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Mesoporous titania with anatase framework synthesized using polyphenolic structure-directing agent: Synthesis domain and catalytic metal loading

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ABSTRACT

Crystalline anatase TiO_2 with nanosponge-like mesoporous morphologies was solvothermally synthesized following the recently reported route using random copolymer (4-vinylphenol and methyl methacrylate) as structure-directing agent. In particular, the synthesis conditions were varied over a wide range of synthesis gel compositions. Crystallinity of the titania products was checked with X-ray powder diffraction. Mesopore diameters, pore volume and specific surface area were analyzed using nitrogen adsorption. The result provided proper synthesis domains for highly mesoporous titania materials. The mesoporous materials were evaluated as supports for catalytic Pt nanoparticles to apply for alcohol-to-aldehyde partial oxidation reactions.

1. Introduction

Crystalline mesoporous titania (TiO_2) has attracted considerable attention because of its high-potential applications in sensors [1,2], dye-sensitized solar cells [3,4], lithium-ion battery technologies [5,6], and photocatalysis [7–9]. Mesoporous TiO_2 has also been widely used as a support for noble metal nanoparticles owing to its strong metal-support interaction [10]. This allows a high metal dispersion, and therefore also a high density of catalytic sites. Various noble metals supported on TiO_2 materials are widely used as catalysts in a number of partial oxidation reactions, such as the transformation of alcohol to aldehyde [11,12]. The versatile applicability of mesoporous titania is attributed to its high surface area, large pore volume, and uniform mesopores, which promote a facile diffusion of reactants and products as well as an increase of active accessible sites through the mesopores [13]. In recent years, many researchers have synthesized nanocrystalline anatase TiO_2 in the form of nanosheets [14,15], nanotubes [16], nanosponges [17], and nanoparticles [18,19] using various processes such as sol–gel method [20,21], solvothermal synthesis [22–24], and sonochemical treatment [25,26].

Conventionally, nanocrystalline mesoporous titania has been synthesized by using amphiphilic organic compounds such as surfactants and block copolymers as structure-directing agents (SDAs) [19,27–30]. In the surfactant-directed synthesis, a large number of surfactant molecules are assembled into micelles, forming a mesostructure. The hydrophilic head group in the surfactants is chosen to bind the inorganic source, similarly to the case of the mesoporous silica synthesis (*e.g.*, MCM-41 and SBA-15) [31,32]. The binding affinity is often van der Waals interactions, hydrogen bonding, coordination bonding, or covalent bonding. Compared to the mesoporous silica synthesis, however, the surfactant–Ti interaction is often unstable. The interaction is easily lost due to rapid hydrolysis of the titania precursor during the mesostructure formation, leading to the agglomeration of TiO_2 into large particles (*i.e.*, >20 nm diameter) [28,33]. Further particle sintering can also occur during a high-temperature treatment (>350 °C) to remove the organic SDA after synthesis, or to convert the amorphous TiO_2 framework to crystalline anatase [33]. The excessive framework sintering is prone to lead to a loss of mesopore volume.

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To overcome the sintering problem, mesoporous crystalline titania is synthesized by the nanocasting method using mesoporous silica as a hard template [34]. The nanocasting method requires infiltration of the template mesopores with a suitable TiO_2 precursor. However, even in the case of full infiltration of the entire volume, the titania yield is quite low as the conversion of the titania precursor to crystalline TiO_2 occurs with a large volume contraction. Thus, it is desirable to develop more advanced strategies to obtain nanocrystalline titania having large surface area.

Recently, Jo et al. reported on the synthesis of mesoporous inorganic materials of various compositions and framework structures, such as aluminosilicate zeolites, aluminophosphates, titania, zirconia, and tin oxide, using linear copolymers of randomly distributed functional groups as SDAs [35]. The mesoporous materials typically had morphologies similar to a nanosponge possessing uniform mesopores. The formation of the nanosponge was explained with a random-graft polymer-directed crystallization mechanism, in which the polymers were equipped with functional groups that could strongly bind to an inorganic precursor. Details of the nanosponge synthesis process indicated that the polymers were gelated through binding with inorganic species, prior to the formation of the crystalline nanosponge. Based on this observation, Jo et al. explained the formation of nanosponges by tight binding of the polymer functional groups to the inorganic species. The binding was thought to be maintained during the course of the inorganic crystallization, so that the neighboring polymer backbones could restrict the crystal growth to a thickness of only a few nanometers. This phenomenon was regarded as a TiO_2-polymer phase separation in nanoscale. In the work of Jo et al., the synthesis of titania nanosponge was briefly presented as an example of inorganic nanosponge synthesis. The synthesis principle for TiO_2 was well established, but nevertheless, there still remained a significant amount of investigation to do regarding the synthesis phase domain to obtain highly mesoporous and crystalline TiO_2.

In this study, therefore, we tried to improve the synthesis method for the anatase nanosponges using random copolymers of 4-vinylphenol and methyl methacrylate—*i.e.*, poly(4-vinylphenol-*co*-methyl meth-acrylate), 'PVP-*co*-PMMA' for brevity—as the SDA. The synthesis conditions were systematically investigated by varying the molar ratios of H_2O/Ti and Ti/PVP-*co*-PMMA in the gel composition. The resultant products were characterized by using powder X-ray diffraction (XRD), transmission electron microscopy (TEM), N_2 adsorption, diffuse reflectance Fourier transform infrared spectroscopy (DR-FTIR), X-ray photoelectron spectroscopy (XPS), UV–vis diffuse reflectance spectroscopy (UV-DRS), and Raman spectroscopy. From the result, we obtained every possible synthesis composition that could potentially generate the anatase nanosponges. In particular, the present synthesis condition was acidic as compared to the previous work. This could promote crystallization of TiO_2 frameworks as synthesized, rapidly at low temperature. Furthermore, we investigated the pore textural properties and thermal stability of the resultant TiO_2 nanosponges, in relation to its applicability as a support for Pt nanoparticles with high dispersion.

2. Experimental

2.1. Materials

Titanium(IV) chloride ($TiCl_4$, 99,9% trace metals basis) and PVP-*co*-PMMA were purchased from Sigma–Aldrich Co. Dimethylformamide (DMF) was purchased from Junsei Chemical Co. Ltd. The distilled water was used in the course of the preparation of the synthetic gel for titania materials.

2.2. Synthesis of TiO_2 nanosponges

The TiO_2 nanosponge was synthesized based on a previously reported method [35]. First, poly(4-vinylphenol-*co*-methyl methacrylate) (PVP-*co*-PMMA, 0.236 g, 1 mol) was dissolved in dimethylformamide (DMF, 20 mL) with magnetic stirring. Titanium(IV) chloride (0.22 mL, 2 mol) was then added dropwise to the solution, followed by reflux for 18 h. After cooling to room temperature, distilled water (0.73 mL, 40 mol) was added to the solution dropwise with continuous stirring. The resulting red-brown transparent solution was placed in an oil bath at 130 °C for 6 h. The gel composition was $1TiCl_4/xH_2O/y$PVP-*co*-PMMA in molar ratio, where x and y were varied over the ranges $1.5 \le x \le 60$ and $0.1 \le y \le 1.65$, respectively. The precipitated product was filtered, washed with ethanol thoroughly, and dried in a convection oven at 60 °C. A calcination treatment was done in O_2 or ozone flow at the desired temperature for 3 h, unless otherwise mentioned. The ozone was generated by an ozone generator (LAB-II, Ozonetech, Korea) where the ozone concentration and flow rate were set to 30% and 200 mL/min, respectively. After the treatment, the reactor was thoroughly purged out with pure oxygen gas, and the resulting product was collected.

2.3. Platinum loading on TiO_2

Samples of Pt supported on either TiO_2 nanosponge or commercial TiO_2 (Aeroxide® P25, Sigma–Aldrich) were prepared by an incipient-wetness impregnation method using an aqueous solution of chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, Sigma–Aldrich). In a typical synthesis, 1 g of calcined TiO_2 material was impregnated with the aqueous solution containing 27 mg of $H_2PtCl_6 \cdot 6H_2O$ by rubbing the mixture with a Teflon-coated spatula. After drying these Pt-impregnated TiO_2 samples at 100 °C, they were then heated in Pyrex tubing with a fritted disk at 300 °C (ramping rate: 1.3 °C min^{-1}) for 2 h under a 50 mL min^{-1} flow of air. The resulting activated samples were then reduced under a 40 mL min^{-1} H_2 flow with linear heating to 300 °C for 4 h and holding for 2 h. Finally, the samples were purged with He (40 mL min^{-1}) at 300 °C for 1 h to remove any chemisorbed H_2.

2.4. Characterization

High-resolution synchrotron X-ray powder diffraction patterns were collected over a 2θ range of 0.4°–5° at 9B beamline at PLS-II. The incident X-rays were vertically collimated by a mirror, and monochromatized to the wavelength of 1.5463(1) Å using a double-crystal Si(111) monochromator. The detector arm of the vertical scan diffractometer is composed of Soller slits, a flat Ge(111) crystal analyzer, anti-scatter baffle, and scintillation detector. XRD patterns were obtained at KAIST with a Rigaku Multiflex diffractometer using Cu Kα radiation ($\lambda = 0.1541$ nm) at 30 kV, 40 mA (1.2 kW). The crystallite sizes were calculated with the Scherrer equation: $d = K\lambda/\beta\cos\theta$, where d is the average crystallite size, K is the shape factor, usually equal to 0.89, λ is the wavelength of the X-ray radiation (0.1541 nm), β is the full width at half-maximum (FWHM) intensity, and θ is the diffraction angle of the (101) peak for anatase ($2\theta = 25.3°$). High-resolution TEM (HR-TEM), selected area electron diffraction (SAED), and elemental mapping images were taken with a FEI Tecnai G2 F30 microscope at an acceleration voltage of 300 kV. Scanning transmission electron microscopy (STEM) images were obtained using a Tiatan cubed G2 60-300 instrument operated at 300 kV and equipped with a spherical aberration corrector. For TEM and STEM imaging, the powder samples were suspended in acetone by sonication and the solution was dropped on a holey carbon grid. The N_2 adsorption–desorption isotherms were measured