A simple synthetic route of polycarbosilane precursor using nanoporous anodized aluminum oxide


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ABSTRACT
A simple catalytic synthesis of polycarbosilane (PCS) from polydimethylsilane (PDMS) was developed by using anodized aluminum oxide (AAO). Three types of AAO catalysts were used: spiral, stirrer, and cylinder. The AAO catalysts can be reused and do not need a filtering process, which can simplify the complex synthetic processes of PCS and save time and cost. The catalytic property of AAO comes from the high specific surface area of its nanopores and its many Lewis acid sites. By including the total synthetic process of spinable PCS, electrospun PCS was also produced.

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1. Introduction
Silicon carbide (SiC) fibers exhibit an excellent high-elastic modulus, high-tensile strength, and high-temperature stability [1,2], excelling over carbon fibers, and are expected to be used as extreme materials in the space shuttle, aircraft, and nuclear fusion fields [3,13], including applications as clean environmental materials, such as for radiation gas burners [3] and high power electrical cables [4]. Fundamentally, the fabrication of SiC fibers depends critically on the spinability of the polycarbosilane (PCS) precursor, including the pyrolysis process. Therefore, the synthesis of spinable PCS has been a key technique in the SiC fiber industry [1–8], since the development of spinable PCS by Yajima et al. [5]. Because PCS and SiC fibers have been considered as strategic materials over country, their synthetic processes are rather unveiled and have not been widely studied. The synthesis of spinable PCS is very complex, involving: (1) alkali-metal reductive coupling of dimethyldichlorosilane (DMDS) to polydimethylsilane (PDMS), (2) catalytic conversion from PDMS to PCS, and (3) thermal polymerization for spinable PCS [9,10]. In particular, the catalytic conversion process from PDMS to PCS is very important because of the “insertion rearrangement of the methyl group” between the Si–Si backbones of PDMS (Kumada rearrangement) [9]. This insertion process happens at high-temperature thermal conversion (commercialized) or at low temperature catalytic conversion on the surface acid sites of catalysts (non-commercialized). A well balanced regular backbone of “Si–C–Si–C” for PCS is essential for the fabrication of homogenous SiC fibers, due to the stoichiometric and geometric balance of carbon and silicon during ceramization (thermal treatment).

Hasegawa and Okamura reported halide catalysts of MCl$_3$ ($M = Al, Mn, V,$ and $Ti$) [9,11]. Duboudin et al. reported monomeric boron catalysts like borane and $B(OMe)$_3 [9,12]. However, these two catalytic methods provided low yields, and it is difficult to separate the catalysts from the finally formed PCS. Recently, Kim et al. reported that ZSM-5 zeolite has good catalytic properties, but is expensive [13,14]. However, with this method it is difficult to separate the powder ZSM-5 from the produced PCS. Here, we report a very simple and good catalytic conversion process from PDMS to pure PCS using very cheap anodized aluminum oxide (AAO), which does not need a filtering process [15]. It should be noted that the filtering process for conventional powdery catalysts needs a dilution process to control the polymer viscosity for filtering and a drying process to remove the solvents. Therefore, the filtering process for powdery catalysts is undesirable in terms of cost, time, and yield for industrial mass production.

2. Experimental
Spiral-, stirrer-, and cylinder-type Al (99%) were degreased and then anodized by applying a voltage of 40 V in a 0.3 M oxalic acid for 3 h at room temperature [15]. As shown in process I of Fig. 1, the produced spiral-type AAO catalyst was inserted into a stainless steel (SS) reaction tube and then PDMS powders (1 g) were...
packed into it. The SS tube diameter and length were 3/8 inch and 20 cm, respectively (Swagelok Co.). Three samples for no catalyst, ZSM-5 (Si/Al = 30) [13], and spiral-type AAO wire were introduced simultaneously into a 350–400 °C furnace to perform a comparison of the effects of the catalysts. PDMS has been synthesized by the continuous reaction of DMDS (KCC Co., Korea) with sodium metal in toluene, as described in a previous paper [14]. The molecular weight distributions were determined using a GPC instrument (Waters 2414 refractive index detector, 515 HPLC pump, and three consecutive Styagel columns (HR1, HR2, and HR3). The PCS structure was characterized by solution-state 29Si NMR.

3. Results and discussion

3.1. Surface and cross-section morphologies of AAO catalysts

Fig. 2 shows scanning electron microscope (SEM) images of the catalytic surface and cross-section of the AAO. Alumina nanopores entirely cover the Al surface. The nanopore size ranges from 40 to 100 nm. Conventional two-step anodizing of high purity aluminum forms regular nanopore arrays due to aluminum pretexture and strain effect [15]. However, this method uses only one-step anodizing for cheap aluminum, resulting in irregular nanopores with a broad size distribution. Nevertheless, the irregular alumina nanopores show an excellent catalytic effect. Thus, this low cost process is very desirable for the mass production of PCS.

3.2. NMR and GPC analysis of PCS

Fig. 3a shows 29Si-NMR spectra for no catalyst, ZSM-5, and spiral-typed AAO wire, respectively, by using process I. There are two main peaks corresponding to SiC4 (0.4 ppm) and SiC3H (−17 ppm) [16]. Small peaks at 7 ppm (SiC3O) and −37 ppm (Si–Si) are caused by the influence of oxygen and the by-product of unreacted PDMS [16]. All three samples showed PCS converted from PDMS. However, as shown in the GPC curves, the three samples clearly show different molecular weight ($M_w$) distributions of PCS. The case of no catalyst shows large amounts of low $M_w$ PCS and small amounts of high $M_w$ PCS.
of high \( M_w \) PCS, while the ZSM-5 and AAO cases show similar \( M_w \) distributions. Therefore, the spiral-type AAO catalyst showed the following two effects: (1) successful catalytic conversion from PDMS to PCS, as much as ZSM-5 and (2) no filtering. The several sharp peaks of low \( M_w \) in the range of 26–28 min (elution time) originate from cyclic polysilane with or without a carbosilane skeleton for a \( M_w \) of 100–200 [11].

3.3. Large-scaled synthesis of PCS

Based on the results of the AAO catalytic effect as shown in the GPC and NMR data for spiral-type AAO, a 1 kg-batch scale production was tried using AAO, as shown in process II (Fig. 4). The large cylinder- and stirrer-type AAO catalysts were used as a reaction chamber wall and stirrer. Powdery ZSM-5 was also used as a comparison with the catalytic effects of AAO. The reaction chamber had a condenser, cooling system, inert gas flow system, and computer-control/monitoring system for temperature and pressure [14]. After placing 1 kg of PDMS into the reaction chamber with the cylinder-type AAO catalyst, the catalytic AAO stirrer was continuously rolled at 350 °C. After terminating the catalytic conversion, the produced liquid PCS (\( M_w \sim 950 \)) was directly extracted from an outlet at the bottom of the reaction chamber, and used without any filtering process. The yields of PCS in the cases of AAO and ZSM-5 were 51% and 49% to 1 kg PDMS, respectively. The liquid PCS was further thermally polymerized for spinable PCS at 400 °C for 10 h. The finished product of spinable solid PCS (\( M_w \sim 1500 \)) is shown in Fig. 5a.

3.4. Preparation of PCS fibers with electrospinning

The solid PCS (dark brown) was dissolved in toluene, and then electrospun. The PCS solution was loaded into a micro syringe with a capacity of 5 ml and subjected to electrospinning using a metallic needle with a diameter of 0.5 mm at a rate of 0.5 mm/h (micro syringe pump) under an applied voltage in the range of 15–30 kV [17]. The PCS solution can be stretched without drop formation up to 23 kV. The distance between the needle tip and the collector, which was covered with a metal mesh for easy separation of the fiber web, was 100 mm. Fig. 5b and d shows that the electrospun PCS fibers are very continuous, and homogeneous in the range of a few micrometers.

Hasegawa and Okamura proposed that the molecular shape of catalytically produced PCS was planar and complex, consisting of linear and ring-type molecular structures with main chains of SiC₄ and SiC₃H and their branched structures [11,16]. The PCS produced from ZSM-5 was also proposed to have the same structure as the “Hasegawa and Okamura proposal”. Based on similar GPC and NMR results, the PCS structure using AAO catalysts may be similar to that using ZSM-5, as shown in the AAO catalytic conversion (Scheme 1). ZSM-5 or zeolite catalysts are well known as a good Lewis acid, which plays a critical role in the conversion from PDMS to...
Kumada rearrangement induces radical formation (Si) by direct bond cleavage of the Si–Si backbone of PDMS [9]. Solid-phase acid catalysts such as zeolites are strongly related to dehydrogenative coupling (SiH) and thereby to bond weakening or the cleavage of SiCH₃ bonds by Lewis acid sites [18]. The AAO surface aluminum cation sites are also known to be good Lewis acids [19,20]. Intuitively, two transition states may be critical for the AAO-induced conversion from PDMS to PCS: The first is that adsorption of PDMS molecules on the AAO catalyst, which is helpful for the direct cleavage of PDMS (reducing the activation energy with the thermal barrier) and radical formation at low temperature. The second is the stabilization of the SiCH₂ states after the production a gaseous silylene and SiH-containing species, together with the weakening of the SiCH₃ bond by the AAO Lewis acid. The radical SiCH₂ species thus stabilized can easily undergo Kumada rearrangement by CH₂ insertion into the Si–Si bond. However, the detailed mechanism and transition states should be further studied by laser spectroscopy. In conclusion, three types of AAO, spiral, stirrer, and cylinder, were produced in an oxalic acid and used as catalysts for the conversion from PDMS to PCS. The AAO surfaces comprise nanopores (high specific surface areas) with many Lewis acid sites. The AAO catalysts clearly show three important facts: (1) catalytic properties as good as ZSM-5, (2) reusability by a simple washing treatment, and (3) no need for a filtering process, which can simplify the complex steps of PCS synthesis. By including the synthetic process of spinnable PCS, homogeneous and continuous PCS fibers were also produced by the electrospinning method.

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