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ARTICLE TYPE

Synthesis of aminonaphtols and β-amino carbonyls in the presence magnetic recyclable Fe_3O_4@MCM-48─$NaHSO_4$ nano catalyst

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In this study, magnetic recyclable Fe_3O_4@MCM-48─$NaHSO_4$ nano catalyst was used for synthesis of aminonaphtols with heteroaromatic amines and β-amino carbonyl during Mannich reaction. For this purpose, magnetite nanoparticles (MNPs) and MCM-48 mesoporous-coated MNPs with particle size lower than 11 nm were synthesized via chemical precipitation methods. Then $NaHSO_4$ was adsorbed on the surface of mesoporous MNPs. The prepared inorganic magnetic catalyst was characterized by FT-IR, XRD, UV-DRS, TEM, VSM and titration. Finally, the applicability of the synthesized solid acid catalyst for catalysis of Mannich reactions was investigated.

Introduction

Consume minimum of energy, reagents or auxiliaries and minimize waste are the principles of “Green Chemistry” for catalyzed organic reactions. Many unrecyclable catalysts are ecologically harmful and didn’t consider to following these principles. Hence, development of new catalysts for synthetic methods has become an important research area, aiming to make the synthesis simpler, to save energy and to prevent toxicity in chemical processes. Consequently, we need a catalyst system that not only shows high activity and selectivity (like a homogeneous system) but also possesses the ease of catalyst separation and recovery (like a heterogeneous system). These goals can be achieved by nanocatalysis based on metal nanoparticles. Nanocatalysis can bridge the gap between homogeneous and heterogeneous catalysis, preserving the desirable attributes of both systems. Clearly, the development of metal nanoparticles with tunable catalytic activity is of great significance for both academia and industry.

However, the recycle problem must be addressed before nanocatalytic processes can be scaled-up, due to the fact that nanoparticles, which include nano-scaled metal catalysts and supports are difficult to separate from the reaction mixture, which can lead to the blocking of filters and valves by the nanoparticle catalyst.[1] Currently, use of magnetic nanoparticles can be solve this problem. Catalysts supported on magnetic nanoparticles, usually iron oxides, can be quickly and easily recovered in the presence of an external magnetic field for reuse.

In the last decade, significant research efforts were devoted to obtain materials with well defined nanoparticles for synthesis of new catalysts. Nanocatalyst based on mesoporous silica materials like MCM-n, SBA-n and FSM, among others, are a fairly new type of material that has pores in the mesoscopic range of 2–50 nm.[2] The performance of these materials as a catalyst is depend directly on the silica network porosity, high surface area, large pores, high hydrothermal stability, easy preparation and etc. This material with particular property can be used as a coating for MNPs. Thereby, synthesis of MNPs functionalized with silica mesoporous leads to increase the surface area and enhance the textural property of MNPs, which allows their usage as a strong and stable support for very organic and inorganic catalysts.

Sulfuric acid is one of the most important catalysts for the production of industrial chemicals. Over 15 million tons of sulfuric acid are annually consumed as an unrecyclable catalyst that don’t follow the principles of “Green Chemistry” because this process is costly, produces high waste and separation of the catalyst from homogeneous reaction mixture is inefficient. These drawbacks can be overcomed by synthesis of mesoporous MNPs-based solid acid with a high density of sulfonic acid groups (─OSO_3H), which can be easily removed from the reaction mixture applying an external magnetic field.[3]

The synthesis of natural molecules, pharmaceuticals and other nitrogenous biologically active compounds for a long time has

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been a significant branch of organic synthesis.[4] The Mannich reaction provides one of the most basic and useful methods for the synthesis of such compounds. Due to the drastic reaction conditions, severe side-reactions, substrate limitations and the long reaction time, the classical intermolecular Mannich reaction is plagued. To overcome the drawbacks of the classic method, the Lewis acid-catalyzed condensation between silyl enol ethers or silyl ketene acetals and imines has been developed. Recently, some Bronsted acid or Lewis aicd-catalyzed one-pot Mannich reactions of unmodified aldehydes, ketones and amines have been catalyzed by HCl,[5] proline,[6] p-dodecyl benzene sulfonic acid (DBSA),[7] polymer-support sulfonic acid (PS-SO3H),[8] Lewis acids[9] as well as Silica-$AlCl_3$.[10] However, the long reaction time, costly catalysts and requirement of special effort for catalyst preparation cannot be avoided. Therefore, it has attracted continuous interest to develop easier methods for the synthesis of b-amino carbonyl compounds.

In the present study, the synthesis of new mesoporous magnetic nano particle based solid acid functionalized with high density of sulfonic acid groups (SO_3H) are reported and its performance as a novel, strong and stable catalyst is discussed. This strategy involves Fe_3O_4 nanoparticle as the magnetic core coated by MCM-48 mesoporous silica as a thin layer and functional groups of sulfonic acid.

Application of MCM-48 as a support for sulfonic acid was reported in previous works,[11-13] but this study focused on the possibility of applying $NaHSO_4$ and nanotechnology for the design of a novel, active and recyclable, sulfonic acid derivative for the first time. Also, the current work shows unique advantages, such as simple usage of the catalyst system in solvent-free conditions, easy separation of catalyst with a permanent magnet and the application of inexpensive and available precursors.

Result and Discussion

Characterization of synthesized MNPs

Magnetite nanoparticles (Fe_3O_4) with 9.0 nm average diameter were prepared by the chemical coprecipitation technique. The sulfonated mesoporous MNPs were synthesized in two steps as follows: (i) preparation of colloidal iron oxide magnetic nanoparticles and (ii) development of a MCM-48 mesoporous structure within the MNPs surface. $NaHSO_4$ was used as the sulfonating agent for synthesis of Fe_3O_4@ MCM-48─$NaHSO_4$ nanoparticles. The new synthesized nanoparticles and solid acid catalysts were characterized via FT-IR, XRD, DRS, TEM, VSM and titration.

The FT-IR spectra of the MNPs, MCM-48, mesoporous-coated MNPs and Fe_3O_4@MCM-48─$NaHSO_4$ MNPs confirm the structure of synthesized particles (see ESI†). For the bare MNPs, the peak at ~ 575 cm^{-1} is attributed to the Fe─O band vibration of Fe_3O_4. In the case of MCM-48 coated nanoporous particle the band at 1085 cm^{-1} is corresponding to Si─O─Si anti symmetric stretching vibrations, being indicative of the existence of SiO_2 in the nanoparticles. The FT-IR spectra of mesoporous-coated MNPs without and with calcination confirm the removal of surfactant template. According to the previous works the stretching and bending vibrations of O–H bonds can be observed at ~ 3500 and 1647 cm^{-1}; respectively. Also, the external vibrations of SiO_4 chains can be observed at ~ 1222 and 789 cm^{-1}; at 962 cm^{-1}, due to asymmetric Si–O vibrations adjacent to sylanol groups; at 580 cm^{-1} due to the presence of double ring vibrations and 454 cm^{-1} due to the angular bending of Si–O units.[14,15] Fe_3O_4 usually presents bands at ~ 570 and 430 cm^{-1}, due to Fe–O vibrations in tetrahedral and octahedral sites, respectively.[16] In the case of Fe_3O_4@MCM-48─$NaHSO_4$ (Figure 1d), the sulfonic acid bonds can be observed at ~1200–1250, 1010–1100 and 650 cm^{-1}, which are attributed to the O=S=O asymmetric and symmetric stretching vibrations and S─O stretching vibration of the sulfonic groups (─SO_3H), respectively. However, in the FT-IR spectra of synthesized nanoparticles, such bands could not be observed because they are probably overlapped by the bands of SiO_2. The increase in the intensities of the bands at 3000– 3500 cm^{-1} suggests that there are more OH groups under the mesoporous MNPs surface after the sulfonation. On the other hand, the band at ~ 3360 cm^{-1} became much broader.

X-ray diffraction (XRD) patterns are shown in Figure 1 for the bare MNPs and Fe_3O_4@MCM-48. The MNPs indicated peaks with 2θ at 29.72, 35.57, 43.17, 57.15 and 62.77 which are characteristic peaks of Fe_3O_4, indicating the purity of the synthesized nanoparticles of Fe_3O_4. The XRD pattern of the mesoporous MNPs showed peaks that could be indexed either mesoporous structure and MNPs, (i) the siliceous mesoporous structure indicated four peaks with 2θ at 1.5-10 or reflection from the 211, 220, 420 and 332, which are characteristic peaks of MCM-48; (ii) the same peaks with MNPs, which indicating the presence of magnetite in the cave of synthesized composite. The same peaks were observed in both bare and mesoporous coated MNPs, which indicated the accuracy synthesis of the Fe_3O_4@MCM-48 MNPs.

X

Figure 1. X-ray diffraction patterns of Fe_3O_4 MNPs (**a**) and Fe_3O_4@MCM-48 (**b**)

Figure 2 shows the diffuse reflectance spectroscopy (UV-DRS) of the synthesized bare MNPs, MCM-48 NPs, mesoporous-coated MNPs and Fe_3O_4@MCM-48─$NaHSO_4$ MNPs, respectively. The MNPs indicated peaks at 220 nm, which indicating the purity of the synthesized Fe_3O_4. The same peaks were observed in all particles. The UV-DRS patterns thus indicate existence of the magnetic core during the all synthesized MNPs.

X

Figure 2. UV-DRS spectra of (**a**) Fe_3O_4; (**b**) Fe_3O_4@MCM-48; (**c**) Fe_3O_4@MCM-48─$NaHSO_4$; (**d**) MCM-48.

The TEM images of the prepared MNPs are shown in Figure 3. Based on the TEM images, analysis of Fe_3O_4 and Fe_3O_4@MCM-48 surface morphology demonstrated the agglomeration of many ultrafine particles with a diameter of about 9.0 and 12 nm, respectively.

X

Figure 3. TEM image of (**a**) Fe_3O_4; (**b**) Fe_3O_4@MCM-48.

It is most important that MNPs and Fe_3O_4@MCM-48─$NaHSO_4$ should possess sufficient magnetic and super paramagnetism property for magnetic carrier technology (MCT) practical application. The magnetic hysteresis curves of MNPs are shown in Figure 4. Bare MNPs and MCM-48 mesoporous MNPs exhibited typical superparamagnetic behavior due to not exhibiting hysteresis, remanence and coercively. The large saturation magnetization of bare MNPs and MCM-48 mesoporous MNPs were 82 emu g^{-1} and 50 emu g^{-1} respectively, which is sufficient for magnetic separation with a conventional magnet.

X

Figure 4. Magnetic hysteresis curves of the Fe_3O_4 and Fe_3O_4@MCM-48.

The amount of $NaHSO_4$ adsorbed on Fe_3O_4@MCM-48 was 3.19–3.22 mmol g^{-1}, which was determined through the neutralization titration of six synthesized samples. We can suggest that $-SO_3H$ group in $NaHSO_4$ can act as Bronsted acid sites in catalytic mechanism. For exhibit magnetic properties of the synthesized solid acid, the sulfonic acid-loaded mesoporous MNPs were dispersed in water, resulting in a dark dispersion. In the presence of an external magnetic field nanoparticles of Fe_3O_4@MCM-48─ $NaHSO_4$ were completely gathered onto one side of the cuvette wall steadily (Figure 5).

X

Figure 5. Photographs of aqueous suspension of Fe_3O_4@MCM-48─$NaHSO_4$ before (**a**) and after (**b**) magnetic capture.

Catalytic properties of Fe_3O_4@MCM-48─$NaHSO_4$

Catalytic properties of Fe_3O_4@MCM-48─$NaHSO_4$ were investigated in the Mannich reaction for synthesis of aminonaphtol derivatives and stereoselective synthesis of β-amino carbonyl compounds.

The Mannich reaction is one of the most important multicomponent reactions, that used for carbon–carbon bond formation. This reaction is a nucleophilic addition of an amine to a carbonyl group followed by dehydration to the Schiff base.

An attractive feature of this method is the use of Fe_3O_4@MCM-48─$NaHSO_4$ as the solid acid catalyst for synthesis of aminonaphtols with high yield in short time and synthesis of β-amino ketones with favor of the anti-isomer.

I) Aminonaphtols: The prepared Fe_3O_4@MCM-48─$NaHSO_4$ magnetic particles have been used as catalysts in three-component, one-pot Mannich reaction for synthesis of aminonaphtol derivatives with heteroaromatic amines. For initial optimization of reaction condition and identification of the best amount catalyst (Fe_3O_4@MCM-48─$NaHSO_4$), benzaldehyde, 3-amino pyridine, naphthalen-2-ol were chosen as model substrates (Figure 6).

X

Figure 6. synthesis of aminonaphtols catalyzed by Fe_3O_4@MCM-48─$NaHSO_4$

The amount of the catalyst is a main factor affecting the synthesis procedure. Thus, after screening different amount of the synthesized catalyst (Table 1), the results show that the product **4** could be obtained in yield range 81 to 95%. Hence, 0.025 g of the Fe_3O_4@MCM-48─$NaHSO_4$ can catalyze the Mannich reaction for synthesis of aminonaphtols.

Table 1. Influence of the amount of synthesized catalyst on the Mannich synthesis of aminonaphtol[a].

Entry	Fe_3O_4@MCM-48─$NaHSO_4$ (g)	Time (min)	Yield (%)[b]
1	0.0125	60	95
2	0.025	18	97
3	0.05	35	90
4	0.1	47	81

[a] Benzaldehyde / 3-amino pyridine / 2-naphtol = 1:1:1, solvent-free, room temperature.

[b] Refers to isolated yield.

Afterwards, we investigated the effect of temperature on the reaction rate as well as the yields of products. According to the obtained results, 25 °C was selected for synthesis procedure (Table 2, entry 2).

Table 2. Influence of temperature on the Fe_3O_4@MCM-48─$NaHSO_4$ catalyzed synthesis of aminonaphtol.[a]

Entry	Temperature (°C)	Time (min)	Yield (%)[b]
1	10	95	85
2	25	13	97
3	50	13	97
4	100	13	95

[a] Benzaldehyde / 3-amino pyridine / 2-naphtol = 1:1:1, solvent-free, 0.025 g of Fe_3O_4@MCM-48─$NaHSO_4$.

[b] Refers to isolated yield.

In summery, the optimal conditions for the Fe_3O_4@MCM-48─$NaHSO_4$ catalyzed Mannich reaction (for synthesis of aminonaphtols) involved combination of Fe_3O_4@MCM-48─$NaHSO_4$ (0.025 g), naphthalen-2-ol **1** (1 mmol), 3-amino pyridine **2a** (1 mmol), benzaldehyde **3** (1 mmol) at room temperature under solvent-free conditions. In view of the obtained results, the optimized reaction condition was selected to determine the scope of this Fe_3O_4@MCM-48─$NaHSO_4$ catalyzed reaction. A wide range of aromatic aldehydes and heteroaromatic amines **2a,b,c,d** were subjected to react with naphthalen-2-ol in presence of 0.025 g Fe_3O_4@MCM-48─$NaHSO_4$ to generate **4,5,6** and **7** (Figure 6), the result summarized in Table 3.

Table3. Fe_3O_4@MCM-48─$NaHSO_4$ catalyzed Mannich synthesis of aminonaphtols **4,5,6,7**.[a]

Amine	R	Product	Time (min)	Yield (%)[b]
2a	H	4a	13	97
2a	3-NO_2	4b	20	94
2a	4-NO_2	4c	17	97
2a	4-Br	4d	15	93
2a	3-Cl	4e	20	93
2a	4-Cl	4f	17	95
2b	H	5a	3	95
2b	4-Me	5b	2	97
2b	4-Br	5c	2	91
2b	4-Cl	5d	1	93
2c	H	6a	2	98
2c	4-Me	6b	2	92
2c	4-Cl	6c	2	92
2d	H	7a	1	94
2d	4-Me	7b	2	97
2d	4-Cl	7c	1	95

[a] All products were characterized by FT-IR, ^{1}H NMR, ^{13}C NMR spectroscopy.

[b] Refers to isolated yield.

II) β-amino carbonyl: After reporting the synthesis of β-amino carbonyl in our previous work,[17] here in we report an efficient and operationally convenient solid acid catalyst for synthesis of β-amino carbonyl compounds with high yields at room temperature and solvent-free conditions.

The one-pot synthesis of β-amino carbonyl compounds was achieved by the three-component condensation of cyclohexanone, aromatic aldehydes and aromatic amines in the presence of Fe_3O_4@MCM-48─$NaHSO_4$ MNPs as a heterogeneous catalyst (Figure 7).

X

Figure 7. One-pot three-component direct Mannich reaction for synthesis of β-amino carbonyl.

Initially, the reaction between benzaldehyde, cyclohexanone and aniline were chosen as model substrates for optimization of conditions. The reaction was carried out by stirring a mixture of cyclohexanone (3.0 mmol), benzaldehyde (2.5 mmol) and aniline (2.5 mmol) in the presence of various amounts of Fe_3O_4@MCM-48─$NaHSO_4$ MNPs as a catalyst in solvent-free condition. The efficiency of the reaction is affected mainly by the amount of Fe_3O_4@MCM-48─$NaHSO_4$ MNPs (Table 4). According to obtained results, to give the product the catalyst is necessary for the reaction. Increasing the amount of the catalyst increased the yield of the product. The optimal amount of Fe_3O_4@MCM-48─$NaHSO_4$ MNPs was 0.05 g (entry 4); increasing the amount of the catalyst beyond this value did not increase the yield noticeably (entries 5).

Table 4. Influence of the amount of synthesized catalyst on the Mannich synthesis of β-amino carbonyl**.**[a]

Entry	Fe_3O_4@MCM-48─$NaHSO_4$ (g)	Time (min)	Yield (%)[b]
1	None	240	None
2	0.0125	120	87
3	0.025	80	92
4	0.05	30	97
5	0.1	55	97

[a] Solvent-free and room temperature condition.

[b] Refers to isolated yield.

The *anti*- and *syn*- isomers of products were identified by the coupling constants (*J*) of the vicinal protons adjacent to C=O and NH in ^{1}H NMR spectra.[17] The coupling constants for *anti*-isomers are reported to be bigger than those of *syn*-isomers.[18] Probably, interaction between catalyst and the transition state in this reaction conduces to the formation of *anti*- or *syn*-isomer.[19,20] Under optimum condition, to show the generality and scope of this new protocol, a wide range of aromatic aldehydes and aromatic amines were used as bearing electron-withdrawing and electron-donating groups in addition to cyclohexanone, which gave product in good to high yields with excellent anti selectivity (Table 5).

Table5. Fe_3O_4@MCM-48─$NaHSO_4$ catalyzed Mannich synthesis of β-amino carbonyl.

Entry	R^1	R^2	Yield (%)[a]	Time (min)	anti/syn[b]
1	H	H	95	30	99/1
2	4-Me	H	80	25	99/1
4	4-Br	H	75	40	70/30
5	4-Cl	H	75	35	99/1
6	4-NO_2	H	90	25	99/1
7	2-Cl	H	90	35	99/1
8	H	4-Br	95	40	99/1
9	H	4-Me	90	20	98/2

[a] Isolated yields, products were confirmed by ^{1}H NMR

[b] anti/syn ratio was determined by ^{1}H NMR.

The different groups substitution of aldehydes and aniline with the same groups located at different positions of the aromatic ring has been shown not to have much effect on the formation of the final product and afford the expected anti-isomer of products. The products were characterized by IR and ^{1}H NMR spectroscopy. Importantly, note that the suuperparamagnetic property of Fe_3O_4@MCM-48─$NaHSO_4$ made the isolation and reuse of this catalyst very easy. After completion of the reaction, the products which connected to catalyst were separated with a permanent magnet. Finally, the reaction product was eluted from the catalyst. The Fe_3O_4@MCM-48─$NaHSO_4$, after washing and drying in air, can be directly reused without any deactivation even after ten rounds of synthesis of product.

A comparison between the result of the proposed catalyst and some of the recently used catalysts for Mannich reaction is summarized in Table 6. This table shows that the heterogeneous catalyst of Fe_3O_4@MCM-48─$NaHSO_4$ is the best in comparison to other mentioned catalysts. The proposed new catalyst has some advantages in comparison with the other catalyst including shorter reaction time, activity as stereoselective catalyst, easy separation via external magnetic field, low consumption of organic solvents and ability to perform reactions in solvent free conditions. It is a stable solid acid catalyst with high densities of sulfuric acid groups that can be easily synthesized in the lab and can be reused for several times. Also, it is more stable respect to non-functionalized or bare magnetite nanoparticles that were synthesized and used in our previous work. [17]

Table 6. Comparison of the characteristic of new synthesized catalyst with some recently used catalysts

Catalyst	Time (min)	Temperature (°C)	Solvent	Stereoselective	Ref.
MgO/ZrO_2	480	80	Acetonitrile	No	21
Cu/C Np[a]	180	r.t[g]	Water/EtOH	No	22
TCT[b]	150	r.t	PEG[i]	Yes	23
TCT	420	r.t	EtOH	No	24
CSA[c]	420	r.t	EtOH	Yes	25
$SiO2-OSbCl_2$	300	r.t	EtOH	No	26
ZnO NP	600	60	H_2O	Yes	27
CBSA[d]	270	r.t	EtOH	No	28
Fe_3O_4[f]	45	r.t	EtOH	Yes	17
Proposed catalyst	60	r.t	Solvent free	Yes	Proposed method

[a] nanoparticle
[b] 2,4,6-Trichloro-1,3,5-Triazine
[c] Cellulose Sulfuric Acid
[d] Carbon-based Solid Acid
[f] Bar magnetite nanoparticle
[g] Room Temperature
[i] Polyethyleneglycol

Experimental

Materials and Apparatus

All chemicals including $FeCl_3$. $6H_2O$, $FeCl_2$. $4H_2O$, tetraethyl ortosilicat (TEOS), NaOH, NaF, $NaHSO_4$. H_2O were purchased with high purity from Fluka and Merck (Darmstadt, Germany). The crystal phases and crystallinity of synthesized MNPs were analyzed by a X-PERTPRO X-ray diffraction (PANalitical) and measured with Cu–Ka radiations in the range of 1.5–70 (2θ), the quality and composition of synthesized nanoparticles were characterized by a Shimadzo Fourier transform infrared (FTIR-470) spectrometer in the range of 400–4000 cm^{-1}. The size and morphology of particles were studying by a PHILIPS transmission electron microscopy (CM10 HT 100KV). The UV-Vis absorption behavior of synthesized MNPs were characterized using a Sinco diffuse reflectance spectrophotometer (DRS, S-4100).

Preparation of the MNPs

MNPs were prepared by addition of aqueous solotion of ammonia to an aqueous mixture of ferrous and ferric salts, according to Faraji et al. method with a little modification.[17] Briefly, 6.3 g $FeCl_3$. $6H_2O$, 4.0 g $FeCl_2$. $4H_2O$ and 1.7 mL HCl (12 mol L^{-1}) were dissolved in 50 mL of deionized water in a beaker in order to prepare the stock solution of ferrous and ferric chloride. After that, the solution was degassed with argon gas and heated to 80 °C in a reactor. Simultaneously, 250 mL of a 1.5 mol L^{-1} ammonia solution was slowly added to the solution under argon gas protection and vigorous stirring (1000 rpm). During the process, the solution temperature was kept constant at 80 °C and argon gas was purged to prevent the intrusion of oxygen. After completion of the reaction, the obtained precipitate of magnetite (Fe_3O_4) nanoparticles were separated from the reaction medium by the magnetic field, and then were washed four times with 500 mL doubly distilled water. Finally, the obtained MNPs were resuspensioned in 500 mL of degassed deionized water. The concentration of obtained MNPs was obtained as 6.2 mg mL^{-1}.

Preparation of Fe_3O_4@MCM-48 and Fe_3O_4@MCM-48─$NaHSO_4$ MNPs

For synthesis of Fe_3O_4@MCM-48, the MNPs (1.5 g) and ammonia solution (5 mL) were mixed with 50 mL distilled water in glass reactor and sonicated for 2 minutes at 40℃. After mixing, TEOS (10 mL), NaOH (0.9 g) and NaF (0.19 g) were added to the mixture and stirred for 2.0 hours. Then, cetyltriammonium bromide (CTAB) (7.0 g) was added to the mixture. The mixture was stirred at 40 °C for 2.0 hours again. At the end of this process, the magnetic composite hydrothermally treated at 120 °C for 48 hours in an autoclave. After two days, the resultant solids were filtered, washed with distilled water and dried at 60 °C. Finally, the template was removed by calcinations of synthesized particles for 3 hours at 300 °C.

For synthesis of functionalized Fe_3O_4@MCM-48 with SO_3H group, the method of Azarifar et al. was used.[29] Fe_3O_4@MCM-48 (1.5 g) was added to 20 ml magnetically stirred aqueous solution of $NaHSO_4.H_2O$ (0.7 g, 5 mmol) at 25 °C over a 60 min period. The mixture was stirred for a further 30 min allowing the sodium bisulfate to adsorbed onto the mesoporous MNPs. Finally, the water was removed and powder was dried in an oven at 90 °C for 2–3 h, which a brown solid of sulfonic acid functionalized MCM-48 mesoporous MNPs (Fe_3O_4@MCM-48─$NaHSO_4$) was obtained.

General procedure for the synthesis of 1-(phenyl(pyridin-3-ylamino)methyl)naphthalen-2-ol

Under the optimum conditions, a mixture of benzaldehyde (1 mmol), 3-amino pyridine (1 mmol), naphthalen-2-ol (1 mmol) and MNPs (0.025 g) was stirred at room temperature and solvent-free conditions for 13 minute. The reaction products were monitored by TLC. After completion of the reaction, the mixture was triturated with ethanol. Afterward, in the presence of a magnetic stirrer bar, Fe_3O_4@MCM-48─$NaHSO_4$ separated and the reaction mixture turned clear. Finally the crude product was recrystallized from EtOH to give a pure product.

General procedure for the synthesis of 2-(phenyl(phenyl amino)methyl)cylohexanone

Under the optimum conditions, The one-pot, three-component Mannich reaction between benzaldehyde (2.5 mmol), aniline (2.5 mmol) and cyclohexanone (3 mmol) in presence of Fe_3O_4@MCM-48─$NaHSO_4$ (0.05 g) was also studied. Hence, the mixture was stirred at room temperature and solvent-free conditions for 30 minute. After completion of the reaction (monitored by TLC), the reaction product was eluted from the MNPs with hot EtOH and the catalyst was removed by a permanent magnet. Then, the EtOH solution of product was kept at room temperature, to crystallize the product. Finally, the collected product was filtrated and washed via EtOH (95%).

Conclusion

The present methodology offers several advantages, such as good yields, short reaction times, solvent-free conditions, room temperature and a recyclable catalyst with a very easy operation. In addition, the obtained results indicated that Fe_3O_4@MCM-48─$NaHSO_4$ as a solid acid can be used as an effective and inexpensive catalyst for synthesis of aminonaphtols and stereoselective synthesis of β-amino carbonyl by one-pot three component reactions.

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Graphical abstract

Sulfonic acid functionalized mesoporous magnetite nanoparticles as an efficient, heterogeneous and recyclable catalyst for synthesis of aminonaphtols and β-amino carbonyls

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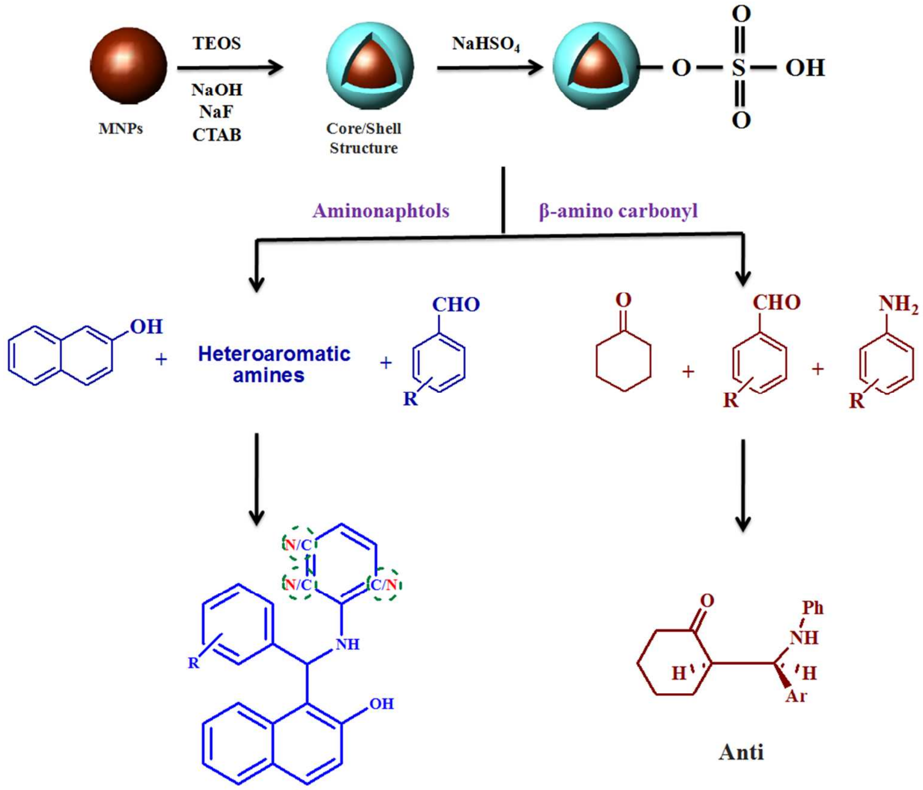

Highlights

- We report, synthesis of Fe_3O_4@MCM-48─SO_3H as a recyclable solid acid catalyst in the Mannich reaction.
- Advantages: good yields, rapid reaction, solvent-free conditions and room temperature.

Figure 1. X-ray diffraction patterns 0f Fe$_3$O$_4$ NPs (**a**) and Fe$_3$O$_4$@MCM-48 (**b**)

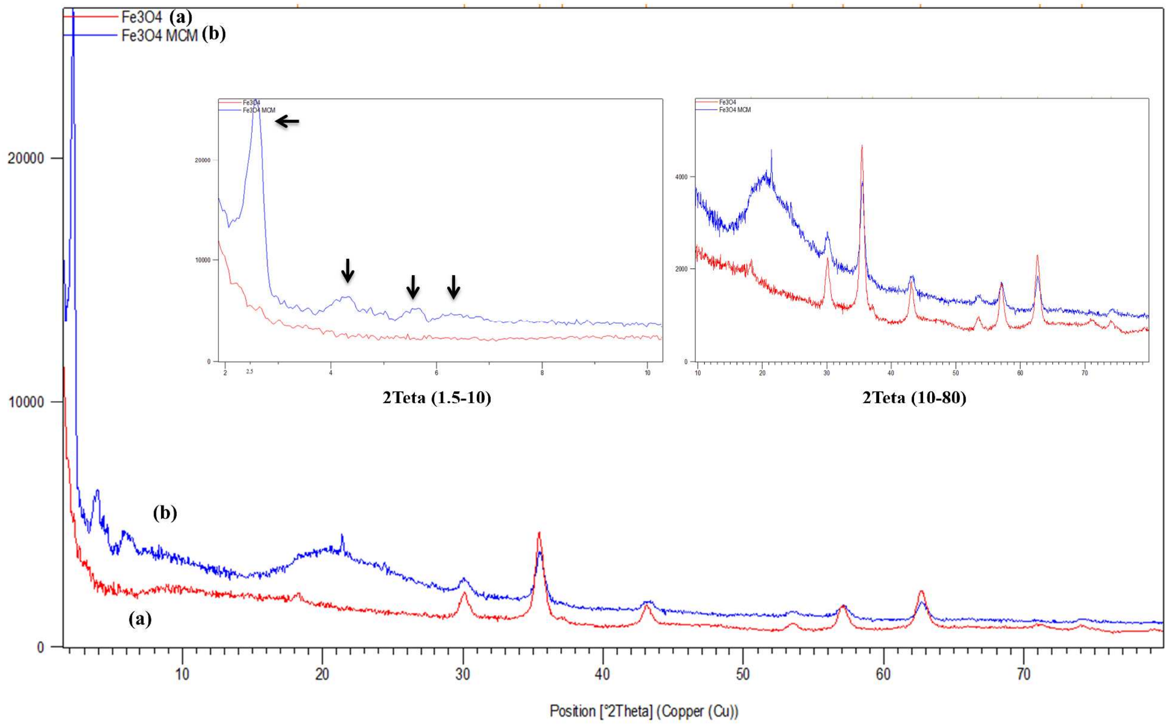

Figure 2. UV-DRS spectra of (**a**) Fe_3O_4; (**b**) Fe_3O_4@MCM-48; (**c**) Fe_3O_4@MCM-48─OSO_3H; (**d**) MCM-48.

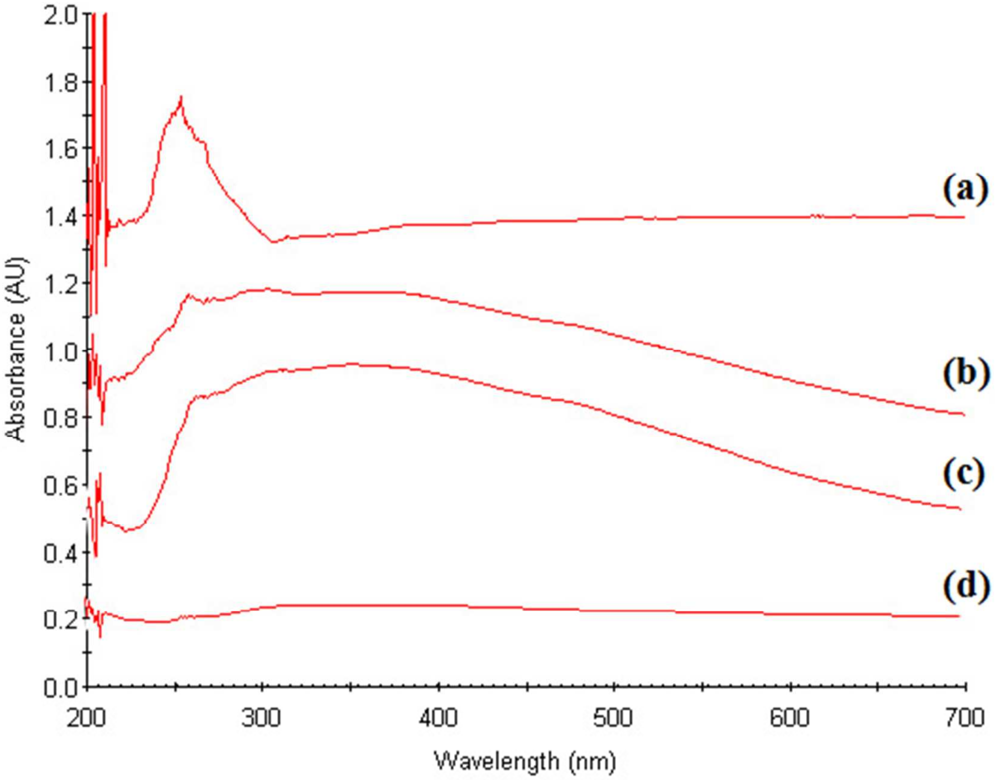

Figure 3. TEM image of (**a**) Fe_3O_4; (**b**) Fe_3O_4@MCM-48.

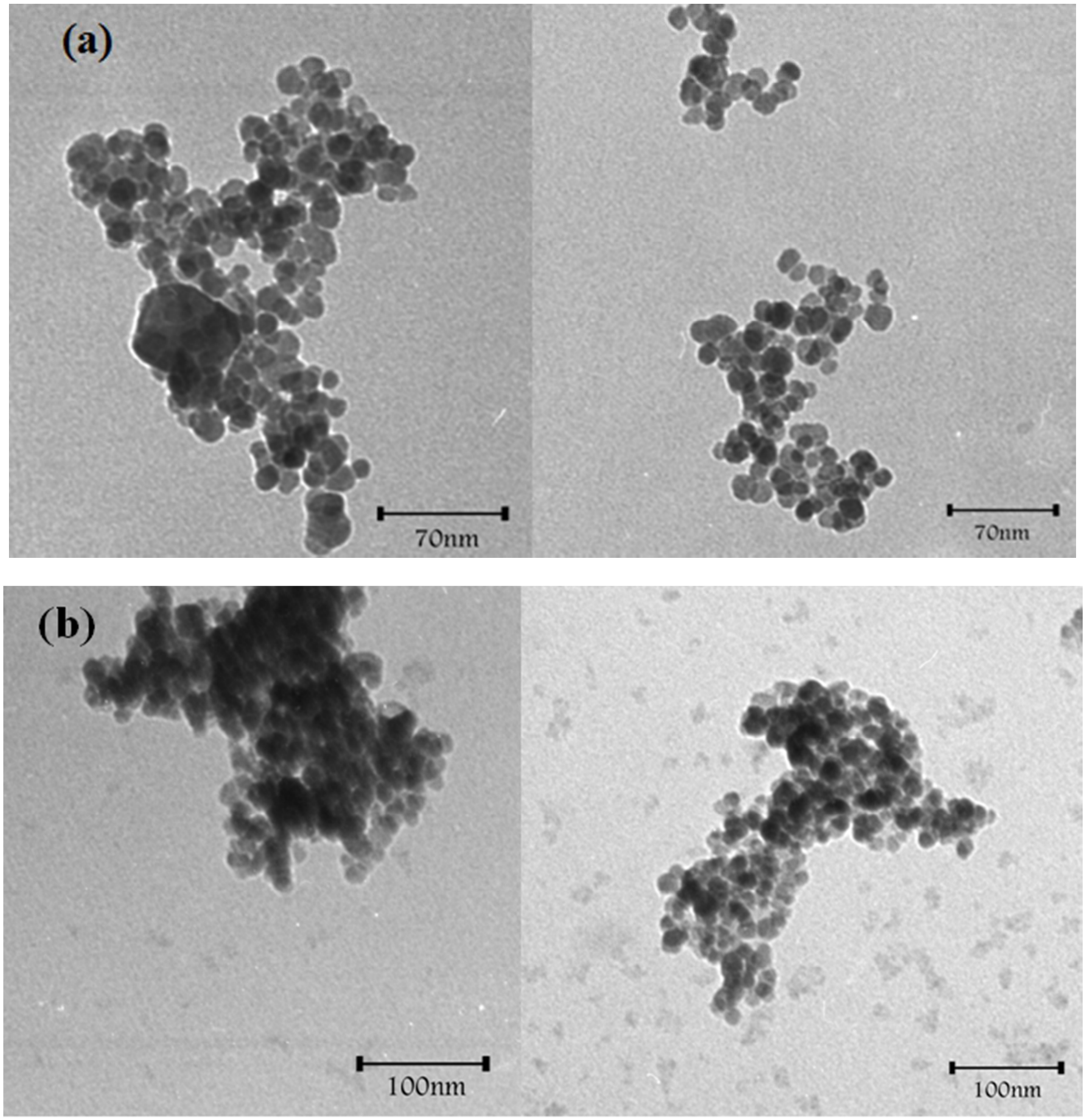

Figure 4. Magnetic hysteresis curves of the Fe_3O_4 and Fe_3O_4@MCM-48.

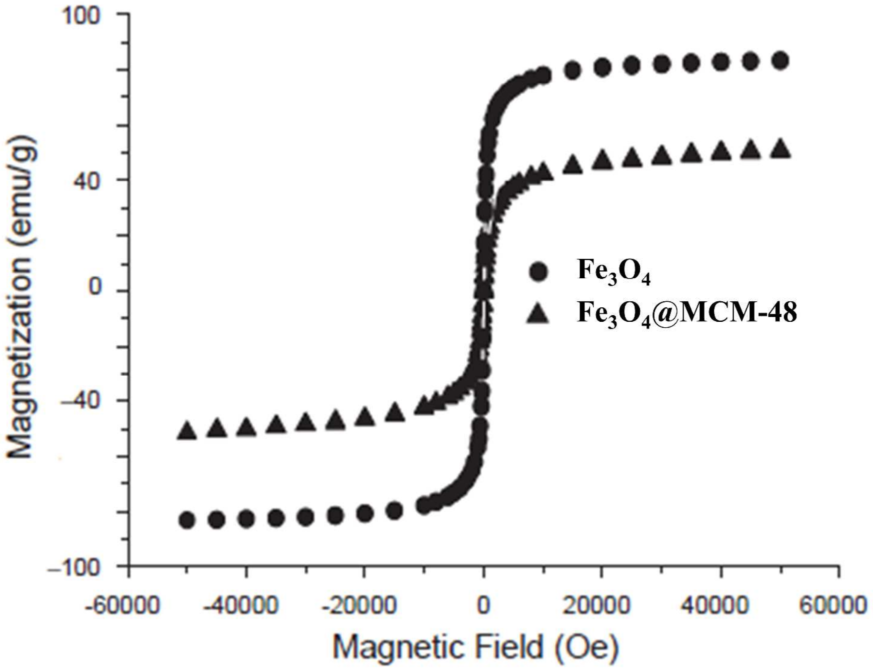

Figure 5. Photographs of aqueous suspension of Fe_3O_4@MCM-48─SO_3H before (**a**) and after (**b**) magnetic capture.

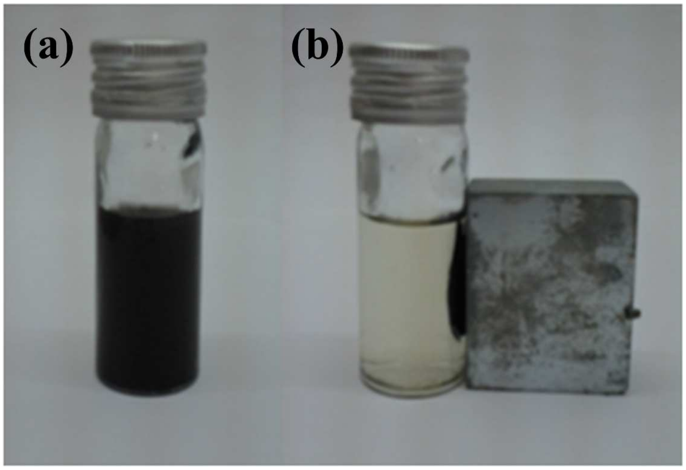

Figure 6. synthesis of aminonaphtol catalyzed by Fe_3O_4@ MCM-48–SO_3H

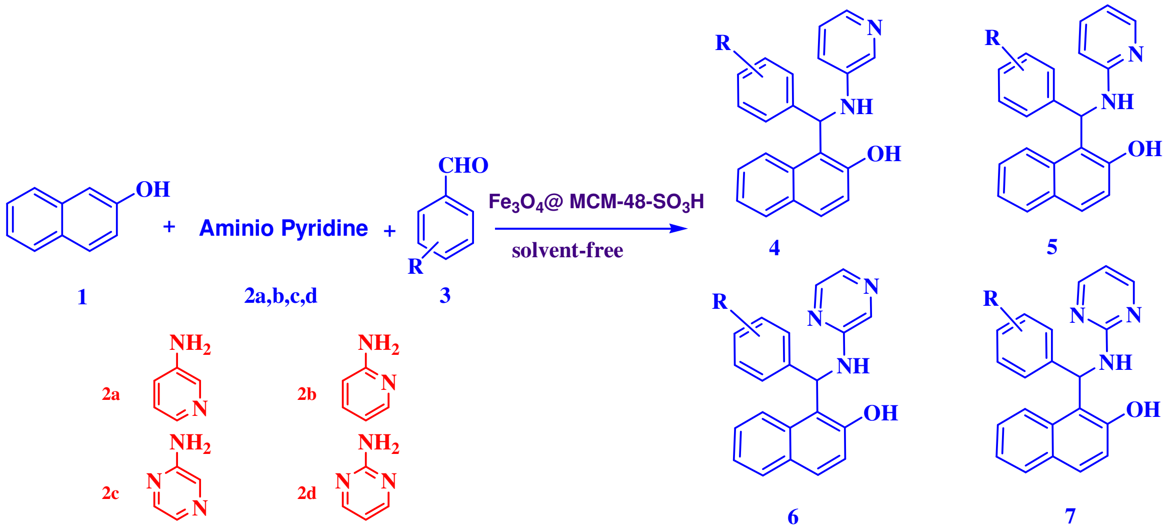

Figure 7. synthesis of aminonaphtols catalyzed by Fe_3O_4@ MCM-48─SO_3H