# Lignin–Silica Hybrids as Precursors for Silicon Carbide

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ABSTRACT: Lignin, prepared by digesting cedar with acetic acid, and tetraethoxysilane have been allowed for a sol-gel reaction in tetrahydrofuran using  $H_2SO_4$  as catalyst to yield lignin-SiO<sub>2</sub> hybrids in the bulk gel form. The solid-state <sup>13</sup>C nuclear magnetic resonance spectra of the hybrids and products formed solely from the lignin under the acidic conditions revealed that the lignin underwent crosslinking during the sol-gel reaction. The degree of crosslinking increased with an increasing amount of H<sub>2</sub>SO<sub>4</sub>. The powdered hybrids have been heated at 1500°C in Ar for carbothermal reduction, resulting in the formation of SiC powders. The lignin-to-tetraethoxysilane mixing ratio of the starting solutions varied free carbon content in the SiC powders. In addition, the amount of carbonaceous residue formed from the lignin upon heating depended on the degree of crosslinking of the lignin. Thus, to adjust the amounts of both the lignin and H<sub>2</sub>SO<sub>4</sub> was necessary for producing the hybrids suitable for precursors for SiC powders with high purity. Critical adjustment of the amounts led to the formation of SiC powders with a free carbon content of 0.57 wt %, implying that the lignin is a beneficial carbon source for the production of SiC powders by the hybrid route. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1321-1328, 1999

**Key words:** lignin; tetraethoxysilane; sol-gel processing; organic-inorganic hybrids; silicon carbide

# **INTRODUCTION**

Lignin is one of main components of lignumized plants, which ranks next to cellulose. A large amount of lignin is formed upon production of pulp. Its use, however, is limited. Then, many efforts have been made so far to develop use of lignin. Concerning its application to inorganic materials, for example, Sudo et al. reported the synthesis of carbon fibers from lignin.<sup>1</sup> We demonstrated the synthesis of lignin–silica (SiO<sub>2</sub>)–

titania  $(TiO_2)$  and lignin– $TiO_2$  hybrid fibers by sol–gel processing and their conversion into Si– Ti–C and titanium carbide (TiC) fibers, respectively, by carbothermal reduction.<sup>2</sup> Overall reactions for the formation of silicon carbide (SiC) and TiC can be expressed as follows.

$$SiO_2 + 3C \rightarrow SiC + 2CO$$
 (1)

$$TiO_2 + 3C \rightarrow TiC + 2CO$$
 (2)

Lignin involved in the hybrid fibers is converted into carbon while preheating for carbothermal reduction, which reacts with the  $SiO_2$  and  $TiO_2$ components to yield SiC and TiC, respectively.

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Thus, lignin plays a role of the carbon source of the carbides.

The lignin–inorganic oxide hybrid fibers, over 30 cm in length, could facilely be prepared from starting solutions with Si-to-Ti atomic (Si/Ti) ratios of 0–1.0 under acidic conditions, which gave the carbide fibers upon heat-treatment at 1500°C in Ar for 4 h along with pretreatment at 150°C in air for cure.<sup>2</sup> However, the hybrid fibers could not be prepared from the solutions with Si/Ti ratios higher than 1.0, which just gave bulk gels. This means that lignin–SiO<sub>2</sub> hybrid fibers and, therefore, SiC fibers, cannot be prepared by the procedure.

Organic–SiO<sub>2</sub> hybrids containing sucrose,<sup>3</sup> phenolic resins,<sup>3–6</sup> or polyacrylonitrile<sup>7</sup> as the organic component have so far been demonstrated to be prominent precursors for SiC powders. Compared with these compounds, lignin is much more cost-effective, and it is therefore anticipated that lignin–SiO<sub>2</sub> hybrids in the bulk gel form would be useful as precursors for SiC powders. In addition, a large amount of lignin would be expected to be processed when applied to SiC powder synthesis.

This study has been aimed at investigating the reaction of lignin during the formation of lignin- $\operatorname{SiO}_2$  hybrids by sol-gel processing under acidic conditions. The hybrids and products formed from the lignin alone under the conditions have been studied by solid-state <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy. On the basis of the measurements, the reason why lignin-SiO<sub>2</sub> hybrid fibers cannot be produced by the procedure has been discussed. Investigation has been made further on the production of SiC powders from the hybrids in the powder form by carbothermal reduction in order to clarify the composition of the hybrids suitable for synthesizing SiC powders with high purity.

## **EXPERIMENTAL**

### **Preparation of Samples**

The lignin used in this study was prepared by digestion of cedar with acetic acid [composition:  $C_9H_{8.33}O_{2.37}(OCH_3)_{0.96}$ ]. The lignin hardly contained any metal impurities.<sup>8</sup> Tetraethoxysilane [Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, TEOS] was used as the SiO<sub>2</sub> source, tetrahydrofuran (THF) as solvent, and H<sub>2</sub>SO<sub>4</sub> as catalyst.

The lignin was added to  $10 \text{ cm}^3$  of THF, followed by the addition of TEOS (15 cm<sup>3</sup>), distilled

water, and  $H_2SO_4$ . Mixtures thus prepared had atomic ratios of C in the lignin to Si in TEOS (C\*/Si ratios) of 2.0-4.0, a  $H_2O$ -to-Si molar ( $H_2O/$ Si) ratio of 1.75, and a  $H_2SO_4$ -to-Si molar ( $H_2SO_4/$ Si) ratio of 0.01. The mixtures were stirred at room temperature for 30 min for intimate mixing and then held at 65°C.

In order to investigate on reactions of the lignin that take place during the sol-gel reaction, the lignin alone was allowed for a reaction in THF at 65°C under the presence of distilled water and  $H_2SO_4$ . The amounts of  $H_2O$  and  $H_2SO_4$  used for the reaction are expressed as the  $H_2O/C^*$  and  $H_2SO_4/C^*$  ratios, respectively, which imply the molar ratios of  $H_2O$  and  $H_2SO_4$ , respectively, to a total amount of C in the lignin.

#### **Conversion into SiC Powders**

The lignin–SiO<sub>2</sub> hybrids were heated at 1500°C in Ar at a flowing rate of 100 cm<sup>3</sup> min<sup>-1</sup> with a tube furnace. Heat-treatment at 1500°C in Ar has been shown to be necessary for converting organic–SiO<sub>2</sub> hybrids into SiC.<sup>9</sup> The heating rate was 10°C min<sup>-1</sup>, and the holding time at 1500°C was 4 h. After the heat-treatment, the furnace was cooled just by exposing to air. Ar gas was kept on flowing at the rate in the tube until when the temperature inside of the tube went down until at least 280°C, where residual carbon in products is not removed by oxidation.

#### **Analytical Procedure**

The lignin–SiO<sub>2</sub> hybrids and products formed by the reaction of lignin alone were analyzed by Fourier transform infrared (FTIR) spectroscopy (the KBr pellet technique) with a Perkin–Elmer System 2000 FTIR spectrometer and solid-state <sup>13</sup>C-<sup>29</sup>Si-NMR spectroscopy using a JEOL and EX270WB spectrometer. The NMR spectra were measured using the high-power <sup>1</sup>H decoupling crosspolarization-magic-angle-spinning (CP-MAS) sequence. The spinning rate was set at approximately 6 kHz. In order to distinguish CH<sub>3</sub> and nonhydrogenated carbons from the other hydrogenated carbons, the MAS-dipolar-dephasing (MAS-DD) sequence, which means the CP–MAS method with dipolar dephasing was also used for the <sup>13</sup>C-NMR measurements. The observed frequencies of <sup>29</sup>Si and <sup>13</sup>C nuclei were 53.54 and 67.80 MHz, respectively. The other analytical conditions were as follows: contact time, 5 ms; repetition time, 5 s; spectral width, 10 kHz; data

point, 8192. Spectra were usually accumulated for 1000–2000 times to achieve a reasonable signal-to-noise ratio. Chemical shifts in the spectra were given with reference to tetramethylsilane.

Products after the heat treatment at 1500°C were analyzed with a Rigaku RINT 1100 X-ray diffractometer using Ni-filtered Cu K $\alpha$  radiation and a Perkin-Elmer System 2000 FTIR spectrometer. Free carbon contents in the products were measured using a Perkin–Elmer Model 240C elemental analyzer. Gases adsorbed on the samples were substituted for helium gas in the sample room of the analyzer maintained at room temperature before the measurement. This means that no heat treatment was made on as-synthesized products prior to the measurement. Si contents in the products were measured by inductively coupled plasma emission spectroscopy with a Shimadzu ICPS-1000IV analyzer onto aqueous solutions prepared from the products subjected to alkali fusion.

# **RESULTS AND DISCUSSION**

# Reaction of the Lignin Taking Place along with the Sol–Gel Reaction

The lignin–TEOS–H<sub>2</sub>O–H<sub>2</sub>SO<sub>4</sub>–THF solutions underwent gelation at approximately 3 h of holding at 65°C. The solutions did not reveal spinnability before gelation in spite of the fact that their viscosity increased with the holding time. The lignin–H<sub>2</sub>O–H<sub>2</sub>SO<sub>4</sub>–THF solutions also gave solid products by holding at the temperature for approximately 3 h.

Figure 1 shows the FTIR spectra of (a) the lignin that was used as the starting material in this study, (b) a product formed by the reaction of the lignin alone at a  $H_2O/C^*$  ratio of 0.58 and a  $H_2SO_4/C^*$  ratio of 0.003, and (c) a gel formed from a solution with a C\*/Si ratio of 3.0, a H<sub>2</sub>O/Si ratio of 1.75 (=a  $H_2O/C^*$  ratio of 0.58), and a  $H_2SO_4/Si$ ratio of 0.01 (=a  $H_2SO_4/C^*$  ratio of 0.003). On the basis of the proposed assignments of bands observed in the infrared spectra of various kinds of lignin,<sup>10</sup> bands observed in Figure 1(a) may be assigned, as summarized in Table I. Since the lignin used in this study was prepared using acetic acid, the spectrum involves bands due to the acetyl group in the lignin in addition to those typically observed for lignin obtained from needle-leaved trees.



**Figure 1** The FTIR spectra of (a) the lignin prepared from cedar with acetic acid, (b) the product formed solely from the lignin by the reaction at a  $H_2O/C^*$  ratio of 0.58 and a  $H_2SO_4/C^*$  ratio of 0.003, and (c) the lignin–SiO<sub>2</sub> hybrid prepared from the solution with a C\*/Si ratio of 3.0, a  $H_2O/C^*$  ratio of 0.58, and a  $H_2SO_4/C^*$  ratio of 0.003 ( $\bigcirc$ : CO<sub>2</sub>;  $\triangle$ : THF occluded in the samples).

These bands are also observed in Figure 1(b). Figure 1(c) gives rise to the same bands, except the range below  $1100 \text{ cm}^{-1}$ . The most intense band in the range of the spectrum  $(1070 \text{ cm}^{-1})$  is ascribable to the asymmetric Si-O-Si stretching vibration.<sup>11</sup> Bands at 958 and 796 cm<sup>-1</sup> are associated with the Si-OH and SiO-H stretching vibrations of terminal silanol groups and the symmetric Si-O-Si stretching vibration, respectively.<sup>11</sup> In the <sup>29</sup>Si NMR spectrum of the gel, an intense signal appears at -100 ppm, which is ascribable to the  $Si(OSi)_3(O^-)$  unit, together with shoulders at -92 and -109 ppm, which are due to the  $\underline{Si}(OSi)_2(O^-)_2$  and  $\underline{Si}(OSi)_4$  unit, respectively. These facts indicate that TEOS underwent hydrolysis and polycondensation to form a siloxane network, and the gel consists of the lignin and  $SiO_2$ components, suggesting the formation of the lignin–SiO<sub>2</sub> hybrids by the sol–gel reaction.

Wave Number (cm <sup>-1</sup> )	Vibrations
818 and 856	C—H out-of-plane deformation (the appearance of the two bands is typical for lignin prepared from needle-leaved trees)
1034	C—H in-plane deformation and C—O—C symmetric stretching
1084	Aliphatic C—O—C stretching
1129	C—H in-plane deformation
1146	C—O—C stretching
1230	C—O stretching in acetic acid ester
1266	Aromatic CH <sub>3</sub> —O—C asymmetric stretching
1368	O—H out-of-plane deformation
(shoulder)	-
1426, 1453,	C—C stretching in aromatic rings
1513, and	
1598	
1463	$ m CH_2$ scissoring
1728	C=O stretching
1800–2000	Over or combination tones of C—H out-of-plane deformation
2848-3003	C—H stretching
3421	O—H stretching

Table IAssignments of Bands Observed in theFTIR Spectrum of the Lignin [Fig. 1(a)]

Figure 2 shows the <sup>13</sup>C CP–MAS NMR spectra of (a) the lignin; (b) the lignin–SiO<sub>2</sub> hybrid prepared from the solution with a C\*/Si ratio of 3.0, a H<sub>2</sub>O/C\* ratio of 0.58, and a H<sub>2</sub>SO<sub>4</sub>/C\* ratio of 0.003; and (c) a product formed by the reaction of the lignin alone at a H<sub>2</sub>O/C\* ratio of 0.58 and a H<sub>2</sub>SO<sub>4</sub>/C\* ratio of 0.333. Because of the complicated structure of the lignin and overlap of signals and spinning side bands, it is impossible to distinguish and assign all signals observed in the spectra; therefore, in this article, the term "signal" is used for "signal group" in some cases, which may be composed of some signals.

On the basis of the assignments of bands observed in the FTIR spectrum of the lignin and proposed assignments of signals seen in <sup>13</sup>C-NMR spectra of lignin-related compounds,<sup>12</sup> the main signals in the spectrum of the lignin [labeled (a)– (h) in Fig. 2(a)] would be assigned as follows: (a) (21 ppm), CH<sub>3</sub> in the CH<sub>3</sub>C(=O)O group; (b) (32 ppm), CH<sub>2</sub>, (c) (56 ppm), CH<sub>3</sub>O and the methyne group; (d) (70–90 ppm), C=O=C(=O)CH<sub>3</sub>; (e) (115 ppm), C=C (olefin) and CH in the benzene ring; (f) (126–133 ppm), C with no C—H linkage in the benzene ring; (g) (147–150 ppm), C attached to the CH<sub>3</sub>O or OH group in the benzene ring; (h) (167 ppm), O—C(=O)CH<sub>3</sub>. In the <sup>13</sup>C MAS–DD NMR spectrum of the lignin, which enables to distinguish signals due to the methyl group and nonhydrogenated carbons from the other carbons, only signals (a), (c), (f), (g), and (h) are observed, which supports the above assignments.

Comparing the spectra shown in Figure 1(a) and (b), signals (a) and (h) decrease in intensity, suggesting that the acetyl group in the lignin was removed by hydrolysis during the sol-gel reac-



**Figure 2** The <sup>13</sup>C CP–MAS NMR spectra of (a) the lignin; (b) the lignin–SiO<sub>2</sub> hybrid prepared from the solution with a C\*/Si ratio of 3.0, a H<sub>2</sub>O/C\* ratio of 0.58, and a H<sub>2</sub>SO<sub>4</sub>/C\* ratio of 0.003; and (c) the product formed solely from the lignin by the reaction at a H<sub>2</sub>O/C\* ratio of 0.58 and a H<sub>2</sub>SO<sub>4</sub>/C\* ratio of 0.333 [S: signals due to occluded solvent (THF); \*: spinning side bands].



**Figure 3** A possible reaction scheme for condensation of the lignin (the small letters correspond to those labeled to <sup>13</sup>C-NMR signals shown in Figure 2.)

tion. With this change, a signal labeled (i) in Figure 2(b) newly appears around 62 ppm, and signals (b) and (f) increase in intensity. Signal (i) would be assigned to the C-OH group, which would be formed by hydrolysis of the acetyl group. The increase in intensities of signals (b) and (f) would be ascribed to increment in the number of CH<sub>2</sub> group and C with no C—H linkage in the benzene ring, respectively. This would indicate that the C—OH group formed upon hydrolysis further underwent polycondensation with the CH group in the benzene ring. This kind of polycondensation, that is, polycondensation between the alkylol group and the CH group in the benzene ring, was demonstrated to take place when 2-hydroxybenzyl alcohol was reacted under the presence of acid catalyst, which yielded a phenolic resin.<sup>13</sup>

In the spectrum of the product formed from the lignin alone under much more highly acidic conditions than those under which the lignin $-SiO_2$  hybrids were prepared [Fig. 1(c)], signals (a) and (h) almost disappear, which would result from the

fact that the acetyl group in the lignin is no longer present by being consumed by hydrolysis. In addition, signal (i) is not visible in Figure 1(c) either, implying that the polycondensation of the lignin was complete. These facts would suggest that the lignin underwent hydrolysis and polycondensation in the acidic solutions to increase the degree of crosslinking, which took place simultaneously with hydrolysis and polycondensation of TEOS. A possible reaction scheme may be illustrated as shown in Figure 3.

Table II shows the ratio by weight of the insoluble portion in the product, formed by the reaction of the lignin alone, against the initial weight of the lignin as a function of the amount of H<sub>2</sub>SO<sub>4</sub>. Because  $H_2SO_4$  occluded in the insoluble portion could not be removed satisfactorily by washing, the value exceeded 100 wt % when the  $H_2SO_4/C^*$ ratio was 0.22 and 0.33. Nevertheless, there appears a tendency that the weight of the insoluble portion increases with increasing  $H_2SO_4/C^*$  ratio. Considering that a polymer with a higher degree of crosslinking has lower solubility, the fact that the amount of the insoluble product increases with increasing amount of H<sub>2</sub>SO<sub>4</sub> would also indicate the formation of lignin with a higher degree of crosslinking by the reaction at a higher  $H_2SO_4/C^*$  ratio.

Regarding the preparation of phenolic resin– SiO<sub>2</sub>–TiO<sub>2</sub> hybrid fibers from phenolic resin– TEOS–titanium tetrakis(2,4-pentanedionate) [Ti ( $C_5H_7O_2$ )<sub>4</sub>, TTP]–H<sub>2</sub>O–H<sub>2</sub>SO<sub>4</sub>–2,4-pentanedione solutions with various Si-to-Ti atomic (Si/Ti) ratios,<sup>14</sup> we showed that the amounts of H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub> had to be varied depending on the Si/Ti ratio of the solutions in order to achieve favorable spinnability of the hybrid fibers. These amounts were directly proportional to the Si/Ti ratio when the solutions showed excellent spinnability. The same proportionality between the Si/Ti ratio and

Table II The Ratio of the Insoluble Portion in Products, Formed by Reacting the Lignin in H<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub>-THF Solutions at 65°C to the Initial Amount of the Lignin

H <sub>2</sub> SO <sub>4</sub> /C* Ratio	The Insoluble Portion (Wt %)		
0.003	61.0		
0.11	92.3		
0.22	102		
0.33	107		

The  $H_2O/Si$  ratio of the solutions was fixed at 0.58.

the amounts of  $H_2O$  and  $H_2SO_4$  was found in the lignin-TEOS-TTP system in the range of Si/Ti ratios of 0-1.0, which gave lignin-SiO<sub>2</sub>-TiO<sub>2</sub> and lignin–TiO<sub>2</sub> hybrid fibers.<sup>2</sup> The lignin-containing hybrid fibers could be prepared from lignin-TEOS-TTP-H<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub>-THF-2,4-pentanedione solutions with H<sub>2</sub>O/(Si+Ti) ratios of 0.3-1.0 and  $H_2SO_4/(Si+Ti)$  ratios of 0.2–0.3 (= $H_2SO_4/C^*$  ratios of 0.05–0.075) when the  $C^{*/(Si + Ti)}$  ratio was fixed at 4.0. By extrapolating these two lines for the proportionality, lignin-SiO<sub>2</sub> hybrid fibers were expected to be prepared from the solution with a C\*/Si ratio of 4.0, a H<sub>2</sub>O/Si ratio of 1.75, and a H<sub>2</sub>SO<sub>4</sub>/Si ratio of 0.01 (=a  $H_2SO_4/C^*$  ratio of 0.0025). The hybrid fibers, however, could not actually be produced from the solution with the composition and those with compositions in the vicinity. Nevertheless,  $SiO_2$  gel fibers could be produced from a  $TEOS-H_2O-H_2SO_4-THF$  with the  $H_2O/Si$  and  $H_2SO_4/Si$  ratios.

On the basis of the fact that the lignin undergoes crosslinking in the acidic solutions and the degree increases with increasing amount of  $H_2SO_4$ , it is inferred that a considerable amount of the lignin would have undergone crosslinking in the solutions with the  $H_2SO_4/C^*$  ratios of 0.05– 0.075, from which the lignin– $SiO_2$ – $TiO_2$  and lignin-TiO<sub>2</sub> hybrid fibers could be prepared. On the other hand, the  $H_2SO_4/C^*$  ratio of 0.0025 would be too low to cause the crosslinking. Considering that the lignin-free solution with the  $H_2SO_4/Si$ ratio of 0.01 (The amount of  $H_2SO_4$  is the same as that in the lignin-containing solution with a  $H_2SO_4/C^*$  ratio of 0.0025.) gave the SiO<sub>2</sub> gel fibers, it is assumed that formation of crosslinked lignin is an important factor for the formation of the lignin-inorganic oxide hybrid fibers by solgel processing. The degree of crosslinking can be increased by adding a larger amount of  $H_2SO_4$  to the starting solution. There is, however, a range of  $H_2SO_4/Si$  ratios suitable for preparing the  $SiO_2$ gel fibers from the lignin-free solutions. Actually, the gel fibers could not be prepared from the solutions with high  $H_2SO_4/Si$  ratios, such as 0.05. Even if the  $H_2SO_4/Si$  ratio can be adjusted to proceed crosslinking of the lignin, the ratio becomes too high to form a siloxane network suitable for the  $SiO_2$  gel fiber formation. Thus, the reason why the lignin-SiO<sub>2</sub> hybrid fiber could not be prepared would be due to discrepancy of the amount of  $H_2SO_4$  optimal for crosslinking of the lignin and hydrolysis and polycondensation of TEOS.



**Figure 4** The XRD patterns of products formed from the lignin–SiO<sub>2</sub> hybrids prepared from the solutions with a C\*/Si ratio of (a) 2.0, (b) 2.5, (c) 3.0, (d) 3.5, and (d) 4.0 by heating at 1500°C in Ar for 4 h. The H<sub>2</sub>O/Si and H<sub>2</sub>SO<sub>4</sub>/Si ratios of the solutions were fixed at 2.0 and 0.01, respectively.

# SiC Powders Produced from the Lignin–SiO<sub>2</sub> Hybrids

The lignin–SiO<sub>2</sub> hybrids were prepared from the solutions with C\*/Si ratios of 2.0-4.0, a H<sub>2</sub>O/Si ratio of 2.0, and a  $H_2SO_4/Si$  ratio of 0.01, which were powdered and then fired at 1500°C in Ar for 4 h. No treatment was conducted to the hybrids prior to the heat treatment. The X-ray diffraction (XRD) patterns of resulting powders are shown in Figure 4. Peaks due to  $\beta$ -SiC phases are dominantly observed in all the patterns. However, cristobalite gives rise to a peak in the pattern of the product whose precursor was prepared from the solution with a C\*/Si ratio of 2.0. This suggests that carbothermal reduction of the SiO<sub>2</sub> component in the hybrid was not complete, which would result from lack of carbon content, that is, the lignin content in the hybrids.

Table III shows free carbon, hydrogen, and nitrogen contents in the products. The free carbon content is lowest (0.57 wt %) in the product whose precursor was prepared from the solution with a

Table III Free Carbon, Hydrogen, and
Nitrogen Contents Found in SiC Powders
Produced from Lignin–SiO <sub>2</sub> Hybrids by
Carbothermal Reduction as a Function of the
C*/Si Ratio of the Starting Solutions

C*/Si Ratio	Free C (Wt %)	H (Wt %)	N (Wt %)
2.0	2.00	0.11	0.08
2.5	1.30	0.10	0.15
3.0	0.57	0.08	0.10
3.5	6.39	0.08	0.09
4.0	12.83	0.15	0.06

C\*/Si ratio of 3.0. It is noteworthy that no heat treatment for removing free carbon involved in the products was conducted prior to the measurements. This means that the free carbon content in the SiC powders can facilely be adjusted by the C\*/Si ratio of the starting solution.

Figure 5 shows the FTIR spectra of the products whose precursors were prepared from the starting solution with a C\*/Si ratio of (a) 2.0 and (b) 3.0. The band at approximately  $822 \text{ cm}^{-1}$  is ascribable to the Si–C stretching vibration.<sup>15</sup> The Si-O-Si stretching vibration gives rise to a band at 1097  $\text{cm}^{-1}$  in Figure 5(a), which is consistent with the fact that the product contains cristobalite as was found with XRD. On the other hand, no apparent band due to the Si-O-Si stretching vibration is observed in Figure 5(b), indicating that  $SiO_2$  or silicon oxide is hardly present in the product synthesized from the solution with a C\*/Si ratio of 3.0. In addition, the total Si content in the product is 69.1%, whereas the theoretical value of Si content in SiC is 70.05%. These facts would suggest that the hybrid prepared from the starting solution with a C\*/Si ratio of 3.0 is optimal for the precursor for SiC powders with high purity. The ceramic yield of the SiC powders is approximately 23%.

The difference in the degree of crosslinking of the lignin caused by the amount of  $H_2SO_4$  varies the amount of carbonaceous residue formed from the lignin upon pyrolysis under a non-oxidizing atmosphere. Table IV shows the ratio by weight of carbonaceous residue formed from the lignin, which was subjected to the reactions at  $H_2SO_4/C^*$ ratios of 0.0025 and 0.33 (The  $H_2O/C^*$  ratio was fixed at 0.58), by heating at 1000°C in Ar for 2 h. The ratio actually increases with increasing amount of  $H_2SO_4$ , that is, increasing the degree of the crosslinking. This would indicate that even if a fixed amount of the lignin is used for the sol-gel reaction to prepare the lignin– $SiO_2$  hybrids, the amount of C formed from the lignin component of the hybrids is variable with the amount of  $H_2SO_4$  used for the reaction, which would further affect purity of the SiC powders. This suggests that both the C\*/Si and  $H_2SO_4$ /Si ratios of the starting solution have to be adjusted in order to prepare the lignin–SiO<sub>2</sub> hybrids appropriate for precursors



**Figure 5** The FTIR spectra of the obtained SiC powders, whose precursors were prepared from the starting solutions with a C\*/Si ratio of (a) 2.0 and (b) 3.0. Their  $H_2O/Si$  and  $H_2SO_4/Si$  ratios were constant at 2.0 and 0.01, respectively.

Table IV The Ratio of Carbonaceous Residue Formed upon Heating the Lignin with Different Degrees of Crosslinking at 1000°C in Ar for 2 h as a Function of the Amount of  $H_2SO_4$  Used for the Formation

$H_2SO_4/C^*$ Ratio	Carbonaceous Residue (Wt %)	
0.003	42.9	
0.33	50.6	

 $H_2O/C^*$  ratio = 0.58.

for SiC powders with high purity. Nevertheless, it can be stated that the lignin can be used as a profitable carbon source for the SiC powder synthesis.

# **CONCLUSIONS**

The lignin–TEOS– $H_2O-H_2SO_4$ –THF solutions underwent a sol–gel reaction to give the lignin– SiO<sub>2</sub> hybrids. During the sol–gel reaction, both the lignin and TEOS underwent hydrolysis and polycondensation. The degree of crosslinking of the lignin depended on the amount of  $H_2SO_4$ added for the sol–gel reaction, and the formation of crosslinked lignin was assumed to be an important factor for the formation of lignin–inorganic oxide hybrid fibers.

SiC powders could be produced by heating the hybrids in the powder form at 1500°C in flowing Ar. The C\*/Si ratio of the starting solutions primarily affected purity of the SiC powders. The degree of crosslinking of the lignin varied the amount of carbonaceous residue formed from the lignin upon pyrolysis. Thus, the amounts of both the lignin and  $H_2SO_4$  were found to be important

factors for producing SiC powders with a low free carbon content. The SiC powders with the lowest free carbon content (0.57 wt %) could be obtained from the hybrid, which was prepared from the starting solution with a C\*/Si ratio of 3.0, a  $\rm H_2O/Si$  ratio of 2.0, and a  $\rm H_2SO_4/Si$  ratio of 0.01.

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