the reaction cell. After allowing the cell to stand for 10 min to deposit carbon on the surface of the Rh-AM or AM, the reaction cell was evacuated and the temperature adjusted to the desired value (150–400 °C). H_2 gas was then injected at ambient pressure. The content of evolved gas was determined by a gas chromatograph (Shimadzu GC-8A) equipped with molecular sieve 13X or Porapak Q columns.

2.3. Temperature-programmed surface reaction

In the measurement of TPSR spectra of the surface carbon, CO_2 gas was injected into the reaction cell containing Rh-AM (1.0 g) at 300 °C. By keeping the reaction cell in the electric furnace (300 °C) for 10 min, carbon was allowed to deposit. It then was evacuated and quenched to room temperature. The TPSR was measured by raising the temperature at a heating rate of 20 °C min^{-1} from room temperature to 700 °C while passing H_2 gas (20 cm^3 min^{-1}) in a flow system through the Rh-AM. The product gases (hydrocarbons) were determined by a gas chromatograph equipped with an FID detector. The gas composition was determined by a chromatograph equipped with a TCD detector.

3. Results and discussion

3.1. Rh-bearing activated magnetite

The X-ray diffraction pattern of Rh-M showed only the peaks corresponding to those of the spinel-type compound, and no other peaks corresponding to α-Fe_2O_3 or iron oxide hydroxides such as α-FeO(OH) were observed. The lattice constant (a_0) of Rh-M was 0.8348 nm, which was close to the value for maghemite (γ-Fe_2O_3; 0.8353 nm). The X-ray diffraction pattern of Rh-AM also showed only peaks corresponding to those of the spinel-type compound, and no peaks for metallic iron were observed. The a_0 of Rh-AM was 0.8394 nm, which was close to the value for stoichiometric magnetite (0.8396 nm: JCPDS card No. 19–629). These results indicate that the magnetite phase is activated by H_2 reduction [1].

3.2. Methanation by various Rh-bearing activated magnetites

Five samples were used for the methanation reaction: (i) Rh-bearing magnetite impregnated at 25 °C (Rh-$M_{T=25}$), (ii) Rh-bearing magnetite impregnated at 60 °C (Rh-$M_{T=60}$; sample 2 in Table I), (iii) magnetite (M), (iv) metallic rhodium (Rh) and (v) a mixture of magnetite and metallic rhodium powder (Rh/M). Each sample was reduced for 2 h by passing H_2 gas through it at 300 °C, followed by CO_2 decomposition to carbon at 300 °C. The methanation reaction was then carried out for the deposited carbon at 300 °C. Fig. 1 shows the time variation of the conversions of carbon. Little CH_4 was evolved on sample Rh (curve E in Fig. 1). Conversions on the samples M, Rh/M and Rh-$AM_{T=25}$ were around 30 to 40% (curves B, C and D in Fig. 1). The highest conversion was obtained on the sample Rh-$AM_{T=60}$ (curve A in Fig. 1) (conversion = 77%, 30 min). In the case of sample M it was essential to pass H_2 gas for 12 h to get good methanation (conversion = 89%, 30 min) [5]. However, in the case of the sample Rh-$AM_{T=60}$, a reactivity comparable to that of sample M could be obtained by 2 h of H_2 reduction. Removal of oxygen ions from the spinel-type structure compound with H_2 was accelerated by the presence of Rh. This enhancement would be due to an increase in the metallic rhodium on the surface of magnetite. In this impregnation method, a colloidal metallic rhodium will possibly be

TABLE I Chemical composition of Rh-bearing magnetite

No.	Chemical composition	Rh/Fe	Fe^{2+}/Fe^{total}	Rh (wt %)	CH_4 conversion[a]
1	$(Rh_2O_3)_{0.004}(Fe_{3.00}O_{4.45})$	2.36×10^{-3}	3.35×10^{-2}	0.30	0.639
2	$(Rh_2O_3)_{0.010}(Fe_{3.00}O_{4.44})$	6.50×10^{-3}	1.89×10^{-2}	0.83	0.980
3	$(Rh_2O_3)_{0.013}(Fe_{3.00}O_{4.40})$	8.63×10^{-3}	3.76×10^{-2}	1.10	0.374

[a] Conversion of C to CH_4 with H_2 at 300 °C for 30 min reaction.

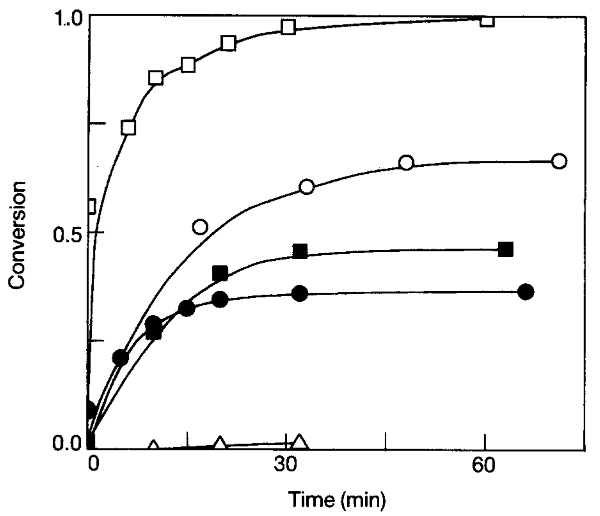

Figure 1 Time variation of the conversion of surface carbon to CH_4 on various samples: (□) Rh-AM$_{T=60}$, (○) Rh-AM$_{T=25}$, (■) M, (●) Rh/M, (△) metallic Rh; C-density 0.4, reaction temperature 300 °C.

deposited on the surface of magnetite, but in sample Rh/M the metallic rhodium will be present in a larger particle size. In the impregnation solution, rhodium ion initially exists in the trivalent state Rh^{3+}. This ion is precipitated to form $Rh(OH)_3 \cdot nH_2O$ by adding NaOH. However, a surface ion-exchange reaction occurs instead of the precipitation in the presence of magnetite. Hydroxide ions adsorbed on the surface of magnetite are replaced by the rhodium hydroxide species. This exchange reaction may contribute to an increase in surface area. It proceeds more readily at 60 °C than at 25 °C. The rhodium-deposited magnetite from impregnation at 60 °C will therefore have a larger surface area which enhances the activity of the material. The activated magnetite, some of whose lattice oxygens are removed by the H_2 reduction, can decompose CO_2 at 300 °C [1]. The reactivity for the decomposition of CO_2 to carbon is enhanced by the increase in oxygen deficiency produced by removal of lattice oxygen from the magnetite [8]. From the above results, metallic Rh is considered to accelerate the removal of oxygen from Rh-M. This acceleration will come from the dissociative adsorption process $H_2 \rightarrow 2H_{ads}$ on the surface of the metallic Rh, where H_{ads} means the atomic hydrogen adsorbed [4]. This H_{ads} will readily react with the lattice oxygen to form H_2O. Therefore the activation of Rh-M will be enhanced with highly dispersed metallic Rh. This large oxygen deficiency produced by the presence of metallic Rh seems to elevate the reactivity for CO_2 decomposition to carbon and to contribute to the rapid methanation of the surface carbon.

Table I shows the chemical analysis of Rh-AM$_{T=60}$ samples with different molar ratios Rh/Fe. Three samples were prepared by the impregnation method at 60 °C. The methanation reactivity of each sample was measured. Each sample was activated for 2 h by passing H_2 gas through it at 300 °C, followed by CO_2 deposition to carbon at 300 °C. Table I also summarizes the conversion ratios of the deposited carbon to CH_4 with H_2 gas at 300 °C for 30 min reaction in the closed system. The most reactive sample was sample 2 containing 0.83 wt % Rh, where a conversion of 0.980 was attained. This sample 2(Rh-M$_{T=60}$) was used for all the following reactions.

3.3. Isothermal methanation reaction

Fig. 2a shows the time variation of the conversion of surface carbon to CH_4 on Rh-bearing activated magnetite with a C-density 0.4 under isothermal conditions in the temperature range 150–300 °C. The surface carbon was converted to CH_4 with a selectivity of nearly 100% without formation of other hydrocarbons. This methanation proceeded above 150 °C, and its conversion and initial rate were at a maximum at 300 °C. In the methanation using magnetite, the reaction consisted of rapid methanation within 10 min and slow methanation after 10 min. The reactive carbon of

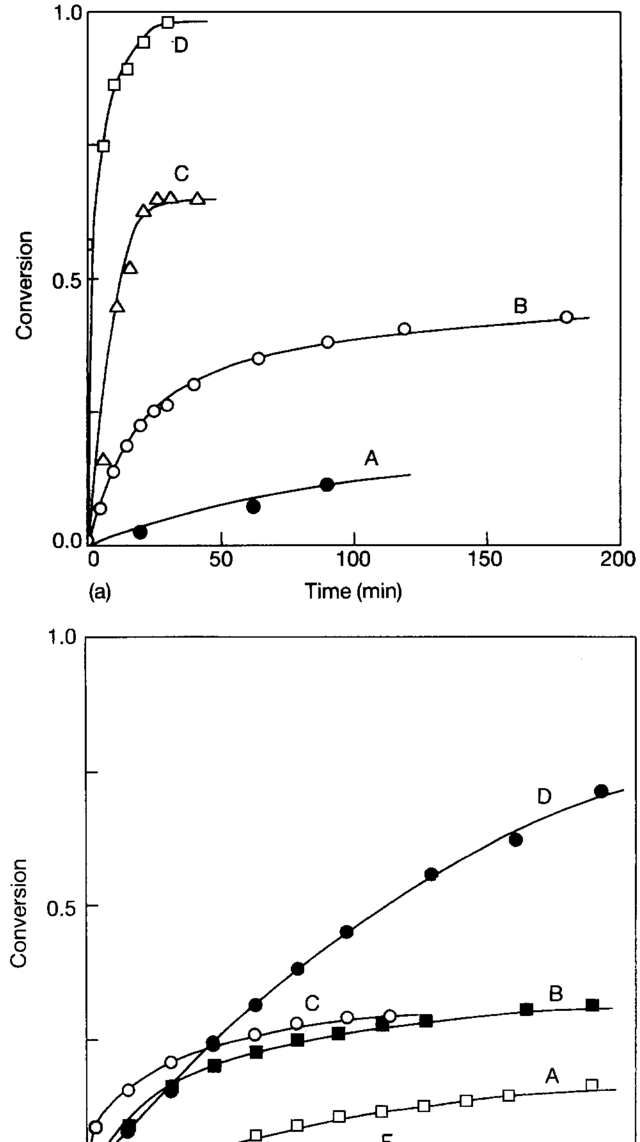

Figure 2 Time variation of the conversion of surface carbon to CH_4 on Rh-AM. (a) C-density 0.4, reaction temperature (●) 150 °C, (○) 200 °C, (△) 250 °C, (□) 300 °C. (b) C-density 2.0, reaction temperature (□) 200°C, (■) 250°C, (○) 300 °C, (●) 350 °C, (△) 400 °C.

TABLE II Activation energy of surface carbon on Rh-bearing activated magnetite

C-density	Reaction temperature (°C)	Activation energy ($kJ\,mol^{-1}$)
2.0	150–300	69.0
0.4	150–300	91.1

the former is called rapidly transformed carbon (RJ-carbon) [5]. The surface carbon (RT-carbon with C-density 0.4) is highly reactive for methanation with H_2 gas below 300 °C. Table II lists the activation energies in the methanation reaction of surface carbon deposited on the sample Rh-$AM_{T=60}$. The activation energy for the methanation of surface carbon deposited on sample Rh-$AM_{T=60}$ with C-density 0.4 (91.1 $kJ\,mol^{-1}$) was larger than that on the sample M with C-density 0.4 (17.7 $kJ\,mol^{-1}$) [5]. However, the methanation rate on sample Rh-$AM_{T=60}$ was faster than on sample M. These results suggest that the methanation reaction of surface carbon is facilitated by metallic Rh, but the reaction temperature is restricted.

The reactivity of the surface carbon is also changed by the C-density. Fig. 2b shows the time variation of the conversion of surface carbon with C-density 2.0 to CH_4 with H_2 under isothermal conditions in the temperature range 200–400 °C in the closed system. This carbon was not transformed to CH_4 with H_2 gas below 200 °C. The reactivity was the highest at 350 °C. The surface carbon was converted to CH_4 with a selectivity of nearly 100% without formation of other hydrocarbons. The surface carbon with C-density 2.0 is less reactive compared with that of C-density 0.4. However, it is surprising that the methanation proceeds above 200 °C on sample Rh-$AM_{T=60}$, although it does not proceed below 400 °C on the sample M. The maximum conversion (0.72 for 60 min reaction) was obtained for methanation at 350 °C on sample Rh-$AM_{T=60}$, whereas the value was 0.11 on sample M. The initial rate of methanation obeyed the Arrhenius plot in the temperature range 200–300 °C. The activation energy was 69.1 $kJ\,mol^{-1}$ for the methanation of surface carbon deposited on sample Rh-$AM_{T=60}$ with C-density 2.0. It was smaller than that on sample M with C-density 2.0 (90.5 $kJ\,mol^{-1}$) [5]. The reactivity of the carbon deposited decreased on sample M when the C-density was large. This is due to the polymerization of the elemental carbon. In contrast, not only elemental carbon but polymerized carbon could be converted to CH_4 on sample Rh-$AM_{T=60}$.

3.4. TPSR spectra

The reactivity of the surface carbon deposited on sample Rh-$AM_{T=60}$ was also studied by temperature-programmed surface reaction. The temperature dependence for the reactivity of carbon may be estimated by TPSR. Fig. 3a shows the TPSR spectrum of the carbon with C-density 0.4 deposited on sample Rh-$AM_{T=60}$. Gas chromatography showed that CH_4 was exclusively formed, and other hydrocarbons, CO or CO_2 were not detected during the TPSR experiment. The results of peak analysis of Fig. 3a (peak temperature and conversion) are given in Table III. One large peak and one small peak (α and β) of CH_4 evolution appeared, indicating that there seem to be two states (mainly α and β) in the surface carbon deposited from CO_2 on Rh-$M_{T=60}$ at 300 °C (C-density 0.4). The conversion of the α-carbon to CH_4 was 0.81. This value is equal to that of the carbon deposited on sample Rh-$AM_{T=60}$ in the isothermal methanation reaction (300 °C, curve A in Fig. 1). In the TPSR of carbon deposited from CO_2 on the surface of sample M, α-carbon appeared at 314 °C and its conversion to CH_4 was 0.43 [5]. This small value is due to the transformation of α-carbon to β- and γ-carbon before the methanation of the α-carbon is completed during raising of the temperature to 300 °C in the TPSR experiment. The β-carbon (polymerized carbon; 314 °C) and γ-carbon (carbide; 437 °C) are less reactive and their conversions to CH_4 were low: 0.28 for β-carbon and 0.29 for γ-carbon. These β- and γ-carbons are not intrinsically present among the deposited carbons, but formed from α-carbon above 300 °C during the TPSR experiment. On the other hand, all the carbons deposited from CO_2 on sample Rh-$AM_{T=60}$ were α-carbon. The peak temperature for α-carbon (236 °C) on sample Rh-$AM_{T=60}$ is lower than on sample M (278 °C) [5], and the methanation of α-carbon was completed below 300 °C before α-carbon was transformed to β- and γ-carbon. These results show that the methanation rate was fast even below 300 °C on Rh-AM. This result corroborates the result from the isothermal methanation reaction.

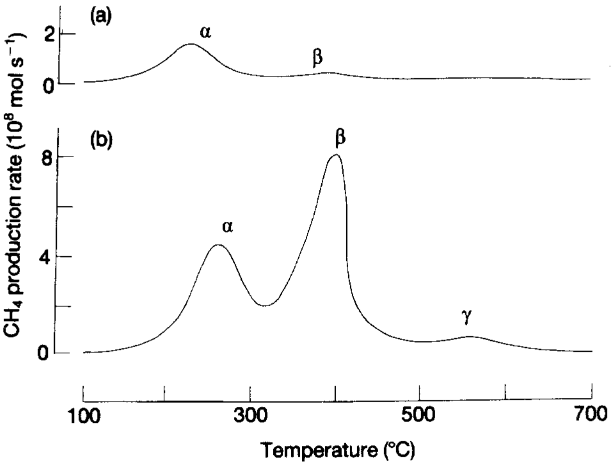

Figure 3 TPSR spectra for the methanation of surface carbon deposited by the decomposition of CO_2 with (a) Rh-bearing activated magnetite (C-density 0.4), (b) Rh-bearing activated magnetite (C-density 2.0).

Fig. 3b shows the TPSR spectrum of surface carbons with C-density 2.0 deposited on sample Rh-$AM_{T=60}$ at 300 °C. Gas chromatography showed that CH_4 was exclusively formed, and other hydrocarbons, CO or CO_2 were not detected. The results of peak analysis of Fig. 3b are given in Table III. Three peaks (large peaks α and β, small peak γ) were observed, indicating that there seems to be mainly two states

TABLE III CH_4 peak temperature in TPSR spectra of surface carbon deposited by decomposition of CO_2 on Rh-bearing activated magnetite.

C-density	State of carbon	Peak temperature (°C)	Conversion
0.4	α	236	0.81
	β	381	1.2×10^{-3}
2.0	α	257	0.34
	β	384	0.53
	γ	534	3.6×10^{-3}

(α and β) in the surface carbon deposited from CO_2 on sample Rh-$AM_{T=60}$ with C-density 2.0 at 300 °C. A certain amount of α-carbon was polymerized to β- and γ-carbon during the carbon deposition from CO_2, but the conversion to CH_4 was 0.34 for α-carbon and 0.53 for β-carbon with a total conversion of 0.87. In TPSR of the carbon deposited from CO_2 on sample M with C-density 2.0, only β-carbon appeared at 322 °C and its conversion to CH_4 was 0.11 [5]. The α-carbon is transformed to β-carbon on sample M at 300 °C when the C-density is large. This small value means that β-carbon is less reactive for hydrogenation even at high temperature (500 °C) in the TPSR. The carbons deposited on sample Rh-$AM_{T=60}$ were α- and β-carbon (Fig. 3b). Polymerization of the α-carbon to β-carbon is due by two processes: one is deposition of an excessive amount of carbon and the other is polymerization during heating above 300 °C. About 60% of the α-carbon deposited was transformed to β-carbon. Almost all the β-carbon was converted to CH_4 while the α-carbon was readily transformed to CH_4 below 300 °C. This result indicates that not only elemental carbon (α-carbon) but polymerized carbon (β-carbon) were transformed to CH_4 on sample Rh-$AM_{T=60}$. This reactivity for methanation can be ascribed to the metallic Rh deposited on the surface of the magnetite. Atomic hydrogen will provide a large extent of oxygen deficiency on Rh-AM which is essential to the methanation. This active atomic hydrogen will be able to transform even polymerized carbon to CH_4.

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