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Application of Surface Modified Magnetite as an Efficient Support for Heteropolyacids and Studying Its Catalytic Activity in Organic Synthesis.

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Research Article

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ABSTRACT

Super paramagnetic Fe_3O_4 nanoparticles have attracted worldwide attention and have been studied extensively due to their biological and technological applications. These magnetic nanoparticles are efficient supports which can facilitate isolation and recycling of expensive catalysts from the reaction media. Herein, Fe_3O_4 Nanoparticles were modified with N-[3-(triethoxysilyl)propyl]isonicotinamide (TPI) linker; then, $H_5PW_{10}V_2O_{40}$ and $H_6P_2W_{18}O_{62}$ were chemically anchored to the surface of the modified magnetite. The prepared catalysts were Characterized using several techniques such as UV-vis, XRD, SEM, TEM, and FTIR. Finally, the catalytic activity of the prepared catalysts was monitored for the synthesis of different substituted bis(indolyl)methanes and 1-amidoalkyl-2-naphthols. This protocol introduced efficient, eco-friendly, and highly recyclable catalysts for the solvent-free, one-pot, and multi-component synthesis of the mentioned synthetic routes.

INTRODUCTION

Metal oxide nanoparticles have been introduced as potential heterogeneous catalysts bearing interesting structures and high catalytic activities[1]. In this respect, magnetic nanoparticles are useful materials which have been applied in catalysis, medicine, and biotechnology[2]. Among this category, Fe_3O_4 nanoparticles have attracted much attention, because of the ease of handling and recovery by using an external magnet. Moreover, high catalytic activity has been detected by these nanoparticles in different organic transformations[3].

Supporting of dodeca-tungstovanadophosphoric acid, $H_5PW_{10}V_2O_{40}$, and diphosphooctadecatungstic acid, $H_6P_2W_{18}O_{62}$, onto the surface of a modified porous material through immobilization and preparation of an organic–inorganic hybrid material has been the target of this research. In this interesting protocol, these two active homogeneous catalysts were chemically immobilizes onto the surface of Fe_3O_4 nanoparticles modified by an organic linker to overcome the potential negative aspects of the catalysts leaching. Then, their catalytic performances were studied in the effective and economic synthesis of substituted bis(indolyl)methanes and different 1-amidoalkyl-2-naphthols under solvent-free conditions.

EXPERIMENTAL

Materials and methods

All starting materials and solvents were commercially available, and their purities were monitored by gas chromatography. All products were identified by comparison of their spectral and physical data with those previously reported [4,5,6]. Progress of the reactions was monitored by TLC. Melting points were recorded on a Bamstead electrothermal type 9200 melting point apparatus. Ultraviolet-visible spectra were recorded on a Shimadzu Model UV-2550 spectrophotometer. Infrared spectra were recorded (KBr pellets) on a 8700 Shimadzu Fourier Transform spectrophotometer. Electron microscopy was performed on Phillips XL-30 scanning electron microscope (SEM). Transmission electron microscopy (TEM) was performed on a Philips CM120 with the magnification of 160 and 200 K. The heteropoly acid catalyst $H_5PW_{10}V_2O_{40}$, was prepared and characterized according to the literature procedures[7].

General procedure for the preparation of bis-(indolyl)phenylmethanes and substituted 1-amidoalkyl-2-naphthols

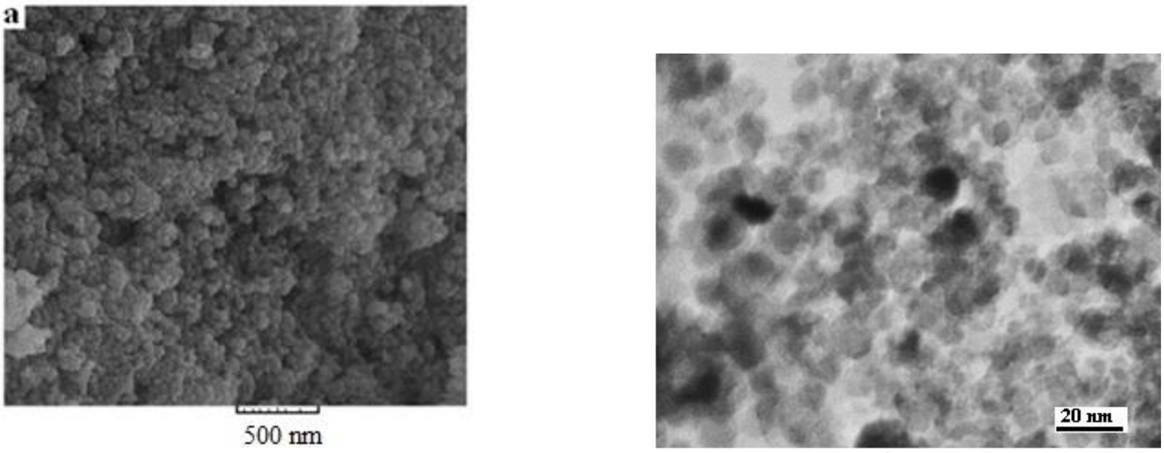
For the preparation of bis-(indolyl)phenylmethanes, a mixture of carbonyl compound (1 mmol), indole (2 mmol) and the nanocatalyst $H_5PW_{10}V_2O_{40}$ /TPI-Fe_3O_4 was stirred at the elevated temperature (100 ºC) for the required time. Finally, as indicated by TLC, acetonitrile (3 ml) was added to the reaction mixture and the catalyst was removed using an external magnetic bar. Then, silica gel (~1g) was added to the filtrate, and after evaporation of the solvent, a dark pinkish solid mixture was obtained. Purification of the product was performed by short column chromatography eluted with ethylacetate/petroleum ether (1/9) to give a pinkish solid product in high yield.

For preparing substituted 1-amidoalkyl-2-naphthols, a mixture of β-naphthol (1.0 mmol), aldehyde (1 mmol), benzamide (1.2 mmol), and $H_6P_2W_{18}O_{62}$/TPI-Fe_3O_4 (20 mg) were added to a small test tube equipped with a condenser, was heated to100 ˚C in an oil bath for the required time. After completion of the reaction (monitored by TLC), the mixture was cooled to 25 ˚C, boiling ethanol was added and the mixture was stirred for 5 min. The catalyst was recovered by using an external magnet. Then, the solution was cooled to room temperature and the resulting solid was filtered off and re-crystallized from aqueous ethanol 15%.

RESULTS AND DISCUSSION

Generally, nanoparticles have been applied as efficient supports for the preparation of functionalized materials because of nano-effects. But, the separation processes become a challenge, because nanoparticles are often readily dispersed in the liquid media. This issue may be overcome by using magnetic materials; they offer the advantage of being magnetically separable by using an external magnetic field. Amongst various metal oxide nanoparticles which have been emerged as potential heterogeneous catalysts, Fe_3O_4 nanoparticles arguably have attracted most attention. The reason would be due to the ease of handling, ease of recovery, as well as the high catalytic activity of Fe_3O_4 nanoparticles in various organic transformations[8,9].

The use of more environmentally benign catalyst coupled with the ease of catalyst separation and reuse are important features of the present report. Magnetic separation of the catalyst nanoparticles was very simple, economical, and promising for industrial application. Studying morphology of $H_5PW_{10}V_2O_{40}$ /TPI-Fe_3O_4 and $H_6P_2W_{18}O_{62}$/TPI-Fe_3O_4 with SEM and TEM micrography clearly indicated homogeneity of the nanohybrid materials and showed that the heteropoly acids were well dispersed in TPI-Fe_3O_4 (Fig. 1). These micrographs clearly indicated homogeneity of the material and also shows that the heteropolyacids were well dispersed in TPI-Fe_3O_4.



a b

Figure 1: The SEM and TEM images of (a) $H_5PW_{10}V_2O_{40}$/TPI-Fe_3O_4 and (b) $H_6P_2W_{18}O_{62}$/Fe_3O_4-TPI, respectively.

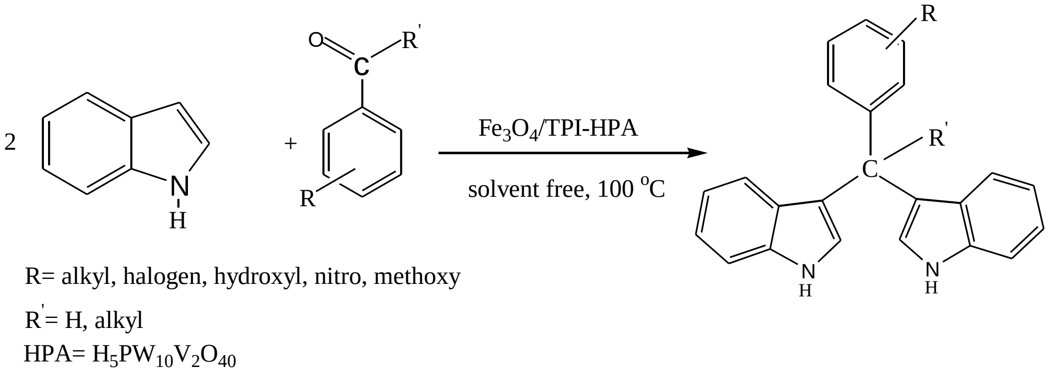
Synthesis of different bis(indolyl)methanes catalyzed by $H_5PW_{10}V_2O_{40}$/TPI-Fe_3O_4

The general nature of the method was demonstrated by using structurally diverse aromatic and aliphatic aldehydes bearing electron withdrawing and electron donating substituents in the reaction with indole under the standard reaction conditions (Table 1). The results revealed that this methodology is effective for a wide range of aldehydes. However, aliphatic aldehydes showed less reactivity towards the condensation reaction than their aromatic analogues.

Synthesis of different α-amidoakyl-β-naphtols in the presence of HPA/TPI-Fe_3O_4 under solvent free conditions

Non-toxicity and chemical stability of the new synthesized organic-inorganic hybrid material HPA/TPI-Fe_3O_4 is amongst the most crucial characteristics of this super paramagnetic iron oxide nanocatalyst. The generality of the protocol was confirmed by using structurally diverse aromatic and aliphatic aldehydes carrying either electron-withdrawing, electron-donating, and halogen groups on their aromatic rings in the condensation reaction and gave the desired products in high yields in short reaction times (Table 2). It was shown that the aromatic aldehydes with electron withdrawing groups reacted faster than their analogues with electron releasing groups. In contrast to the previously reported methods[10,11], in which aliphatic aldehydes were not transformed into the corresponding 1-amidoalkyl-2-naphtols, they were converted into the desired product in good yields in the current methodology. Findings revealed that this protocol is effective for a wide range of aldehydes. However, aliphatic aldehydes showed less reactivity toward condensation reaction than aromatic analogues.

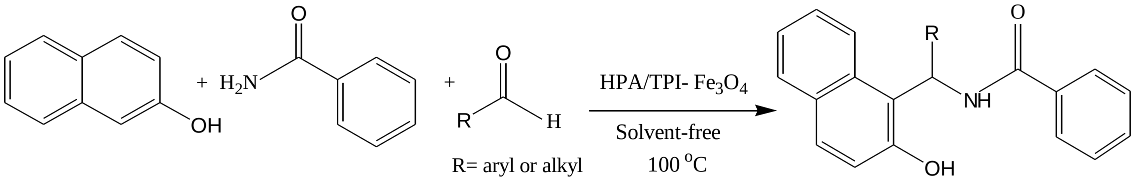
Table 1: Synthesis of various bis(indolyl)methane derivatives in the presence of HPA/TPI-Fe_3O_4 under solvent-free conditions.



Entry	Aldehyde	Time (min)	Yield (%)	MP (m.p./lit.m.p.(°C)
1	benzaldehyde	25	96	147-148/145
2	4-NO_2- benzaldehyde	15	92	219-222/ 222
3	4-Cl- benzaldehyde	40	65	78-79/ 79
4	2-Cl-benzaldehyde	25	98	107-109/107
5	3-Br- benzaldehyde	10	85	189-191/190
6	2-OMe- benzaldehyde	10	82	170
7	2-Cl- benzaldehyde	15	97	201

Reaction conditions are as described below Table 1. 0.01g of HPA/TPI-Fe_3O_4, including 1.9mg of $H_5PW_{10}V_2O_{40}$ (0.06 mol%) was used in all cases.

Table 2: Synthesis of various α-amidoakyl-β-naphtol derivatives in the presence of HPA/TPI-Fe_3O_4 under solvent free conditions.



Entry	Aldehyde	Time (min)	Yield (%)	M.P. (lit. mp)
1	benzaldehyde	30	92	235 (235-237)
2	4-NO_2-benzaldehyde	25	94	237 (239-241)
3	3-NO_2-benzaldehyde	30	88	239 (240-242)
4	4-Cl-benzaldehyde	30	91	177 (176-177)
5	2-Cl-benzaldehyde	35	75	286 (284-285)
6	3-Br-benzaldehyde	35	83	230-232
7	4-Br-benzaldehyde	35	87	243-244
8	2-Me-benzaldehyde	40	85	215 (215-216)
9	acetaldehyde	45	48	247-248
10	formaldehyde	60	57	235 (233-235)

Reaction conditions are described below Table 1.

CONCLUSION

Novel magnetic inorganic–organic nanohybrid materials $H_5PW_{10}V_2O_{40}$ /TPI-Fe_3O_4 and $H_6P_2W_{18}O_{62}$/TPI-Fe_3O_4 were fabricated and performed as an efficient, eco-friendly, and highly recyclable catalyst for the solvent-free, one-pot, and multi-component synthesis of different substituted substituted bis(indolyl)methanes and 1-amidoalkyl-2-naphthols. The nanohybrid catalysts were prepared by the chemical anchoring of the two heteropolyacids onto the surface of the modified Fe_3O_4 nanoparticles with N-[3-(triethoxysilyl)propyl]isonicotinamide (TPI) linker. This protocol is developed a safe and convenient alternate method for clean organic synthesis. The present approach offers several promising advantages such as higher yield, easy handling, reduced reaction time, easy and green work-up, and versatility. These advantages, in general, highlight this protocol as a useful and attractive methodology, among the methods reported in the literature, for the rapid synthesis of biologically active materials.

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