Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

In situ synthesis of catalytic metal nanoparticle-PDMS membranes by thermal decomposition process

Anubha Goyal [a], Melinda Mohl [b], Ashavani Kumar [a], Robert Puskas [b], Akos Kukovecz [b], Zoltan Konya [b], Imre Kiricsi [b], Pulickel M. Ajayan [a,*]

[a] Department of Mechanical Engineering and Materials Science, Rice University, Houston, TX 77005, USA
[b] Department of Applied and Environmental Chemistry, University of Szeged, Rerrich B. tér 1, 6720 Szeged, Hungary

ARTICLE INFO

ABSTRACT

Nanoparticles of various transition elements such as palladium, iron, and nickel were synthesized in situ in the polydimethylsiloxane (PDMS) matrix by thermal decomposition of their corresponding acetylacetonate salts. Various complementary techniques such as XRD, TEM and XPS were used to characterize the nanoparticles formed in the polymer matrix. This synthesis route results in relatively monodisperse nanoparticles with a narrow particle size distribution. In addition, the composite films are pore-free and mechanically stable, making them attractive for a range of applications. Palladium-PDMS membranes can be used as catalytic membrane reactors and show enhanced catalytic activity in ethylene hydrogenation.

1. Introduction

Metal nanoparticles have unique physical and chemical properties, significantly different from the bulk material, which make them useful for a broad range of applications [1–4]. But they suffer from issues related to particle aggregation and oxidation which can compromise some of these attractive characteristics. Embedding nanoparticles in a polymer matrix is an effective method to overcome some of these detriments. The polymer matrix functions not only as a dispersion medium but also stabilizes the nanoparticles against aggregation and helps in controlling the polydispersity in particle size. The matrix can also impart additional functionality to the system. Synergistically, nanoparticles can influence the polymer matrix by enhancing its mechanical, optical or electrical properties. The properties of polymer–nanoparticle composite are governed by both the intrinsic behavior of the nanoparticle and polymer, and by their mutual interactions. These nanocomposites have many novel properties and find extended, diverse applications such as biosensors, optical devices and catalytic reactors [5–8].

Various ex situ and in situ routes have been explored for synthesizing polymer nanocomposites, including physical and chemical vapor deposition, sol–gel techniques and the simultaneous metal salt reduction and matrix polymerization [9–11]. Thermal decomposition of metal salts is another synthesis technique wherein the mixture of metal precursor and polymer is heated to the decomposition temperature of the salt, resulting in the formation of metal nanoparticles in the polymer matrix. For example, using this technique, silver nanoparticles have been created in situ in poly(methyl methacrylate) and copper nanoparticles have been stabilized on the surface of polytetrafluroethylene nanograins [12,13]. In an alternative approach, a site-selective, lithographic process was developed by carrying out local heating using laser-assisted irradiation to form II–IV group nanocrystals, CdS and ZnS in polystyrene and topas matrices [14]. Horiuchi and co-workers have synthesized metal nanoparticles in polystyrene, polypropylene and polyamides by vaporization and reduction of metal salt on polymer films; but the penetration depth of the metal was limited to only 100 μm [15].

Though the thermal decomposition technique has been explored before, some process limitations restrict the use of many polymers. Chemical intolerance of the polymer to the solvent used [16] and the inability of the polymer to polymerize in the presence of a metal precursor can present major challenges. Additionally, the metal loading in the polymer matrix is affected by the solubility of the metal precursor in the polymer and also by the solubility of both of components in the common solvent. The physical properties of the polymer such its melting point and glass transition temperature can add further constraints.

Taking into account all these factors, polydimethylsiloxane (PDMS) would be a highly suitable polymer because of its good thermal and mechanical stability and chemical inertness, the latter being particularly important for reactive environments [17]. PDMS is a transparent, low cost, flexible and non-toxic polymer, which is widely used for microfluidics, biomedical applications and gas

* Corresponding author.
   E-mail address: ajayan@rice.edu (P.M. Ajayan).

separation membranes [16]. The presence of metal nanoparticles would further impart additional properties to it and extend its applications. Therefore, we have synthesized a range of nanoparticles such as iron, nickel and palladium in the PDMS, thereby making the nanocomposite attractive for various magnetic and catalytic applications. There are no previous reports on fabrication of nanocomposites using thermal decomposition of metal acetylacetonates [M(acac)$_2$] in a bulk PDMS matrix. Metal acetylacetonates were chosen as the precursor over carbonyls or fatty acids due to their lower decomposition temperature. Metal salt solution was added to PDMS elastomer which was then cured at room temperature. A further heat treatment resulted in the formation of metal nanoparticles in the polymer matrix. This route resulted in nanoparticles with a narrow range of size distribution. These features are attractive for many applications as the properties of nanoparticles depend critically on their size. The palladium-PDMS nanocomposite was tested for accessibility and catalytic activity using ethylene hydrogenation as a model reaction.

2. Material and methods

To synthesize these nanocomposites, PDMS elastomer (Sylgard 184, Dow Corning) was used as received. The polymer kit contains elastomer (PDMS) and curing agent which were mixed in the weight ratio of 10:1 and then degassed under vacuum to remove entrapped air bubbles. All the other chemicals were purchased from Sigma Aldrich. 0.1 mol/L solution of palladium acetylacetonate [Pd(acac)$_2$] was prepared in methylene chloride. Ten millilitres of this solution was added to 5 g PDMS to finally obtain 2 wt.% palladium content after decomposition. The amount of salt solution added was varied to give films with different metal content. The solution concentration was kept at 5×10^{-3} mol/L and 10^{-3} mol/L for iron acetylacetonate [Fe(acac)$_2$] and nickel acetylacetonate [Ni(acac)$_2$] respectively. These concentrations are lower than that used for palladium due the limited solubility of the metal salts in the solvent. 5 ml of each of these solutions was added to 10 g PDMS, which was then cast on glass slides and cured at room temperature under vacuum. The solvent was allowed to completely evaporate from the films. The as-cured films were then heated at 623 K for an hour. An inert argon-15% hydrogen atmosphere was maintained during heating to prevent the oxidation of metal. A visible color change was seen in all the films indicating the formation of nanoparticles and further characterization was carried out.

Detailed morphological analysis was carried out using Transmission Electron Microscopy (JEOL 2010). Imaging was done at 100 kV on drop casted samples prepared on carbon coated copper grids. The crystalline nature of the products was determined by X-ray diffractometer (Rigaku D/Max Ultima II) operated at 40 kV and equipped with a Cu Kα radiation source. X-ray photoelectron spectroscopy (XPS) was performed by a spectrophotometer (PHI Quantera SXM), using a monochromatic Al Kα radiation (1486.6 eV). Thermogravimetric (TGA, Seteram Labsys TG–DTA) analysis of the membranes was carried out from room temperature to 1073 K in nitrogen atmosphere at a heating rate of 10 K min^{-1}. The catalytic activity was studied through a continuous flow, fixed-bed microreactor system equipped with on-line GC–MS product analysis.

3. Results and discussion

Fig. 1A (inset) is the photograph of a pure PDMS film and PDMS film containing [Pd(acac)$_2$] before and after the heat treatment. Pure PDMS film is transparent but after the addition of metal salt, it takes the color of the salt and turns yellow. There is an evident color change (to black) after heating, a strong visual indication of the formation of palladium particles in the film. The particles were

extracted from the film by swelling finely cut membrane pieces in diisopropylamine and were then analyzed using TEM to determine their shape and size. TEM micrographs (Fig. 1A and B) reveal non-aggregated nanoparticles which are spherical in nature with the shape and size being widely uniform. The size distribution histogram obtained from the TEM images shows the average particle diameter to lie in the range of 3–6 nm (Fig. 1C). Fig. 1D is the XRD spectrum obtained from the film which conclusively shows the crystalline nature of nanoparticles. The peaks can be indexed corresponding to the {1 1 1}, {2 0 0} and {2 2 0} reflections from fcc palladium (JCPD #00-005-0681). This result concurs with the reported study on the decomposition of Pd(acac)$_2$ in various organic solvents where Esumi et al. have shown the formation of palladium nanoparticles in the diameter range of 8–10 nm [18]. The chemical state of the metal and its interaction with the matrix were analyzed using XPS. The general survey scan showed the presence of C1s, Si2p, O1s and Pd3d core levels. The Gaussian-fitted XPS spectrum for palladium is shown Fig. 2A. Binding energy of 284.5 eV for adventitious carbon (C1s) was used as the internal standard. Spin-orbital coupling effect results in the splitting of the 3d emission from palladium into two discrete peaks centered at 336 eV and 341.4 eV, which correspond to 3d$_{5/2}$ and 3d$_{3/2}$ core levels of metallic palladium [19]. As seen in Fig. 2B, the Si2p peak originating from PDMS is centered at 102.2 eV which is same as that for pure PDMS [19]. This observation eliminates the possibility of any significant chemical interaction between the palladium nanoparticles and the surrounding PDMS matrix. Similar to palladium, the iron and nickel containing films also underwent a color change on heating and the TEM analysis confirmed the formation of nanoparticles (Supporting information).

PDMS is a widely studied polymer for catalytic reactions as it has good diffusivity for gases besides the before-mentioned attributes of good chemical and mechanical properties [20]. The dense PDMS membranes can be made catalytically active to serve the dual purpose of separation and reaction in a single step [21]. As an example, Kopinke and co-workers have synthesized Pd-PDMS composites by the chemical reduction route using NaBH$_4$ and have used this membrane for hydrodechlorination of chlorobenzene contaminant present in ground water [22]. As palladium nanoparticles are well-known for hydrogenation activity [23] we have tested the Pd-PDMS membranes for the hydrogenation reaction of ethylene.

To determine the activation temperature, thermogravimetric analysis was carried out. The starting sample weight was 10 mg and final weight loss was found to be 45% as inferred by the data in Fig. 3. In agreement with the previously reported studies, the decomposition started just below 673 K. For example, Jana et al. found the initial decomposition temperature for pure PDMS to be 636 K [24]. Consequently, the activation of membrane catalysts was carried out at 623 K in hydrogen atmosphere. In all experiments, 10 mg of membrane (cut to 1 mm^2 pieces) was mixed with 1 g of inert Stober silica before activation, yielding a catalyst bed volume large enough to ensure adequate contact between the gaseous reactants and the catalyst. The catalytically inactive, monodisperse silica particles (170 nm) were synthesized using the well-known Stober procedure [25]. Blank experiments were done with pure SiO$_2$ nanoparticles and pure PDMS membranes to determine the presence of any background reaction. No activity was observed in these control experiments, thereby making silica nanoparticles an appropriate diluting matrix for the PDMS membranes.

The membranes mixed with silica were placed into an 8 mm internal diameter glass tube and tested at atmospheric pressure. The tubular reactor was placed in a furnace equipped with a temperature controller and the catalyst mixed with inert Stober silica was subjected to reductive treatment prior to the hydrogenation reaction by annealing it at 623 K and exposing it to a 30 cm^3 min^{-1}