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Anchoring sulfonic acid on silica surface through Si—C bond for immobilization of catalyst for polyketone synthesis

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ABSTRACT

Sulfonic acid groups were anchored on a silica surface through robust Si—C bonds. The successive treatment of dehydroxylated silica with benzylmagnesium chloride and H_2SO_4 resulted in the surface tethering of $—CH_2C_6H_4SO_3H$ groups at a high coverage rate (0.50-$CH_2C_6H_4SO_3H$/nm^2). The pore structure of the silica remained unchanged during this surface-modification process. Next, the $—CH_2C_6H_4SO_3H$ groups on the surface were successfully used for preparing a supported catalyst for CO/ethylene copolymerization; the $≡Si—CH_2C_6H_4SO_3H$ groups on the surface were reacted with [1,3-bis(di(2-methoxyphenyl)phosphino)propane]Pd$(OAc)_2$ to generate dicationic palladium species, which were anchored on the silica surface through ionic interactions with the sulfonate anions generated on the surface. The supported catalyst prepared in this way exhibited a high activity (up to 43 kg/g-Pd or 0.61 kg/g-cat) with respect to CO/ethylene copolymerization. The morphology of the obtained polymer particles replicated that of the silica particles. Thus, a polymer powder that exhibited a high bulk density (0.30 g/mL) could be obtained while causing minimal reactor fouling.

1. Introduction

Polyketones are thermoplastic polymers that are prepared by the alternating copolymerization of carbon monoxide (CO) and olefins [1–5]. A highly active catalyst for synthesizing polyketones was developed by Shell in the 1980s and was commercialized under the trade name Carilon (Scheme 1) [6,7]. Shell shut down the project in early 2000; however, the commercial development of this catalyst has continued, especially in Asian countries [8–13]. Commercially relevant polyketone is available in the form of a CO/ethylene copolymer and a CO/ethylene/propylene terpolymer; these are semicrystalline polymers having melting temperatures (T_m) of 270 and ~220 °C, respectively. The highly active catalyst developed by Shell is a homogeneous catalyst composed of a dicationic palladium center, a 1,3-bis[di(*o*-methoxyphenyl)phosphino]propane ligand, and a noncoordinating anion such as *p*-toluenesulfonate (*p*TsO$^-$) (**1** in Scheme 1) [14]. Typically, the copolymerization is performed in methanol at ~90 °C in the presence of CO and ethylene; the thus-synthesized catalyst exhibits an activity as high as 8–10 kg/g-Pd h. The copolymer is insoluble in methanol, and the polymer precipitates in the form of irregular-shaped white particles or lumps. This irregular particle morphology lowers the bulk density, which reduces the productivity per unit reactor volume. Some of the polymer particles stick to the reactor wall and the agitator, hindering a large-scale commercial processing; this is called "reactor fouling". Shell reported that this problem could be overcome by feeding a seed powder at the start of the batch polymerization process and by using an excessive amount of a strong acid in the recipe of catalyst preparation [7]. The use of the seed powder and a strong acid promotes the agglomeration of the synthesized polymer particles, consequently building up the bulk density to 0.3–0.4 g/mL. To control the morphology and to circumvent the problem of reactor fouling, the suspension polymerization technique, which involves the use of a two-phase water/1-octanol system, was introduced by us; using this technique, polymer chains can be grown in droplets of 1-octanol dispersed in water, resulting in well-controlled polymer particles and the prevention of reactor fouling [15].

In the commercial production of polyethylene or polypropylene, being able to control the morphology of the synthesized polymer particles while preventing reactor fouling is also of a critical importance. Morphology control is typically achieved by using a supported catalyst; a homogeneous metallocene catalyst should be immobilized on a silica support for use in the slurry or gas phase process [16–19]. Polymer chains are subsequently grown from the silica surface, and the morphology of the synthesized polymer particles replicates that of the silica support. Reactor fouling can be

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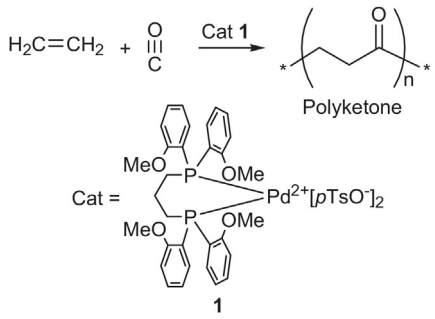


Scheme 1. Polyketone synthesis using the catalyst developed by Shell.

avoided by preventing the leaching of the catalyst. In this study, we synthesized a supported catalyst for producing polyketone [20]. Sulfonic acid units were anchored on a silica surface through robust Si—C bonds to prepare the supported catalyst (Scheme 2(b)).

2. Experimental

2.1. General remarks

All the manipulations were performed in an inert atmosphere using a standard glove box and Schlenk techniques. Diethyl ether was dried using Na/benzophenone and CH_3CN, CH_2Cl_2 and $CDCl_3$ were purified by being stirred over CaH_2 for 1 day. CO gas (99.99%), ethylene (99.0%), and methanol were used as purchased (*i.e.*, without purification) for the polymerization reactions. The silica samples used (XPO2412 from Grace Davison, ES70X from PQ) were provided by the polyolefin industry, while MCM-41 was purchased from Aldrich. Benzylmagnesium chloride and phenylmagnesium bromide were purchased from Aldrich. The elemental analyses were performed at the Analytical Center, Kyung Hee University. The ^{13}C CP TOSS NMR (500 MHz) spectral analyses were performed at the Analytical Center, Seoul National University. The XRD measurements were made at the Analytical Center, Ajou University. The N_2 adsorption–desorption isotherms, obtained at liquid N_2 temperature, were measured using an Autosorb-1 system (Quantachrome). Before the measurement, the silica samples were degassed for 24 h at 140 °C to remove the physically adsorbed water. The bisphosphane ligand [1,3-bis(di(2-methoxyphenyl)phosphino)propane] was prepared according to the procedure reported in the patent [40].

2.2. Attachment of —$CH_2C_6H_5$ group on silica surface

The silica sample was dehydroxylated through weak purging in nitrogen gas at 850 °C for 15 h. Benzylmagnesium chloride (12.0 mmol, 1.0 M in diethyl ether) was added to a slurry of the dehydroxylated silica (3.0 g) in diethyl ether (8 mL) at room temperature, and the resulting mixture was made to react for 12 h without being stirred. Because silica particles can undergo fragmentation when stirred using a magnetic bar, the mixture was made to react in the absence of stirring. An aqueous HCl solution (2.5 N, 75 mL) was added to the mixture, and the modified silica was isolated through filtration. The isolated solid was washed thoroughly and successively with water, methanol, and diethyl ether. Finally, the isolated silica was dried under vacuum for 6 h.

2.3. Sulfonation

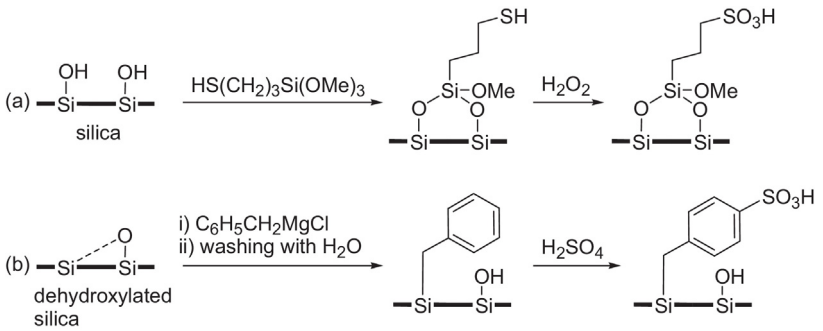
Sulfuric acid (95%, 12 mL) was added to the silica (3.00 g) with the surface-tethered benzyl groups at room temperature. The resulting silica dispersion in sulfuric acid was made to react for 12 h without being stirred. Next, the mixture was poured into water (250 mL), and the silica was isolated through filtration. The isolated silica was thoroughly washed with copious amount of water (~750 mL). The isolated silica was the dried under vacuum at 150 °C for 4 h. Finally, the dried silica (200 mg) was dispersed in water and titrated with a standard NaOH (0.010 N) solution.

2.4. Preparation of **2** [41]

To a stirred solution of $(CH_3CN)_2PdCl_2$ (200 mg, 0.770 mmol) in CH_2Cl_2 (20 mL) was added a solution of 1,3-bis(di(2-methoxyphenyl)phosphino)propane (410 mg, 0.770 mmol) in CH_2Cl_2 (4.0 mL). The solution mixture was stirred for 6 h at room temperature. The removal of the solvent yielded a yellow solid, which was triturated in diethyl ether. The solid was dissolved in methanol (12 mL), and AgOAc (258 mg, 1.54 mmol) was rapidly added to the solution while it was being stirred in an inert atmosphere. After overnight stirring, the precipitated AgCl was filtered using Celite. The solvent was removed under vacuum, yielding a yellow residue, which was dissolved in CH_2Cl_2 and then filtered again to remove the residual AgCl. After the solvent had been removed, the complex was triturated in diethyl ether to isolate a yellow solid (547 mg, 94%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.60–7.35 (br, 4*H*, CH), 7.00–6.90 (br, 8*H*, CH), 46.90–6.70 (br, 4*H*, CH), 3.73 (s, 12*H*, OCH_3), 2.60–2.30 (br, 4*H*, PCH_2), 2.10–1.80 (br, 2*H*, CH_2), 1.24 (s, 6*H*, $C(O)CH_3$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 176.67, 160.28, 134.00–132.00 (br m), 122.00–120.00 (br m), 117.00–115.00 (br m), 110.71, 57.72 (OCH_3), 23.00–22.00 (m, PCH_2), 20.50 (CH_2) ppm. Anal. Calc. ($C_{35}H_{40}O_8P_2Pd$): C, 55.53; H, 5.33. Found: C, 55.76; H, 5.67%.

2.5. Preparation of **3**

To a stirred solution of (COD)Pd(CH_3)Cl (223 mg, 0.841 mmol) [42] in CH_2Cl_2 (20 mL) was added a solution of 1,3-bis(di(2-methoxyphenyl)phosphino)propane (448 mg, 0.841 mmol) in



Scheme 2. Attaching sulfonic acid groups on a silica surface: (a) conventional method and (b) method used in this study.