ELSEVIER

Materials Science and Engineering B 135 (2006) 20–24

MATERIALS SCIENCE & ENGINEERING B

www.elsevier.com/locate/mseb

Influence of solvents on the formation of Pd and PdO nanoparticles in SBA-15

Seoung-Soo Lee, Ho-In Park, Byoung-Kyu Park, Song-Ho Byeon [*]

College of Environment and Applied Chemistry, Kyung Hee University, Kyung Ki 449-701, Republic of Korea

Received 19 June 2006; received in revised form 5 July 2006; accepted 9 August 2006

Abstract

SBA-15 supported Pd and PdO nanoparticles have been synthesized and compared in three different solvents, ethanol (EtOH), tetrahydrofuran (THF), and supercritical carbon dioxide ($scCO_2$). The particle size distribution and dispersion are strongly influenced by the nature of solvents. When the impregnation of $Pd(hfac)_2$ on SBA-15 without surface functionalization is carried out in ethanol, strong aggregation of Pd nanoparticles is induced on the external surface during evaporation and the size distribution is extremely poor. Loading of Pd precursors in THF induces PdO and Pd nanoparticles both in the mesoporous channels and on the external surface of the silica support. However, the particles even on the external surface are relatively well dispersed and the growth of particle is not significant. In contrast, the impregnation of $Pd(hfac)_2$ precursor in $scCO_2$ solvent results in well dispersed Pd and PdO nanoparticles in the mesoporous channels of SBA-15, where the particle size (∼6 nm) is limited by the mesopore diameter.

Keywords: Pd nanoparticle; PdO nanoparticle; Mesoporous; Supercritical carbon dioxide

1. Introduction

As one of the diverse strategies for the synthesis of nanomaterials, an increasing amount of attention has been paid to the synthesis of nanoparticles and nanowires on templates in the past few years. In particular, the synthesis and deposition of nanoparticles in the pores of mesoporous materials have become rather commonplace [1]. Confinement of the particles in the mesoporous materials can induce narrow size distribution and high dispersion of nanometer-sized metals and metal oxides. Various studies on coating thin layers or loading small particles in the pores of ordered porous materials, such as zeolites, MCM-41, FSM-16, and SBA-15 have been carried out using mainly liquid solvents [2–6].

Palladium metal and palladium alloys are used in a variety of technologically important applications including catalysts and gas sensors [7,8]. Obviously, the porous materials with well-defined pore geometry are attractive as supports and adsorbents for highly selective catalytic reactions by palladium or palladium alloys. The incorporation of Pd into the pores of SiO_2 monoliths was induced by submerging the prepared monoliths in $PdCl_4^{2-}$ solution followed by reduction with either aqueous $NaBH_4$ or gaseous H_2 [9]. Nanometer-sized Pd in the channels of a lyotropic liquid crystal polymer was prepared by the ion exchange reaction, followed by reduction under hydrogen [10]. Impregnation of H_2PdCl_4 on FSM-16 and HMM-1 was investigated to synthesize Pd nanowires by subsequent UV-irradiation [11]. Pd and PdO nanoparticles (∼1.1 nm) were synthesized also in complementary SBA-15 micropores by the ion exchange of surface silanol groups in $Pd(CH_3COO)_2$ ammonia solution [12].

Typically, the low diffusivity, wettability, surface tension, and high viscosity could prevent liquid solvents from penetrating into the porous structures of substrates. The process using the vapor phase is one of the effective methods for the impregnation of Pd into the mesopores. For instance, Pd nanowire was prepared in MCM-41 with the chemical vapor deposition and the thermal decomposition of Pd complexes [13]. In that process, one of disadvantages is that the precursors are limited to those with a high volatility and thermal and moisture stability.

Supercritical fluids (SCFs) exhibit characteristics of both a liquid and a gas. The lack of surface tension between interfaces of solids and SCFs minimizes the mass transport limitations that are usually present in liquid deposition techniques. Yet, SCFs easily dissolve a broad range of chemical compounds that would

---

[*] Corresponding author. Tel.: +82 31 201 2457; fax: +82 31 202 7337.
E-mail address: shbyun@khu.ac.kr (S.-H. Byeon).

0921-5107/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.mseb.2006.08.028

otherwise exhibit very low solubilities under ambient conditions [14]. Therefore, they have been used as solvents for coating or loading the metal particles on porous substrates. The supercritical cabon dioxide ($scCO_2$), for example, has been applied for deposition of metal thin films or metal and alloy particles within porous alumina disks or mesoporous silica templates [15,16]. In the present work, SBA-15 supported Pd and PdO nanoparticles were synthesized using three different solvents, ethanol (EtOH), tetrahydrofuran (THF), and supercritical carbon dioxide. Special attention was paid to investigate the difference in size distribution and dispersion of Pd and PdO particles when the adsorption processes for $Pd(hfac)_2$ precursors on SBA-15 were carried out in different solvents.

2. Experimental

Tetraethyl orthosilicate (TEOS), palladium(II) hexafluoroacetylacetonate ($Pd(hfac)_2$), tetrahydrofuran (THF), poly (ethylene oxide)-block–poly(propylene oxide)-block–poly (ethylene oxide) triblock copolymer $EO_{20}PO_{70}EO_{20}$ were purchased from Aldrich Chemical Co. EtOH and THF were dried prior to use and other materials were used as received.

Mesoporous SBA-15 was prepared according to the literature procedure [17]. TEOS and triblock copolymer $EO_{20}PO_{70}EO_{20}$ (Pluronic P123) was used as the silica source and the structure-directing agent, respectively. The copolymer template was removed by calcination at 500 °C for 8 h. Residual powder was heated at 150 °C for 20 h in a vacuum. Palladium(II) hexafluoroacetylacetonate [$Pd(hfac)_2$] was selected as a Pd precursor because of its relatively high solubility in $scCO_2$ [18]. $Pd(hfac)_2$ (Pd, 10.0 wt.%) was dissolved in ethanol (10 mL) containing SBA-15. The mixture was stirred for 24 h, evaporated, and dried under vacuum for 4 h. The same procedure was repeated using THF (10 mL) as a solvent. Impregnations from CO_2 were conducted in 200 mL high-pressure stainless steel reactor sealed with a high-pressure needle valve at both ends and equipped with a pressure gauge. SBA-15 (0.5 g) and $Pd(hfac)_2$ (∼10.0 wt.% in CO_2 solution) were loaded into the separated stainless holders at ambient condition. Both holders were placed in the reactor and allowed to equilibrate to 60 °C. Carbon dioxide was then added to 100 bar using a high-pressure syringe pump (Isco Inc. Model 260D) that was maintained at the desired temperature using a water jacket. The reaction was allowed to stand for a period of 5 h. Two kinds of $Pd(hfac)_2$-loaded SBA-15 ($Pd(hfac)_2$/SBA-15), which were prepared in ethanol and THF, respectively, were also treated under $scCO_2$ in the same condition to induce a possible migration of adsorbed Pd precursors. Each $Pd(hfac)_2$/SBA-15 was calcined in air at 400 °C for 3 h to form PdO/SBA-15 and then reduced for 1 h in $H_2(4\%) + Ar(96\%)$ mixed gas atmosphere at 300 °C to form Pd/SBA-15.

X-ray diffraction patterns of SBA-15 supported Pd and PdO were compared before and after calcination and reduction. Wide-angle X-ray diffraction was performed on a rotating anode source installed diffractometer (MacScience Model M18XHF) with X-ray source of 40 kV, 300 mA. The Cu Kα radiation used was monochromated by a curved-crystal graphite. The amounts of loaded Pd and PdO were calculated from the impregnated quantities of $Pd(hfac)_2$ which were determined by the thermogravimetric (TG) analysis of $Pd(hfac)_2$/SBA-15. Transmission electron microscopy observations of Pd/SBA-15 and PdO/SBA-15 were made with a Philips CM200 operating at 200 kV. Typically, the powder samples were dispersed in dry ethanol and deposited on a carbon-coated 200-mesh copper grid. The excess liquid was removed with a filter paper.

3. Results and discussion

To maintain the narrow size distribution of the nanoparticles only in the mesopores, it should be ensured that no particle nucleates on the external surface during the deposition process. The ion exchange reaction is usually adopted to introduce the metal precursors if the silanol groups are preserved in a mesoporous silica support. Otherwise, a surface functionalization with ionic (organo) groups should precede the ion exchange with ionic metal precursors in liquid solution. When the impregnation is not performed by the ion exchange reaction, however, the ionization and decomposition of metal precursors in the liquid solvents can lead to large metal or metal oxide particles on the external surface of mesoporous supports. Moreover, the evaporation process of organic or aqueous solvents often causes an aggregation of metal precursors on the external surfaces. Consequently, the improvement of particle size distribution and dispersion would be strongly dependent on the nature of solvents. In order to compare the exclusive solvent effect, no surface modification of the silica support was performed before the impregnation of Pd precursor.

SBA-15 loaded with $Pd(hfac)_2$ in ethanol solution exhibited a gray color which was retained after evaporation. Considering that the ethanol solution of $Pd(hfac)_2$ was orange colored, the observation of gray color suggested a formation of Pd metal during loading process. Such a possibility is confirmed by the wide-angle X-ray diffraction (WAXD) as shown in Fig. 1a, the powder sample after evaporation of ethanol revealing characteristic reflections from the (1 1 1) and (2 0 0) Pd crystal planes. Thus, a part of precursors already forms Pd metal before any reduction process. In contrast, no reflection for PdO is observed at this stage. A calcination of the powder sample in air produces a large amount of PdO as evidenced by a strong PdO(1 0 1) and (1 1 0) reflections in Fig. 1b, but a considerable amount of Pd metal remains. PdO is readily converted to Pd metal by subsequent H_2 reduction (Fig. 1c). The large difference in intensities of both Pd and PdO reflections before and after thermal decomposition (Fig. 1a and b, respectively) indicates that $Pd(hfac)_2$ precursors are adsorbed dominantly as molecular states on the support. $Pd(hfac)_2$/SBA-15 prepared in ethanol solution was treated under $scCO_2$ to induce a possible migration of Pd precursors adsorbed on the external surface into the mesopores of SBA-15. As shown in Figs. 1d–f, no significant difference is observed between WAXD patterns before and after $scCO_2$ treatment.

If Pd metal is formed in ethanol solution, the evaporation process can induce an aggregation of metal precursors on the external surfaces of SBA-15. Fig. 2 shows TEM images of Pd/SBA-15 prepared using ethanol. Without $scCO_2$ treatment,