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HPA-dendrimer functionalized magnetic nanoparticles (Fe_3O_4@D-NH_2-HPA) as a novel inorganic-organic hybrid and recyclable catalyst for the one-pot synthesis of highly substituted pyran derivatives

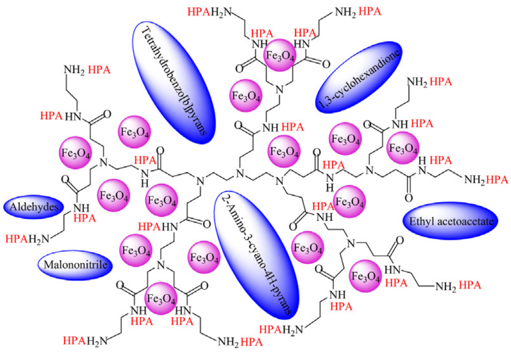
Ali Jamshidi, Behrooz Maleki*, Farrokhzad Mohammadi Zonoz, Reza Tayebee

Department of Chemistry, Hakim Sabzevari University, Sabzevar, 96179-76487, Iran

HIGHLIGHTS

- A novel magnetic nanoparticle catalyst was prepared and characterized.
- Environmentally benign reaction conditions for pyran synthesis.
- High catalytic activity and excellent recyclability.
- Facile recovery of the catalyst by external magnet.
- For the first time, $H_9[H_3P_2V_6W_{12}O_{62}].18H_2O$ has been used to create heterogeneous catalyst.

GRAPHICAL ABSTRACT



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ABSTRACT

An environmentally friendly HPA-dendrimer functionalized magnetic nanoparticle (Fe_3O_4@D-NH_2-HPA) was successfully prepared and evaluated for the first time as novel and efficient nanocatalyst for the one-pot synthesis of highly substituted pyran derivatives. The nano-magnetic catalyst was characterized by Fourier transform infrared (FT-IR), powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and vibrating sample magnetometry (VSM). Furthermore, the catalyst can be easily recovered and reused without a significant loss of activity.

1. Introduction

One of the most important classes of heterocyclic compounds are pyran derivatives. Due to the hallmark biological [1] and pharmacological activities of these compounds such as anticoagulant, spasmolytic, diuretic, anticancer, antianaphylactin properties [2], Alzheimer's disease, AIDs associated dementia and myoclonus [3], they have attracted a lot of attention. Pyran rings such as pyranopyrimidines, pyranopyridines, pyridine-2-ones, pyranopyrazoles and polyazanaphthalenes have a high intrinsic reactivity, through which they can provide a variety of synthetic methods for producing a wide range of heterocycles [4]. In the last years, different methods have been reported by the articles for the synthesis of these compounds. The easiest way for the synthesis of pyran derivatives is one-pot, three-component condensation of malononitrile, aldehyde and 1,3-dicarbonyl compounds in various conditions. The various catalysts such as diammonium hydrogen

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* Corresponding author.
E-mail address: malekibehrooz@gmail.com (B. Maleki).

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phosphate [5], tetrabutylammonium bromide [6], L-proline [7], $H_{14}[NaP_5W_{30}O_{110}]$ [8], *N*-methylmorpholine [9], hexadecyldimethylbenzyl ammonium bromide [10], ionic liquids [11–14], magnetic core–shell titanium dioxide nanoparticles [15], silica coated magnetite polyoxometalate nanoparticles [16], nanostructured diphosphate ($Na_2CaP_2O_7$) [17], Silica-coated magnetic $NiFe_2O_4$ nanoparticle-supported Preyssler heteropolyacid ($H_{14}[NaP_5W_{30}O_{110}]$) [18], Silica-coated magnetic $NiFe_2O_4$ nanoparticles-supported $H_3PW_{12}O_{40}$ [19], Nano α-Al_2O_3 supported ammonium dihydrogen phosphate ($NH_4\ H_2PO_4/Al_2O_3$) [20], nano ZnO [21], piperazine [22], sodium selenite [23], and 1-butyl-3-methyl imidazolium hydroxide ([bmim]OH) [24], and ammonium acetate have been used in this synthetic method [25]. However, these catalysts in spite of their potential utility show some limitations due to the usage of toxic and corrosive reagents, the tedious work-up procedure, and long reaction times.

Over the past decade the usage of magnetic nanoparticles (MNPs) presented a lot of merits because these nanoparticles had magnetic and electrical characteristics, high specific surface area and hallmark applications in various area such as drug delivery systems, targeted gene therapy, magnetic resonance imaging (MRI), sensors, saving information, separation metal ion environmental remediation, biomedicine particularly in the fields of pharmacology and catalysis [26–28]. Moreover, the surface of MNPs was also functionalized and modified by various organic and inorganic materials such as silica, polymers, biomolecules, metals, etc. which enabled them to be used as selective and efficient catalysts in a wide range of catalytic reactions [29,30].

Dendrimer is derived from Greek words Dendron means “tree” and meros means “part” synthesized in the late 1970's by Fritz Vögtle and co-workers [31]. These branched, star-shaped macromolecules are nano-sized, radially outward symmetric molecules with well-defined, homogeneous, and monodisperse structure. Dendrimer has molecular chains that branched out from a common core, and there is no involvement between each dendrimer molecules [32]. Such molecules have extensive applications in supramolecular chemistry, particularly in host-guest reactions and self-assembly processes [33]. These compounds are characterized by special features that make them promising candidates for a lot of applications. The Application of these branched structures generally depend on connecting other chemical species to the surface of dendrimer which enable them to operate as targeting constituents, detecting agents (like a colored molecule), radio-ligands, imaging factors, pharmaceutically active materials, drug delivery, gene delivery, sensors, blood substitution, and catalyst. Due to the ability of dendrimer to form multivalent structures, they can display a variety of these applications. That is to say, a dendrimer molecule has a lot of possible places to join to an active species [34–39]. According to the above, the surface of dendrimers is very important because they have many functional groups that are able to connect to other catalysts such as heteropolyacids (HPAs) through electrostatic bonding. Therefore, dendrimers can increase their catalytic efficiency by increasing the loading of catalysts onto their surface [40].

Recently, HPAs are famous as environmentally friendly and economically viable solid acids have gained importance among scientists. The structure of these compounds, which form an exceedingly great and diversified class of polyoxometalates (POMs), includes one or more p-, d-, or f-*block* “heteroatoms”, the d^0 and/or d^1 transition metal cations (addenda atoms) and oxide anions. Among various types of POMs, Keggin ($X^{n+}M_{12}O_{40}^{(8-n)\text{-}}$) ($X = P^{5+}$, As^{5+}, Si^{4+}, Ge^4+, B^{3+}, etc., M = Mo, W, V, and sometimes Nb) and Wells-Dawson ($X_2^{n+}M_{18}O_{62}^{(16-2n)\text{-}}$) structures have attract considerable interest as catalysts [41,42]. Among a variety of solid acids, HPA have distinctive chemical characteristicss because their acidity is considerably higher than that of general mineral acids. Moreover, these compounds have an ability to protonate and activate the substrates, and are sometimes more effective than typical mineral acids and traditional acid catalysts. Due to the high solubility of HPA, the separation of these compounds from the reaction environment is very difficult. So they are immobilized on the high surface supports which enable them to use as catalysts in a variety of organic reactions [43–45].

In this paper, we have tried to use the capabilities of three major catalytic groups of MNPs, dendrimers and HPAs simultaneously. For this reason, a new compound called inorganic-organic magnetic hybrid was synthesized and identified, and also its catalytic effect was studied in the preparation of tetrahydrobenzo [*b*]pyrans and 2-amino-3-cyano-4H-pyrans.

2. Experimental section

All reagents were of analytical grade and were used as received from commercial sources without further purification. FT-IR spectra were recorded in the range 400–4000 cm^{-1} on an Alpha Centaurt FT-IR spectrophotometer using a KBr pellet. All NMR spectra were measured at room temperature using a Bruker Avance 300 or 400 (300 or 400 MHz for ^1H, 75 or 100 MHz for ^{13}C) NMR spectrometer. All chemical shifts are reported in δ-scale as parts per million (ppm) relative to the solvent residual peaks as the internal standard. Abbreviations used for signal multiplicity: ^1H NMR: s = singlet, d = doublet, t = triplet, q = quartet. Melting points were determined in open capillary tubes in a Stuart BI Branstead Electrothermal cat no. IA9200 apparatus and uncorrected. X-ray diffraction (XRD) patterns obtained from an XPert MPD diffractometer with Cu Kα radiation at 40 keV and 30 mA, and scanning rate was set to 3°min^{-1} in the 2θ range from 5° to 80°. The morphology and distribution of particles of the synthesized catalyst were characterized with a field emission scanning electron microscopy (FESEM) was carried out on a HITACHI S-4160 with gold coating. Thermogravimetric analyses were performed on TGA-50 Shimadzu thermal analyzer in the flowing air atmosphere with the heating rate of 10 °C min^{-1} in the temperature region of 30–700 °C. Magnetic characteristics of compound were measured by Vibrating samples magnetometer (VSM, MDK, Model 7400).

2.1. Preparation of $H_9[H_3P_2V_6W_{12}O_{62}].18H_2O$

The potassium salt $K_9\ [H_3P_2V_6W_{12}O_{62}].18H_2O$ was prepared according to Roland Contant and coworkers litruture [46]. This vanadium–substituted Wells-Dawson hetropolyanion was converted into the corresponding acid by passing it through a column of Dowex-50w-X8 ion exchange resin. A sample of $K_9[H_3P_2V_6W_{12}O_{62}]\cdot 18H_2O$ (5 g) was dissolved in 100 ml water; then, the solution passed through the resin column in the H^+ form. This process was repeated for three times. Pure $H_9[H_3P_2V_6W_{12}O_{62}].18H_2O$ was obtained by the slow evaporation of final solution.

2.2. Preparation of nano-Fe_3O_4

Nano-Fe_3O_4 was synthesized From the method outlined in the article [47]. For this reason, $FeCl_3.6H_2O$ (2 mol) and $FeCl_2.4H_2O$ (1 mol) was dissolved in deionized water (20 ml). Under vigorous magnetic stirring (600 rpm), pH was risen piecemeal to approximate 10 by pouring (dropwise around 2 min) 25% NH_3 solution (5 ml) and the mixed solution was stirred at room temperature for an hour. Ultimate magnetic nanoparticles were aggregated by exterior electric field and washed several times with absolute ethanol and deionized water. Then, the product was dried in vacuum oven at 40 °C for 8 h.