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Magnetic nanoparticles functionalized ethane sulfonic acid (MNESA): as an efficient catalyst in the synthesis of coumarin derivatives using Pechmann condensation under mild condition

Marjaneh Samadizadeh[1] · Saeed Nouri[1] · Faeze Kiani Moghadam[2]

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Abstract This paper reports an efficient heterogeneous catalyst based on sulfonic acid functionalization of magnetic nanoparticles. This new catalyst was prepared using the reaction between magnetic nanoparticles and sodium 2-bromoethane-1-sulfonate. Magnetic nanoparticles functionalized ethane sulfonic acid (MNESA) was found as efficient catalyst for the synthesis of coumarin derivatives using Pechmann condensation under mild condition. This reaction was catalyzed by MNESA under solvent-free condition at 90 °C, to give the corresponding products in excellent yields. The catalyst is easily separated from the reaction condition and can be reused for several times with consistence in the activity.

Keywords Heterogeneous catalyst · Coumarin · Pechmann reaction · Magnetic nanoparticles

Introduction

There are widespread interests in the preparation of heterogeneous acid catalyst for application in acid catalyzed organic transformations [1–4]. In recent years, magnetic nanoparticles (MNPs) have been used as an efficient support for synthesis of heterogeneous catalyst. This material is an abundantly available and highly stable substrate, mainly characterized by the fact that organic groups can be linked to its surface

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✉ Marjaneh Samadizadeh
mar.samadizadeh@iauctb.ac.ir

[1] Department of Chemistry, Islamic Azad University, Central Tehran Branch, 19379-58814 Tehran, Iran

[2] Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran

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with strong bonding to generate catalytic sites [5–7]. Development of magnetic reusable catalysts for organic synthesis based on solid acids has become an environmental chemical procedure for academic and industrial applications [8]. Several types of magnetic nanoparticle sulfonic acids have been prepared and applied in chemical transformations in recent years [9–11]. All of these magnetic nanoparticles based on sulfonic acid catalyst are suitable for some acid catalyzed organic transformations, but such preparation often suffers from some deficiency such as expensive starting reagents and requires more than two steps for the preparation [9–14].

Our aim was to have magnetic nanoparticles react directly with sodium 2-bromoethane-1-sulfonate to generate SO_3H groups on the surface of the magnetic nanoparticles. In this way, we introduced a new solid acid catalyst based on magnetic nanoparticles. However, to the best of our knowledge, there are no examples of silica-based ethane-1-sulfonic acid catalysts that have been prepared according to our approach.

In this study, we wished to evaluate the catalytic performance of this new catalyst in the "Pechmann reaction" as an acid catalyzed process. Although various methods have been reported for this reaction, they suffer from disadvantages such as long reaction time, using expensive and/or nonstable catalyst and using heterogeneous catalysts [15–21]. There is widespread interest in the synthesis of new coumarin derivatives, because of their applications in organic synthesis, biology, medicine, perfumes and cosmetics fields [22, 23]. Also some of the coumarin derivatives are known as antioxidant compounds, due to their radical scavenging properties [24]. In material science, they have been used as fluorescence dyes in composite with other heterocyclic moieties [24]. Furthermore, for DNA and RNA labeling, some fluorescent materials containing a coumarin moiety have been reported [25]. Due to these properties, coumarins have been given attention by chemists, and a range of methods have been reported for their synthesis [26–39].

Among them, the Pechmann reaction is a simple protocol for the synthesis of coumarin rings using a two-component coupling reaction between phenol and β-ketoester under acid catalyst condition. This reaction has been studied with different homogeneous, heterogeneous and Lewis acid catalysts [16, 40–51]. Although these methods are suitable for this process, they often suffer from one or more deficiencies such as low yield, prolonged reaction time, tedious work-up processes, expensive reagents and hazardous reaction conditions [52–54]. Considering the above reports, it seems that preparation of a new catalyst to replace these catalyst procedures with environmentally more acceptable protocols, based on improved solvent toxicity and recoverable catalysts, is reasonable.

Experimental

Chemicals were purchased from Fluka and Aldrich chemical companies and were used without further purification. The known products were characterized by the comparison of their spectral and physical data with those reported in the literature. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 250 MHz spectrometer in $CDCl_3$ solution with tetramethylsilane (TMS) as an internal standard. FT-IR spectroscopy (Shimadzu FT-IR 8300 spectrophotometer), was employed for

characterization of the catalyst and products. The scanning electron micrograph (SEM) for the MNESA catalyst was obtained by SEM instrumentation (SEM, XL-30 FEG SEM, Philips, at 20 kV). Transmission electron microscopy (TEM) was obtained using a TEM apparatus (CM-10-Philips, 100 kV) for characterization of the catalyst. X-ray diffraction (XRD, D8, Advance, Bruker, axs) was also used to characterize the catalyst. Elemental analyses for C, H, N and S were performed using a Heraeus CHNS Rapid analyzer. Melting points were determined in open capillary tubes in a Barnstead Electro-thermal 9100 BZ circulating oil melting point apparatus. The reaction monitoring was accomplished by TLC on silica gel PolyGram SILG/UV254 plates.

Preparation of catalyst

Synthesis of Fe_3O_4 nano particles

Fe3O4 nanoparticles were synthesized by using a coprecipitation process [55]. Briefly, FeCl3·6H2O and FeCl2·4H2O (2:1 molar ratio) were loaded into a three-neck flask and dissolved in 100 mL Millipore water. Ammonia hydroxide was then added dropwise into the vigorously stirred solution at 40 °C. After ammonia ran out, an additional 15 min was required to form stable nanoparticles. Then the Fe3O4 nanoparticles were collected by permanent magnetic field and washed with water to remove unreacted ammonia. Tetramethylammonium hydroxide (TMAOH) solution (25 wt% in water) was added into the collected Fe3O4 and stirred for 30 min to form stable colloid. Nitrogen was used in the whole process to prevent the particles from oxidation.

Synthesis of Fe_3O_4@SiO_2 nano particles

The silica coated magnetic nanoparticles were prepared based on the literature with some modifications [56]. In a conical flask, 250 mL of heptanes, 50 mL of i-PrOH, 40 mL of PEG-300 and 20 mL of water and 4 g of Fe_3O_4 were added. Then, the mixture was stirred by mechanical stirrer under nitrogen gas for 45 min. Then, 40 mL of tetraethyl orthosilicate (TEOS) was added to the mixture, and the solution was stirred for 12 h at 35 °C. Afterward, 20 mL of ammonia was added, and the solution was stirred continuously for another 12 h. The precipitates were washed with ethanol (3 × 10 mL) and collected by an external magnetic field. The obtained Fe_3O_4@SiO_2 nanoparticles were dried in an oven under vacuum overnight.

Synthesis of Fe_3O_4@SiO_2@$EtSO_3H$ (MNESA) catalyst

In a conical flask (100 mL), a mixture of Fe_3O_4@SiO_2 (4.0 g) in dry toluene (50 mL), TBAB (0.5 g), K_2CO_3 (8 mmol, 1.1 g) and sodium 2-bromoethane-1-sulfonate (1.7 g, 8 mmol), was mechanically stirred at 110 °C for 24 h. Then, the mixture was cooled down to room temperature, and filtered and washed with EtOH (2 × 10 mL) and water (3 × 10 mL). After the dark solid was dried in an oven, it was stirred in a HCl solution (0.1 M) for 6 h in order to exchange protons to obtain the desired catalyst.

General procedure for Pechmann reaction in the presence of MNESA catalyst

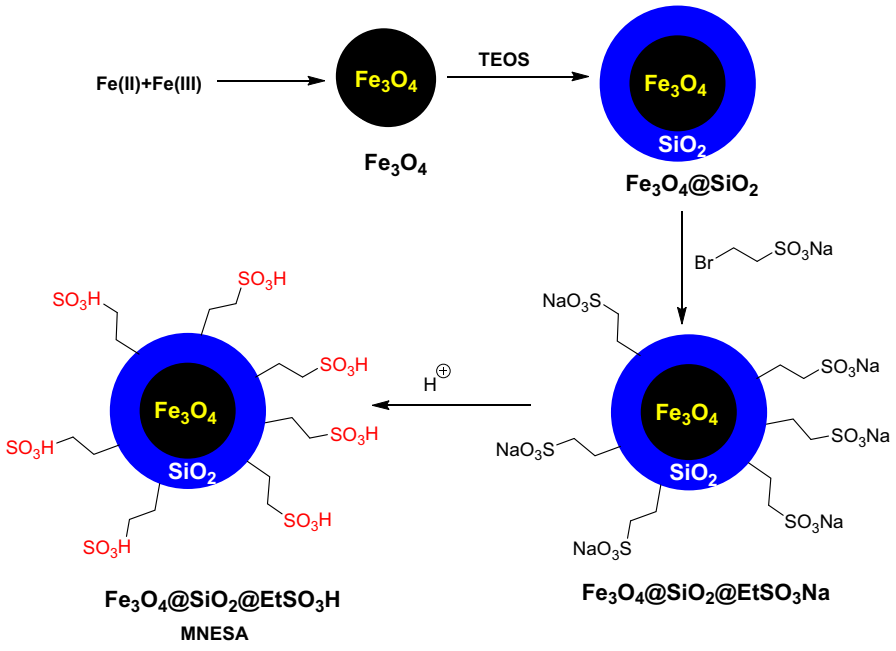
A mixture of phenol (1.0 mmol), β-ketoester (1.5 mmol) and MNESA (0.075 g) was stirred at 90 °C in a round-bottomed flask for the appreciated time. After completion of the reaction as confirmed by TLC, the reaction mixture was cooled down to room temperature and the catalyst was separated from the reaction mixture using an external magnetic field. Some water was then added to the reaction mixture and the product was extracted using EtOAc (2 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to yield the crude product. For more purification, the crude product was purified by recrystallization in ethanol to obtain the desired purity.

Results and discussion

Catalyst preparation and characterization

We prepared the MNESA catalyst based on the following operation (Scheme 1).

First, magnetic nanoparticles (Fe_3O_4) were synthesized according to the procedure in the literature [55]. Then Fe_3O_4 nanoparticles were coated with a silica layer in order to prevent their aggregation [28]. Finally, silica-coated magnetic



Scheme 1 Our synthetic method for the synthesis of MNESA catalyst

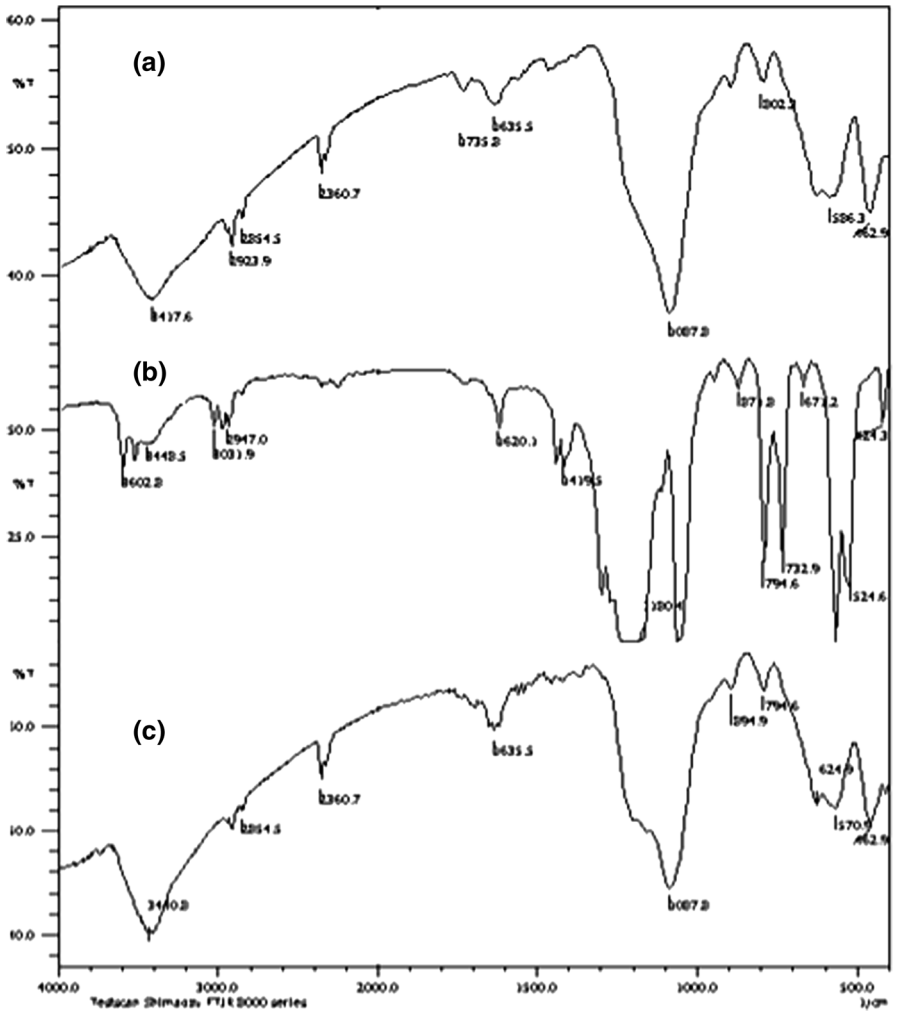


Fig. 1 A comparison between the FT-IR spectra of $Fe_3O_4@SiO_2$ (**a**), sodium 2-bromoethane-1-sulfonate (**b**) and MNESA (**c**)

nanoparticles were allowed to react with sodium 2-bromoethane-1-sulfonate in toluene at 110 °C to produce MNESA catalyst.

We next characterized the MNESA catalyst using some different microscopic and spectroscopic techniques such as FT-IR, TEM, SEM, XRD and elemental analysis.

The FT-IR spectra of the $Fe_3O_4@SiO_2$ (a), sodium 2-bromoethane-1-sulfonate (b) and MNESA (c) are shown in Fig. 1.

A comparison between the FT-IR spectra of $Fe_3O_4@SiO_2$, sodium 2-bromoethane-1-sulfonate and MNESA shows the existence of ethane sulfonic acid moiety on the surface of magnetic nanoparticles, which clarifies the efficiency of our methodology

for synthesis of this heterogeneous catalyst system. The FT-IR transmission spectrum of the MNESA (Fig. 1c) shows the following peaks: characteristic absorption at 3444.8 cm^{-1} that is associated with the free –OH site on magnetic nanoparticles and –OH of $–SO_3OH$ group [60], stretching frequency in 2850 cm^{-1} related to C–C and C–H bond vibrations [58] (this peak confirms the presence of alkyl chain on the magnetic nanoparticles), the medium bond in 624 cm^{-1} presumably is due to the stretching frequency of S–O bond [60], and two peaks at 1085.5 and 1185.5 cm^{-1} related to asymmetric and symmetric stretching of O–S–O bond, respectively [57]. The observed peak at 586 cm^{-1} is related to Fe–O or Fe–O–Fe bond [59]. Also, the strong peak at 1088 cm^{-1} corresponds to Si–O–Si bond, which confirms the existence of an SiO_2 layer around magnetic nanoparticles [60].

The TEM images of the MNESA catalyst (Fig. 2) show that nanoparticles of the catalyst with near spherical morphology are assembled with relatively good monodispersity. It seems that nanoparticles formed in the range of 20–30 nm are suitable in view point of catalytic activity.

According to the SEM image (Fig. 3), it is clear that the catalyst particles are regular in shape and are arranged in an approximately good orderly manner. The SEM image has also confirmed the point that the MNESA nanoparticles are produced with near spherical morphology.

The bare magnetic nanoparticles and final catalyst were analyzed using x-ray diffraction (XRD) technique, and their XRD patterns are shown in Figs. 4 and 5, respectively.

The peak at $2\theta = 18.5°$ corresponds to the SiO_2 shell and the peaks indexed as (220), (311), (400), (422), (511), and (440) are the planes of the Fe_3O_4 nanoparticles [61].

The presence of these peaks in the XRD pattern of catalyst shows the successful synthesis of magnetic base of this catalyst and indicates that the structure of bare magnetic nanoparticles remained after the surface modification.

According to vibrational sampling magnetometer (VSM) analysis, the catalyst exhibits a superparamagnetic property. After structural characterization of MNESA

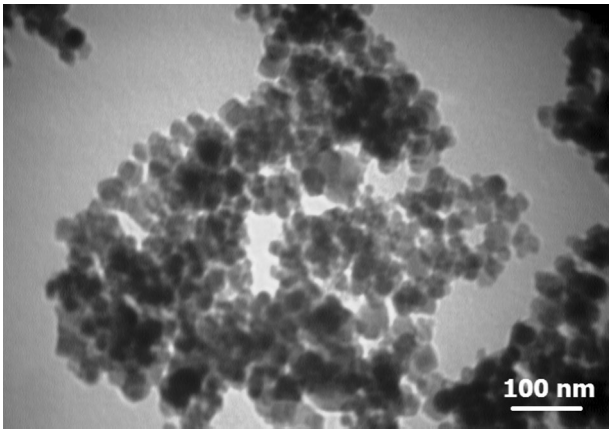


Fig. 2 The TEM image of MNESA catalyst

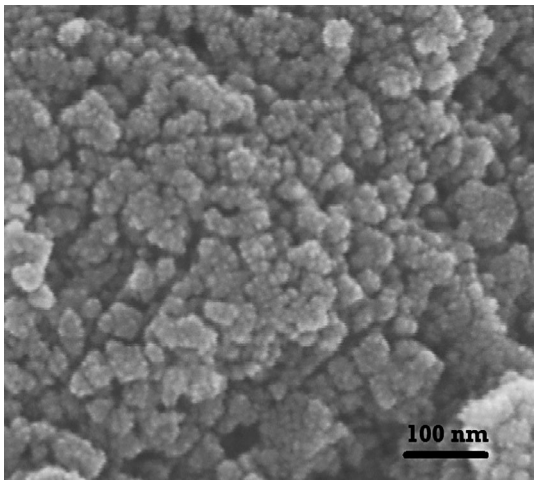


Fig. 3 The SEM image of MNESA catalyst

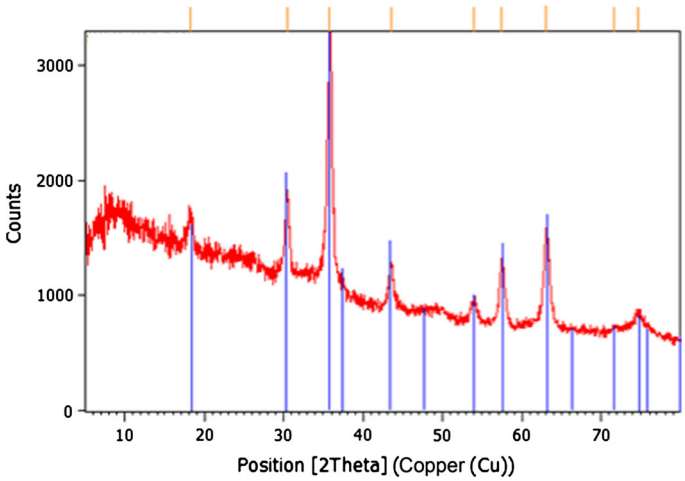


Fig. 4 The XRD pattern of bare Fe_3O_4@SiO_2

catalyst, it was analyzed with elemental analysis in order to estimate the $–SO_3H$ content of this material for the determination of catalyst loading. The obtained sulfur content of the catalyst was 4.8 %. It is possible to calculate the mmol of —SO_3H group per 1 g of catalyst, which is equal to 1.5 mmol per 1 g of catalyst. Thus the catalyst loading is equal to 1.5 mmol/g (Fig. 6).

Pechmann condensation using MNESA catalyst

After characterization of the catalyst, its catalytic activity was evaluated in the Pechmann condensation for one-pot synthesis of coumarin derivatives. The reaction

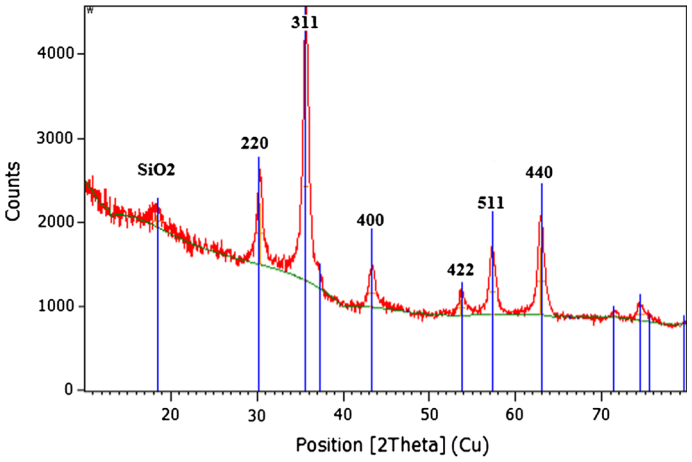


Fig. 5 The XRD pattern of MNESA catalyst

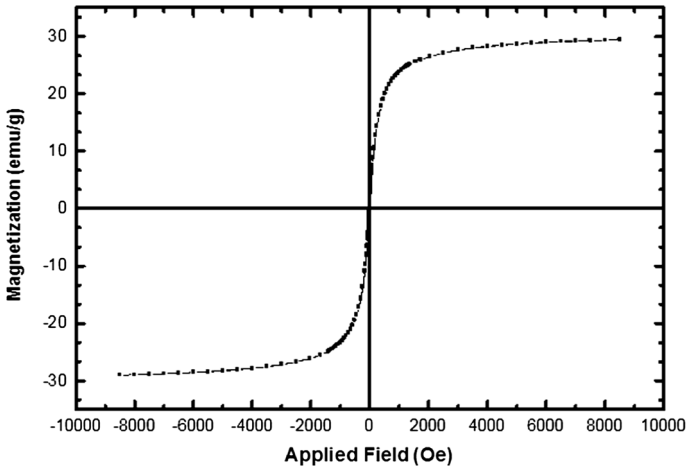
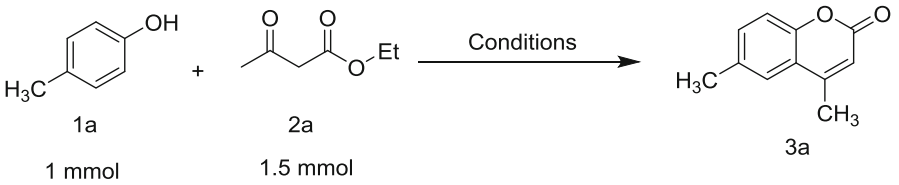


Fig. 6 The VSM of MNESA catalyst

between *p*-cresol (*p*-methyl phenol) and ethyl acetoacetate was chosen as a model reaction to find optimization conditions for preparation of the coumarins. The results are summarized in Table 1.

As shown in Table 1, in the absence of catalyst, no product was observed. In the presence of magnetic nanoparticles, only 20 % of product was produced. The results of the optimization study show that the MNESA catalyst is an efficient catalyst for the Pechmann condensation for one-pot synthesis of coumarins. Some solvents were tested and under solvent-free condition, maximum yield of product was observed. Also, 0.075 g of catalyst (11 mol%) was optimal for this reaction. A temperature of 90 °C was recognized to be the best condition to obtain maximum yield of product. Overall, the optimized conditions for this reaction are shown in Scheme 2.

Table 1 Optimization of the reaction condition for synthesis of coumarins using Pechmann condensation in the presence of MNESA catalyst[a]



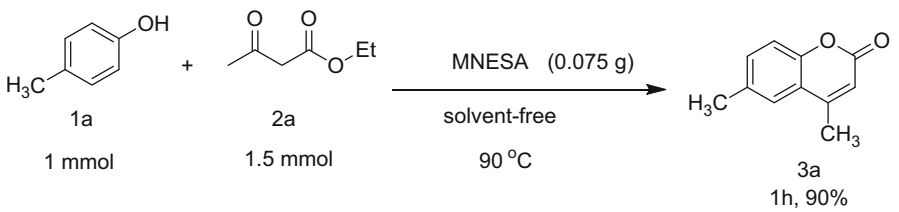
Entry	Catalyst (catalyst loading)	Solvent	T (°C)	Time (h)	Yield (%)[b]
1	–	–	100	6	0
2	Fe_3O_4@SiO_2 (0.1 g)	–	100	6	20
3	MNESA (0.1 g)	–	100	1	90
4	MNESA (0.1 g)	EtOH	Reflux	6	55
5	MNESA (0.1 g)	Toluene	110	6	60
6	MNESA (0.1 g)	H_2O	Reflux	12	Trace
7	MNESA (0.1 g)	CH_2Cl_2	Reflux	6	50
8	MNESA (0.05 g)	–	100	1	82
9	MNESA (0.075 g)	–	100	1	89
10	MNESA (0.025 g)	–	100	2	75
11	MNESA (0.075 g)	–	rt	12	Trace
12	MNESA (0.075 g)	–	80	1	86
13	MNESA (0.075 g)	–	50	1	54
14	MNESA (0.075 g)	–	90	1	90
15	MNESA (0.075 g)	–	90	1	91[c]
16	MNESA (0.075 g)	–	90	1	83[d]

[a] Reaction conditions: *p*-cresol (1 mmol), ethyl acetoacetate (1.5 mmol) and solvent (3 mL), catalyst (11 mol%)

[b] Isolated yield

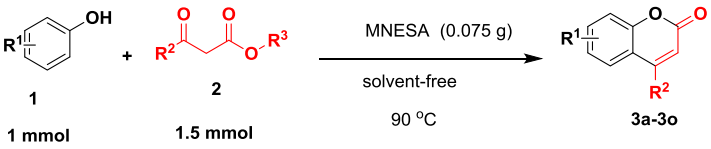
[c] 2 mmol of 2a was used

[d] 1.2 mmol of 2a was used



Scheme 2 Optimized conditions for synthesis of coumarins using Pechmann condensation in the presence of MNESA catalyst

Table 2 Diversity of the reaction for the synthesis of coumarins using Pechmann



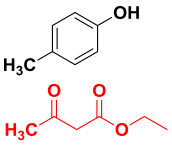
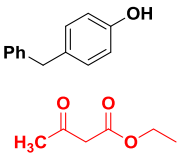
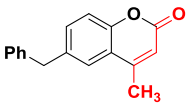
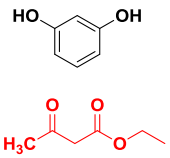
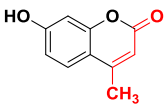
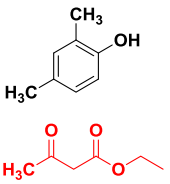
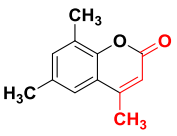
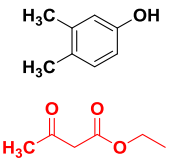
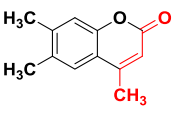
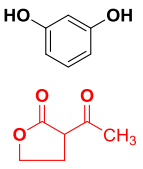
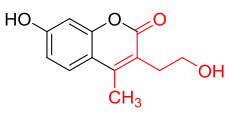
Entry	Starting materials	Products	Time (h)	Yield (%)[a,b]
1		 **3a**	1	90
2		 **3b**	1	91
3		 **3c**	1.5	93
4		 **3d**	1	90
5		 **3e**	1	92
6		 **3f**	3	88

Table 2 continued

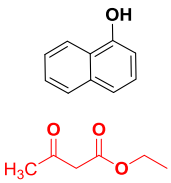
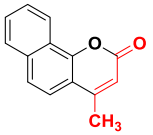
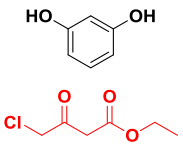
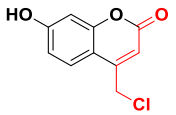
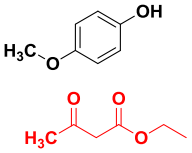
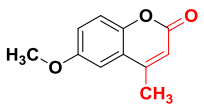
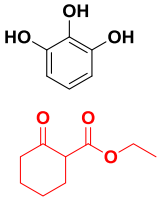
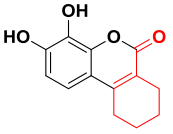
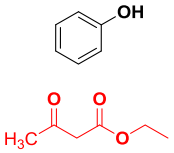
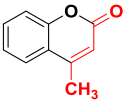
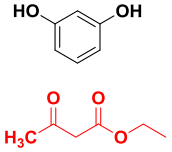
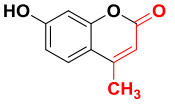
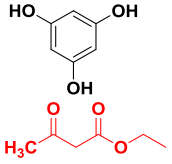
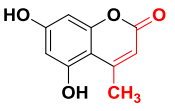
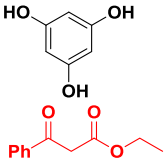
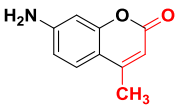
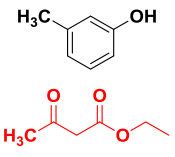
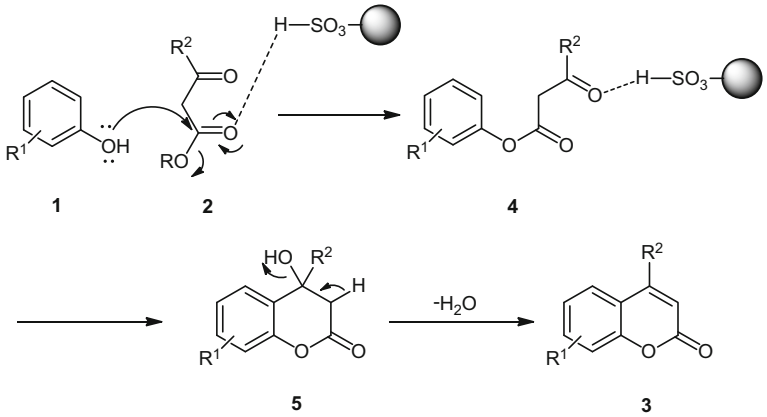
Entry	Starting materials	Products	Time (h)	Yield (%)[a,b]
7		 **3g**	2	90
8		 **3h**	5	91
9		 **3i**	3	89
10		 **3j**	2	92
11		 **3k**	4	87
12		 **3l**	2	90
13		 **3m**	10	75

Table 2 continued

Entry	Starting materials	Products	Time (h)	Yield (%)[a,b]
14		 **3n**	5	85
15		 **3o**	3	90

[a] Isolated yield

[b] Reaction conditions: phenol (1 mmol), β-ketoester (1.5 mmol), MNESA (0.075 g), temperature 90 °C



Scheme 3 Mechanism for the synthesis of coumarins using Pechmann condensation in the presence of MNESA catalyst

To determine the scope of the designed protocol for preparation of coumarin derivatives, a number of commercially available phenols were condensed with some β-ketoesters under optimized reaction conditions, and the results are depicted in Table 2.

Table 2 clearly demonstrates that the MNESA is effective for the synthesis of coumarin derivatives under solvent-free conditions at 90 °C temperature. As clearly shown in Table 2, catalytic activity of MNESA depended on both phenol and β-ketoester substrates, and all phenols were rapidly converted to the corresponding products in good to excellent yields.

Table 3 The reusability of catalyst

Entry	Catalyst (g)	Time (h)	Yield (%)[a,b]
1	0.150	1	90
2	0.143	1	89
3	0.140	2	88
4	0.138	2	87
5	0.132	5	85

[a] Isolated yield

[b] Reaction conditions: phenol (1 mmol), β-ketoester (1.5 mmol), MNESA (0.075 g), temperature 90 °C

A plausible mechanism of Pechmann condensation reactions for the synthesis of coumarins between β-ketoester compounds and phenols has been proposed according to literature (Scheme 3) [15–21]. At first, esterification reaction of phenol 1 and β-ketoester compound 2 in the presence of catalyst lead to intermediate 4. Then, Friedel–Crafts reaction between carbonyl group of ketone and benzene ring and dehydration lead to coumarin 3.

For practical applications of MNESA catalyst, the level of reusability was evaluated. The possibility of recycling the catalyst was tested using the reaction of *p*-cresol with ethyl acetoacetate under optimized reaction conditions. When the reaction was complete, the reaction mixture was washed with hot ethanol three times (3 × 5 mL). Then, the filtered solid acid was dried and reused for subsequent runs. The recycled catalyst could be reused five times. No observation of any appreciable loss in the catalytic activity of the MNESA was observed (Table 3).

After being reused five times, the S content of catalyst was analyzed by elemental analysis, and it was shown that the amount of sulfur is 4.58 %. This experiment revealed that our introduced catalyst is heterogeneous in nature.

To examine whether there was any leaching and if the catalyst completely acts as a heterogeneous catalyst, we removed the catalyst by external magnet 5 min after the beginning of the reactions. We observed that the reaction did not reach completion even after 48 h. This clearly confirmed that the acidic function did not leach into the solvent and that the catalyst acts as a heterogeneous catalyst.

Conclusion

In summary, a magnetic nanoparticles supported sulfonic acid was successfully prepared and utilized as effective catalyst for preparation of coumarin derivatives using Pechmann condensation under solvent free condition. This new catalyst system efficiently catalyzed this reaction and a range of coumarins were produced in good to excellent yields. The catalyst system can be reusable using an external magnetic field. It can therefore be concluded that the reusability (the catalyst was reusable for at least five times) and easy workup are the main advantages of this catalyst system. This catalyst can also be useful for applications in other organic transformations in the future.

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