Organic/inorganic hybrid composed of modified polyacrylamide grafted silica supported Pd nanoparticles using RAFT polymerization process: Controlled synthesis, characterization and catalytic activity

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HIGHLIGHTS

- Preparation of PdNPs on modified polyacrylamide grafted silica as a new catalyst.
- "Grafting to" and "grafting from" approaches used to prepare polymer grafted silica.
- Control of both MW and density of grafted chains obtained *via* RAFT polymerization.
- The catalyst used in the Heck coupling for the preparation of butyl cinnamate.

GRAPHICAL ABSTRACT
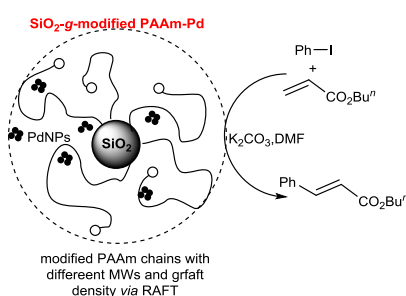
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ABSTRACT

Reversible addition-fragmentation chain transfer (RAFT) polymerization was utilized for the preparation of polyacrylamide brushes grafted onto silica particles (SiO$_2$-g-PAAm) *via* "grafting to" and "grafting from" approach in a controlled manner. Control of both the polymer's molecular weight and the density of grafted chains can be achieved by these methods. The polymer grafted silica was further modified to convert it to phosphinite ligand. Complexation of this ligand with Pd(OAc)$_2$ was performed in order to obtain the Pd catalytic system. Various techniques such as FT-IR, TGA, XRD and electron microscopy systems such as SEM and TEM were conducted as characterization methods. Moreover, X-Ray photo-electron spectroscopy (XPS) of the catalyst disclosed the binding energy of Pd in zero oxidation state properly. This organic-inorganic hybrid catalytic system showed proper activity in Heck coupling reaction. The catalyst was successfully reused in repeating cycles with negligible change in its efficiency. Characteristic of the catalyst such as size and shape, chemicophysical stability and the structure of catalyst are retained almost unchanged even after successive reactions.

1. Introduction

Free radical vinyl polymerization recognized as the most employed chain growth polymerization method due to the versatility in reaction conditions and functional groups tolerance [1]. However, conventional free radical processes is unsuitable for the preparation of macromolecules with specific composition due to the poor control over chain length, molecular weight distribution and end groups of the final polymer. As a result, reversible-deactivation radical polymerization (RDRP) (historically known as

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living or controlled radical polymerization–CRP) is constructed to solve the problem [2]. RDRP represents key strategies for the easy production of complex architectures with precise design, foreseeable molecular weights and sharp dispersity. There are several individual RDRP techniques [3]. The primitive one is nitroxide mediated polymerization (NMP) method [4]. Atom transfer radical polymerization (ATRP) [5] and reversible addition–fragmentation chain transfer (RAFT) polymerization [6] are the most common used methodologies. Newer examples of RDRP are radical polymerization mediated with tellurium [7] and organostibene [8] and quinone transfer radical polymerization [9].

Of these methods, RAFT has made a great contribution in designing polymer [10]. The main potential of RAFT polymerization concerns to its versatility regarding kinds of monomers and reaction conditions, toleration toward a broad range of functionality, applicability to the production of water-soluble polymers or copolymers such as polyacrylamide and acrylic acid and stimuli-responsive polymers, simple implementation and inexpensive procedure compared to competitive technologies. Furthermore, compared with ATRP, RAFT is a process with no contamination of the polymer by transition metal catalyst which is of vital importance in biomedical applications. The appropriate choice of chain transfer agent (CTA or RAFT agent) is crucial for the success of RAFT polymerizations. RAFT agents are thiocarbonylthio species belonging to dithioesters, dithiocarbamates, trithiocarbonates and xanthates general families. The so-called R and Z groups determine the reactivity of the RAFT agents [11].

Graft polymers are segmented polymers consist of a backbone with randomly distributed branches. They have been applied in the chemical and agricultural industries, environmental field, pharmaceutics and in general analytical methods [12]. Their potential applications have expanded with the development of controlled radical polymerization. Recently, the combination of surface modification and RAFT polymerization technique has been widely explored as a route to produce polymer brushes with structural and grafting density control [13]. In this regard, different policies are utilized such as: immobilization of a RAFT agent to the surface *via* either R-class [14] or Z-class [15] approaches or attachment of an initiator to the backbone ("grafting from") [16], modification of the surface with a polymerizable group ("grafting through") [17], grafting polymers prepared *via* RAFT process to the backbone ("grafting to") [18] and using macro-monomers [19]. "Grafting to" of polymer chains onto surfaces *via* covalent bond can also be obtained through "click" chemistry manner [20].

Palladium-catalyzed coupling of haloarenes with unsaturated halides (or triflates) (Mizoroki-Heck reactions) has emerged recently as powerful method for construction of C-C bonds and preparation of highly complex molecules [21]. Despite the synthetic efficacy of various homogenous catalytic systems for Heck reaction [22], this process suffers from inefficient separation and reusability of the catalyst and contamination of products by Pd species. To overcome this issue, immobilized catalysts having high activity attract great interest [23]. Several types of heterogeneous materials such as zeolites [24], alumina [25], silica [26], graphene [27], carbon nanotubes [28], magnetic nanoparticles [29] and organic or bio polymers [30] have been used to support palladium species. In this regard, applying polymer grafted silica [31] benefited from the properties of both a linear polymer and high mechanical and thermal stability and good dispersion of silica particles. Furthermore, utilizing controlled polymerization techniques for preparing polymers enable us to control catalyst activity with modifying branch density and chain length of the polymers.

In continuation of our previous report [32] and considering the excellent properties of silica grafted polymers and RAFT polymerization strategy, herein a proper procedure is outlined for grafting of polyacrylamide onto silica particle *via* "grafting to" and "grafting from" approach through RAFT polymerization. Using living polymerization method such as RAFT for the synthesis of this type of catalyst lead to control MW and graft density of the polymer and adding probable blocks with different characteristic to the catalyst for future study. In addition, in order to explore their prospective applications, phosphinite functionalities was further immobilized onto SiO_2-*g*-PAAm with transamidation followed by reaction with $ClPPh_2$. Then, complexation of the corresponding ligands with $Pd(OAc)_2$ afforded Pd nanoparticles (PdNPs) supported on modified polyacrylamide grafted silica (SiO_2-*g*-modified PAAm-Pd). These practical supported catalysts were then employed successfully in Mizoroki-Heck coupling reaction.

2. Experimental section

2.1. General remarks

2.1.1. Materials

Aminopropyl silica gel (product number 09297) used in this study with a mean particle size of 15–35 μm and the density of the NH_2 group of 0.95 mmol g^{-1} supplied from Sigma-Aldrich. Azobisisobutyronitrile (AIBN, Merck, 98%) and acrylamide (Fluka, 97%) were recrystallized from methanol and chloroform, respectively. 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (Sigma-Aldrich, 98% HPLC) dried under vacuum prior to use. 1,4-Dioxane (Fluka, 99.5%) dried using calcium chloride as preliminary drying agent and then final drying was accomplished almost exclusively with distillation of refluxed solution of Na wire (1% w/v) and benzophenone (0.2% w/v) until the blue color of the mixture due to the benzophenone ketyl radical anion perseveres. All other materials were used without further purification.

2.1.2. Characterization techniques

TLC (silica gel polygrams SIL G/UV 254 plates) and GC (Shimadzu GC-14A) were used to follow the progress of the coupling reactions. Gas chromatograph equipped with a 3-m length glass column packed with DC-200 stationary phase, flame ionization detector and N_2 as the carrier gas. The product was identified by spectral data and all conversions are based on the starting material. FT-IR spectra were collected using Shimadzu FTIR-8300 instrument. The solid samples were prepared for IR measurement by grounding with KBr and then pressing into a pellet. NMR analyses were carried out on a Bruker Avance DPX instrument (250 MHz & 400 MHz) using D_2O as solvent. Elemental analyses were achieved using a thermo finnigan FIASHEA 1112 series elemental analyzer. X-Ray powder diffraction (XRD) diagrams were collected at room temperature on a Bruker AXS D8-Advance X-ray diffractometer (Cu Kα radiation with λ = 1.541874 A°) and a 2θ scan range of 10–90°. Pd loadings were carried out on samples by acid digestion followed by ICP-OES analysis on a Varian, Vista-Pro with CCD Simultaneous spectrometer. Thermal analysis of the samples was conducted using a Perkin-Elmer Pyris Diamond TG/DTA thermal analyzer. The samples were scanned within the temperature range from ambient to 1000 °C under nitrogen atmosphere at the heating rate of 10 °C min^{-1}. Samples ranging between 1.5 up to 3.5 mg in weight were tested in platinum pans. Scanning electron micrographs were obtained by SEM, KYKY-EM3200, at 26 kV. The samples are sputter-coated with Au using sputter coater KYKY SBC12 with physical vapor deposition technique (PVD) prior to SEM observation. TEM images were obtained on a Zeiss (Germany)-EM10C instrument with an accelerating voltage of 80 kV on the Holey carbon coated grid Cu (Mesh 300). Sonicators (Misonix- S3000) used for dispersing the sample in distilled water before TEM analysis. X-Ray photoelectron spectroscopy (XPS) measurements were conducted