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Synthesis of Functionalized Iron Oxide Nanoparticle with Amino Pyridine Moiety and Studies on Their Catalytic Behavior

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Research Article

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ABSTRACT

Aim: The main objective of this paper is to study the synthesis of functionalized iron oxide nanoparticle and its reactivity towards chromene synthesis

Study design: Functionalized iron oxide nanoparticle study.

Place and duration of study: Department of Studies and Research in Industrial Chemistry, School of Chemical Sciences, Kuvempu University, Shankaraghatta, between December 2009 and July 2010.

Methodology: This paper describes synthesis of stable functionalized iron oxide nanoparticles through surface modification of magnetic iron oxide nanoparticles by amino pyridine. Iron oxide nanoparticles were synthesized by co-precipitation method and the surface modification process was achieved by treating the nanoparticles with (chloro propyl trimethoxy silane) CPTS and aminopyridine. The developed functionalized iron oxide nanoparticle was evaluated as the catalyst for synthesis of chromones under MW irradiation conditions.

Results: The catalysts were magnetically recovered and reusable without significant loss of their catalytic efficiency. To receive morphological and structural information on the obtained functionalized nanoparticle, the samples were analyzed by X-ray diffraction (XRD) measurements, FTIR and scanning electron microscopy (SEM) imaging. All synthesized chromene derivatives were characterized using analytical techniques such as IR, ¹H NMR, and mass spectroscopy. Also the identity of these compounds was easily established by comparison of their melting point with those of reported samples.

Conclusion: In summary, we have developed a new magnetically recyclable and

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efficient functionalized magnetic nano catalyst for the chromene synthesis. Magnetic nanoparticle catalyst achieves a simple separation of catalyst without filtration including high yield in product.

Keywords: Iron oxide nanoparticle; 2-amino-4H-chromenes; catalyst; green chemistry;

1. INTRODUCTION

In recent years, functionalized iron oxide nanoparticle are of increasing interest in the variety of field such as cell biology, biotechnology (Hu, et al., 2008), diagnostics, nanoanalytics and pharmaceuticals mostly due to their super-paramagnetic property present at small particle sizes (Scherer et al., 2005; Raming et al., 2002). Metal-organic solids are hybrid materials created by the association of the metal ion and organic ligands, which have already shown a wide range of promising properties in gas sorption, sensing, catalysis, ion exchange, magnetism, optics, etc. (Mornet et al., 2004; Chorny et al., 2007; Gu et al., 2006). Because of the vast range of the properties, one of the actual challenges is the miniaturization of this system to design and fabricating novel metal-organic nanoparticles. Magnetic nanoparticles have been immobilized on various catalyst supports, including polymers, carbons, and silicas, (Teunissen et al., 1999; Yoon et al., 2003; Yoon et al., 2007; Yang et al., 2004; Stevens et al., 2005; Lee et al., 2006; DSlaigh et al., 2007) since easily recoverable and reuseable heterogeneous catalyst is still in high demand, a striking feature of supported magnetic nanoparticle catalyst is that they can be readily separated using an external magnet, which achieves a simple separation of catalyst without filtration. Additionally they not only show high catalytic activity but also a high degree of chemical stability and they do not swell in organic solvents. In recent years, extensive research has been performed on magnetic catalyst (Polshettiwar et al., 2008) which has led to substantial advances in nanomaterial synthesis.

Chromones constitute one of the major classes of naturally occurring compounds, and interest in their chemistry continues unabated because of their usefulness as biological and pharmacological aspects (Kidwai et al., 2005). Much effort has been focused towards the development of catalyst for the synthesis of chromone derivatives using (Mg/Al) hydrotalcite (Surpur et al., 2009), cetyltrimethyl ammonium bromide under ultrasound (Jin et al., 2004), TiCl₄ (Kumar et al., 2006), preyster heteropoly acid (Heravi et al., 2007), PEG 400 (Nana et al., 2010), N,N-dimethylaminoethylbenzyl dimethyl-ammonium chloride (Lu et al., 2009) and most recently nanostructured Na₂CaP₂O₇ (Solhy et al., 2010), nanosize MgO (Kumar et al., 2007) as efficient heterogeneous catalyst. One of the primary problems of these heterogeneous catalysts is their separation and reuse through nanofiltration membrane which are associated with reaction mixture. Even though the search for more active catalysts, novel materials and methodology for exposing more active sites in a catalyst for a particular reaction continues, catalyst's selectivity has become a crucial issue recently. As part of our ongoing research aimed at the development of reusable catalysts for various organic transformations (Girija et al., 2011; Naik et al., 2009), here in we focus on developing functionalized iron oxide nanoparticle and its catalytic application for synthesis of chromones under MW irradiation conditions.

2. EXPERIMENTAL DETAILS

2.1 Materials and Reagents

All chemicals (AR grade) were commercially available and used without further purification. The melting points of the products were determined by open capillaries and are uncorrected. Thin-layer chromatography was performed using commercially prepared 60-mesh silica gel plates and visualization was effected with short wavelength UV light (254 nm). The IR spectra were recorded on a Shimadzu model impact 400D FT-IR Spectrophotometer using KBr pellets. ¹H NMR were recorded on a Buckner AC-300F 300 MHz spectrometer in CDCl₃

2.2 General Experiment

2.2.1 General procedure for the synthesis of magnetic silica nanoparticles (MSN)

Magnetic Fe₃O₄ nanoparticles used in the experiment were produced by chemical co precipitating Fe²⁺ (FeCl₂•4H₂O) and Fe³⁺ (FeCl₃•6H₂O) ions in ammonia solution, according to the reported procedure (Bee et al., 1995; Yoon et al., 2005) with slight modification. To introduce reactive silanol on the surface of magnetic nanoparticle (MNP) 2.0 g of the synthesized Fe₃O₄ nanoparticles diluted with water, alcohol and ammonia aqueous were ultrasonicated for 1 h. Then TEOS was slowly added to this dispersion, and mechanical stirring was continuous for 12 h. The precipitates were washed several times with deionized water by magnetic decantation and treated with 1M HNO₃ solution for 12h. Then the TEOS modified Fe₃O₄ nanoparticles were treated with (chloro propyl trimethoxy silane) CPTS and aminopyridine.

2.2.2 Preparation of 3-chloropropyl-functionalized magnetic silica nanoparticles (MSN-CI)

Magnetic silica nanoparticles (100 mg) were dried at 110°C under vacuum conditions for 90 minutes. Afterwards, the amount of 15 mL dry xylene was added under nitrogen atmosphere. After addition of 3- chloropropyltrimethoxysilane (200 µl), the reaction mixture was allowed to stir for overnight under reflux conditions (Zheng et al., 2009). The functionalized MSN-CI was separated by centrifugation and washed with each 30 mL of xylene, methanol and water before being dried at 60°C for 12 hours.

2.2.3 Preparation of pyridin-2-amine functionalized magnetic silica nanoparticles (MSN-AP)

The obtained MSN-CI was added to 10 mL of a saturated solution of amino pyridine in xylene. The resulting mixture was stirred at 90°C for overnight. The material was obtained by magnetic separation followed by two times washing with 30 mL of xylene and ethanol sequentially before being dried at 60°C for 12 hours.

2.3 General Procedure for the Preparation of 2-Amino- 3 Cyano-Chromene Derivatives

The mixture of aldehyde (2 mmol), malononitrile (2 mmol) and MSN-AP (~ 0.4 mmol) was taken in a 50 ml flask and irradiated under microwaves for the time indicated in (Table 2) and the completion of the reaction was monitored by TLC. After completion of reaction, the

reaction mixture was cooled to room temperature and got solidified within hour. The resulting solidified mixture was diluted with ethyl acetate (5 ml) and the catalyst was separated. The filtrate obtained was washed twice with water and evaporation of the solvent under reduced pressure yielded the crude product, which was further purified by recrystallization. All synthesized chromene derivatives were characterized using analytical techniques such as IR, ¹H NMR, and mass spectroscopy. Also the identity of these compounds was easily established by comparison of their melting point with those of reported samples (Table 2) (Jin et al., 2004; Heravi et al., 2007; Lu et al., 2009; Kumar et al., 2007) using TMS as an internal standard with ¹H resonant frequency of 300 MHz.

3. RESULTS AND DISCUSSION

In the present study, tetraethyl orthosilicate (TEOS) were employed to introduce highly reactive silanols on the surface of magnetic Fe₃O₄ to improve the affinity of Fe₃O₄ nanoparticles for the target species. Then the TEOS modified Fe₃O₄ nanoparticles were then treated with 3 chloro propyltriethoxysilane (CPTS), which can bind covalently to the free –OH groups at the surface of the particles and the ended chloro group couples with amino pyridine forming pyridin-2-amine functionalized magnetic silica nanoparticles (MSN-AP) Figure 1.

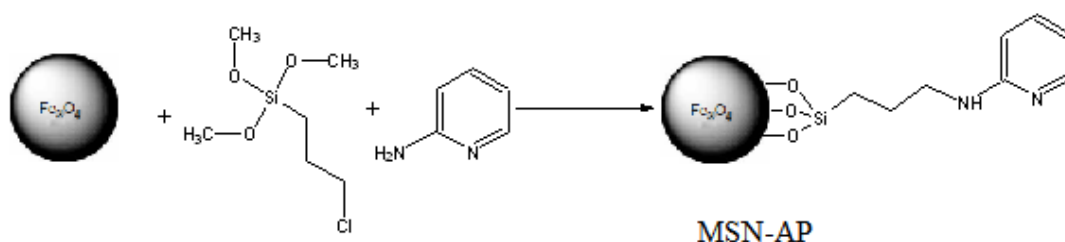


Fig. 1. Synthesis of pyridin-2-amine functionalized magnetic silica nanoparticles (MSN-AP)

The crystalline structures of the MSN-AP catalyst were determined by powder X-ray diffraction (XRD) (Figure.2); the diffraction patterns and relative intensities of all the peaks matched well with those of magnetite (JCPDS card no. 00-002-1035). Broad XRD peaks clearly indicate the nanocrystalline nature of the material. The average crystallite size D was calculated using the Debye–Sherrer formula

$$D = K \lambda / (\cos \theta)$$

where K is Sherrer constant, λ is the X ray wavelength, θ is the peak width of half-maximum, and θ is the Bragg diffraction angle. The crystallite size thus obtained from this equation was found to be about 28 nm. Same characteristic peaks can also be found in Figure 2b which illustrated that the characteristic peaks did not change but only the peak intensity and width after coated with silane and amino pyridine, showing the crystalline structure of the modified nanoparticles was not varied.

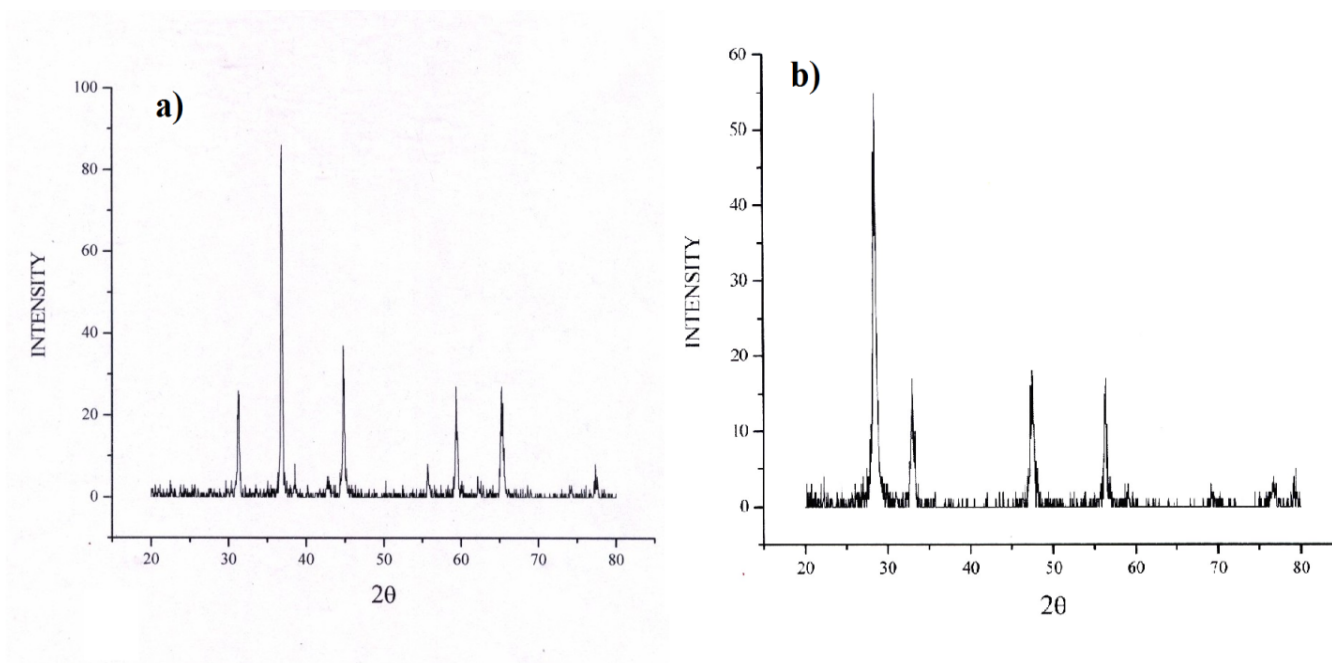


Fig. 2. XRD pattern of MNP a) and MSN-AP (b)

Scanning electron microscopy (SEM) analysis (Figure 3) of the organocatalyst showed uniform-sized particles with spherical morphology with an average size range of 30–32 nm. Anchoring of amine on the surface of magnetic nanoparticles was examined by FT-IR spectroscopy.

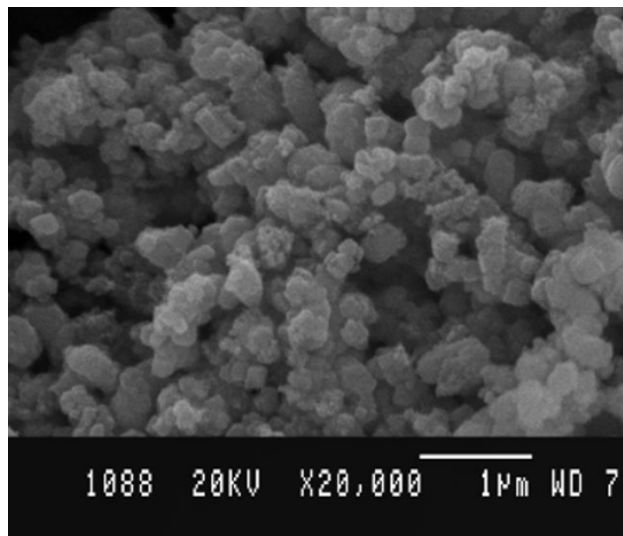


Fig. 3. SEM images of synthesized MSN-AP

To study the surface group on magnetic nanoparticle, very dilute samples were examined by ^1H NMR (Willis et al., 2005), ^1H NMR resolved spectra of ligands bound to a paramagnetic nanocrystal are difficult to perform due to large broadening effects caused by paramagnetic features.

The FTIR spectrum for the magnetite nanoparticles (Figure 4) alone shows a stretching vibrational 3474 cm^{-1} which incorporates modes of the O-H bonds which are attached to the surface iron atoms. The presence of an adsorbed water layer is confirmed by a stretch for the vibrational mode of water found at 1623 cm^{-1} , The absorption band at 587 cm^{-1} is attributed to the Fe-O bonds. In the spectrum for the catalyst loaded nanoparticles, additional stretches are attributed to the presence of the catalyst. Alkyl C-H stretches is found at 2957 and 2874 cm^{-1} . The amine C-N stretch is found at 1292 cm^{-1} which was covered by a stronger absorption of Si-O bonds at 1139 cm^{-1} . The stretch found at 855 cm^{-1} is due to the presence of Fe-O-Si bonds in the sample.

The supported catalyst was evaluated for chromene synthesis using benzaldehyde, malononitrile and naphthol. Initially, the reaction was performed with several solvents and monitored for the best possible combination, the reaction condition was optimized for the chromene synthesis using benzaldehyde as a substrate, under microwave (MW) irradiation conditions. MW-assisted chemistry was used due to the efficiency of the interaction of microwaves with the polar nano-catalyst as they allow rapid heating of the reaction mixture to required temperatures with precise control. In each case, the substrates were mixed together with 0.25 g MSN-AP agitated with 10 mL solvent. The results are shown in Table 1. The polar solvents such as water and ethanol or acetonitrile, afford better yields than nonpolar ones, and the mixture of water and ethanol is the most effective solvent.

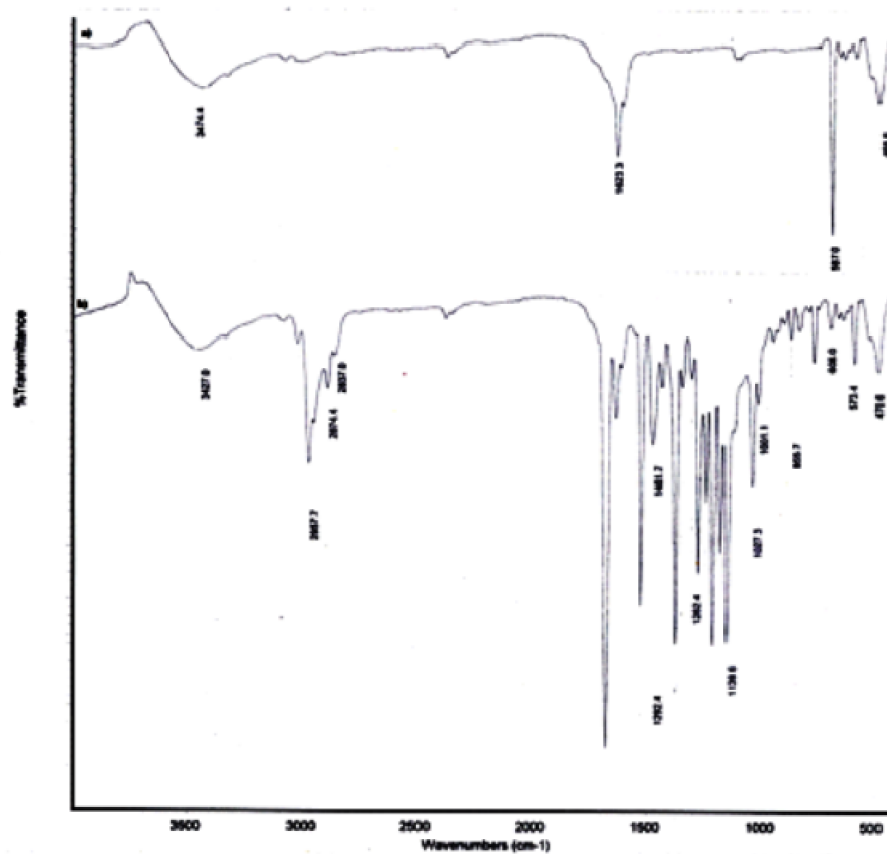
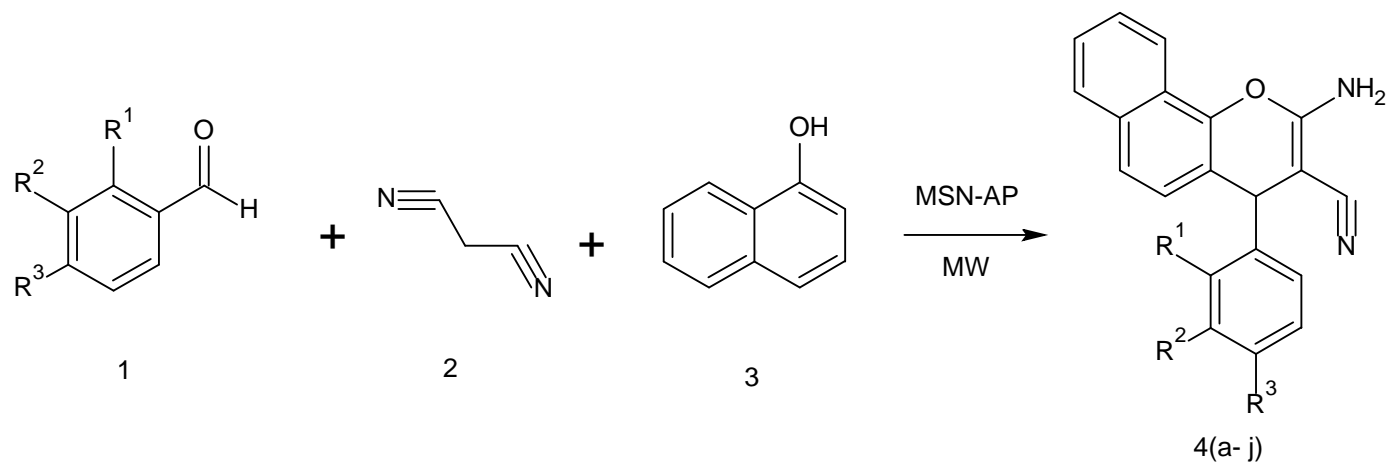


Fig. 4. FT-IR spectra of bare MNP (a) and MSN-AP (b)



Scheme 1. MSN-AP promoted 2-amino-4H-chromenes

Table 1. Solvent effect on the synthesis of chromene derivatives presence of MSN-AP

Entry	Solvents	Time (min)	Yield ^a (%)
1	DMF	20	57
2	Toluene	16	67
3	ACN	14	73
4	Ethanol	12	90
5	H ₂ O/ Ethanol	8	95

Subsequently, In order to investigate the scope of this reaction, a variety of different substituted benzaldehyde compounds were subjected to this reaction (Table 2). A variety of substituted benzaldehyde possessing a wide range of electron-donating functional groups such as hydroxyl, alkoxy (entries **2, 4-6**), and electron-withdrawing functional groups such as chloro (entries **7-8**), nitro group (entries **3-9**) afforded the corresponding products in good yields.

Table 2. A one-pot multi-component reaction for synthesis of 2-amino-chromenes in presence of MSN-AP catalyst

Entry	R ¹	R ²	R ³	Time (mins)	Product	Yield (%)	M.P. (°C) Found	M.P. (°C) Reported
1	H	H	H	8	4a	95	209-210	210-211
2	H	H	NMe ₂	12	4b	98	204-206	203-205
3	H	H	NO ₂	10	4c	96	233-235	231-234
4	H	OMe	OH	12	4d	88	137-138	137-139
5	H	H	OMe	10	4e	90	189-191	191
6	H	H	OH	10	4f	94	243-245	245
7	H	H	Cl	15	4g	93	232-237	231-232
8	Cl	H	H	12	4h	95	237-239	236-237
9	H	NO ₂	H	9	4i	85	209-210	208-211
10	furyl	H	H	10	4j	91	169-170	169-172

Nature of the substituents on the aromatic ring shows a strong effect in term of reaction time under the given condition. When electron donating groups were employed longer reaction time was required than those of electron withdrawing groups on aromatic ring.

To test the lifetime and the feasibility of repeated use of the catalyst, we conducted the experiments using the recycled nano organo catalyst After the completion of the first reaction, the reaction mixture was diluted with ethyl acetate and the organic layer was removed by decantation and the catalyst was recovered magnetically, the separated catalyst was directly used for the next run without any pretreatment. It was observed that the developed catalyst could be used at least four times without any change in activity (Figure 5).

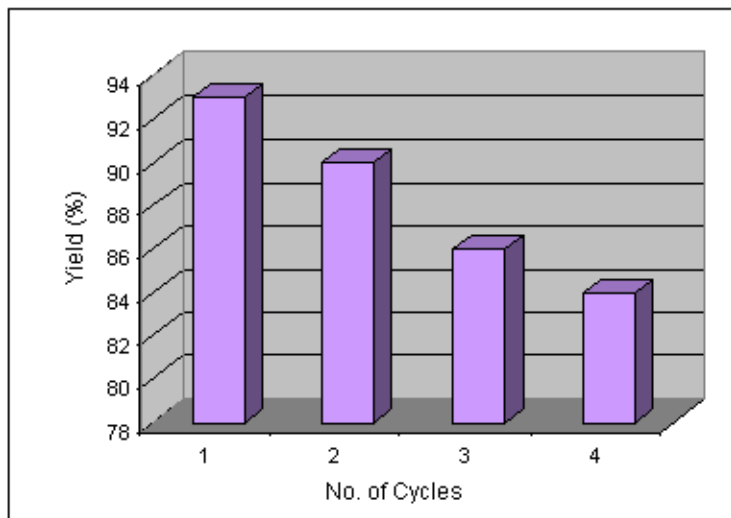


Fig. 5. Recyclability of pyridin-2-amine functionalized magnetic silica nanoparticles (MSN AP)

4. CONCLUSION

In summary, we have developed a new magnetically recyclable and efficient functionalized magnetic nanocatalyst for the chromene synthesis. The catalysts show environmental friendly character, with recyclability of the catalyst makes for the development of a greener strategy. Moreover, the procedure offers several advantages including high yields, operational simplicity, clean reaction conditions and minimum pollution of the environment, which makes it a useful and attractive process for the synthesis of these chromene derivatives. Further investigation and synthesis of supported –MNP catalyst is in progress.

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