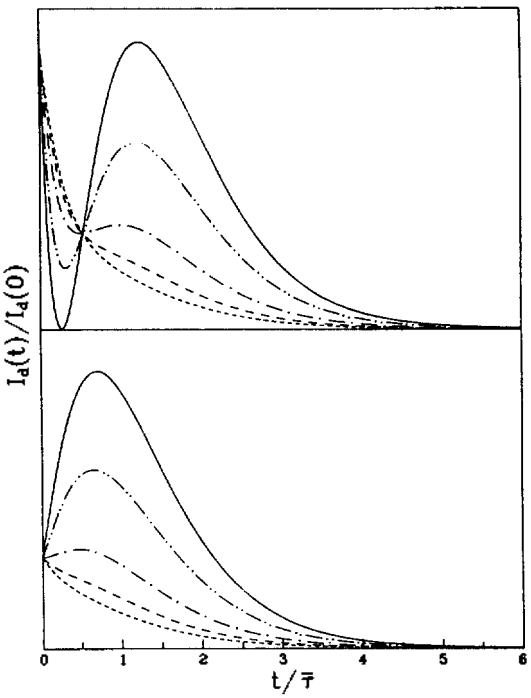

Figure 1. Simulated FRS decay profiles showing how mixed amplitude and phase grating contribution affects the shape of decay profiles for decay-growth-decay type profile (upper plot) and after pulse growth type (lower plot). respectively. They are simulated according to Eq. (4) and relative amplitude of the complementary grating pair is fixed as $A_1/A_2=9.4/8.4$ for easy comparison with ref. 13. The upper plot is for the case of $(\tau_1-\tau_2)/\tau=-0.4$ and the lower one is for $(\tau_1-\tau_2)/\tau=0.4$ where $\tau=(\tau_1-\tau_2)/2$. Each line corresponds to different $\Delta\varphi$; $\Delta\varphi=180°$ (——), 175° (—·—·—), 170° (—·—·—), 165° (------), and 160° (·····).

the effect is only distinct for a decay-growth-decay type FRS signal (the upper plot, the cases of $A_1>A_2$, $\tau_1<\tau_2$ or $A_1<A_2$, $\tau_1>\tau_2$)[12,13] where the phase effect is easily discernible from its intensity at the dip position having non-zero values. On the other hand, for the case of after pulse growth type singnal (the lower plot, the cases of $A_1>A_2$, $\tau_1>\tau_2$ or $A_1<A_2$, $\tau_1<\tau_2$), the phase effect is not clearly visible. Therefore one should be extremely careful in the analysis of the signal if the probe in either its shifted or unshifted state absorbs the reading beam. Even for the decay-growth-decay type signal, for instance in the report by Rhee *et al.*,[3] such phase effect was seemingly not taken into proper account in the analysis.

We close this report by emphasizing the importance of the knowledge on the photochemical properties of chosen probes in order for the correct interpretation of FRS data. It seems to be advantageous for simpler interpretation to choose the experimental condition as either a pure phase or amplitude grating limit. If possible, however, carrying out an experiment at various wavelengths will not only be helpful in deducing correct diffusion coefficients, but also enable us to gain access to other attendant photochemical properties of the system.

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References

1. H. Hervet, L. Leger, and F. Rondelez, *Phys. Rev. Lett.*, **42**, 1861 (1979).
2. H. Kim, T. Chang, J. M. Yohanan, L. Wang, and H. Yu, *Macromolecules*, **19**, 2737 (1986).
3. K. W. Rhee, D. A. Gabriel, and C. S. Johnson, Jr., *J. Phys. Chem.*, **88**, 4010 (1984).
4. M. Antonietti, J. Coutandin, R. Grutter, and H. Sillescu, *Macromolecules*, **17**, 798 (1984).
5. J. Zhang and C. H. Wang, *J. Phys. Chem.*, **90**, 2296 (1986).
6. W. J. Huang, T. S. Frick, M. R. Landry, J. A. Lee, T. P. Lodge, and M. Tirrel, *AIChE J.*, **33**, 573 (1987).
7. Q. Tran-Cong, T. Chang, C. C. Han, and Y. Nishijima, *Polymer*, **29**, 2261 (1988).
8. N. Nemoto, M. Kishine, T. Inoue, and K. Osaki, *Macromolecules*, **23**, 659 (1990).
9. J. Lee, T. Park, J. Sung, S. Park, and T. Chang, *Bull. Korean. Chem. Soc.*, **12**, 596 (1991).
10. H. Kogelnik, *Bell Syst. Tech. J.*, **48**, 2909 (1969).
11. K. A. Nelson, R. Casalegno, R. J. D. Miller, and M. D. Fayer, *J. Chem. Phys.*, **77**, 1144 (1982).
12. C. S. Johnson, Jr., *J. Opt. Soc. Am. B*, **2**, 317 (1985).
13. S. Park, J. Sung, H. Kim, and T. Chang, *J. Phys. Chem.*, **95**, 7121 (1991).

Trisilaalkanes; New Precursors for Ultrafine β Silicon Carbide Powders

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Ultrafine silicon carbide powders have been recognized as the material for the high temperature engineering ceramics because of its excellent thermal shock resistance, high-temperature strength and oxidation resistance.[1] These powders are usually prepared by gas phase pyrolysis method of silicon compounds since this method provides many advantages such as high purity, loose aggregation, small particle size, spherical particle shape, and a narrow particle size distribution, suitable for the structural ceramics with the perfection in microstructure.[2]

Silicon carbide powders have been synthesized by several gas phase processes including plasmas,[3,4] laser radiation[5,6] and conventional gas phase reactions in heated furnace tube.[2,7-9] Though conventional gas phase reaction in the furnace requires high energy, it is regarded as a simple and convenient method for powder synthesis and has advantages of large production rate and capability of using various reactants.

Until now, most of the reactants employed in gas phase

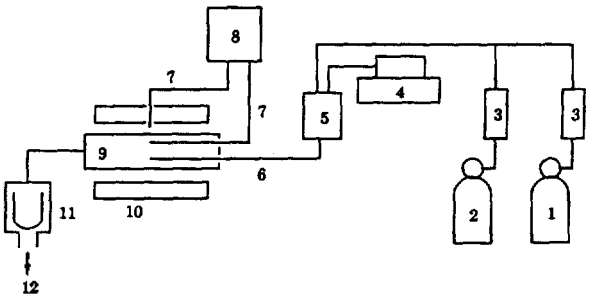
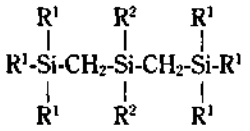


Figure 1. Schematic diagram for pyrolysis of trisilaalkanes. (1) H_2 gas, (2) Ar gas, (3) flowmeter, (4) syringe pump, (5) preheater, (6) stainless steel nozzle, (7) thermocouple, (8) temp. controller and recorder, (9) alumina tube, (10) SiC resistance furnace, (11) stainless steel filter with micron cloth filter bag, (12) gas outlet

processes to produce SiC powder are monosilanes and volatile polysilanes such as silane,[9,10] dimethylsilane,[11] trimethylsilane,[11] tetramethylsilane,[2] methyltrichlorosilane,[3,4] methyldichlorosilane,[7,8] 1,2-dimethyldisilane,[11] 1,1,2,2-tetramethyldisilane[11] and 1,1,2,3,3-pentamethyltrisilane.[11] Generally, silane and methylsilanes are difficult to synthesize and handle, and inadequate for large production. Methylchlorosilanes are readily available materials but they are thermally stable and difficult to decompose so that the powder yields are low. Also sometimes products are hard agglomerates or contain free silicon.[7] Polysilanes have been reported as good precursors for silicon carbide powders but they are even more difficult to synthesize, either from Wurtz type condensation of methylchlorosilanes with sodium or as by-products in small quantities from the direct reaction of metallic silicon and methylchloride.[12,13] Recently it was reported that 1,3-disilacyclobutane could be utilized for silicon carbide.[14]

Herein we wish to report that trisilaalkanes prepared by the direct reaction of α-chloromethylsilanes with metallic silicon[15] can be new precursors for ultrafine silcon carbide powders by the conventional gas phase reaction in a simple furnace tube. Trisilaalkanes (I) have a molecular backbone of silicon and carbon in alternating pattern and are expected to be good precursors for silicon carbide materials due to the polycarbosilane backbone.[16-18]



wherein R^1=CH_3, Cl, H; R^2=Cl, H

When various trisilaalkanes[19] were pyrolyzed,[20] the products were ultrafine β SiC powders with diameters less than 100 nm, measured from SEM and TEM photographs (Figure 2a, b). These results are listed in Table 1. Photographs also showed spherical shape of the particles. Those particle sizes were consistent with the average particle diameters calculated from the specific surface areas, measured by BET methods. Crystal structure of the powders was identified to be β SiC from XRD patterns showing the peaks at 2θ=35.7, 60.0, 71.8° (Figure 3). The crystallites,[3,5,11] which were constituting the particle, could be identified in the TEM photographs and the sizes were estimated as less than 10 nm, reasonably close to the calculated value of about 2 nm from the Scherrer equation using halfwidth of the (111) peak at 35.7° of XRD results.[22] Therefore it was concluded that SiC powders could be prepared by the simple pyrolysis of trisilaalkanes at the temperature of 1200-1400℃ with the high powder yields and that the products were ultrafine particles of SiC each having a spherical configuration of 0.01 to 0.1 μm in diameter formed of crystallites of β type SiC with a size of 2 to 5 nm.

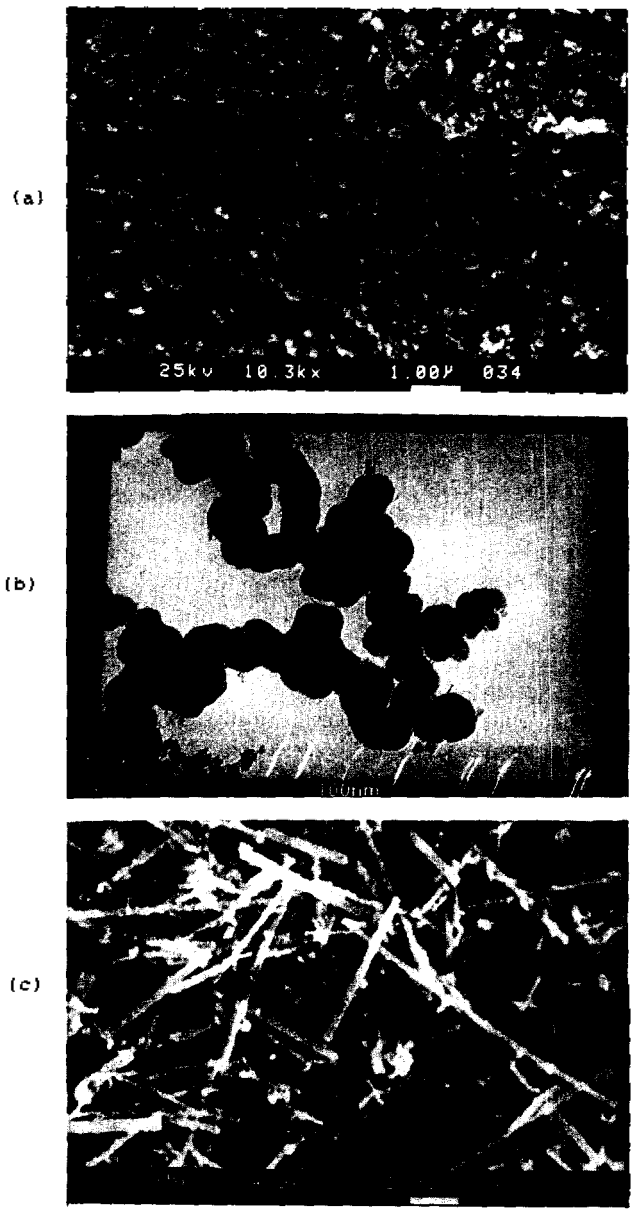


Figure 2. (a) SEM and (b) TEM photographs of SiC powders from 2,6-Dimethyl-2,4,6-trisilaheptane (Ar), and (c) SEM photograph of SiC fibers from 2,6-Dimethyl-2,4,4,6-tetrachloro-2,4,6-trisilaheptane (H_2).

However the powder products showed the characteristics of the reactants and carrier gases. When pyrolyzed in Ar atmosphere, 2,4,6-trisilaheptane and 2,6-dimethyl-2,4,6-trisilaheptane (Exp. 1, 2; Si : C ratio=3 : 4; 3 : 6) gave black pow-

Table 1. Silicon Carbide Powders from Various Trisilaalkanes

Exp.	Trisilaalkane	Carrier gas	Temp. (℃)	*SiC Powders* Powder yield (%)	Specific surface Area(m^2/g)	Particle size (μm) TEM	Particle size (μm) Surf. Area	Crystallite size (nm) XRD	Crystallite size (nm) TEM
1	CH_3-SiH_2-CH_2-SiH_2-CH_2-SiH_2-CH_3	Ar	1200	94.1	23.0	0.080-0.100	0.087	1.9-2.1	<10
2	$(CH_3)_2$SiH-CH_2-SiH_2-CH_2-SiH$(CH_3)_2$	Ar	1200	93.1	22.0	0.080-0.100	0.091	1.7-1.9	<10
3	SiH_3-CH_2-SiH_2-CH_2-SiH_3	Ar	1300	81.1	29.3	0.040-0.060	0.068	2.8-3.3	<10
4	SiH_3-CH_2-SiH_2-CH_2-SiH_3 and CH_3-SiH_2-CH_2-SiH_2-CH_2-SiH_2-CH_3 (1 : 1)	Ar	1400	68.1	50.6	0.015-0.020	0.040	1.9-2.8	<10
5	$(CH_3)_2$SiH-CH_2-SiH_2-CH_2-SiH$(CH_3)_2$	H_2	1400	62.9	19.0	0.060-0.080	0.105	2.4	<10
6	$(CH_3)_2$ClSi-CH_2-$SiCl_2$-CH_2-SiCl$(CH_3)_2$	H_2	1400	44.1	33.5	0.030-0.040	0.060	4.2-5.2	<10

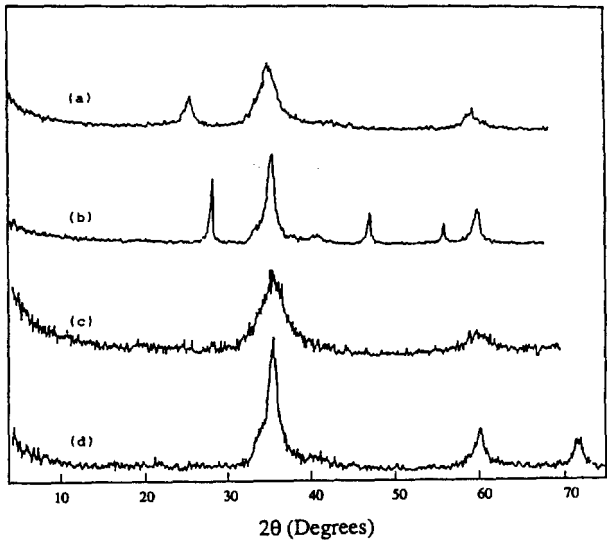


Figure 3. XRD patterns of SiC Powders from (a) 2,4,6-Trisilaheptane (Ar), (b) 1,3,5-Trisilapentane (Ar), (c) 2,6-Dimethyl-2,4,6-trisilaheptane (H_2), and (d) A mixture of 2,4,6-Trisilaheptane and 1,3,5-Trisilapentane (Ar).

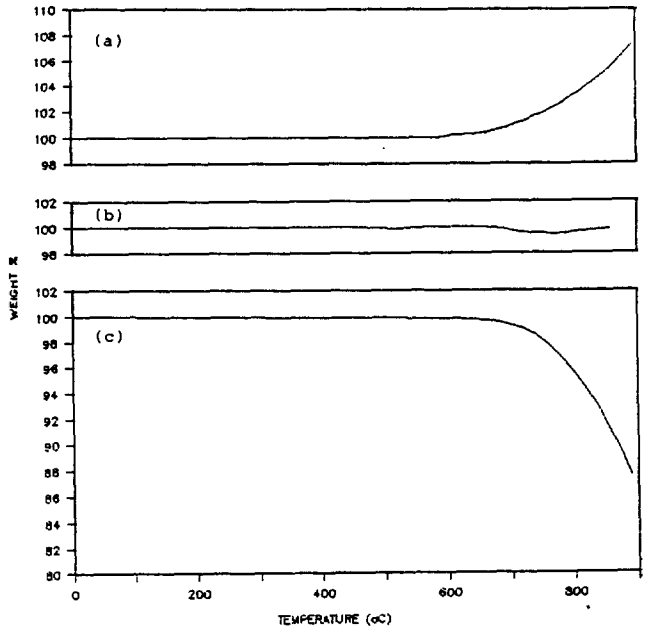


Figure 4. TGA (Air, 20℃/min) of SiC powders from (a) 1,3,5-Trisilapentane (Ar), (b) A mixture of 1,3,5-Trisilapentane and 2,4,6-Trisilaheptane (Ar), and (c) 2,4,6-Trisilaheptane (Ar).

ders with the yields of 94.1 and 93.1%, respectively. These powders showed graphite peak at $2\theta = 25°$ in XRD patterns (Figure 3a), weight loss in TGA in the air due to the oxidation of graphite to CO_2 (Figure 4c), Si : C mole ratio of 1 : 1.31 and 1 : 1.44 from the elemental analysis, indicating free carbon in SiC. On the contrary, 1,3,5-trisilapentane (Exp. 3; Si : C ratio = 3 : 2) gave gray-brown powders with the yield of 81.1%. The brown powders showed free silicon peaks at $2\theta = 28.3$, 47.3, 56.0° in XRD pattern (Figure 3b), weight gain in TGA in the air due to the formation of SiO_2 (Figure 4a), Si : C mole ratio of 1 : 0.72, indicating free silicon in SiC. When reactants were mixed for equal composition of silicon and carbon (Exp. 4, Si : C ratio = 6 : 6), products were white-gray powders with the yield of 68.1%. This powders showed only β-SiC peaks in XRD pattern (Figure 3d), no weight changes in TGA in the air (Figure 4b) and equivalent Si : C mole ratio. In cases of Exp. 1 and 2, it was believed that the deposition of free carbon or silicon might increase the powder yields and the compositions of powders could be controlled by changing trisilaalkanes.

Carbon-rich 2,6-dimethyl-2,4,6-trisilaheptane was pyrolyzed again under H_2 (Exp. 5) and white-gray powders were obtained with the yields of 62.8%. Though more carbons are present in the reactant, products and yield were similar to Exp. 4, showing β SiC peaks only in XRD pattern (Figure 3c), no weight change in TGA in the air. Therefore it was thought that the excess carbon was removed by H_2 as CH_4 effectively.

When 2,6-dimethyl-2,4,4,6-tetrachloro-2,4,6-trisilaheptane (Exp. 6, Si : C ratio = 3 : 6) was pyrolyzed under H_2, the products were a mixture of loosely aggregated fibers and powders with gray-brown color. They yield was 44.1%, quite lower than others. H_2 was employed because H_2 was necessary to break Si-Cl bond for the pyrolysis of chlorine containing silanes.[3,7] SEM photograph (Figure 2c) showed that the fiber products were about 0.5 μm in diameter. However TEM photograph of powder product showed spherical particles of the size of about 50 nm. Judging from the color and XRD patterns, the powder products contained free silicon in SiC. This

was rather peculiar results because more carbons were present in the reactant. It was reported that when methyldichlorosilane (Si : C ratio=1 : 1) was pyrolyzed under H_2, the products were also brown.[7] When Exp. 5 and 6 were compared, the only difference was the presence of chlorine in the reactant. Therefore the presence of chlorine must be the reason for presence of free silicon, the lower yield and the formation of fiber products.

The mechanisms for gas phase pyrolysis are regarded to be complex.[2,3,5] When heated, trisilaalkanes decompose to the fragments. Fragments may be gaseous atoms or radicals of silicon or carbon. Recombination of gaseous silicon and carbon followed by condensation gives SiC in solid state. The advantages of using trisilaalkanes are recombination to or formation of silicon carbide may be easy because of Si-C polycarbosilane structure. Also high powder yields are expected as shown in the results. However when silicon or carbon is in excess in the reactant, that element in gaseous state condense alone to give the same element in excess in products. The excess carbon can be removed by pyrolyzing under H_2 giving SiC only. Since pyrolysis of chlorotrisilaalkane under H_2 gives free silicon containing SiC, it is assumed that free silicon can not be removed by H_2.

The effect of chlorine in the pyrolysis is difficult to deduce. But in order to explain free silicon in SiC from carbon-rich trisilaalkanes, gaseous chlorine or chlorine containing fragments must interfere recombination of gaseous silicon and carbon, providing more chances for carbon being removed by H_2 gas leaving free silicon in the products.[23] This may be the reason for the low powder yield. It is not clear how chlorine interfere recombination but further investigations for effects of chlorine are in progress.

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References

1. W. H. Rhodes and S. Natansohn, *Am. Ceram. Soc. Bull.*, **68**, 804 (1989).
2. H. D. Wu and D. W. Readey, in "Ceramic transactions, Vol. II, Silicon Carbide"; J. D. Cawley and C. E. Semler, Eds., Am. Chem. Soc.; Westerville, OH, 1989.
3. A. Kato, T. Ozeki, and J. Hojo, *J. Less-Common met.*, **92**, L5 (1983).
4. H.-S. Park, H.-S. Seon, S.-H. Rhee, K.-H. Lee, and S. Baik, *J. Mat. Sci.*, **26**, 5957 (1991).
5. Y. Suyama, R. A. Marra, J. S. Haggerty, and H. K. Bowen, *Am. Ceram. Soc. Bull.*, **64**, 1356 (1985).
6. R. A. Marra and J. S. Haggerty, *Ceram. Eng. Sci. Proc.*, **3**, 3 (1982).
7. S. Takenaka, Jpn. Kokai Tokkyo Koho 61307 (1989).
8. S. Takenaka, Jpn. Kokai Tokkyo Koho 83510 (1989).
9. L. Chen, T. Goto, and T. Hirai, *J. Mater. Sci.*, **24**, 3824 (1989).
10. C. H. Pai, K. Koumoto, S. Takeda, and H. Yanagida, *J. Mater. Sci.*, **24**, 3679 (1989).
11. M. Endou, M. Takamizawa, T. Hongu, T. Kobayashi, A. Hayashida, N. Urasato, H. Ohsaki, N. Suzuki, and T. Toide, U. S. Patent 4571331 (1986).
12. R. J. H. Voorhoeve, "Organohalosilanes, Precursors to Silicones", Chap. 4, Elsevier Publishing Co., New York, 1967.
13. W. Noll, "Chemistry and Technology of Silicones", Chap. 2, Academic Press, New York, 1968.
14. D. J. Larkin and L. V. Interrante, *Chem. Mater.*, **4**, 22 (1982).
15. I. N. Jung, G.-H. Lee, S. H. Yeon, and M. Y. Suk, *Bull. Korean Chem. Soc.*, **12**, 445 (1991).
16. J.-H. Hong, J. S. Han, G.-H. Lee, and I. N. Jung, *J. Organomet. Chem.*, **437**, 265 (1992).
17. I. N. Jung, G.-H. Lee, and C.-H. Song, Korea Patent Appl. 4705 (1992).
18. I. N. Jung, G.-H. Lee, M. Y. Suk, and S. H. Yeon, *Bull. Korean Chem. Soc.*, **12**, 705 (1991).
19. Chlorotrisilaalkanes were synthesized by the direct reaction of metallic silicon and α-chloromethylsilanes in a stirred bed reactor as described in a literature (Ref. 15). Trisilaalkanes have been reported and were prepared by the reduction of chlorotrisilaalkanes by lithium aluminum hydride in dibutylether, 2,4,6-trisilaheptane (*cf.* Ref. 21a) from 2,2,4,4,6,6-hexachloro-2,4,6-trisilaheptane, 2,6-dimethyl-2,4,6-trisilaheptane (*cf.* Ref. 21b) from 2,6-dimethyl-2,4,4,6-tetrachloro-2,4,6-trisilaheptane and 1,3,5-trisilapentane (*cf.* Ref . 21c) from 1,1,1,3,3,5,5,5-octachloro-1,3,5-trisilapentane.
20. Trisilaalkanes or chlorotrisilaalkane were pyrolyzed in alumina tube (internal diameter 65 mm, length 1200 mm; heating zone 600 mm) at the temperature of 1200-1400℃ under Ar (UHP grade and purified), or H_2 (UHP grade) atmospheres. A scheme of the reaction system was shown in Figure 1. Liquid trisilaalkanes were introduced to the preheater (150℃, filled with glass beads) for vaporization by a syringe pump (KASP-005/150 MT. Keun-a Mechatronics Co., with Hamilton gas tight syringe) and the carrier gas pushed the reactant vapor to the furnace. The nozzle for reactant-carrier gas was extended to the center of the tube where the exact temperature was monitored. Injection rates of reactants were about 2 g/hr with the carrier gas flowrates of 600-900 ml/min. Reactant concentration in the carrier gas were about 0.5 to 5 vol%. Usually injection was continued for 1-6 hours. After injection, the temperature was maintained for 30 minutes under same carrier gas for the completion of pyrolysis. The products were collected mainly from the tube, distributed from the nozzle to the end of the tube in the direction of the carrier gas, as loosely aggregated form of powders in case of trisilaalkanes or a mixture of powders and fibers in case of chlorotrisilaalkane. Small amount of product, which was carried away during the reaction, was collected at the micron cloth filter outside the reactor. However, there was no hard deposition on the tube. The products were characterized by X-ray diffraction (CuKα) for the phases in the silicon carbide; FT-IR spectroscopy for composition; BET method for specific surface area; electron microscopy for the shape, size and strucutres of the particles; TGA in the air for excess carbon and silicon; elemental analysis for Si : C mole ratio.
21. (a) G Fritz and J. Honold, *Z. Anorg. Allg. Chem.*, **556**, 23 (1988); (b) G. Fritz, J. Maas and A. Hornung, *Z. Anorg. Allg. Chem.*, **460**, 115 (1980); (c) G. Fritz and K. H. Schmid, *A. Anorg. Allg. Chem.*, **441**, 125 (1978).

22. B. D. Cullity, "Elements of X-Ray Diffraction", 2nd ed., pp. 102; Addison Wesley Publishing Co., Reading, MA, 1978.
23. When the same chlorodisilaalkane was pyrolyzed under H_2 or H_2+Ar (1 : 2), dilution of H_2 with Ar changed the color of powder products from brown-gray to white-gray, compositions from free silicon containing SiC to SiC only. When H_2 was diluted with Ar, it was thought that scavenging of carbon by H_2 might be decreased, recombination of SiC increased (Unpublished Results).

Liquid Chromatographic Resolution of α-Arylpropionic Acids on a π-Basic Chiral Stationary Phase

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Many of nonsteroidal antiinflammatory drugs (NSAIDs) are α-arylpropionic acids. Two enantiomers of some of these drugs have been known to show different metabolic pathway and different pharmacological activity, the (S)-enantiomers being generally more active.[1] For example, the inactive (R)-(−)-enantiomer of ibuprofen (see Figure 1 for the chemical structures of NSAIDs) is known to be converted to the active (S)-(+)-enantiomer *in vivo*.[2] The decreased rate of metabolism and excretion of benoxaprofen in elderly patients exerted by the inversion of (R)-(−)-enantiomer of benoxaprofen to its (S)-(+)-enantiomer has led to the hepatotoxicity and the withdrawal from the market.[3] However, among the commercial NSAIDs, only naproxen is sold as a single enantiomer form.

Because of the biological significance of the stereochemistry of NSAIDs, the accurate and convenient means of measuring the optical purity of NSAIDs has been required and the chromatographic separation of enantiomers on chiral stationary phases (CSPs) has been the choice. Previously, several research groups have reported the chromatographic separation of the enantiomers of NSAIDs as their π-basic amide derivatives or without derivatization on the CSP derived from (R)-N-(3,5-dinitrobenzoyl)phenylglycine[4] or on the CSP based on protein or cellulose.[5] More recently, the improved CSP for the stereoselective separation of naproxen without derivatization has been developed.[6] However, the π-basic CSP which is known to be useful for the resolution of π-acidic compounds has not been fully studied for the resolution of NSAIDs.[7] In this paper, we report the resolution of various NSAIDs as their 3,5-dinitroanilide derivatives **1** on CPS **2** which has been widely used for the resolution of variety of racemates[8] and we propose the possible chiral recognition mechanism.

The stereoselective π-π interaction between CSP **2** and the analytes has been known to be essential for the chiral recognition.[8] CSP **2** has a strong π-basic functionality such as 6,7-dimethy-1-naphthyl group and, in consequence, is expected to resolve racemic NSAIDs as their π-acidic derivatives. In this study, nine kinds of NSAIDs purchased from drug stores were converted to 3,5-dinitroanilide derivatives **1** by simply treating the acid chlorides of NSAIDs with 3,5-dinitroaniline in dry methylene chloride at room temperature and then resolved on CSP **2**. As shown by the chromatographic resolution results summarized in Table 1, it was found that CSP **2** was reasonably good in resolving two enantiomers of NSAIDs as their 3,5-dinitroanilide derivatives. The elution orders for ibuprofen and naproxen shown in Table 1 were determined by chromatographing the partially resolved ibuprofen obtained by the known classical resolution method with (R)- or (S)-α-phenylethylamine[9] and the optically pure naproxen which is commercially available.

To explain the chromatographic resolution results, from the study with space filling molecular model we propose the chiral recognition model shown in Figure 2. The conformation of CSP **2** shown in Figure 2 has been thought to be heavily populated.[8] Similarly, the analyte shown in Figure 2 is presumed in the lowest energy conformation in which the methine hydrogen on the stereogenic center is eclipsed with the amide hydrogen[10] and, in consequence, approxima-

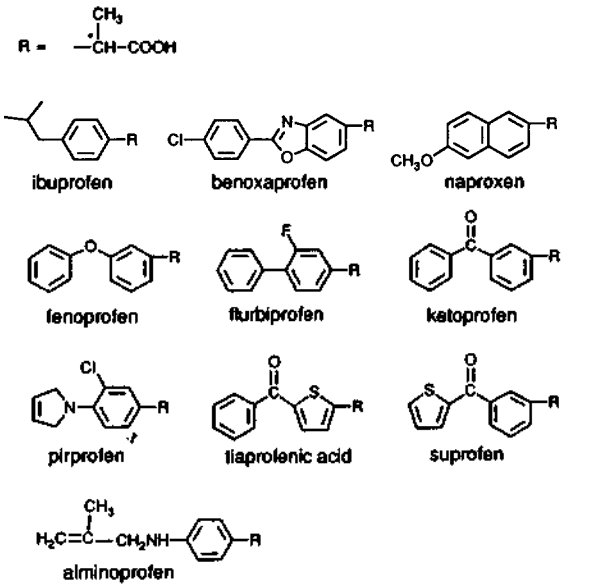

Figure 1. Chemical structures of α-arylpropionic acids (NSAIDs) mentioned in this study.