Synthesis and Physicochemical Analysis of Polystyrene-Anchored Pd(II) Metal Complex

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ABSTRACT

A polystyrene (PS)-anchored Pd(II) metal complex was synthesized on cross-linked polymer by heating a mixture of chlorometylated polystyrene with phenyldithiocarbazate and carbon disulfide in the presence of potassium hydroxide (KOH) in dimethylformamide (DMF). The reaction mixture was heated at 80 °C to form the corresponding phenyldithiocarbazate-functionalized polymer. Then, it was treated with bis(benzonitrile)palladium(II) chloride. The properties of dark colored polymer, impregnated with the metal complex was then characterized by various spectroscopic technique such as Fourier Transform Infrared (FTIR), Scanning Electron Microscopy/Energy Dispersive X-ray (SEM/EDX), CHNS elemental analysis, BET surface area, X-ray Diffraction (XRD), Thermogravimetric (TGA) and Inductively Coupled Plasma-Optical Emission (ICP-OES) spectroscopy.

***Keywords**: Polystyrene; Palladium; Catalyst*

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INTRODUCTION

Recent interest in the development of environmentally, simple and efficient heterogeneous catalyst for organic transformation has become a common goal for many researchers. Ideally, the catalyst was prepared to improve the thermal and chemical stabilities, can be used repeatedly as well as can be stored for long periods without any appreciable loss of catalytic activity. The development of reusable supported catalyst for chemical transformation has meet the highest demand for stringent environmental. The synthesizing of heterogeneous catalyst can give an alternative solution to overcome the homogeneous one [1]. Moreover, the development of green chemistry becomes the most exciting research. Recently, Bakherad *et al*. studied a functionalized poly-vinyl chloride resin-supported Pd(ll) complex in C-C bond formation [2]. While, Yurdakoc and co-workers reported that Siral 80 was use as a supported material for Ni and Cu acetylacetonates complexes [3].

Currently polymers have become the option in the synthesizing of reusable supported catalyst [4]. So, polystyrene is one of the solid supports that most widely reported due to its ready availability, mechanical robustness, product selectivity, chemical inertness and facile functionalization [5-9]. The interaction that normally occurred between polystyrene and metal complexes either by forming chemical bonds or through physical interactions such as covalent bonding, hydrogen bonding or donor-acceptor interaction [10].

On the other hand, palladium has found to be the best metal for the catalytic cycle due to its insensitivity towards oxygen and moisture, and even to acidic condition [11]. Significantly, palladium catalyst offers an abundance of possibility of carbon-carbon bond formation which there is no other transition metals can offer such as palladium metal. Consequently, the use of palladium in catalytic study is considered to be the most desirable even though palladium is known as a noble metal and very expensive element.

The work presented herein shows the report of our investigation concerning the preparation of a new PS-anchored Pd(II) complex which highly potential to be used in C-C bond formation. This supported catalyst was also successfully characterized by various physicochemical and spectroscopic techniques.

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EXPERIMENTAL

Materials, Method and Instruments

All reagents were obtained commercially and used without further purification. Merrifield's polymer, chloromethyl poly (styrene-divinyl benzol) 2% was supplied by Sigma-Aldrich. Bis(benzonitrile)palladium(II) chloride, $PdCl_2(PhCN)_2$ and other reagents were purchased from Merck. FTIR spectra were recorded as potassium bromide (KBr) disc on a Perkin Elmer Spectrum 100 FTIR spectrometer in the range of 400 to 4000 cm^{-1}. CHN elemental analyses were performed on a Flash EA1112 to collect microanalytical data (C, H and N). The thermal stability of sample was determined using a Perkin Elmer Pyris 1 DSC. Surface morphology and the particle size of parent polystyrene and its functionalized metal complex were analyzed using a scanning electron microscope JOEL JSM 6360 equipped with Energy Dispersive X-Ray facility (SEM-EDX). X-ray diffraction (XRD) pattern were measured using a Rigaku Miniflex II X-ray Diffractometer and was obtained in the range 3-70°, with 2θ scale and counting time of 1 sec/step. BET surface area was calculated by using Thermo Finnigan Qsurf Surface Analyzer. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was performed using Vista-Pro Varian ICP-OES.

Preparation of PS-anchored palladium(II) complex

A 250 mL round bottom flask equipped with a condenser and magnetic stirrer bar containing DMF (15 mL) was added with chloromethylated polystyrene (1.5 g), phenylhydrazine (2.5 mL), potassium hydroxide (0.14025 g, 2.5 mmol), and carbon disulphide (0.198 g, 2.5 mmol). The mixture was stirred for 36 h at 90 °C under air atmosphere. The PS-functionalized ligand was subsequently filtered and washed thoroughly with DMF, and air-dried. The resulting bright yellow PS-functionalized polymer (1.0 g) was treated with bis(benzonitrile)palladium(II) chloride (1.0 g) in DMF and the resulting mixture (Scheme 1) was heated at 80 ºC for 20 h. The resultant catalyst was filtered off by vacuum filtration and the solid filtrate washed with acetonitrile. The residue was dried in air for 24 h to afford the black supported catalyst.

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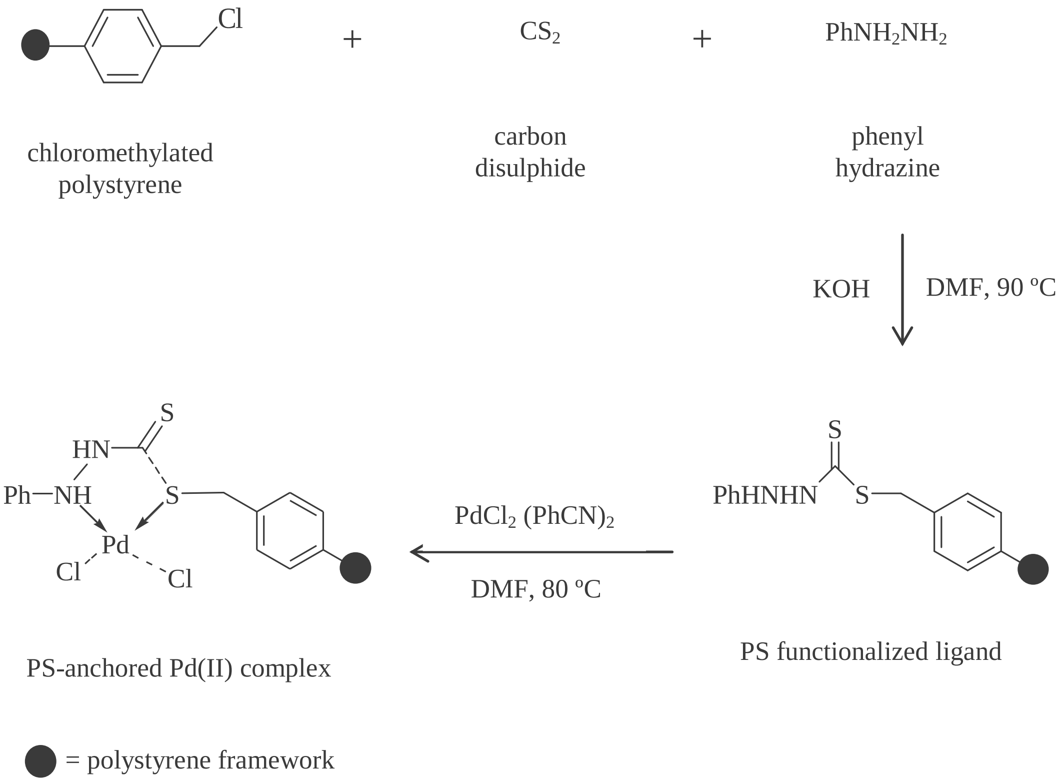

Scheme 1: Synthesis of the PS-anchored Pd(II) complex

RESULTS AND DISCUSSION

PS-anchored Pd(II) complex was successfully synthesized by heating a mixture of PS with carbon disulphide and phenylhydrazine to produce the corresponding PS functionalized ligand, which was then reacted with $PdCl_2(PhCN)_2$ to yield the PS-anchored Pd(II) complex. The catalyst obtained was well characterized using BET surface area, CHNS elemental analysis, FTIR, SEM/EDX, ICP-OES, TGA and XRD.

The BET surface area of PS and PS-anchored Pd(II) complex were 6.42 m^2/g and 3.60 m^2/g, respectively. However, a significant decrease in the surface area was observed for PS-anchored Pd(II) due to the partially blocked of pores during the complexation reaction [12-13]. Complete incorporation of elements in the supported catalyst was confirmed by elemental analysis. The nitrogen and sulfur content was obtained to be 1.596 mmol/g and 0.1617 mmol/g, respectively. The amount of palladium loading in the supported catalyst was found 1.536 mmol/g.

The FTIR spectrum of PS exhibits a sharp absorption band at 1264 cm^{-1} which is assigned to ν(CH_2-Cl) group in polymer [14]. However the disappearance of –C-Cl_2 band and the appearance of a strong band at 3426 cm^{-1}, 1116 cm^{-1} and 1491 cm^{-1} in the suggested the involvement of the ν(-NH stretch), ν(C=S) and ν(-NH deformation) groups, respectively [15]. The stretching vibrations of the ν(C=C) appeared at 1598 cm-1 for phenyldithiocarbazate-functionalized PS.

SEM was also recorded to understand the morphological changes which occurred on the surface of PS after palladium metal loading and the micrographs are presented in Figure 1. A clear change in the morphology was observed with the spherical shape of the particles is more visible throughout the specimen. The presence of palladium has also caused changes which affected the particle size and roughness of the surface of parent PS [16-17]. The EDX data (Figure 2) clearly supported the presence of palladium metal on the surface of polymer matrix.

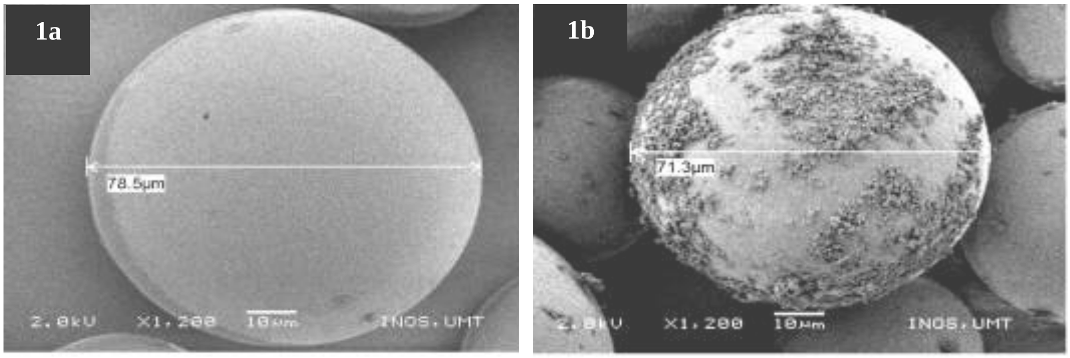

Figure 1: SEM image for (a) PS (b) PS-anchored Pd(II) complex

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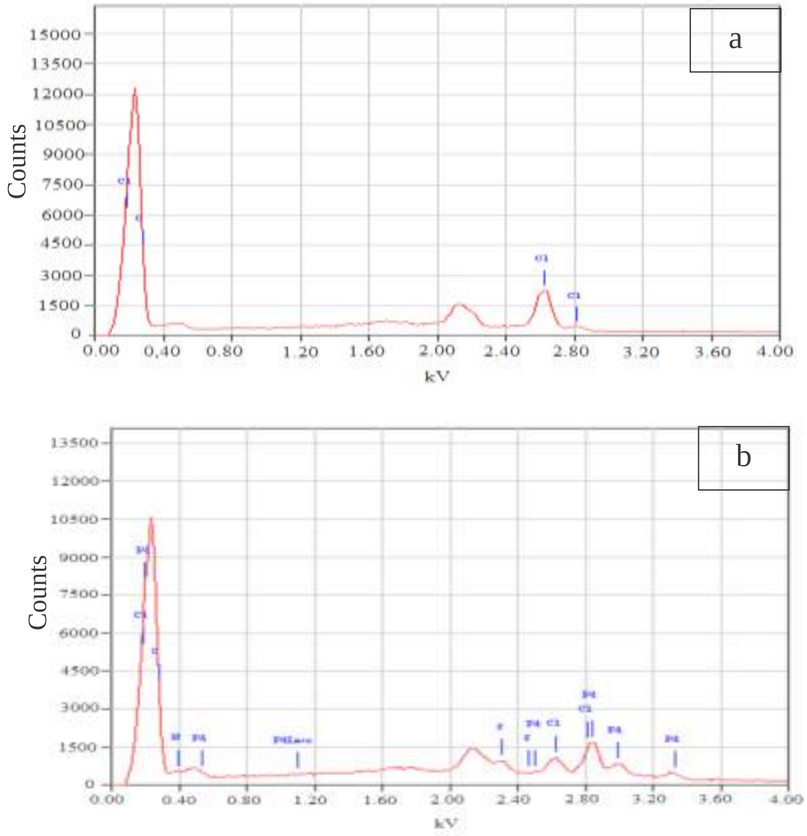

Figure 2: EDX spectra for (a) PS (b) PS-anchored Pd(II) complex

Thermogravimetric analyses of PS and its supported catalyst (Figure 3) were carried out at a heating rate of 10 ºC min^{-1} in nitrogen over a temperature range of 25-700 °C which to measure the weight loss due to degradation. TGA data demonstrated that the PS-anchored Pd(II) complex was stable to 280 °C and decomposed above this temperature. The thermal stability of the supported catalyst was slightly improved after complexation reaction. The TGA study indicates that the PS-anchored Pd(II) complex degrades at very high temperature.

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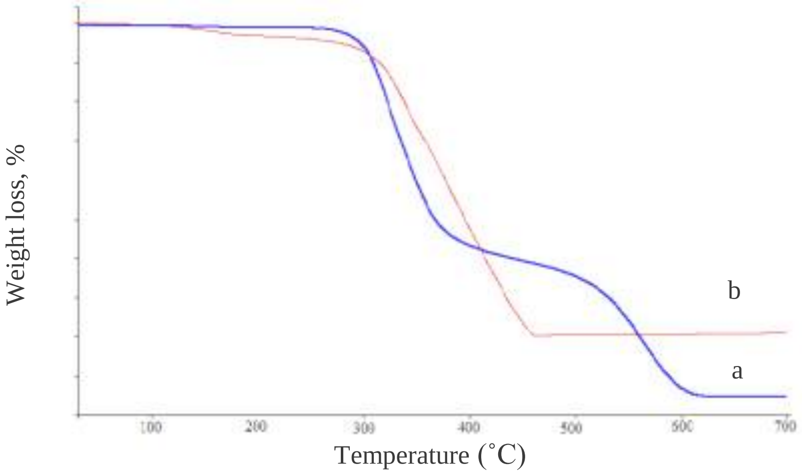

Figure 3: TGA curves for the (a) parent PS (b) PS-anchored Pd(II) complex

XRD measurements were performed to assess the quality and structural ordering of PS and its supported catalyst. The diffractogram of PS-anchored Pd(II) complex (Figure 4) showed dramatic changes compared to PS structure. A sharp peak at the range of 40.42º-42.80º indicated the presence of palladium metal in the supported catalyst [18-20].

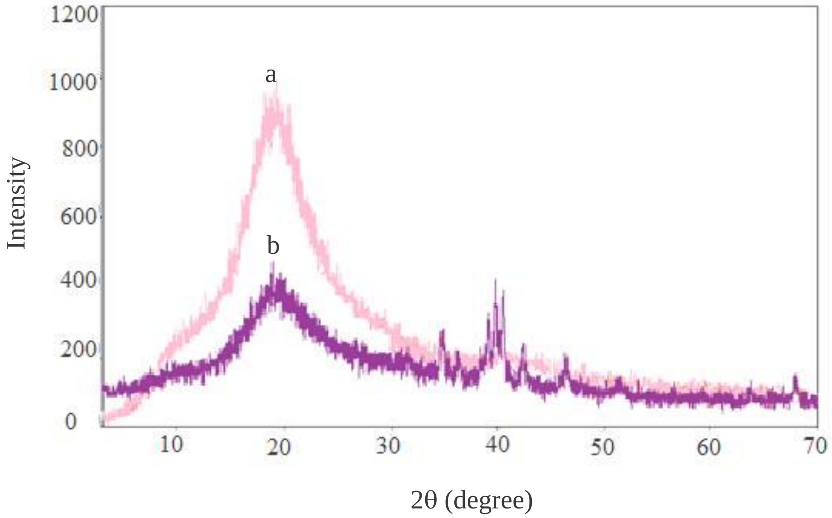

Figure 4 XRD pattern of PS (a) PS-anchored Pd(II) complex (b)

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CONCLUSION

In summary, a supported catalyst was successfully synthesized and characterized via several spectroscopic and analytical techniques. The ease of preparation, stability towards air and moisture will make this PS-anchored Pd(II) complex as an ideal supported catalyst for C-C bond formation.

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