PREPARATION AND CHARACTERIZATION OF PALLADIUM SUPPORTED ON NANOMAGNETIC Fe3O4@HYPERBRANCHED POLYETHYLENIMINE (Fe3O4@HPEI.PD) AS A NEW ORGANIC-INORGANIC HYBRID NANOMATERIAL AND STUDY OF ITS CATALYTIC ROLE IN THE AQUEOUS-PHASE OXIDATION OF ALCOHOLS IN THE PRESENCE OF OXONE AND H2O2

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Abstract- Palladium immobilized on magnetic nanoFe3O4@hyperbranched polyethylenimine (Fe3O4@HPEI.Pd) is an active, stable, and reusable catalyst for the selective oxidations of alcohols applying oxone (potassium hydrogen monopersulfate) and H2O2 as an oxidant in the presence of water as solvent at room temperature. Primary and secondary alcohols gave the corresponding products in good yields. In addition, the catalyst could be reused up to 13 runs without significant loss of activity.

Keywords- Nanomagnetic catalyst; Palladium; Oxidation; Alcohols; Carbonyl compounds; Oxone.

I. INTRODUCTION

Magnetic separation supplies a convenient method to remove and recycle magnetized species by utilizing an appropriate magnetic field. Most of these utilizations require the nanoparticles to be chemically stable, uniform in size, and well scattered in liquid media. It has been illustrated that the formation of a passive coating of inert materials such as polymers, carbons, and silicas on the surfaces of iron oxide nanoparticles could help prevent their aggregation in liquid and make their chemical stability better and better.

II. DETAILS EXPERIMENTAL

Fe3O4@HPEI (0.3 g) was charged into a round-bottomed flask containing an acetonitrile solution (10 mL) and sonicated for 20 minutes. Palladium chloride (0.6 mmol) was charged into another round-bottomed and sonicated for 20 minutes. Then, this mixture was added drop wise to the above mixture under an argon atmosphere and sonicated for 30 minutes. Then, this mixture stirred under an argon atmosphere for 48 h. The resultant catalyst was filtered off and washed with acetonitrile followed by acetone. The residue was dried in a vacuum oven for 24 h. Also, the same procedure was used Co and Cu incorporation into the nanomagnetic catalyst by using cobalt and copper chloride.

Alcohol (1 mmol), water (2 mL) and catalyst (1 mol% of Pd, 30 mg) were added into a round-bottomed flask. The reaction mixture was stirred for two minutes, then oxone (0.6 mmol) was added in three portions due 15 minutes. The reaction mixture was stirred at room temperature. Progress of the reaction was followed by TLC (EtOAc-cyclohexane, 2:10) in comparison with the standard samples of corresponding alcohols and carbonyl compounds. After the completion of the reaction, the product was extracted with dichloromethane. The organic phase was evaporated under reduced pressure to give the corresponding aromatic products. Purification of the residue using flash column chromatography (silica gel) provided the pure carbonyl compounds. The products were characterized via comparison their spectral data (IR, 1H NMR) with authentic samples. The aliphatic products in dichloromethane were dried by using anhydrous MgSO4 and detected by GC-FID in comparison with the standard samples of corresponding alcohols and carbonyl compounds. The GC yields of the aliphatic products were calculated based on their corresponding gas chromatogram. The selectivity of the oxidized products was determined from their 1H NMR spectra of corresponding crude samples.

III. RESULTS AND DISCUSSION

In this work, the amine groups of hyperbranched polyethylenimine (HPEI) were reacted with the epoxy groups of [3-(2,3-Epoxypropoxy)propyl]trimethoxysilane (EPO) and then the resulted polymer was grafted to the Fe3O4 magnetic nanoparticles (MNPs) via the reaction of its trimethoxysilane group with OH groups of MNPs. Finally, it is assumed that the prepared Fe3O4@HPEI has good nitrogenous ligand for palladium chelating and could be effective for uniform reoxidation of Pd(0) in the cycle of reaction. Palladium immobilized on magnetic nanoFe3O4@hyperbranched polyethylenimine (Fe3O4@HPEI.Pd) is an active, stable, and reusable catalyst for the selective oxidations of alcohols applying oxone (potassium...
hydrogen monopersulfate) and H$_2$O$_2$ as an oxidant in the presence of water as solvent at room temperature. Primary and secondary alcohols gave the corresponding products in good yields. In addition, the catalyst could be reused up to 13 runs without significant loss of activity.

The prepared nanomagnet (Fe$_3$O$_4$@HPEI.Pd) is an active, stable, and reusable catalyst for the selective oxidations of alcohols applying oxone and H$_2$O$_2$ as an oxidant in the presence of water as solvent at room temperature. Primary and secondary alcohols gave the corresponding products in good yields. In addition, the catalyst could be reused up to 13 runs without significant loss of activity. The catalyst was characterized by IR, UV-Vis, TEM, SEM, XRD, TGA, VSM, ICP and EDX techniques (Figures 1 & 2).

CONCLUSIONS

In conclusion, we have introduced a direct and effective method for the oxidation of alcohols to their corresponding carbonyl compounds utilizing oxone in the presence of Fe$_3$O$_4$@HPEI/Pd catalyst at room temperature in water. The use of non-toxic and inexpensive materials, stability of the oxidative system, simple method, short reaction times, good yields of the products and mild reaction conditions are the advantages of this method. In comparison with the other oxidants such as O$_2$ or TBHP, oxidation with oxone accomplished at low temperatures and in short times. The extension of the application of this nanocatalyst to different oxidation reactions is currently under investigation in our laboratory.

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Biography: Ali Ramazani has completed his Ph.D from TMU in the Iran. He currently works as a full professor in Chemistry at University of Zanjan in the Iran. His studies focused on organic synthesis and nanochemistry and he has published more than 300 papers. He is an Editorial Board Member of the international Journal Nanochemistry Research. He has received several national and international awards, including the 2013 kharizmi international award, several top-cited author awards and best-paper awards from leading ISI Journals, Best Researcher Awards, and the Best Lecturer Awards at the University of Zanjan.

REFERENCES


Fig. 1. SEM (a,b) and TEM (c,d,e) images of Fe$_3$O$_4$ and Fe$_3$O$_4$@HPEI.

Fig. 2. Recycling of the Fe$_3$O$_4$@hpei.pd catalyst for the oxidation of benzyl alcohol.

REFERENCES