THESIS INFORMATION

Title: INVESTIGATION OF USING SUPERPARAMAGNETIC NANOPARTICLES $CoFe_2O_4$ AS CATALYST SUPPORT FOR KNOEVENAGEL, SONOGASHIRA, SUZUKI AND HECK REACTIONS

Major: Chemical engineering of organic compounds

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Abstract:

Cobalt superparamagnetic ($CoFe_2O_4$) nanoparticles were synthesized following a microemulsion method and functionalized by using the supported ligand and palladium acetate to form the immobilized palladium complex catalyst with a palladium loading of 0.33 mmol/g. The catalyst was characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), vibrating sample magnetometry *(VSM)*, Fourier transform infrared (FT-IR), atomic absorption spectrophotometry (AAS), and nitrogen physisorption measurements. The results proved that the Pd(II)-$CoFe_2O_4$ magnetic nanoparticles were as an efficient catalyst for several C-C couplings including the Suzuki reaction between 4'-bromoacetophenone with phenylboronic acid, the Sonogashira reaction between 4'-bromoacetophenone with phenylacetylene, and the Heck reaction between 4'-bromoacetophenone with styrene under conventional and microwave irradiation conditions. Efficiency of catalysts in reactions was evaluated by conversion which was determined by gas chromatography. The catalysts could be reused several times without significant degradation in catalytic activity.

Main results:

Firstly, two types of catalysts based on magnetic nanoparticles were synthesized, including amino-functionalized nanoparticles (2N-MNPs), and palladium-immobilized nanoparticles (Pd-1N-MNPs, Pd-2N-MNPs and Pd-3N-MNPs). Their physical-chemical charateristics, thermal and magnetic properties were determined.

- The thesis scope includes four C-C coupling reactions: (i) Knoevenagel, (ii) Heck, (iii) Suzuki, and (iv) Sonogashira transformations. The results proved that both types of catalysts exhibited good catalytic activity with high reaction conversion being achieved under conventional heating or under microwave irradiation conditions. The best conditions for four reactions were found, and effects of electron-withdrawing and donating groups on reaction conversions were also investigated.
- Catalysts based on magnetic nanoparticles were demonstrated as heterogenous catalysts for these reactions. The catalysts could be recycled by simple magnetic decantation, and could be reused five times with reaction conversion of over 93% being observed.
- This is the first time in which crystalline structure, thermal and magnetic properties of reused catalysts (5 times) were studied. The results proved that high structural and characteristic stabilities could be obtained for the magnetic nanoparticles during the course of the reaction.

Our results here demonstrate the feasibility of applying magnetic nanoparticles as catalyst supports for immobilizing homogeneous catalysts. The unique properties of the particles such as nanometer-sized, magnetic, and facilely functionalized *via* silane chemistry, offer potential advantages over conventional catalyst support materials. The research could be expanded to the design and the immobilization of several catalysts on superparamagnetic nanoparticles for a wide range of organic transformations.

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