

# Synthesis and Application of Hyperbranched Polyester-Grafted Polyethylene (HBPE-g-PE) Containing Palladium Nanoparticles as Efficient Nanocatalyst

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Abstract In nowadays, palladium-catalyzed reactions are of utmost importance in synthetic organic chemistry. Due to advantages of heterogeneous catalysts such as the easy handling and good recyclability, usually these types of catalysts are first choice in constructing a new catalytic system. Here we report a facile approach to prepare hyperbranched polyester-grafted-polyethylene supported palladium nanoparticles as an efficient catalyst in Suzuki reaction and solvent-free aerobic oxidation of alcohols. The reactions were carried out in different conditions with various reagents and the efficiency was determined. Because of the amplification effect of hyperbranched polyester, high loading capacities (around 0.276 mmol  $g^{-1}$ for Pd) was achieved. The catalyst was characterized with X-ray powder diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy, transmission electron microscopy, differential scanning calorimetry and thermogravimetric analysis. This metal nanocatalyst has a very low leaching loss, high activity and selectivity, excellent thermal stability and can be reused at least five times without deactivation of catalytic activity.

**Graphical Abstract** In this work, a hyperbranched polyester based on 2,2-bis (methylol) propionic acid (bis-MPA) was synthesized and grafted onto carboxylic acid functionalized polyethylene powder. The final nanocatalyst was prepared via solution loading of PdCl<sub>2</sub> and reduction to palladium nanoparticles on the HBPE-g-PE. The activity and stability of prepared polymer-supported heterogeneous

Hossein Mahdavi hmahdavi@khayam.ut.ac.ir catalyst was carefully examined for Suzuki reaction and solvent-free oxidation of alcohols.



**Keywords** Polyethylene-support · Hyperbranched polyester · Palladium nanoparticles · Suzuki reaction · Oxidation of alcohols

# **1** Introduction

Transition-metal catalyzed reactions are fundamental transformations in organic synthesis. Palladium is one of the most important metals, which has been used as a catalyst in synthesis of a wide variety of organic compound [1]. The most well-known palladium-catalyzed reactions are coupling of aryl halides with organoboronic acids (Suzuki–Miyaura reaction), coupling of aryl halides with alkenes (Mizoroki–Heck reaction), oxidation of alcohols, etc. These types of reactions have a great industrial potential for the synthesis of pharmaceuticals, functional materials, and natural products [2–5].

Both heterogeneous and homogeneous systems can be used to carry out these reactions. Despite the excellent

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activity and selectivity of homogeneous catalysis, they have several drawbacks such as difficult separation and recycling of the catalyst. In contrast, the heterogeneous catalysis could be recycled by simple filtration or centrifugation, which in turn decrease environmental pollution caused by residual toxic palladium metal in waste. In addition, they have other excellent features including ease of handling and good reusability. Therefore, heterogeneous catalyst is much affordable in catalytic reactions [6, 7]. In recent years, significant efforts have been made for heterogenization of catalysts to solid supports. Many organic and inorganic supports such as polymers [8], zeolites [6], silica [9], carbon nanofiber [10], clay [11], metal oxides [12], partially reduced graphene oxide (PRGO) [13], and alumina [14] have been used in preparation of efficient and environmental-friendly heterogeneous catalytic systems. Immobilizing palladium nanoparticles onto the support prevents aggregation of metal particles and increases surface area and activity of catalyst [15]. In comparison to inorganic supports, better control on catalytic activity was obtained with polymer supports [16]. In the past decade, there has been increasing interest on the preparation of polymer supported palladium nanoparticles with narrow size distribution for Pd-catalyzed transformations due to their much enhanced catalytic activity and selectivity. Oberhauser and co-workers employed carboxylic acid endfunctionalized poly(lactic acid) (PLA)-based stereocomplexes containing PdNPs as heterogeneous catalyst for chemoselective hydrogenation of the C=C double bond in cinnamaldehyde. For 3-phenylpropanal, 90 % chemoselectivity at 88 % conversion was obtained [17]. Siyo et al. prepared different sized PVP stabilized Pd NPs with a mean diameter between 1.8 and 4.4 nm for the aerobic oxidation of 5-hydroxymethylfurfural into 2,5-furandicarboxylic acid in an alkaline aqueous solution. The influence of the particle size on conversion and product yield in the presence of different sized Pd NPs was investigated [18]. Raspolli Galletti et al. employed polyketone as a support and stabilizing agent for Pd nanoparticles in order to examine its catalytic performance in the selective hydrogenation of cinnamaldehyde to hydrocinnamaldehyde. The sample with smaller nanoparticle size and a narrower metal particle size distribution show the highest selectivity (87.7 %) [19].

Polyolefins like polyethylene (PE) and polypropylene (PP) are good choices for solid supports among commercial polymers. These types of polymers have excellent chemical and physical properties along with low cost, good recyclability, and simple process-ability. Despite these superior features, lack of the reactive groups has limited the interaction of polyolefins with other materials and polymers, which leads to solubility restrictions in common solvents [20]. However, strong interactions between polyolefins and

substrates having polar surfaces can be provided in presence of polar functional groups, such as -OH, -COOH, -NH<sub>2</sub>, and halides onto the surface of inert polyolefins [20, 21]. Surface properties of polyolefins such as wetability, hydrophilicity, and biocompatibility are improved via modification approaches. These functional groups provide the selective sites for subsequent polymer grafting [21]. There are three strategies for modification of the surfaces and preparing hyper-graft polymers [22]. These strategies are called "grafting onto", "grafting from", and "grafting through". In all grafting routes, we need proper functional groups onto the surface of the solid support. Various chemical reactions such as oxidation can provide these functions onto the surface. Several functional polymer side chains can be created onto the polyolefin backbone by grafting methods, which offers various practical advantages [20, 21].

Metal nanoparticles can be stabilized with polymers containing heteroatoms. Dendrimers and hyperbranched polymers are excellent model systems, which act as capping agents and stabilize metal nanoparticles [23]. Hyperbranched polymers are more easily made by simple onestep polymerizations in contrast to dendrimers. Hyperbranched polymers are highly branched macromolecules with dendritic architecture, which contain numerous functional end groups [24]. High density of functional groups can increase the loading capacity of the metal nanoparticles and improve catalytic activity of the catalyst. High dispersion and narrow size distribution of metal particles play a key role in improvement of catalytic performance [23]. Therefore, hyperbranched grafting onto the PE-support provides numerous functional groups, which increase loading capacity of palladium nanoparticles and stabilizes the reduced form of Pd-NPs.

In the present work, we synthesized a hyperbranched polyester based on 2,2-bis (methylol) propionic acid (bis-MPA) and then, this hyperbranched polyester grafted onto carboxylic acid functionalized polyethylene powder. The final nanocatalyst was prepared via solution loading of PdCl<sub>2</sub> and reduction to palladium nanoparticles on the HBPE-g-PE. The activity, selectivity, and stability of prepared polymer-supported heterogeneous catalyst were carefully examined for Suzuki reaction and solvent-free oxidation of alcohols.

# 2 Experimental

#### 2.1 Materials

Granular low density polyethylene LH 0075 (melt flow index: 0.75 g/10 min) was purchased from Bandar Imam Petrochemical Company. 2,2-Bis (methylol) propionic acid

(Bis-MPA), 2-Ethyl-2-(hydroxymethyl)-1,3-propanediol (TMP) and *p*-Toluenesulfonic acid were supplied from Merck. Palladium (II) chloride ( $\geq$ 99.9 %) was purchased from Sigma-Aldrich. All solvents and other chemical reagents were purchased from Merck and Sigma-Aldrich and used without any further purification.

#### 2.2 Characterization

The amount of palladium nanoparticles supported on HBPE-g-PE was analyzed on a Varian VISTA-MPX inductively coupled plasma-optical emission spectrometry (ICP-OES) instrument.

X-ray diffraction (XRD) pattern of the catalyst was recorded on a Philips analytical X-ray diffractometer (XPert MPD) with monochromatized Cu/K $\alpha$  radiation ( $\lambda = 0.15424$  nm). Diffraction data were collected from 10° to 90° (2 $\theta$ ).

Scanning electron microscopy (SEM) images of the samples were obtained on AIS2100 scanning electron microscope and (TESCAN-VEGA3 XMU) field emission scanning electron microscope equipped with EDX and elemental mapping accessories. Transmission electron microscopy (TEM) observations were performed on a Philips CM30 electron microscope at an accelerating voltage of 200.00 kV in order to obtain the mean particle size of Pd nanoparticles.

Thermal properties of the samples were analyzed by Thermogravimetric (TG) and Differential scanning calorimetric (DSC) analysis using TGA Q50 V6.3 Build 189 and DSC Q100 V9.0 Build 275 instruments, respectively. The analyses were performed under nitrogen atmosphere and a heating rate of 10 °C min<sup>-1</sup>.

The yields of catalytic reactions were determined by gas chromatography using Shimadzu gas chromatograph.

ATR-FTIR spectra of the samples were run on EQUT-NOX55 BRUKER spectrometer with DTGS detector.

#### 2.3 Preparation of Hyperbranched Polyester

Bis-MPA (6.71 g), TMP (0.745 g), and p-TSA (33.6 mg) were mixed in a three-necked flask equipped with an argon inlet, a drying tube, and a stirrer. The reaction was carried out in preheated oil bath in 140 °C under a stream of argon (for removing of water formed during the reaction). After 2 h, the argon stream was removed and the flask connected to a vacuum for 1 h. For synthesis of third generation of hyperbranched polyester, Bis-MPA (8.94 g) and p-TSA (44.8 mg) were added to the mixture and the argon stream was turned on for 2 h. Then the argon stream was removed and the vacuum was applied for 1 h. Forth generation of hyperbranched polyester (HBPEG4) was synthesized by removing the vacuum and addition of Bis-MPA (17.875 g)

and p-TSA (0.056 mg) into the reaction mixture. Argon passing and connecting to the vacuum steps were repeated in this stage, too. Synthesized polymer was dissolved in acetone for 24 h and then precipitated in n-hexane [25].

Fourth generation of poly (Bis-MPA) was prepared by this methodology with  $M_n = 6620 \text{ g mol}^{-1}$ .

### 2.4 Catalyst Preparation

#### 2.4.1 Chemical Modification of Polyethylene Powder

Low density polyethylene (LH0075) (2.0 g) were dissolved in hot xylene (20 ml) at 110–120 °C under stirring. PE powder was collected by precipitation into methanol and then was dried in the vacuum. The obtained white powder was extracted with methylene chloride in a soxhlet apparatus at 40–50 °C to remove any commercial additives. In a 100 mL round-bottomed flask, Potassium dichromate (5.0 g) was dissolved in distilled water (30 ml) and sulfuric acid (%98, 21 ml). Then, 2.0 g of PE powder were added into the mixture. The reaction mixture was heated under reflux and stirring on an oil bath at 90 °C for 4 h. Yellow oxidized polyethylene (PE–COOH) was collected by filtration and washed thoroughly with distilled water and dried at 50–60 °C for 24 h under vacuum.

In order to converting prepared carboxylic acid groups on the PE surface to the corresponding acid chloride, thionyl chloride (15 ml), a drop of dimethylformamide, and PE–COOH (2.0 g) were mixed in 50 ml round-bottomed flask. The mixture was heated at 60–70 °C for 14 h under reflux and N<sub>2</sub> purge. To minimize hydrolysis, the powder was collected and washed with THF and transferred to the subsequent reaction solution immediately.

# 2.4.2 Grafting of Hyperbranched Polyester onto the Modified Polyethylene

In a 25 mL round-bottomed flask, HBPE (G4) (0.6 g) was dissolved in dioxane (12 ml). A drop of pyridine as an acid scavenger was added into the mixture and then 2.0 g of PE–COCl was added and the mixture was placed in an oil bath under reflux and stirring at 60–70 °C for 24 h. The prepared HBPE-g-PE was washed with acetone and dried under vacuum.

The percentage of hyperbranched grafting was calculated by following equation:

$$Grafting(\%) = \frac{W_g - W_o}{W_o} \times 100$$

where  $W_g$  is the weight of hyperbranched-grafted polyethylene and  $W_o$  is the weight of polyethylene before hypergrafting.

To achieve the more effective functional groups to complex with Pd ions, the surface hydroxyl groups were transformed into carboxylic acid functionality. Therefore, HBPE-g-PE (2.0 g) was added to a flask containing dimethylformamide (30 ml), succinic anhydride (1.6 g), and triethylamine (2.8 ml). The reaction mixture was stirred at 90 °C for 6 h under reflux. The collected powder was washed with methanol and dried under vacuum.

# 2.4.3 Formation of Pd Nanoparticles on the Synthesized Polymer Support

A mixture of palladium chloride (10 mg) and sodium chloride (66.2 mg) in deionized water (15 ml) was heated to achieve the dark-red aqueous solution of Na<sub>2</sub>PdCl<sub>4</sub>. Then, 2.0 g of supported polymer was added to the solution and in order to better dispersion, the mixture was placed under ultrasonic waves for 5 min and then was stirred at room temperature for 48 h. The yellow powder was collected and washed with deionized water three times to remove any residual palladium ions from the surface of support. To determine the Pd content, 1.0 g of solid was treated with mixture of concentrated HCl and H<sub>2</sub>SO<sub>4</sub> (3/1)(8 ml) at 50–60 °C. The filtrate was diluted to 250 ml with distilled water and analyzed with ICP spectroscopy using calibration curve method. The loading amount of Pd (II) is calculated to be 0.276 mmol/g of polymer support.

1.0 g of collected solid was redispersed in aqueous solution (25 ml) of freshly prepared NaBH<sub>4</sub> (1.0 M) and stirred for 60 min at room temperature. The yellow powder became black due to reduction of Pd (II) to Pd (0).

#### 2.5 General Procedure for Suzuki Reaction

HBPE-g-PE containing Pd nanoparticles (7.0 mg), aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), and  $K_2CO_3$  (2.0 mmol) were added to mixture of  $H_2O/DMF$  (1:1) (2.5 ml). The reaction mixture was stirred in a flask at 90 °C under reflux for the indicated time. The reaction was monitored by TLC. On completion of the reaction, the catalyst was separated by simple filtration. Ethyl acetate was added to the mixture and decanted. After evaporation of solvent, the products were subjected to GC analyzer to obtain yields of the reactions.

# 2.6 General Procedure for Solvent-Free Aerobic Oxidation of Alcohols

Oxidation of alcohols with palladium nanoparticles supported on PE-HBPE was performed using molecular oxygen in the absence of solvent. For this purpose, 5.0 mg of the catalyst was dispersed in alcohol (5.0 ml) in a threenecked round flask with a reflux condenser under stirring. Oxygen flow was bubbled at a flow-rate of 20 ml/min. After the allowed reaction time duration, the catalyst was removed from the mixture, and the products were analyzed using gas chromatography.

### 2.7 Reusability of the Catalyst

After completion of the reaction in the first run, the catalyst was removed by simple filtration and washed with acetone. It was dried under vacuum and then was added to another vessel containing the starting materials. The sequential reaction was carried out under the same conditions as discussed before. The recycling was repeated successfully for five cycles without significant loss of catalytic activity.

### **3** Results and Discussion

# 3.1 Preparation and Characterization of the Catalyst

Contrary to the commercial application of polyolefins, the lack of reactive groups has restricted many uses of these kinds of polymers, including interaction with other materials. Chemical modification of polyolefins, introduces a controlled amount of functional groups onto the polyolefin backbone, which improve some properties such as solubility, hydrophilicity, and ability of metal loading [20]. One of the most useful ways for creating appropriate functional groups on the surface of inert polymers is grafting of dendrimers or hyperbranched polymers [21]. Hyperbranched grafting provides useful functional groups on the polyethylene backbone.

One of the most employed methods for surface modification of polyolefins is the oxidation reaction using various soluble manganese and chromium oxidants, such as potassium dichromate or chromium trioxide in sulfuric acid. With this manner, carboxylic acid and ketones are the most functional groups which be formed on the polymer surface [26, 27]. These functional groups provide the selective sites for the subsequent hyperbranched grafting.

Thus, we focused on chemical modification of polyethylene and then hyperbranched grafting to provide sufficient functional groups for loading of palladium. The hyperbranched polyester-grafted-polyethylene (HBPE-g-PE) supported palladium catalyst was synthesized following the simple procedure shown in Scheme 1.

Oxidized-PE powder with carboxylic acid functional groups (PE–COOH) was obtained by oxidation of PE with mixture of  $K_2Cr_2O_7/H_2SO_4/H_2O$  as the oxidant. The content of created carboxylic acid by oxidation reaction is low for immobilizing high amount of palladium on the surface. Therefore, hyperbranched polyester with highly amounts of

palladium



**HBPE-g-PE** supported PdNPs

terminal hydroxyl groups was used to enhance loading capacity of palladium. For this aim, hyperbranched polyester as the palladium nanoparticles template was attached to modified polyethylene. Esterification reaction between carboxylic acid of oxidized-PE and hydroxyl group of hyperbranched polyester is slow and needs high temperature. Hence, the carboxylic acid groups of oxidized-PE were converted to acid chloride functionality using thionyl chloride to accelerate grafting process. In order to prevent hydrolysis of acid chloride groups with moisture, the prepared powder was isolated and employed in next step immediately.

Fourth generation of hyperbranched polyester (HBPEG4), with a well-defined structure and numerous terminal hydroxyl groups was synthesized via the melt polymerization of 2,2-Bis (methylol) propionic acid (AB<sub>2</sub> monomer) and 2-Ethyl-2-(hydroxymethyl)-1,3-propanediol (B<sub>3</sub> monomer, as the core moiety) using p-Toluenesulfonic acid as the catalyst in a pseudo-one-step reaction [25] and then was covalently linked to the modified PE-support through "grafting to" approach. Degree of grafting was estimated to be 33.3 % by weighting the powder before (2.0 g) and after (2.66 g) grafting. After grafting, in order to achieve better chelating of Pd (II), terminal hydroxyl groups of HBPEG4 were converted to carboxylic acid functionality in presence of succinic anhydride.

For preparation of Pd nanoparticles supported system, at first the Pd salt were coordinated with functional groups of the support and then reduced to Pd particles by reducing agent. Palladium deposition onto the HBPE-g-PE support was accomplished by immersing the powder in Na<sub>2</sub>PdCl<sub>4</sub> aqueous solution, which leads to homogeneous dispersion of palladium on the surface of the support through chelating of Pd (II) with hyperbranched polyester end groups. NaBH<sub>4</sub> is a very convenient reducing agent, which reduces Pd (II) to Pd (0) easily at room temperature. Reduction of Pd (II) to Pd (0) causes the yellow powder turned to brown and then dark after 1 h. There is no need to use stabilizers in the reaction mixture because it seems that highly numerous functional groups of hyperbranched polyester are capable of stabilizing the Pd nanoparticles and prevent aggregation, which increases surface area and activity of the catalyst. The palladium loading content was determined to be 0.276 mmol/g by ICP analysis.

Figure 1 displays the ATR-FTIR spectra of synthesized hyperbranched polyester, neat PE, oxidized-PE, and HBPE-g-PE. For hyperbranched polyester, the absorption frequencies of carbonyl and C–O appear at 1722 and 1100–1200 cm<sup>-1</sup> respectively and a broad peak is observed at around 3370 cm<sup>-1</sup> related to terminal hydroxyl groups. For polyethylene, the observed absorbance at 1467 cm<sup>-1</sup> corresponds to C–C stretching and C–H stretching peaks are observed at 2849 and 2916 cm<sup>-1</sup>. For oxidized-PE containing carboxylic acid groups, new peak is observed at 1710 cm<sup>-1</sup> due to the carbonyl stretch of



Fig. 1 ATR-FTIR spectra of HBPEG4, PE, PE-COOH, and HPBE-g-PE

carboxylic acid. The broad band at around  $3390 \text{ cm}^{-1}$  is attributed to carboxylic acid O–H stretch and the C–O stretch appears in the region 1100–1200 cm<sup>-1</sup>. Therefore, oxidation of polyethylene and creating carboxylic acid functionality has occurred successfully after 4 h. The ATR-FTIR spectrum of HBPE-g-PE shows the absence of absorption band corresponding to carbonyl stretch of carboxylic acid at 1710 cm<sup>-1</sup> and the presence of the estercarbonyl band at 1729 cm<sup>-1</sup> corresponding to hyperbranched polyester. The peaks at 1100–1200 cm<sup>-1</sup> and a wide band in the region 3300–3400 cm<sup>-1</sup> due to C–O and terminal hydroxyl groups, respectively, are implying the successful grafting of hyperbranched polyester onto the surface of modified PE.

The surface morphology of prepared material was studied using scanning electron microscopy (SEM). Figure 2 presents the SEM images for pure PE, PE-COOH, HBPE-g-PE and HBPE-g-PE containing palladium nanoparticles. Surface morphology of polyethylene was clearly changed by creation of different functionalities. The surface of pure polyethylene is very smooth and flat. After the oxidation process, some functional groups are generated in the surface and change the surface morphology. Examination of Fig. 2c shows that the stiffness of surface is more increased after grafting and creation of highly functional groups related to hyperbranched polyester. Comparison of Fig. 2a–c shows increasing trend of surface stiffness along oxidation and grafting of hyperbranched polyester.

The elemental distribution of C, O and Pd within HBPEg-PE containing palladium nanoparticles and EDX spectrum of HBPE-g-PE supported Pd catalyst are presented in Fig. 3a, b. Typical carbon, oxygen and palladium peaks are detected by EDX analysis, which prove Pd is successfully loaded into HBPE-g-PE support. Alternatively, elemental maps further confirm the successful loading of Pd into the support with homogeneous dispersion and uniform size distribution. Histogram of the Pd particles size distribution (Fig. 3c) was determined by counting about 350 particles. It could be observed that Pd particles are in diameters from 2 to 19 nm, and the average particle size is  $\sim 11.5$  nm. Then it is possible to conclude that the palladium particles are well dispersed within the catalyst in nanometer scale.

Figure 4 shows the TEM images of the HBPE-g-PE containing palladium nanoparticles and the histogram of the PdNPs size. The dark spots are the Pd nanoparticles with a size in the range of 2.0–16 nm. The size distribution diagram estimated from the TEM image shows that the mean size of Pd is  $\sim$  7.0 nm, which is in agreement with results obtained from elemental maps. These observations revealed good stabilizing properties of hyperbranched polyester (HBPE), which prevent the aggregation of nanoparticles. These relatively small particles with narrow size distribution and high surface area can perform

Fig. 2 SEM images of (a) neat

polyethylene, (b) oxidizedpolyethylene, (c) HBPE-g-PE and (d) HBPE-g-PE containing palladium nanoparticles 30 µm 30 µm 30 µm um (a) **(b)** 15000  $\mathbf{O}$ C 10000 cps/eV 5000 POLB ٥ 10 0 5 Pd O C Pd Energy (KeV) (c) 45 40 Relative frequency % 35 30 25 20 15 10 5 0 4 9 13 14 18 19 2 7 Particle diameter (nm)

Fig. 3 (a) SEM mapping photograph of C, O and Pd in HBPE-g-PE containing palladium nanoparticles; (b) EDX pattern of the catalyst; and (c) Histogram of the Pd nanoparticles size

catalytic reactions in high activity and selectivity. Thus, HBPE with numerous functional groups is an attractive supporting agent for palladium catalysts.

The presence of highly hydroxyl groups increases surface hydrophilicity and therefore, HBPE-g-PE should have an acceptable dispersion in polar solvents. Low density polyethylene has semi-crystalline structure and consists of carbon and hydrogen chains with no functionality. Thus, solubility of LDPE is very low in existing solvents at the ambient temperature. Polar carboxylic acid groups caused

Fig. 4 (a) Low and high magnification TEM images of HBPE-g-PE containing palladium nanoparticles and (b) histogram of the Pd nanoparticles immobilized on HBPE-g-PE





better dispersion of PE-COOH in polar solvents. After grafting of hyperbranched polyester on the surface of polyethylene and creating highly amounts of terminal hydroxyl groups, solubility of powder was further increased. Figure 5 illustrates enhancement of dispersion of polyethylene in DMF as polar solvent at room temperature after surface modification and grafting process. As expected, increasing surface functional groups enhances dispersing ability of polyethylene in polar solvents.

X-ray powder diffraction (XRD) pattern of HBPE-g-PE containing palladium nanoparticles is shown in Fig. 6. Observed diffraction peaks at 43.58, 49.38, 70.62, and 84.41° correspond to (111), (200), (220), and (311) crystallographic planes of Pd (0) nanoparticles, respectively. The sharp peaks are appeared at 21.66 and 23.83° correspond to (110) and (200) planes of (CH<sub>2</sub>)<sub>n</sub> chains of polyethylene, respectively. The crystallite size of nanoparticles was calculated by using Scherrer equation from XRD pattern data to be 10.6 nm which is in a good agreement with the mean particle size observed from TEM and SEM mapping images.



Fig. 5 Dispersion ability of (a) polyethylene (b) oxidized-polyethylene (c) HBPE-g-PE in DMF as polar solvent at room temperature

Thermal studies were conducted to determine the applicability of catalyst in reactions operating at the high temperatures. Thermal stability of neat polyethylene was compared to HBPE-g-PE and HBPE-g-PE containing



Fig. 6 XRD patterns of hyperbranched polyester-g-polyethylene containing palladium nanoparticles



Fig. 7 TGA curves of neat polyethylene, HBPE-g-PE, and HBPE-g-PE containing palladium nanoparticles (HBPE-g-PE/PdNPs)

palladium nanoparticles (HBPE-g-PE/PdNPs) by means of TGA upon heating the samples at the rate of 10 °C min<sup>-1</sup> from 25 to 600 °C. Breaking the C-C bonds of polyethylene backbone is accomplished at high temperatures and requires high energy. As shown in Fig. 7 for PE, the weight loss due to decomposition starts above 420 °C which indicating excellent stability of polyethylene at elevated temperatures. Thermal decomposition of hyperbranched polyester starts at about 250–275 °C [28]. Grafting of HBPE onto the polyethylene surface induces that decomposition starts at lower temperatures (310 °C). Comparing the HBPE-g-PE and HBPE-g-PE/PdNPs curves shows that the weight loss of HBPE-g-PE/PdNPs occurs at a higher temperature (360 °C) which may be attributed to the presence of Pd nanoparticles in the polymer matrix. Therefore, the prepared catalyst shows excellent thermal stability and preserves its activity and structure at high temperatures. Therefore, using the catalyst in catalytic reactions conditions has no limitation.

DSC analyses of pure PE and HBPE-g-PE containing palladium nanoparticles are shown in Fig. 8. Comparison of the diagrams indicated a significant increase in glass



Fig. 8 DSC thermograms of (a) neat polyethylene; (b) hyperbranched polyester-g-polyethylene containing palladium nanoparticles

transition temperature of polyethylene after grafting and immobilizing of Pd nanoparticles. LDPE is a semi-crystalline polymer with low glass transition temperature (-47.09 °C) and grafting of hyperbranched polyester increases amorphous segments in polymer backbone. Hydrogen-bonding of hydroxyl end groups of hyperbranched polyester that are not coordinated with palladium, increases T<sub>g</sub> of the support. In addition partial loss of the conformational freedom of hyperbranched polyester segments due to complexation with palladium enhances glass transition temperature.

On the other hand, the presence of palladium between polymer chains facilitates segmental motions of chains and decreases glass transition temperature slightly. All these reasons cause the glass transition temperature of HBPE-g-PE to be observed at 9.45 °C. Melting point of pure PE and HBPE-g-PE supported palladium nanoparticles are 110.28 and 109.74 °C, respectively. Due to grafting is performed in amorphous areas of polyethylene and crystalline areas of PE remain intact, melting point of polyethylene will not change remarkably.

# 3.2 Catalytic Activity Study of the Catalyst in Suzuki–Miyaura Reaction

Nowadays, the Suzuki reaction is one of the most popular coupling reactions in organic synthesis. Here, the catalytic property of the prepared catalyst was initially examined in Suzuki reaction. The coupling reaction between aryl halide and arylboronic acid with electron-donating and electronwithdrawing substituents proceeded effectively to obtain corresponding products in good to excellent yields. The coupling of iodobenzene with phenylboronic acid was studied initially as a model reaction. The HBPE-g-PE supported catalyst acted as a heterogeneous catalyst in this catalytic reaction successfully. To optimize reaction condition, the catalytic reactions were carried out with different solvents, bases and at different temperatures. Optimization studies determine how solvent, base, and temperature influence the coupling reaction. Tetrabutylammonium bromide as a phase transfer agent was added to enhance the performance of the catalyst in the aqueous medium. The Results that are given in Table 1 summarize Suzuki coupling of aryl halide and arylboronic acid containing various substituents. Isolated yields of the products were good to excellent within short reaction times and high selectivity toward substituted biphenyl products have been achieved for all substrates. Examination of Table 1 indicates that 86 % cross-coupling yield can be achieved by low content of catalyst for the reaction of iodobenzene with phenylboronic acid within just 1 h.

A product yield of 78 % was observed when the substrates were 1-iodo-4-methylbenzene and phenylboronic acid (entry 7). With the aryl halide substrate changed to 4-iodonitrobenzene, the best yield (96 %) was obtained at 90 °C and within 1 h.

A moderately good yield of 76 % was observed for idodobenzene and 4-bromophenylboronic acid substrates. Compared to iodobenzene, the reaction took longer when the substrate was bromobenzene. Decrease in activity was observed when the halide substituent was changed to chloride. Chlorobenzene was generally less reactive toward Suzuki reaction under the same condition. The best result was observed when the reaction was performed in DMF/  $H_2O$  (1:1). Further catalytic reactions in  $H_2O/DMF$  (1:1) using different bases were carried out, and it was found that  $K_2CO_3$  act as the best bases (entries 12–14). Other bases such as K<sub>3</sub>PO<sub>4</sub>, and NaOH were slightly less effective to obtain high product yield. When the reaction was carried out without a significant content of base, no activity was observed even at a prolonged reaction time. Therefore, the presence of base as the activator of organo-boron compounds is necessary in the reaction mixture. Influence of

	X + (H	O) <sub>2</sub> B-	cataly solvent,	base R <sup>1</sup>		<del>ر</del> 2		
Entry	Aryl halide	Arylboronic acid	Time (h)	Temperature (°C)	Solvent	Base	Yield (%)	Selectivity toward related biphenyl product (%)
1	C <sub>6</sub> H <sub>5</sub> I	$C_6H_5B(OH)_2$	1	90	DMF/H <sub>2</sub> O (1:1)	K <sub>2</sub> CO <sub>3</sub>	86	100
2	C <sub>6</sub> H <sub>5</sub> Br	$C_6H_5B(OH)_2$	4	90	DMF/H <sub>2</sub> O (1:1)	$K_2CO_3$	81	100
3	C <sub>6</sub> H <sub>5</sub> Cl	$C_6H_5B(OH)_2$	6	90	DMF/H <sub>2</sub> O (1:1)	$K_2CO_3$	72	100
4	C <sub>6</sub> H <sub>5</sub> I	$CH_3C_6H_4B(OH)_2$	1	90	DMF/H <sub>2</sub> O (1:1)	K <sub>2</sub> CO <sub>3</sub>	92	100
5	C <sub>6</sub> H <sub>5</sub> I	BrC <sub>6</sub> H <sub>4</sub> B(OH) <sub>2</sub>	3	90	DMF/H <sub>2</sub> O (1:1)	K <sub>2</sub> CO <sub>3</sub>	76	100
6	IC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	$C_6H_5B(OH)_2$	1	90	DMF/H <sub>2</sub> O (1:1)	$K_2CO_3$	96	100
7	C <sub>7</sub> H <sub>7</sub> I	$C_6H_5B(OH)_2$	1	90	DMF/H <sub>2</sub> O (1:1)	$K_2CO_3$	78	100
8	C <sub>6</sub> H <sub>5</sub> I	$C_6H_5B(OH)_2$	2	90	H <sub>2</sub> O/Dioxane	$K_2CO_3$	75	100
9	C <sub>6</sub> H <sub>5</sub> I	$C_6H_5B(OH)_2$	2	90	Dioxane	$K_2CO_3$	62	100
10	C <sub>6</sub> H <sub>5</sub> I	$C_6H_5B(OH)_2$	2	90	$H_2O$	$K_2CO_3$	77	100
11	C <sub>6</sub> H <sub>5</sub> I	$C_6H_5B(OH)_2$	1	90	DMF	$K_2CO_3$	78	100
12	C <sub>6</sub> H <sub>5</sub> I	$C_6H_5B(OH)_2$	3	90	DMF/H <sub>2</sub> O (1:1)	None	-	100
13	C <sub>6</sub> H <sub>5</sub> I	$C_6H_5B(OH)_2$	2	90	DMF/H <sub>2</sub> O (1:1)	$K_3PO_4$	78	100
14	C <sub>6</sub> H <sub>5</sub> I	$C_6H_5B(OH)_2$	2	90	DMF/H <sub>2</sub> O (1:1)	NaOH	73	100
15	C <sub>6</sub> H <sub>5</sub> I	$C_6H_5B(OH)_2$	1	70	DMF/H <sub>2</sub> O (1:1)	K <sub>2</sub> CO <sub>3</sub>	72	100
16	C <sub>6</sub> H <sub>5</sub> I	$C_6H_5B(OH)_2$	1	100	DMF/H <sub>2</sub> O (1:1)	$K_2CO_3$	78	100

Table 1 Suzuki coupling of aromatic halides with different Arylboronic acids

temperature was investigated by performing the reaction at 70, 90, and 100 °C. Efficiency was increased with increasing temperature from 70 to 90 °C. Partial decrease was observed at 100 °C which can be attributed to the agglomeration of palladium nanoparticles and then decreasing the available number of active sites. Thus, the best system for this reaction was 2.5 ml of H<sub>2</sub>O/DMF (1:1) as solvent and K<sub>2</sub>CO<sub>3</sub> as base (2.0 mmol) at 90 °C. The reactions were performed well under this optimized condition, and the appropriate products were obtained in good to excellent yields within 1–4 h.

# 3.3 Performance of the Catalyst in Solvent-Free Aerobic Oxidation of Alcohols

Nowadays, oxidation of alcohols is performed using stoichiometric oxygen donors such as permanganate or chromate in a commercial scale. Recently, some attempts were conducted to replace molecular oxygen for oxidation of alcohols to reduce environmental concerns [29]. One of the most useful transformations among Pd-catalyzed reactions is the selective oxidation of alcohols to corresponding carbonyl compounds including aldehydes and ketones. Palladium catalysts can oxidize alcohols using molecular oxygen without any use of base and under mild solventfree reaction conditions [30].

In this work, we chose a number of primary or secondary alcohols to perform oxidation reaction and prepare relevant aldehydes or ketones under solvent-free condition. The low content of prepared catalyst (5.0 mg) revealed good activity and high selectivity toward corresponding aldehydes or ketones in aerobic oxidation of various alcohols. Various alcohols oxidize to aldehydes or ketones with different boiling temperature. Considering that, temperature of the reactions was changed according to the boiling point of final products. As presented in Table 2, conversion yield increases at elevated temperatures, but products selectivity is still high (95–100 %) at lower temperature. Performing the reaction under solvent-free condition has several advantages such as saving costs, reducing environmental pollution, removing solvent separation step, and raising purity of oxidized alcohols.



Fig. 9 Recycling experiments of supported Pd catalyst in (a) Suzuki coupling of iodobenzene and phenylboronic acid; and (b) aerobic oxidation of benzyl alcohol

Table 2 Solvent-free aerobic oxidation of various alcohols R'								
Entry	Alcohols	Temperature (°C)	Time (h)	Yield (%)	Selectivity <sup>a</sup> (%)			
1	Benzyl alcohol	90	2	80	95			
2	Cyclohexanol	90	4	74	100			
3	1-Butanol	65	5	78	98			
4	2-Propanol	40	6	71	100			

<sup>a</sup> Selectivity refers to the corresponding aldehyde or ketone; for benzyl alcohol, by-products are toluene and benzoic acid; for 1-butanol, by-product is butyric acid

Entry	Catalyst	Condition	Time	Yield (%)	Ref.
1	SMNPs-Salen Pd (II)	DMF/H <sub>2</sub> O, K <sub>2</sub> CO <sub>3</sub> , 100 °C	1 h	100	[1]
2	Pd/MIL-53(Al)-NH <sub>2</sub>	H <sub>2</sub> O/EtOH, Na <sub>2</sub> CO <sub>3</sub> , 40 °C	30 min	99	[2]
3	FemSILP-NHC-Pd complex	DMF, K <sub>3</sub> PO <sub>4</sub> , reflux temperature	20 min	52	[3]
4	Chitosan-2(diphenylphosphino)imine-Pd	Xylene, K <sub>2</sub> CO <sub>3</sub> , 130 °C	6 h	34	[4]
5	Pd/g-C <sub>3</sub> N <sub>4</sub>	PEG/H <sub>2</sub> O, K <sub>2</sub> CO <sub>3</sub> , r.t.	30 min	99.9	[5]
6	Pd-1/FSG	MeOH/H <sub>2</sub> O, K <sub>2</sub> CO <sub>3</sub> , 80 °C	6 h	98	[ <mark>6</mark> ]
7	Pd–ZnFe <sub>2</sub> O <sub>4</sub> MNP	Ethanol, K <sub>2</sub> CO <sub>3</sub> , reflux temperature	4 h	92	[ <b>7</b> ]
8	Chitosan-pyridyl imine Pd complex	Xylene, K <sub>2</sub> CO <sub>3</sub> , 143 °C	1 h	85	[8]
9	8.64 %Pd(B)-MCM41	DMF/H <sub>2</sub> O, Et <sub>3</sub> N, 80 °C	2 h	56	[ <mark>9</mark> ]
10	Polymer-anchored Pd(II) complex	DMF/H <sub>2</sub> O, K <sub>2</sub> CO <sub>3</sub> , 80 °C	5 h	100	[ <mark>10</mark> ]
11	Pd@g2Amino-Si(HIPE)P2	Dioxane, K <sub>2</sub> CO <sub>3</sub> , 115 °C	72 h	98	[11]
12	HBPE-g-PE/Pd NPs	DMF/H <sub>2</sub> O, K <sub>2</sub> CO <sub>3</sub> , 90 °C	1 h	86	This work

Table 3 Suzuki coupling reaction of iodobenzene with phenylboronic acid catalyzed by different heterogeneous Pd-based catalysts

Table 4 Comparison of the catalytic performance of resulting HBPE-g-PE/PdNPs catalyst with different reported heterogeneous Pd-based catalyst employed in solvent-free aerobic oxidation of benzyl alcohol

Entry	Catalyst	Temperature (°C)	Time (h)	Yield (%)	Ref.
1	Pd-GC	110	6	72.5	[12]
2	2.5 % Au + 2.5 % Pd/TiO <sub>2DP2</sub>	140	3	80	[13]
3	1Pd/MPTMS-TUD	160	1	26.3	[14]
4	1Au5Pd/APS-S16	140	1	22.3	[15]
5	2 %Pd/SBA-15-900 N	120	4	70	[16]
6	Pd/NaX	100	4	66	[17]
7	Pd@C-Glu <sub>A</sub> -550	80	7	70	[18]
8	Pd/2.5MnO <sub>x</sub> /CNT	160	1	15.4	[19]
9	Pd/CeO <sub>2</sub>	120	1	95.7	[20]
10	HBPE-g-PE/Pd NPs	90	2	80	This work

Effect of  $O_2$  as co-oxidant and hydrogen acceptor [30] was evaluated by carrying out the oxidation of 2-propanol in presence and absence of oxygen. Presence of oxygen enhances catalytic performance of the catalyst and facilitates the oxidation process.

# 3.4 Hot Filtration Test

Hot filtration test is a way to show the catalyst acts heterogeneously in the reaction condition. Metal leaching is a common problem for the heterogeneous catalysts [3]. To investigate content of palladium leached into the reaction mixture, the catalyst was separated by simple filtration after completion of catalytic reactions, and the filtrate was analyzed by ICP. No palladium leaching was observed by ICP analysis of the filtrate after the end of the reaction. Thus, the immobilized palladium was very stable in reaction condition and the obtained products were free of contamination with palladium, and the synthesized catalyst could be used as a heterogeneous catalyst in catalytic reactions.

#### 3.5 Recycling of the Catalyst

Recycling of the catalyst was studied in Suzuki coupling of iodobenzene and phenylboronic acid, and aerobic oxidation of benzyl alcohol as the model reactions. As presented in Fig. 9, after five consecutive runs, the catalytic activity of collected powder was still high and the catalyst required a bit longer time to achieve high conversion.

Slight loss of activity in third run can be attributed to aggregation of nanoparticles and poisoning of the active sites. Thus, the recovery can be successfully accomplished up to five cycles without significant loss of activity. Reusability of the catalyst leads to using low toxic and expensive palladium and reducing the cost of products in large-scale processes. A comparison of the activity of various heterogeneous Pd-based catalysts with HBPE-g-PE/PdNPs in the Suzuki coupling reaction and solvent-free aerobic oxidation of alcohols published in the literature is listed in Tables 3 and 4 [30–49].

Some of listed heterogeneous catalysts require higher temperatures or prolonged reaction times in order to obtain excellent yields for both catalytic reactions (e.g., Pd@g2Amino-Si(HIPE)P2 for Suzuki reaction and Pd-GC for solvent-free aerobic oxidation of benzyl alcohol).

# 4 Conclusions

In summary, we have prepared an efficient palladium catalyst supported hyperbranched polyester-grafted-polyethylene, which was used for Suzuki reaction and solventfree aerobic oxidation of alcohols. Hyperbranched polyester grafted on the modified PE support acts as both stabilizer and well-defined template for high loading of palladium nanoparticles with homogeneous distribution in this process. Prepared catalyst displayed a good conversion and excellent selectivity in these catalytic reactions, suggesting the effective catalytic activity within short reaction times. The catalyst could be recovered by simple filtration and reused for five successive runs without significant loss of activity. No palladium leaching was observed during reactions. The hyperbranched polyester has a high ability to entrap palladium without remarkable leaching of the catalyst into the reaction mixture. The TGA results confirmed the excellent thermal stability of the catalyst at high temperatures, which has no restriction for carrying out the reactions at evaluated temperatures. Therefore, short reaction times, high product yields, excellent selectivity, simple separation, good reusability, excellent thermal stability, low cost, and no Pd leaching which lead to low contamination of isolated products are main features of the prepared catalyst.

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