Catalysis Letters 14 (1992) 75–87

Catalytic behavior of silicon carbide for hydrogen activation

Yasuo Iizuka [1], Hiroshi Kawauchi, Shigeyoshi Arai and Kazunori Kijima

Department of Chemistry, Faculty of Engineering and Design, Kyoto Institute of Technology,
Matsugasaki, Sakyo-ku, Kyoto, 606, Japan

Received 4 March 1991; accepted 30 March 1992

The catalytic activities for hydrogen–deuterium exchange were examined at 473 K for three kinds of SiC powders with different particle sizes. Three SiC powders showed a high activity after outgassing at high temperatures above 873 K. The thermodesorbed gases from SiC were mainly H_2 and CO, and they were produced from the thermal decomposition of adsorbed water on SiC surfaces. The extent of decomposition was found to be parallel to the catalytic activity at 473 K. Therefore, the sites of the decomposition are responsible for the catalytic activity.

Keywords: Silicon carbide; hydrogen exchange; thermodesorbed gases; decomposition of adsorbed water

1. Introduction

In the past 20 years, the catalytic properties of transition metal carbides have been examined extensively, since physical and chemical properties of transition metals changed significantly by the introduction of carbon into metal lattices [1–6]. The observation of analogies between the catalytic properties of WC and those of noble metals has stimulated many investigators [3]. However, the catalytic properties of SiC have rarely been studied yet from this view point. Whereas, the interesting photoelectrocatalytic reduction of carbon dioxide to form organic compounds has been found for SiC powders suspended in water. Reduced compounds such as formaldehyde and methyl alcohol were produced most efficiently on SiC among various photosensitive semiconductor powders [7,8].

Recently Kijima et al. succeeded in the synthesis of ultrafine SiC powder with a nanometer particle size and an ultra high purity (99.999%) by r.f. plasma CVD

---

[1] To whom correspondence should be addressed.

Table 1
Purity and impurities by ICP emission spectrochemical analysis of each type of SiC

	Kijima et al.	Ibiden	Showa Denko
SiC [a]	99.999	99.1	balance
free SiO_2 [a]	– [b]	0.3	0.32
free C [a]	–	0.4	1.32
B [c]	–	47	11
Al	–	650	115
Ca	–	460	361
Ti	–	130	40
Cr	–	46	47
Fe	5	480	325
Cu	–	15	8
Zn	–	18	3
Mg	1	58	82
Zr	–	14	–
Na	–	30	36
Co	–	–	7
Ni	–	–	29
V	–	18	14
Ba	–	10	–
K	–	30	3
Mn	–	–	5

[a] SiC, free SiO_2, and free C (wt%).
[b] – non detected.
[c] Each element (ppm).

[9]. The surface properties of this SiC powder have attracted our attention, because both effects of an ultrafine particle size and of the introduction of carbon into the lattice of silicon on its catalytic properties have been unknown.

Since transition metal carbides exhibit interesting properties in isomerization [1,3,4], hydrogenolysis [2,4], hydrogenation [4,5], and hydrogen oxidation [3], we decided to examine the catalytic behavior of SiC for the activation of hydrogen.

2. Experimental

Three kinds of SiC powders from different sources were used in this study. Ultrafine particles of SiC were synthesized by r.f. plasma CVD using a chemical system of SiH_4–CH_4–Ar according to the similar procedure described in ref. [9]. The other two kinds of commercial submicron SiC powders synthesized by carbothermal reduction of silica and by the Acheson method were obtained from Ibiden Co. and Showa Denko Co., respectively. The purities and the spectrochemical analyses of three SiC powders are given in table 1. Ultrafine fumed silica (Aerosil 300) with ultrahigh purity, produced by the hydrolysis of silicon tetrachloride in the flame of hydrogen–oxygen mixtures, was obtained from Nippon Aerosil Co. Two kinds of graphite powders were obtained from Toho Carbon Industry Co. One is high purity graphite (EG-36H), and its principal impurities are Fe (1.8 ppm) and Si (1.2 ppm). The other (EG-36) contains comparatively large amounts of metal impurities (Fe, 600 ppm; Mg, 250 ppm; Si, 100 ppm; Al, 60 ppm). Hydrogen was purified by passing through liquid nitrogen-cooled traps. Deuterium above 99.5% purity purchased from Takachiho Trading Co. was purified in the same way. Heavy water above 99.8% purity obtained from CEA was purified in the vacuum system by several cycles of freezing, evacuation, and thawing.

The XRD spectrum was recorded on a Nihon Denshi powder X-ray diffractometer with nickel-filtered CuK_α radiation. A specific surface area was measured by the BET method using N_2 as adsorbate at liquid nitrogen temperature. The pore volume was also measured using the BET apparatus.

A Pyrex-glass recirculatory reaction system was used for pretreatments and catalytic activity measurements. This apparatus could be evacuated below 1.3×10^{-3} Pa. The total surface areas of three SiC powders in a fused quartz reactor were made equal to each other as much as possible. The heating of the catalyst was performed by an IR gold image furnace (ULVAC RHL-E25) controlled by a HPC-8000 multiprogrammable temperature controller (ULVAC).

After pretreatment of the catalyst, the activity of SiC for a hydrogen–deuterium equilibrium reaction was measured at 473 K in a static system. Equimolar mixtures of hydrogen and deuterium at a constant total pressure of 13 Pa were introduced into the reactor. The variations of the isotopic composition were followed by a direct inlet mass spectrometer (ULVAC MSQ-400 type quadrupole mass analyzer) connected to the reactor through a Granville-Phillips variable leak valve.

3. Results and discussion

3.1. PHYSICAL PROPERTIES

XRD patterns of SiC powders produced by plasma CVD and by carbothermal reduction of silica revealed that these two samples have mainly 3C type crystal forms, while SiC powder obtained by the Acheson method has mainly 6H type crystal form. However, three SiC powders as-received did not show any signal attributable to graphite or silica.

Table 2 summarizes crystal forms, BET surface areas, pore volumes, and calculated particle sizes (diameter) from BET surface areas of these three SiC powders. It can be seen that SiC powder synthesized by plasma CVD has a much larger surface area and smaller particle size than the other two. Table 2

Table 2
Characteristics of silicon carbide powders

SiC	Surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Particle size (nm) [a]	Crystal form	Abbreviated symbols
r.f. plasma CVD	160	0.37	12	3C	β-SiC(12)
carboreduction of silica	19	0.040	99	3C	β-SiC(99)
Acheson method	15	0.033	120	6H	α-SiC(120)

[a] Calculated from BET surface area assuming sphere.

also shows the abbreviated symbols of three SiC powders based on their crystal forms and particle sizes, which are referred to in this paper hereafter.

3.2. HYDROGEN-DEUTERIUM EXCHANGE

Hojo reported that the surface of SiC is oxidized by oxygen and/or water in air even at room temperature [10]. Therefore, two different pretreatments were carried out to remove the surface oxygen. One is the reduction with circulating hydrogen at several fixed temperatures between 873–1173 K for 1 h. However, β-SiC(12) did not permit us to use circulating hydrogen at a pressure above 665 Pa because of scattering of the powder in a fused quartz tube reactor. Accordingly, three SiC powders were in a similar manner reduced with circulating hydrogen at 665 Pa. However, an evident activity for hydrogen exchange could not be observed for any SiC even after the reduction at 1173 K.

The other pretreatment was the evacuation of SiC powder at elevated temperatures between 473–1173 K for 1 h. In this case, noticeable amounts of gases were liberated from all SiC powders. In spite of continuous evacuation, the pressure in the reactor could not be lowered below 1.3×10^{-2} Pa at 1173 K. After the evacuation, all three SiC powders exhibited a high hydrogen exchange activity at 473 K. The HD content in a hydrogen isotopic mixture increased rapidly and finally reached to an equilibrium value of 48.8% at 473 K. The decrease of hydrogen pressure could not be detected during the exchange reaction.

The change of HD percentage in an isotopic mixture with time can be expressed by the following first-order equation:

$$-\ln\left[\left(X_{\mathrm{HD}}^{\mathrm{e}} - X_{\mathrm{HD}}\right)/X_{\mathrm{HD}}^{\mathrm{e}}\right] = rt/N, \tag{1}$$

where $X_{\mathrm{HD}}^{\mathrm{e}}$ expresses an equilibrium percentage of HD at 473 K, X_{HD} a percentage of HD at reaction time t (min), r a reaction rate of hydrogen exchange, N the total mole number of hydrogens in the reactor. The first-order plots of this exchange reaction according to eq. (1) were found to show a good linearity during the initial period of reaction time for all SiC powders evacuated

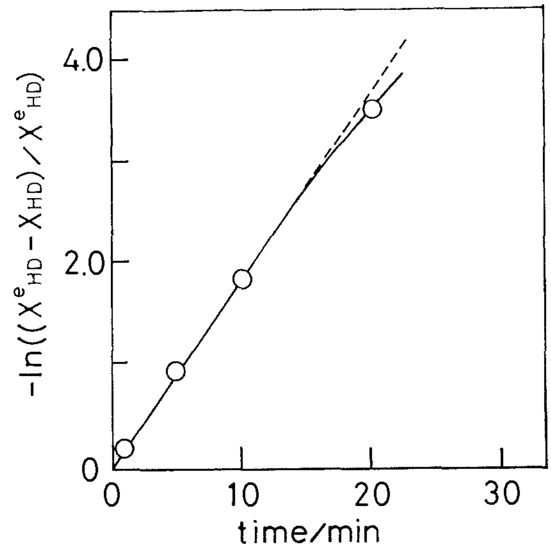

Fig. 1. A typical result of the first order plots of a hydrogen–deuterium exchange reaction according to eq. (1) at 473 K on α-SiC(120) degassed at 873 K for 1 h.

over 873 K. However, as the exchange proceeded, the plots deviated from the initial straight line. A typical result on α-SiC(120) evacuated at 873 K for 1 h is shown in fig. 1. After reaching an equilibrium, the hydrogen isotope mixture was exhausted at 473 K, and again the equimolar hydrogen and deuterium mixture at 13 Pa was introduced into the reactor. The catalyst showed considerable lowering of exchange activity. Accordingly, the deviation of the plots from the initial straight line may be caused by the deactivation of the catalyst.

The specific hydrogen exchange rates per unit surface area for three SiC powders were calculated from the slopes of the initial linear portions of the plots and the surface areas. The results are plotted in fig. 2 as a function of degassing temperature. The exchange activity rapidly increases with a rise of degassing temperature. Comparing the plots of α-SiC(120) with those of β-SiC(99), we found that the difference in crystal form does not give an important effect on the exchange activity.

The specific activity of β-SiC(12) is much smaller than those of α-SiC(120) and β-SiC(99) powders under the same pretreatment conditions. However, β-SiC(12) evacuated at 1173 K showed almost the same level of exchange activity as the other two SiC powders evacuated at 873–973 K. Since β-SiC(12) does not contain metal impurities except for 5 ppm of Fe and 1 ppm of Mg as shown in table 1, the revelation of hydrogen exchange activity is not due to impurities. Both β-SiC(99) and α-SiC(120) contain much more metal impurities than β-SiC(12). However, the cause of the revelation may be the same among them, because three SiC powders show a similar temperature behavior in the revelation of hydrogen exchange activity.

3.3. THERMODESORBED GASES FROM SILICON CARBIDE

In order to elucidate the revelation of the exchange activity by outgassing at high temperature, β-SiC(12) was heated at a constant rate after evacuation at room temperature. The thermodesorbed gases accumulated in the reactor were analyzed every 10 min by a quadrupole mass spectrometer. The peak intensities are plotted in fig. 3 as a function of temperature. It can be seen that the peak intensities at mass numbers 2 and 28 grow rapidly with a rise of the temperature. The peak at mass number 2 was attributed to hydrogen. The peak at mass number 28 was attributed to CO, because the peak intensity ratio of 28 to 12 coincided with that of pure CO. The minor peaks at 12, 15, and 18 corresponded to C^+, CH_3^+, and H_2O^+, respectively. Thermodesorption of CO and H_2 was observed for all SiC powders.

Cappelen et al. reported that the gas-phase products of the continuous oxidation of SiC with water vapor (0.05 MPa) at 1773 K in the absence of oxygen are CO and H_2, and that CO is oxidized to some extent to CO_2 with excess

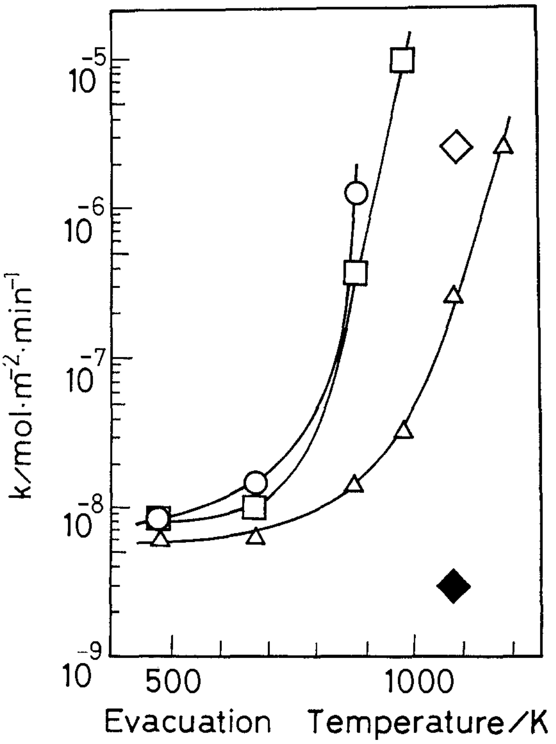

Fig. 2. Effect of evacuation temperatures on the specific hydrogen–deuterium exchange rates of three SiC powders. The equimolar mixture of hydrogen and deuterium at a constant total pressure of 13 Pa was introduced to the catalyst at 473 K. Also plotted are the specific hydrogen–deuterium exchange rate of α-SiC(120) after exposure to water vapor of about 0.1 Pa at 473 K for 15 min (◆) and that of reactivated α-SiC(120) after exposure to water vapor (◇).

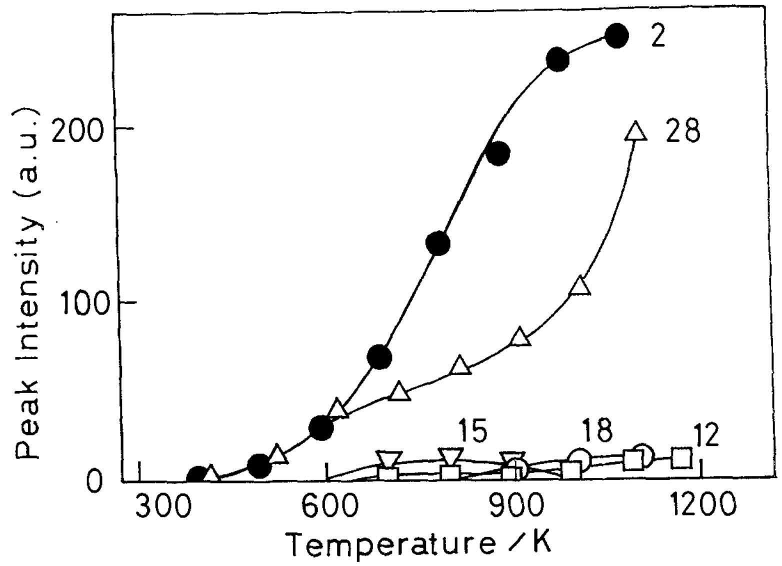

Fig. 3. Change of the mass peak intensities of thermodesorbed gases with a rise of the catalyst temperature. β-SiC(12) was heated at a constant rate (10 K/min) and the thermodesorbed gases were accumulated in the reactor.

water vapor [11]. Since (i) Hojo, as already mentioned, reported that the surface of SiC is oxidized by oxygen and/or water vapor in air even at room temperature [10] and (ii) our thermal desorption experiment was carried out at least at the beginning under vacuum, i.e. without excess water, we considered that H_2 and CO arised from the reaction between SiC and water adsorbed on it in air at room temperature, and that both products were liberated from the surface of SiC with the rise of the temperature. This was confirmed by the following experiment. α-SiC(120) degassed at several temperatures between 298 and 1173 K for 1 h was exposed to saturated D_2O vapor at room temperature for 24 h. After evacuation of the D_2O vapor, it was heated at a constant rate (10 K/min) up to 1173 K. The thermodesorbed gases accumulated in the whole heating process were analyzed by a mass spectrometer. Fig. 4 shows the mass spectra of thermodesorbed hydrogens as a function of the evacuation temperature. The deuterium content in hydrogen isotopes is plotted against the evacuation temperature in fig. 5. It can be seen in fig. 4 that thermodesorbed gases from SiC powder evacuated at 298 K already show three peaks at mass number 2, 3, and 4. The appearance of the peaks at mass number 3 and 4 indicates that D_2O adsorbed on the surface of SiC at room temperature caused the production of HD and D_2 with a rise of the catalyst temperature through such reaction steps as OH or OD bond scission and H or D atom recombination. The mass spectrum of thermodesorbed hydrogens in the heating process from the catalyst evacuated at 573 K is almost the same as that from SiC powder evacuated at 298 K. This fact shows that the concentration of hydrogen (H) on the surface of SiC

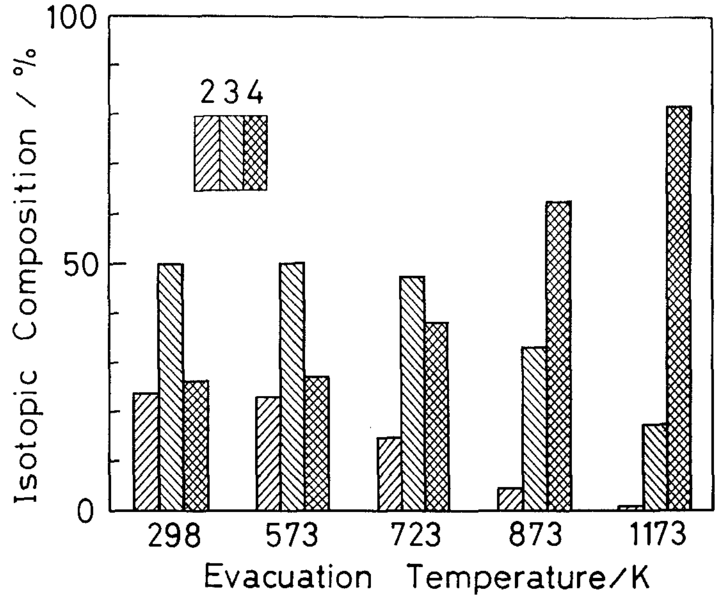

Fig. 4. The change of the mass spectrum of hydrogens thermodesorbed from α-SiC(120) which was exposed to D_2O vapor at room temperature for 24 h after degassing at several temperatures between room temperature and 1173 K for 1 h.

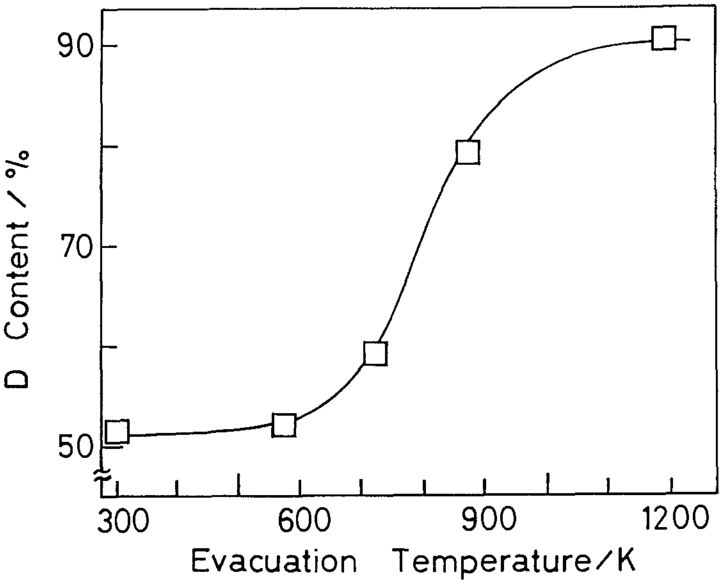

Fig. 5. The change of the deuterium content in hydrogen isotopes thermodesorbed from α-SiC(120) with a rise of the degassed temperature. D content (%) = [2D (%) + HD (%)] × 100/2 [H_2 (%) + HD (%) + D_2 (%)].

after evacuation at 573 K did not differ from that after evacuation at 298 K. When the catalyst was evacuated above 723 K, the percentage of D_2 increased and those of HD and H_2 decreased with the evacuation temperature. The deuterium content in thermodesorbed hydrogens increases above 723 K. This fact shows that the hydrogen (H) concentration on the surface of SiC decreases by the evacuation at 723 K, that is, the thermal decomposition of adsorbed water followed by desorption of hydrogen isotopes proceeded at this temperature. Thermodesorbed hydrogens from SiC evacuated at 1173 K for 1 h were mainly D_2 and HD, and the deuterium content in the thermodesorbed hydrogens became nearly 90%. This result shows that a large part of adsorbed water on the surface of SiC is removed by the evacuation at 1173 K. It can be concluded from the above results that the decomposition of adsorbed water in vacuum proceeds gradually between 723–1173 K on the surface of SiC.

3.4. DECOMPOSITION OF ADSORBED WATER AND EXCHANGE ACTIVITY

From the facts that (i) the thermal decomposition of adsorbed water on the surface of SiC proceeded with a rise of the evacuation temperature and (ii) the higher the evacuation temperature became, the higher the exchange activity did all SiC powders show, one can consider that the thermodesorption sites of water on the surface probably participate in the exchange activity. In order to ascertain this view, α-SiC(120) evacuated at 1073 K for 1 h was exposed to water vapor (0.1 Pa, the saturated water vapor pressure at 195 K) at 473 K. The exposure time was only 15 min. The specific hydrogen exchange activity of α-SiC(120) is also given in fig. 2. It is obvious that the exposure to water vapor caused the serious deactivation of the hydrogen exchange. Subsequently, the α-SiC(120) was again evacuated at 1073 K for 1 h. The specific hydrogen exchange activity after the second evacuation is also plotted in fig. 2. It can be seen that α-SiC(120) almost regained its former activity.

These experimental results show directly that the adsorption of water vapor on active sites caused the serious deactivation of the hydrogen exchange activity of α-SiC(120) and that the thermal decomposition of adsorbed water followed by the desorption of hydrogen and carbon monoxide caused the revelation of a hydrogen exchange activity. Accordingly, the previous experimental result that SiC powders prereduced with circulating hydrogen did not show the notable hydrogen isotopic exchange activity may be explained as follows. The readsorption of water vapor produced during the hydrogen reduction occurred on the thermal decomposition and/or thermodesorption sites of water on the surface of SiC to poison active sites for hydrogen exchange. The cause of the deactivation during the hydrogen exchange reaction observed in fig. 1 may also be explained in a similar manner.

Comparing the experimental results shown in fig. 5 with those shown in fig. 2, we can find that the temperature at which the deuterium content in thermodesorbed hydrogens began to increase significantly almost coincides with the temperature at which α-SiC(120) powder shows a noticeable hydrogen exchange activity. As the deuterium content in thermodesorbed hydrogens increases, α-SiC(120) shows the higher hydrogen exchange activity. It can be concluded from all these results that the water adsorbed on the surface of SiC at room temperature reacts with SiC above 700 K to produce CO and H_2, and that the desorption sites of these gases operate as active sites for hydrogen exchange. The higher the evacuation temperature, the more the decomposition of adsorbed water proceeds and the higher catalytic activity for hydrogen exchange α-SiC(120) reveals.

In order to examine whether hydrogen atoms in adsorbed water are active in hydrogen exchange or not, pure deuterium of 13 Pa was introduced to α-SiC(120) outgassed at 873 K. It was confirmed that a detectable amount of HD or H_2 was not produced at 473 K. Since α-SiC(120) evacuated at this temperature still retains a part of adsorbed water undecomposed as shown in figs. 4 and 5, and since it shows a high hydrogen exchange activity, this result shows that hydrogen atoms in adsorbed water are inactive for the hydrogen exchange at least at 473 K.

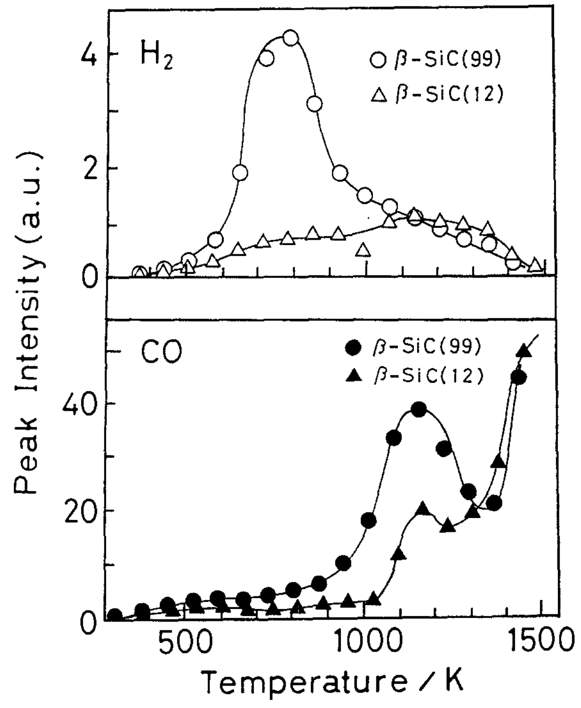

Fig. 6. TPD spectra of hydrogen and carbon monoxide preceded by the decomposition of adsorbed water on the surface of β-SiC(12) and β-SiC(99). The catalysts were heated at a constant rate (10 K/min) from room temperature. The peak intensities at massnumber 2 and 28 were recorded every 7 min as a function of the catalyst temperature.

The thermal decomposition behavior of adsorbed water on SiC powders was then examined in connection with the specific hydrogen exchange rates observed for SiC powders with different particle sizes. β-SiC(12) and β-SiC(99) were heated at a constant rate after evacuation at room temperature. Fig. 6 shows TPD spectra of hydrogen and carbon monoxide from both SiC powders. It can be seen that β-SiC(99) shows a clear desorption peak of hydrogen at 773 K, whereas β-SiC(12) shows only a broad maximum around 1120 K. This shows that the thermal decomposition of adsorbed water on β-SiC(99) takes place at much lower temperatures than β-SiC(12). Since the thermal decomposition of adsorbed water participates in the revelation of the exchange activity, this different decomposition behavior must be responsible for a higher specific exchange activity of β-SiC(99) than that of β-SiC(12), when they were treated under the same outgassing conditions.

The TPD spectrum of CO shows two desorption peaks at much higher temperatures as compared to that of H_2. There was no difference in the peak temperatures between β-SiC(99) and β-SiC(12). Oxygen still remains on the surface of SiC even after the desorption of hydrogen. Both β-SiC(99) and β-SiC(12) liberate oxygen in the form of CO above 1000 K irrespective of particle size. Two desorption peaks of CO, which can be seen in both SiC samples, may correspond to two kinds of adsorbed oxygen or carbon species on the surface of SiC. CO desorption peak from β-SiC(99) is much larger than that from β-SiC(12).

3.5. SURFACE COMPOSITION OF SiC AND EXCHANGE ACTIVITY

Miyoshi and Buckley investigated the (0001) surface of a single crystal silicon carbide heated at various temperatures up to 1773 K in vacuo using X-ray photoelectron and Auger electron spectroscopies [12]. The photoelectron emission lines for C 1s of the silicon carbide showed asymmetric doublet peaks due to the different carbonaceous species. For specimen preheated above 673 K the carbon contamination peak disappears from the spectrum, and the graphite and carbide peaks are seen. Both peak heights of graphite and carbide increase with an increase in preheating temperatures. At 1173 K the carbide peak height was smaller than that at 1073 K, but the graphite peak height was larger. At 1273 K the height of the carbide peak decreased and became smaller than that of the graphite.

It can be noticed here that (i) the temperature range where three types of SiC powders begin to show the hydrogen exchange activity almost coincides with that where the graphite peak appears on the surface of single crystal of silicon carbide and (ii) with an increase of preheating temperature all SiC powders show the higher exchange activity and the peak height of graphite from the surface of single crystal SiC grows larger. The experimental facts of Miyoshi and

Buckley, therefore, indicate that the hydrogen exchange activity of SiC powder may be caused by the graphite precipitated on the surface of SiC.

Accordingly, XRD spectra of three types of SiC powders were examined after preheating them at 1173 K in vacuum, although any three types of SiC powder did not show the XRD peak of graphite before heat treatment. It was found that β-SiC(12), which showed the poorest hydrogen exchange activity, showed the distinct peak of graphite at an angle of 26.4°. As for β-SiC(99), which showed the highest hydrogen exchange activity, only a trace peak of graphite could be found, and as for α-SiC(120), no trace of graphite peak could be found.

In order to confirm the contribution of graphite phase to the hydrogen exchange activity, two kinds of graphite powders (EG-36H and EG-36), which had different amounts of metal impurities, were degassed at 1173 K and the hydrogen exchange activities were measured at 473 K. Neither graphite powder did show the activity irrespective of the amounts of metal impurities. We consider from these findings that the probable precipitation of graphite on the surface of SiC does not cause the hydrogen exchange activity.

Fumed silica (280 m^2/g, 0.51 cm^3/g) which has almost the same surface area and pore volume as β-SiC(12), was confirmed not to show any hydrogen exchange activity even after it had been evacuated at 1173 K for 1 h. This result suggests that the surface of SiC is not totally covered with a silica layer. If the surface of SiC is covered with a thin layer of adsorbed water or oxide layer to a limited extent, they may be removed at least partially on evacuation at high temperatures.

Acknowledgement

The authors wish to thank Professor B. Delmon of Université Catholique de Louvain for his kind and valuable discussions.

References

[1] J.M. Muller and F.G. Gault, Bull. Soc. Chim. France 2 (1970) 416.

[2] J.H. Sinfelt and D.J.C. Yates, Nature Phys. Sci. 27 (1971) 229.

[3] R.B. Levy and M. Boudart, Science 181 (1973) 547.

[4] M. Boudart, S.T. Oyama and L. Leclercq, in: *Proc. 7th Int. Congress on Catalysis*, Tokyo, 1980, eds. T. Seiyama and K. Tanabe (Elsevier, Amsterdam, 1981) p. 578.

[5] I. Kojima, E. Miyazaki, Y. Inoue and I. Yasumori, J. Catal. 59 (1979) 472.

[6] M. Boudart, J.S. Lee, K. Imura and S. Yoshida, J. Catal. 103 (1987) 30.

[7] T. Inoue, A. Fujishima, M. Konishi and K. Honda, Nature 277 (1979) 637.

[8] S. Yamamura, H. Kojima, J. Iyoda and W. Kawai, Electroanal. Chem. 225 (1987) 287; 247 (1988) 333.

[9] K. Kijima, H. Noguchi and M. Konishi, J. Mat. Sci. 24 (1989) 2929.

[10] J. Hojo, *SiC Ceramics*, eds. S. Somiya and Y. Inomata (Uchida Rokakuho, Tokyo, 1988) p. 115.

[11] H. Cappelen, K.H. Johansen and K. Motzfeldt, Acta Chem. Scand. A35 (1981) 247.

[12] K. Miyoshi and D.H. Buckley, Surf. Sci. 10 (1982) 357.