Preparation of ultrafine Fe–Si–C powders in a radio-frequency thermal plasma and their catalytic properties

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Ultrafine Fe–Si–C powders were prepared from mixed gases of SiH_4–CH_4–$Fe(CO)_5$ using a newly developed thermal-plasma apparatus with a dual-radio-frequency-coupled-plasma-torch system. The phases of the powders prepared were classified into two groups; one composed of β-$FeSi_2$ which was prepared by rapid quenching, while the other was composed of α-Fe, Fe_3Si, Fe_5Si_3, FeSi, β-SiC and amorphous Si, which were prepared by slow quenching. The diameters of these powders were in the range 5–50 nm. The catalytic activities of these powders for Fischer–Tropsch synthesis were examined. The ultrafine β-$FeSi_2$ powder was very active for the selective formation of olefin. On the other hand, powders of α-Fe, Fe_3Si and Fe_5Si_3 were low in their selectivity but gave high CO conversion. Relations between the plasma conditions for the preparation of ultrafine Fe–Si–C powders and their catalytic properties are discussed.

1. Introduction

Ultrafine powders of 1–50 nm have remarkable properties which are different from those of bulk materials. One of their most hopeful fields of application is as a catalyst.

The diameter of a catalyst is one of the main factors controlling both the activity and selectivity of a catalytic reaction. Ultrafine powders have very large specific surface areas. Therefore, they are expected to promote catalytic reactions. Moreover, the surface structure of ultrafine powders is thought to be different from that of a bulk material. This phenomenon would also be expected to give high selectivity in a catalytic reaction.

The phase of a catalyst is also important. New phases of carbides and nitrides in ultrafine powders have recently been paid strong attention because of their potential as new catalysts [1]. However, it has been very difficult to prepare these powders by a conventional wetting method. Many kinds of ultrafine powders of oxides and metals used as catalysts, on the other hand, have been prepared by the conventional method.

Fe, Co or Ru metal are usually used as catalysts for the Fischer–Tropsch reaction, but they are lacking in their selectivity and stability [2]. Therefore, Yardley and Gupta [3] prepared ultrafine Fe–Si–C powders preliminarily by a CO_2 laser chemical vapour deposition (CVD) method. They found that mixed phases of $FeSi_2$, Si and SiC gave high selectivity for the olefin formation in the Fischer–Tropsch synthesis reaction. The laser CVD, however, is at a disadvantage because at least one of the starting materials should be excited

by the laser and it is very difficult to prepare large amounts of product.

Radio-frequency (r.f.) thermal plasmas have been a powerful method of preparing ultrafine carbide powders. They are deposited after the rapid quenching of clusters and crystalline nuclei produced in the plasma. In the case of the thermal-plasma CVD method, large amounts of ultrafine powders are produced from many kinds of reactants which do not need to be excited by photons as is the case with laser CVD. Recently the authors developed a new r.f. thermal-plasma system, which is called a dual-r.f.-thermal-plasma-torch system. The features of this system have already been reported by Kameyama *et al.* [4].

This report studies the preparation of ultrafine Fe–Si–C powders using the dual-r.f.-plasma apparatus and examines their catalytic activities in the Fischer–Tropsch synthesis reaction.

2. Experimental procedure

2.1. Dual-r.f.-thermal-plasma-torch system

Fig. 1 shows a schematic drawing of the dual-r.f.-thermal-plasma-torch system for preparing ultrafine Fe–Si–C powders. R.f. power is loaded to the plasma gas through the electromagnetic work coil. A small plasma torch for ignition of the main plasma is composed of coaxial double quartz tubes and two nozzles as shown in Fig. 1. The small plasma is first ignited under argon gas at atmospheric pressure by a conventional Tesla coil in an argon stream of $4\,l\,min^{-1}$ supplied from port (1) and $10\,l\,min^{-1}$ from port (2) with a power of 1.0 kW at a frequency of 27.12 MHz.
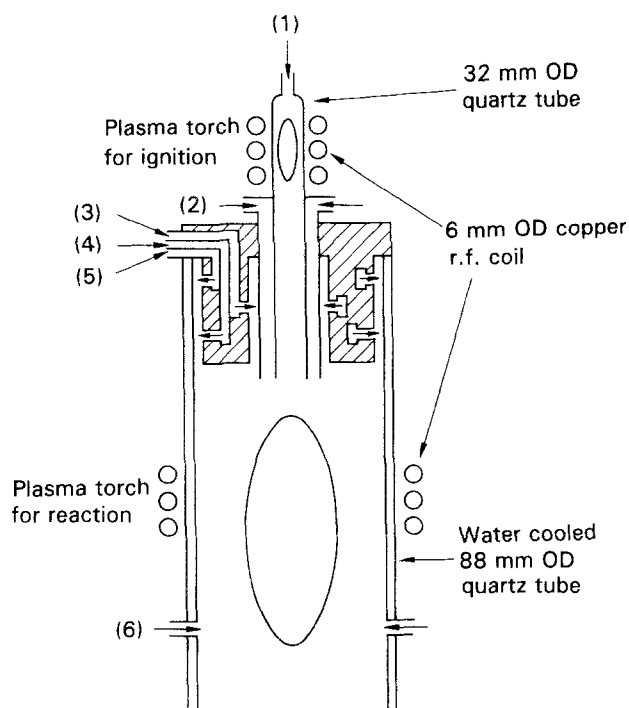
Figure 1 Drawing of a dual-r.f.-torch system. Ar gas is fed from the following ports: (1) axially, (2) tangentially, (3) tangentially inside, (4) radially outside, (5) tangentially outside and (6) radially. (OD is the outer diameter.)

Figure 2 A chamber for the preparation of ultrafine Fe–Si–C powders. The powders are collected at: (A) the inner wall of the torch, (B) a quartz tube, and (C) a copper cylinder. Ar gas is fed from (1) and (2) for plasma generation and from (3), (4) and (5) for the quenching reaction. The reactant gases are fed mainly from (2).

The main plasma torch for the reaction is composed of a small plasma-torch head, coaxial double quartz tubes, and four nozzles. Cooling water is introduced between the outer and inner quartz tubes. Argon gas for both cooling the inner quartz tube and confining the plasma in the quartz tube is introduced tangentially from port [5]. Argon gas flows in both the inner tangential direction, (3), and the outer radial direction, (4), also play important roles in forming a plasma flame and controlling its shape. The main plasma is lit by the small plasma at atmospheric pressure.

2.2. Preparation of ultrafine Fe–Si–C powders

Ultrafine Fe–Si–C powders were prepared by using the new dual-r.f.-thermal-plasma-torch system. Fig. 2 shows the chamber for preparing ultrafine Fe–Si–C powders. It consists of two r.f. plasma torches, a reactor chamber, a supply system for plasma gas and reactant gas, a water-cooling system and an exhaust system.

The experimental conditions are shown in Table I. Mixed reactant gases of CH_4, SiH_4, and $Fe(CO)_5$ are introduced mainly into the upper part of the main plasma flame from port (2) or (3) with an argon carrier gas as shown in Fig. 1. In some cases, only $Fe(CO)_5$ is introduced from port (6) separately. $Fe(CO)_5$, which is liquid at room temperature, is heated up to 60°C, and its vapour was carried by argon gas. The flow rate of $Fe(CO)_5$ is controlled by the argon-gas flow rate. The output power and argon-gas flow rate were constant through all the runs. Each run was done for 1 h.

Powders formed in the main plasma were deposited on the following three places as shown in Fig. 2: the
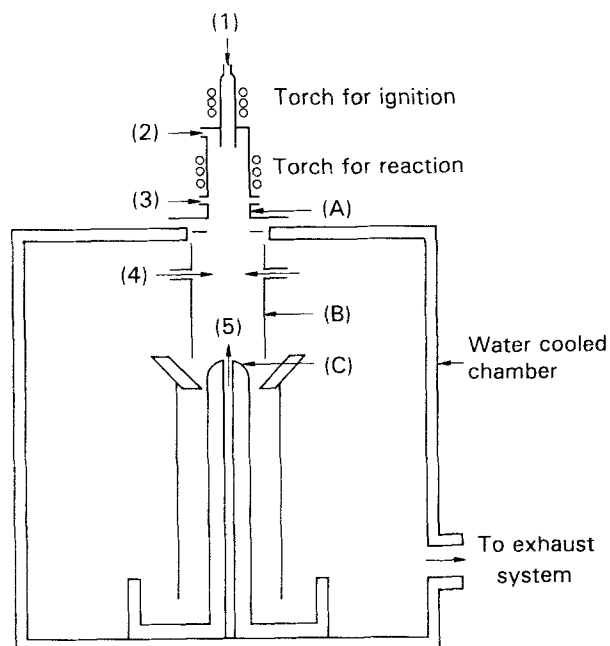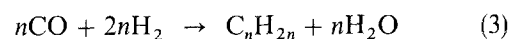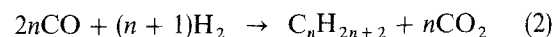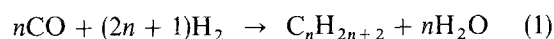
wall of a plasma torch, (A); a quartz-tube collector (B), of 140 mm diameter and 600 mm length; and a copper cylinder, (C), cooled with water.

Characterization of the powders were carried out by the following methods. The phases of powders were identified by an X-ray powder diffraction (XRD) method. The diameters of the powders and their shapes were observed by transmission electron microscopy (TEM). The contents of Si, Fe, free C and total C were measured by inductively-coupled-plasma (ICP) spectroscopy.

The catalytic properties of powders prepared for the Fischer–Tropsch synthesis were examined. Fischer–Tropsch synthesis is a hydrocarbon-formation reaction from CO and H_2. It contains the following reactions.

$$nCO + (2n + 1)H_2 \rightarrow C_nH_{2n+2} + nH_2O \quad (1)$$

$$2nCO + (n + 1)H_2 \rightarrow C_nH_{2n+2} + nCO_2 \quad (2)$$

$$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O \quad (3)$$

$$2nCO + nH_2 \rightarrow C_nH_{2n} + nCO_2 \quad (4)$$

Besides these products, alcohols, esters, etc. are formed. Olefins are very important as raw materials in the chemical industry. The CO_2 formation in Reactions 2 and 4 is not desirable, because it wastes carbon. So reaction 3 is favourable from the view point of olefin formation without CO_2 as a byproduct.

Fig. 3 shows a schematic apparatus for measuring the catalytic activity of ultrafine Fe–Si–C powders. The measurement was conducted in a flow-type-fixed-bed microreactor of stainless steel. About 1.0 g of prepared powder was charged in the reactor as a

TABLE I Conditions for preparing ultrafineFe–Si–C powders

1. Output r.f. power for the reaction:	10 kW, 3 MHZ
2. Output r.f. power for ignition:	1.0 kW, 27.12 MHz
3. Flow rate of argon gas for the plasma:	

Port (1)[a] axially	$4 \, l \, min^{-1}$
Port (2) tangentially	$10 \, l \, min^{-1}$
Port (3) inside, tangentially	$6 \, l \, min^{-1}$
Port (4) outside, tangentially	$10 \, l \, min^{-1}$
Port (5) outside, radially	$4 \, l \, min^{-1}$
Port (6) radially	$6 \, l \, min^{-1}$

Flow rate of reactant gas:	$SiH_4(0.05 \, l \, min^{-1}) + Ar(2 \, l \, min^{-1})$
	$CH_4(0.01 \sim 0.05 \, l \, min^{-1}) + Ar(4 \, l \, min^{-1})$
	$Fe(CO)_5^c(0.008 \, l \, min^{-1} \sim 0.05 \, l \, min^{-1}) + Ar(0.08 \, l \, min^{-1})$

[a]The port numbers are those shown in Fig. 1.
[b]From Port (3) inside, tangentially
[c]In some cases, only $Fe(CO)_5$ is introduced from port (6) as shown in Fig. 1.
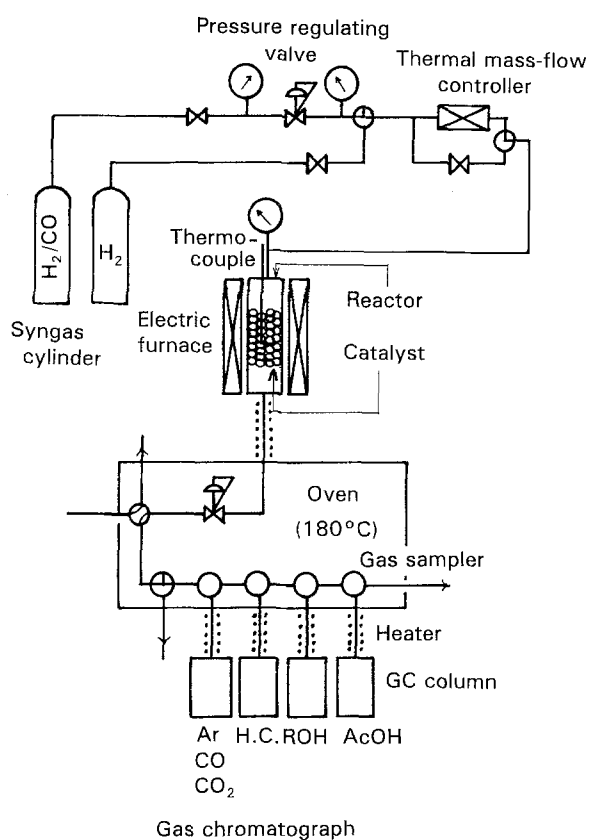

Figure 3 Schematic apparatus for measuring the catalytic behaviour of ultrafine Fe–Si–C powders. The reaction condition are as follows: catalyst charge, 1.0 g; reaction pressure, 1–30 atm; reaction temperature, 250–280 °C; flow rate, 100 ml min^{-1} and syngas ratio (H_2/CO), 2.

catalyst. The reaction temperature was in the range 250–280 °C. The reaction pressure was in the range 1–30 atm. The syngas, which is a mixture of H_2 and CO, and all the products in the reactor were kept hot so that the products were not condensed in the pipe connected to the gas chromatograph. The ratio of H_2 to CO gas was 2, and the flow rate of mixed reactant gases was 100 ml min^{-1}. All the gases through the

reactor were directly introduced into the gas chromatograph. Columns for gas chromatography (such as PEG 1500, VZ 10) and squalane were used for the analysis of the alcohols and esters, and the hydrocarbons and inert gases, respectively.

3. Results and discussion

Ultrafine powders prepared in a thermal plasma were deposited on the inner wall of the plasma torch (A), the quartz tube in the chamber, (B) and the copper cylinder, (C), as shown in Fig. 2. The amounts of the products collected on the copper cylinder, (C), was very small. Table II shows the flow rates of the reactant gases and the phases of the products. The products in run number 1 collected on the torch wall, (A), and on the quartz tube in the chamber, (B), will be called 1A and 1B, respectively. The powders prepared from an equivalent mole of reactant gases in run numbers 1–5, and then collected at the torch wall, (A),

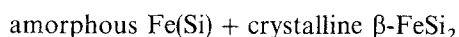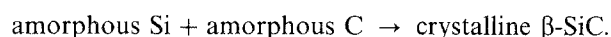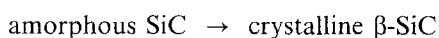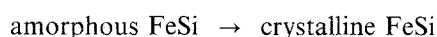TABLE II Reactant gases and products

Run No.	reactant gas flow rate (ml min^{-1}) (port number)[a]			Products	
	SiH$_4$	CH$_4$	Fe(CO)$_5$	A (torch)	B (chamber)
1	50	50	50	Amorphous,	β-SiC, Fe$_3$Si,
	(3)	(3)	(3)	β-FeSi$_2$	amorphous
2	50	50	10	Amorphous,	β-SiC,
	(3)	(3)	(3)	β-SiC	amorphous
3	50	50	50	Amorphous,	α-Fe, Fe$_3$Si,
	(3)	(3)	(6)	Si, β-SiC	β-SiC
4	50	50	10	Amorphous,	FeSi, α-FeSi$_2$,
	(3)	(3)	(6)	Si, β-SiC	Si, β-SiC
5	50	50	50	Amorphous	FeSi, amorphous,
	(2)	(2)	(2)	β-FeSi$_2$	β-SiC
6	50	11	7.5	Amorphous,	α-FeSi$_2$,
	(3)	(3)	(3)	α-FeSi$_2$, Si	Si, β-SiC

[a]The numbers in parentheses show the port, in Fig. 1, through which the reactant gas was injected into the plasma.

mainly had a β-FeSi₂ phase, and small contents of the amorphous phase were also present. Whereas, the powders collected at quartz tube, (B), in the chamber were composed of crystalline Fe₃Si, β-SiC, FeSi and large amounts of the amorphous phase. In addition to these crystalline phases, α-FeSi₂, and Si were also deposited at other runs, as shown in Table II.
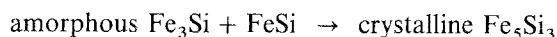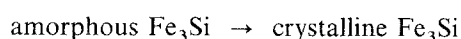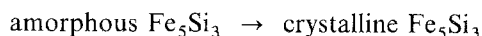
In order to clarify the chemical formula of the amorphous phases in the prepared powders – shown in Table III as Am(A) collected at the torch wall, (A), and Am(B) collected at the quartz tube, (B) – as-deposited powders were calcined at 900 °C for 5 h in Ar which resulted in complete crystallization. The degrees of magnetization were also measured qualitatively using a magnet. The total contents of Fe in the samples were determined by X-ray-fluorescent spectroscopy, the results are shown in Table III. After the calcination, no amorphous phase was detected by the XRD method. α-Fe, amorphous Fe with a small Si content, Fe₃Si, and Fe₅Si₃ were all well magnetized by a magnet because they were ferromagnetic phases [5]. Therefore, during the calcination process, the following reactions must take place corresponding to the phase diagram in [6].

1. In the case of amorphous A, that is Am(A)

   amorphous FeSi → crystalline FeSi

   amorphous SiC → crystalline β-SiC

amorphous Si + amorphous C → crystalline β-SiC.

   amorphous Fe(Si) + crystalline β-FeSi₂

   → crystalline FeSi

Fe(Si) means that small contents of Si are dissolved in an Fe matrix. Thus, amorphous A is thought to have been composed of SiC, Si, C, FeSi and Fe(Si) in the above chemical formulas.

2. In the case of amorphous B, that is Am(B)

   amorphous Fe₅Si₃ → crystalline Fe₅Si₃

   amorphous Fe₃Si → crystalline Fe₃Si

   amorphous Fe₃Si + FeSi → crystalline Fe₅Si₃

Thus, amorphous B is thought to have been composed of Fe₅Si₃, Fe₃Si, and FeSi in these chemical formulas.

The contents of Fe, Si, free C and total C in the prepared powders were analysed by ICP spectroscopy; the result is shown in Table IV. Based on the

TABLE IV Chemical analysis of powders (wt %)

Powders	FCᵃ	TCᵇ	Fe	Si	Total
1A	1.50	3.11	42.67	47.92	93.70
1B	16.14	16.97	36.44	34.88	88.29
3B	–	23.61	30.19	40.71	94.51
4B	–	24.17	2.37	65.98	92.52
5A	0.387	0.85	46.66	47.69	95.20
5B	5.86	6.40	47.72	33.64	87.76
6A	–	0.17	14.24	60.98	75.39
6B	–	7.57	8.53	74.87	90.97

ᵃ Free carbon. ᵇ Total carbon

results shown in Table II–IV, the contents of the phases were assigned as shown in Table V. The phases of the powders prepared are, therefore, classified into two groups: β-FeSi₂ deposited on the torch wall; and α-Fe, Fe₃Si, Fe₅Si₃, FeSi and amorphous Si, deposited on the quartz tube in the chamber.

Fig. 4 shows the TEM photographs of samples, 5A and 5B. They are conglomerates of small particles, whose diameters are from 5 to 50 nm. Other powders showed a similar appearance. They are ultrafine powders, therefore, they are expected to have high catalytic activities.

The catalytic behaviours of these ultrafine Fe–Si–C powders were examined by a Fischer–Tropsch synthesis reaction. The results are summarized in Table VI. Catalysts 1A and 5A give high olefin selectivity; that is, the olefin/paraffin ratios are in the range 15.1–17.5, while this ratio was about 1 in the case of the conventionally prepared Fe catalyst [7]. Catalysts 1B, 3B, and 5B, on the other hand, give high CO conversions of 4.6–6.3%, while their olefin selectivities are very low.

Relations between the catalytic activity of ultrafine Fe–Si–C powders and their phases are shown in Fig. 5. It becomes clear that the β-FeSi₂ phase gives high olefin selectivity. While, the α-Fe, Fe₃Si and Fe₅Si₃ phases give low olefin selectivity but they remarkably promote CO conversion. The reason why β-FeSi₂ gives high olefin selectivity is not clear but some speculations are proposed. It seems to depend on β-FeSi₂ being a semiconducting phase [8] and on the valency of iron in β-FeSi₂ being very high. It has been thought that the high valency of Fe in the catalyst

TABLE III Characterization of the amorphous phase in the prepared Fe–Si–C powders

Run	Feᵃ (wt %)	As-deposited Phase	Magnetizationᵇ	Calcinationᶜ Phase	Magnetization
1A	30.9	Am(A), β-FeSi₂	+ +	FeSi, β-SiC	–
5A	34.2	Am(A), β-FeSi₂	+ +	FeSi, β-SiC	–
1B	34.1	Am(B), Fe₃Si, β-SiC	+ + +	Fe₃Si, Fe₅Si₃, β-SiC	+ + +
5B	43.5	Am(B), FeSi, β-SiC	+ + +	Fe₃Si, Fe₅Si₃, β-SiC	+ + +

ᵃ Total content of Fe in the as-deposited powder
ᵇ + + +, strong; + +, medium; +, weak; –, zero.
ᶜ 900 °C, 5 h, Ar

TABLE V Content of phases of prepared ultrafine Fe–Si–C powders

Phase (mol%)

1A	1B	3B	4B	5A	5B	6A	6B
β-FeSi$_2$ (84)	C (40.7)	β-SiC (68.6)	β-SiC (91.4)	β-FeSi$_2^a$ (96.8)	FeSi (33)	Si (68)	Si (50.2)
SiC (9.8)	Fe$_3$Si + Fe$_5$Si$_3$ (29.6)	Fe$_3$Si^a (9.2–15.4)	Si (6.1)	SiC (2.0)	Fe$_5$Si$_3$ (26.6)	α-FeSi$_2^a$ (32)	β-SiC (36.6)
C (4.6)	Si (25.7)	α-Fe^a (6.8–15.4)	α-FeSi$_2$ (1.5)	C (1.2)	C (18.9)		α-FeSi$_2$ (13.2)
Si (1.6)	β-SiC (4.0)		FeSi (1.0)		Si (18.7)		
					β-SiC (3.4)		

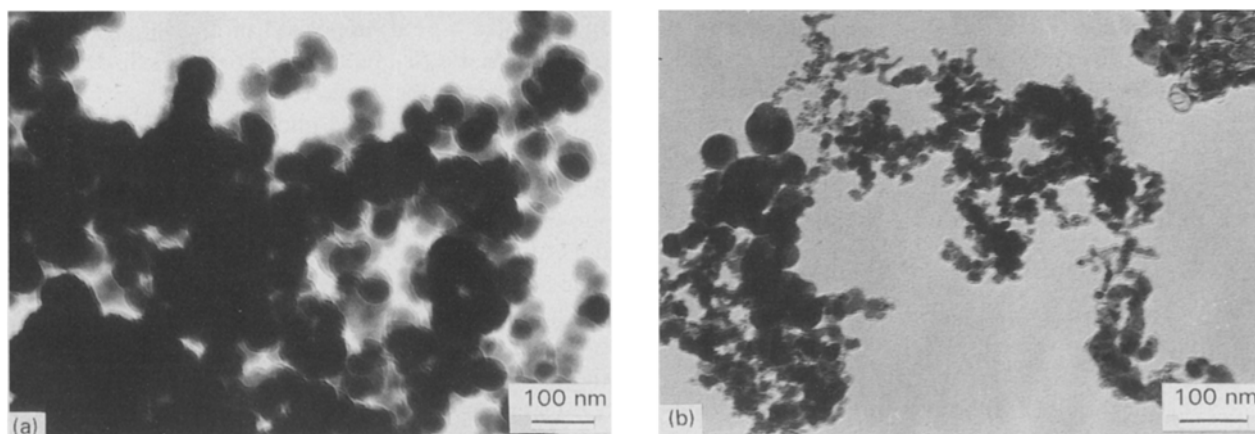^{a}Some carbides are present in the matrix.

Figure 4 TEM observations of Fe–Si–C powders. The phases of (a) 5A and (b) 5B are shown in Table V.

TABLE VI Catalytic behaviour of Fe–Si–C ultrafine powder

Catalyst number[c]	Catalyst charge (g)	H$_2$/CO	T (°C)	P (atm)	CO conv. (%)	Selectivity in carbon efficiency (%)											$\dfrac{C_2^{2-} + C_3^{2-}}{C_2 + C_3}$
						CH$_4$	C$_2^a$	C$_2^{2-\,b}$	C$_3$	C$_3^{2-}$	C$_4$	C$_4^{2-}$	C$_5$	C$_5^{2-}$	CO	Others	
1A	0.7	2	280	1	0.2 ~ 0.3	55.3	1.9	19.8	0.6	18.3	0.0	4.1	0.0	0.0	0.0	0.0	15.2
1B	0.7	2	280	1	6.3	25.7	6.8	4.7	3.1	12.9	2.2	5.7	1.4	3.5	9.5	24.5	1.8
3B	0.7	2	280	1	4.0	32.9	7.7	7.0	3.5	14.6	2.3	5.8	1.4	0.5	0.0	24.3	1.9
4B	0.7	2	280	1	0.4	46.5	5.3	9.4	3.7	12.9	2.5	5.2	0.0	0.0	0.0	0.0	2.5
5A	1.0	2	260	1	0.4	42.4	2.0	21.1	0.6	18.2	0.0	4.0	0.0	0.0	0.0	11.5	15.1
5A	1.0	2	280	1	Trace	42.4	1.9	24.0	0.5	17.9	0.0	4.2	0.0	0.0	0.0	8.9	17.5
5A	1.0	2	280	30	2.05	30.7	7.8	4.9	3.3	11.1	2.4	5.2	1.6	3.3	4.5	22.1	1.4
5B	0.5	2	260	1	5.7	25.2	6.3	4.1	3.5	12.0	2.6	5.9	1.8	3.7	15.5	18.2	1.6
6A	0.4	2	280	1	Trace	76.5	4.6	9.5	2.0	7.3	0.0	0.0	0.0	0.0	0.0	0.0	2.5
6A	0.4	2	280	1	Trace	77.6	3.7	9.9	1.5	7.2	0.0	0.0	0.0	0.0	0.0	0.0	3.3
6B	0.1	1	250	1	0.21	93.6	0.0	6.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	–
6B	0.1	1	256	20	0.13	87.2	3.1	9.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.1

^{a}Ethane. ^{b}Ethylene. ^{c}The number and alphabetical letter of the catalyst show the run number of synthesis and the sampling position, respectively, their phases are shown in Table V.

promotes the olefin selectivity. β-FeSi$_2$ is also expected to work actively as a catalyst under high temperatures because the small content of carbon responsible for the formation of some carbides in the powders of β-FeSi$_2$ may suppress the grain growth and the agglomeration of these ultrafine particles. Thus, they must constantly work as catalysts, even at high temperatures.

Some relations between the thermal-plasma features and phases of the ultrafine Fe–Si–C powders prepared in the plasma are summarized in Fig. 6. Both the temperature and the flow-rate profiles of Ar in a r.f. thermal plasma have already been calculated by Yoshida *et al.* [9]. The maximum temperature near the centre of the plasma was 7000–10 000 K and the minimum temperature was 4000–6000 K around
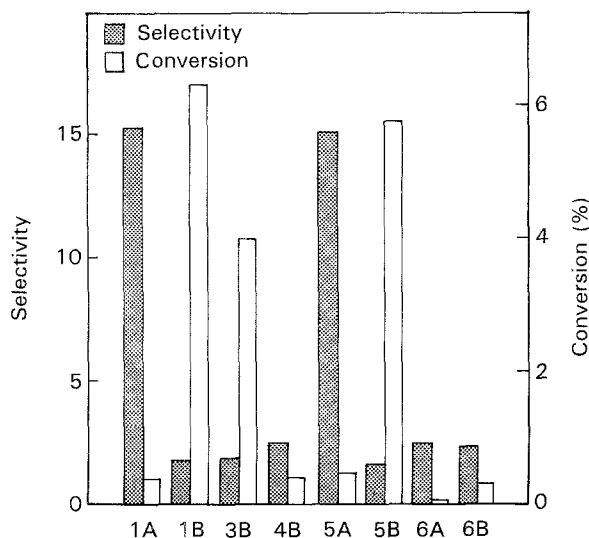
Figure 5 Catalytic activities of ultrafine Fe–Si–C powders. Their phases are shown in Table V.

the margin of the plasma. The flow rates of Ar through the centre of the plasma and around the margin were calculated as 16 m s^{-1} and 4 m s^{-1}, respectively. The maximum temperature of the plasma used in this study was measured as 7500 K by argon-emission spectroscopy [10]. This value seemed to support the above calculated temperature profiles. Using this datum the quenching rates for the ultrafine powders deposited at the torch wall, (A), and quartz tube, (B), were estimated to be 10^6 Ks^{-1} and 10^4 Ks^{-1} respectively. Therefore, ultrafine β-FeSi$_2$ powders, which have a high olefin selectivity in the Fischer–Tropsch synthesis reaction are thought to have been prepared by the rapid quenching process in the r.f. thermal plasma.

From the actual catalyst viewpoint, the authors hope to prepare composite powders of β-FeSi$_2$ at the nanolevel, with α-Fe, or Fe$_3$Si and small contents of carbide, which would give a high olefin selectivity and
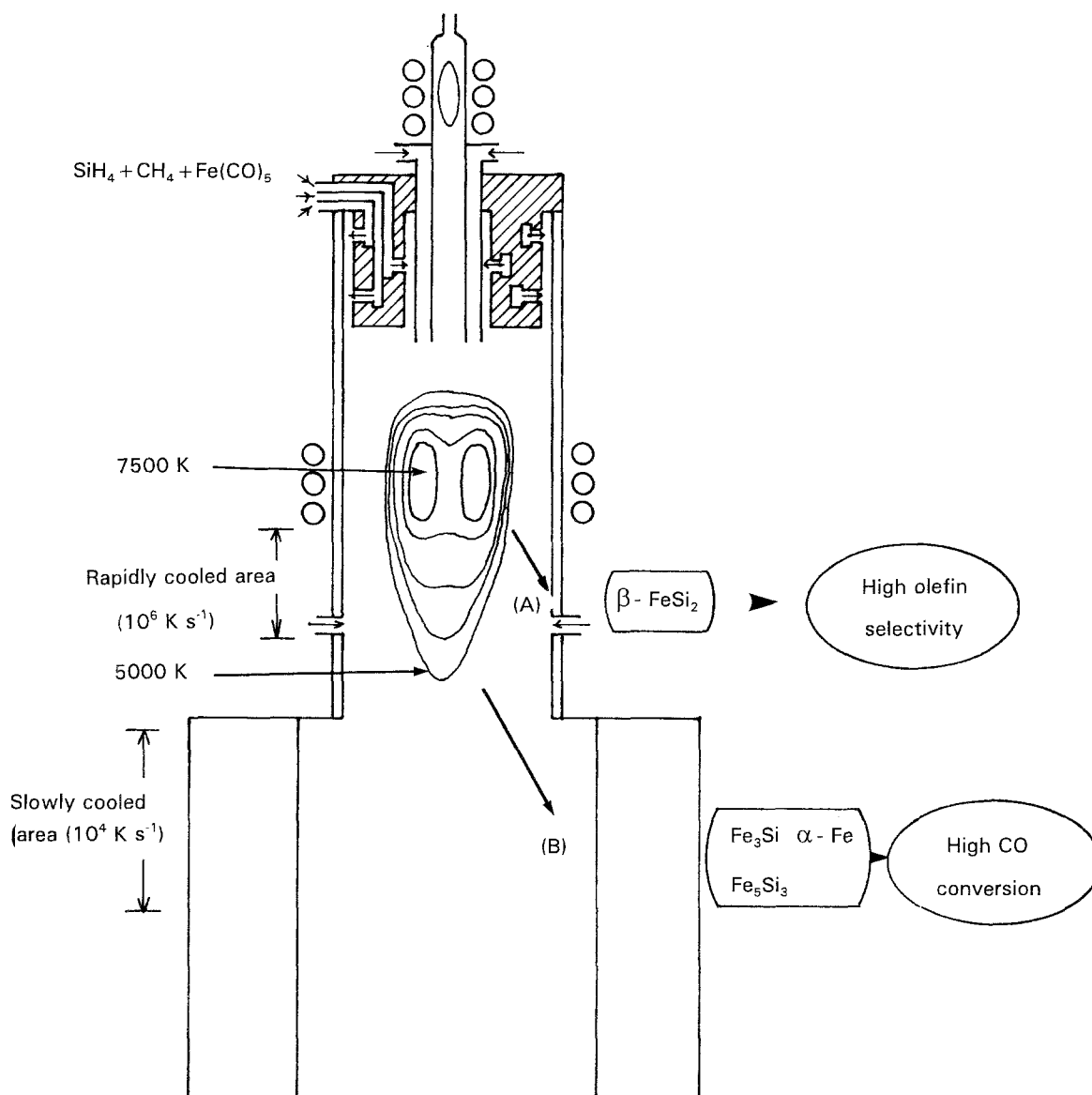

Figure 6 Plasma features and catalytic activities of ultrafine Fe–Si–C powders.

a high CO conversion without degradation of the catalyst under high temperatures.

4. Conclusions

1. Ultrafine Fe–Si–C powders were prepared by a newly developed thermal plasma apparatus with a dual-radio-frequency-plasma-torch system.

2. The phases of the powders prepared from mixed gases of SiH_4–CH_4–$Fe(CO)_5$ were classified into two groups: β-$FeSi_2$, which was deposited at the site of rapid quenching, and a mixed group with α-Fe, Fe_3Si, Fe_5Si_3, FeSi and β-SiC, which were prepared at the site of relatively slow quenching. The diameters of these powders were in the range 5–50 nm.

3. Ultrafine β-$FeSi_2$ powders gave a high olefin selectivity of 15–17 in the Fischer–Tropsch synthesis reaction, while powders composed of α-Fe, Fe_3Si, and Fe_5Si_3 gave a low olefin selectivity of about 2, promoting the CO conversion.

4. The dual-r.f.-thermal-plasma-torch system should become an attractive apparatus for the preparation of ultrafine carbide powders which have great possibilities as new catalysts.

Acknowledgements

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