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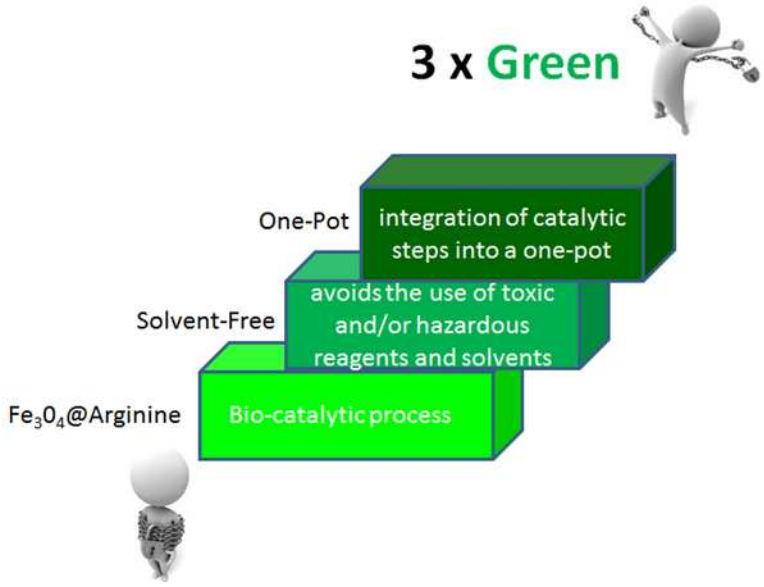

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ARTICLE TYPE

Ultrasound Irradiation for the Green Synthesis of Chromenes Using Arginine-Functionalized Magnetic Nanoparticles as a Recyclable Organocatalyst

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A practical, convenient, and cheap methodology is developed for the synthesis of a series of chromene derivatives *via* cyclocondensation of α- or β-naphthole, malononitrile and aromatic aldehydes, in the presence of Arginine-immobilized magnetic nanoparticles, under ultrasound irradiation, in high yields. This catalyst can be easily separated from the reaction by an external magnet and recycled four times without its activity loss. This methodology has shown shorter reaction times when compared with conventional thermal heating.

Arginine is one of the 20 most common natural amino acids. The side chain of Arginine composed of three carbon atoms of aliphatic straight chain which is capped by a complex guanidinium group. Because of the presence of positively charged guanidinium group in side chain, Arginine is a most basic, positive charged amino acid. The isoelectric point of Arginine has high pH value due to the extra positive charge on side chain. Because of the conjugation between the double bond and the nitrogen lone pairs, the positive charge is delocalized, enabling the formation of multiple H-bonds.[2]

Arginine is the most basic amino acid, with a side-chain pK_a for the guanidinium group of about 12.5 (pK_a=12.48).[3] Actually, Arginine-immobilized magnetic nanoparticles could also be obtained by attaching Arginine onto the surface of MNPs through COOH group without using any linkers. Availability, non-toxic and eco-friendly natures of Arginine are enough reasons for using it as efficient supported base on the magnetic surface.

Magnetic particles may be used in the industries because of simple and economical applications and their convenient isolation from the reaction mixture.[4] Also, in small-scale laboratory reactions, this separation method is much more effective than filtration or centrifugation.[5]

Chromenes constitute one of the major classes of naturally occurring compounds. The basic structural skeleton of these compounds is an ordinary characteristic of polyphenols[6] found in tea, fruits, vegetables and red wine. Fused chromenes exhibit antimicrobial,[7] mutagenicitical,[8] antiviral, antiproliferative, antitumoral properties and be employed as cosmetics and pigments. These compounds can be used as potential biodegradable agrochemicals.[9]

Chromenes synthesis for having medicinal and biological properties has been interested in recent years.[10, 11] To date, numerous homogeneous and heterogeneous catalysts have been used to promote the chromenes synthesis such as cetyltrimethylammonium bromide under ultrasonic waves ,[12] cetyltrimethylammonium chloride,[13] montmorillonite KSF clay,[14] triethylamine,[15] I_2/K_2CO_3,[16] alumina coated with potassium fluoride,[17] basic ionic liquid,[18] piperidine,[19] 1,8-diazabicyclo[5.4.0]undec-7- ene (DBU),[20] $Ca(OH)_2$ [21]and Mg–Al hydrotalcite.[22] As previously reported methods tolerate shortages, such as toxic catalysts, tedious work-up steps,[9,23,24,25] so the application of some of these methods is limited because of the moderate yields of the products or laborious workup procedure. Therefore, finding the efficient ways to synthesize of chromenes is highly regarded.

The use of ultrasonic irradiation facilitates an organic transformation at ambient conditions which otherwise require drastic conditions of temperature and pressure..[26] The interaction between molecules and ultrasound isn't direct but the energy of theses long wavelength can cause cavitation which makes the reaction faster.[27]

In continuation of our laboratory work on environmentally procedures [28,29] now we expose to view Fe_3O_4@Arginine nanoparticles as an alternate magnetic organocatalyst for the synthesis of chromenes *via* cyclocondensation of α- or β-naphthole, malononitrile and aromatic aldehydes by using ultrasonic irradiation. Also this reaction was done in one pot manner and under solvent free conditions.

Result and Discussion

Characterization of Fe_3O_4 @Arginine nanoparticles:

To confirm the alteration of the nanoparticles surface with Arginine, the FT-IR spectra of Fe_3O_4@Arginine nanoparticle was recorded (Fig.1).

Bare magnetite nanoparticles are easily distinguished by strong absorption peaks at 561 cm^{-1} and the transmissions around 500 cm^{-1} characteristic of the Fe-O band of magnetite (a). The typical stretching frequencies of pure Arginine involve: NH_2 and OH stretching at around of 2800-3300 cm^{-1} as broad band and (COO) at about 1600 cm^{-1} (b). The FT-IR measurement of nanoparticle Fe_3O_4@Arginine reveals the stretching bands of Fe-O stretching shifted to a higher wave number (614 cm^{-1}) as low intensity peak and (COO) at 1622 cm^{-1}(c).

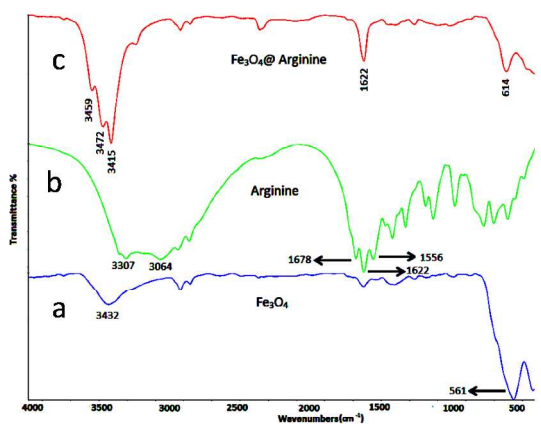


Fig. 1: FT-IR spectra of nanoparticle Fe_3O_4@Arginine

It means that the Arginine was supported on the magnetite surface. Also the disappearance of the OH broad peak confirms the previous conclusion.

The earned lattice parameter of the nanoparticle Fe_3O_4@Arginine using XRD technique was coincided to the standard parameters of magnetite. The pattern of nanoparticle Fe_3O_4@Arginine is depicted in Fig. 2.

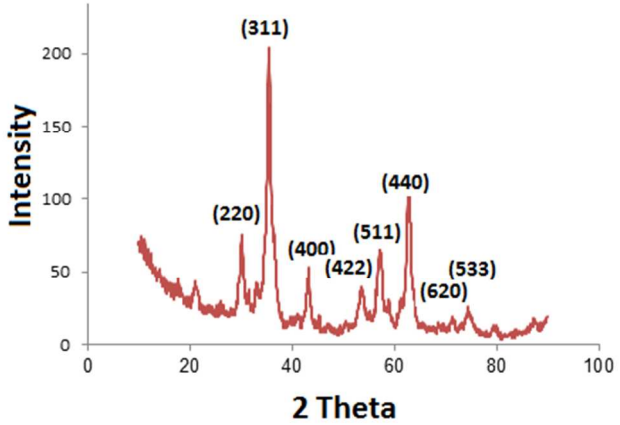


Fig. 2: The X-ray diffraction patterns of nanoparticle Fe_3O_4@Arginine

The next proof on the bond formation between Arginine and nanoparticles can be deduced from thermogravimetric/differential thermal analyses (TG/DTA) (Fig. 3). Violet curve shows the mass loss of the functional groups on the magnetic surface as it decomposes upon heating. The weight loss of nanoparticle Fe_3O_4@Arginine below 200 °C can be assigned to the release of physically adsorbed solvent and organic groups. Exothermic peak accompanied with mass loss of 7.3% at the temperature range of 200–600 °C in the TGA curve of nanoparticle Fe_3O_4@Arginine was mainly attributed to the decomposition of organic groups grafted to the Fe_3O_4 surface. Through the TGA analysis, the Arginine content of nanoparticle Fe_3O_4@Arginine was evaluated to be 0.42 mmol/g.

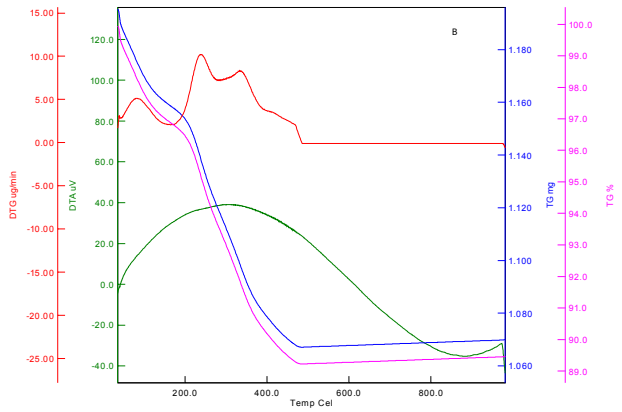


Fig. 3: Thermogravimetric and Differential Thermogravimetric of nanoparticle Fe_3O_4@Arginine

The high activity of the Fe_3O_4@Arginine supposedly results from its high surface area. Nano-scale features of the catalyst coherent with this hypothesis (Fig. 4).

Fig. 4: SEM Analysis of the nanoparticle Fe_3O_4@Arginine

Transmission electron microscopy (TEM) confirmed the formation of single-phase Fe_3O_4 nanoparticles, with spherical morphology and a size range of 15 nm. Congestion of Arginine as the external walls can be seen on the Fe_3O_4 as the core (Fig. 5).

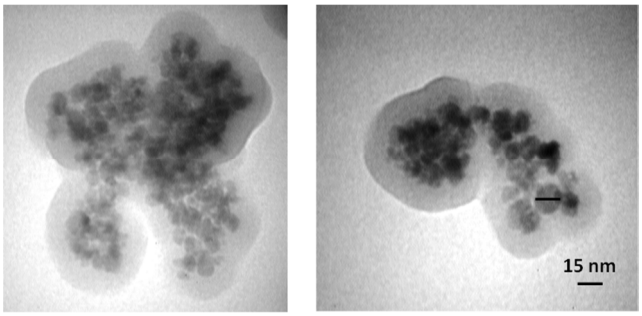


Fig. 5: TEM micrographs of Fe_3O_4@Arginine

The magnetic possession of the nanoparticle Fe_3O_4@Arginine was deliberated by vibrating sample magnetometry (VSM). Magnetization (emu/g) as a function of applied field (Oe) was depicted in Fig. 6 with the confined field from −10000 to 10000

Oe. Fe_3O_4@Arginine nanocrystals owner high saturation magnetization of 60 emu/g at room temperature. These covered magnetic nanoparticles have a lower magnetic value than the bare MNPs (74.3 emu/g).[30] Large saturation magnetization (>32 emu/g) means it can be strongly attracted by magnetic fields.[31] VSM shows the hysteresis loops of the Fe_3O_4@Arginine at room temperature. Zero remanence and coercivity of magnetization curve demonstrate that these nanoparticles have super paramagnetic properties.

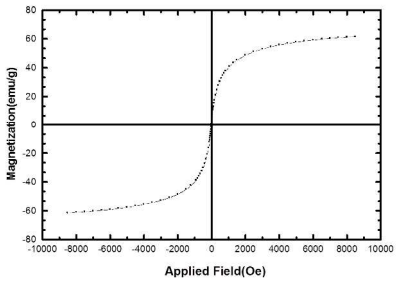
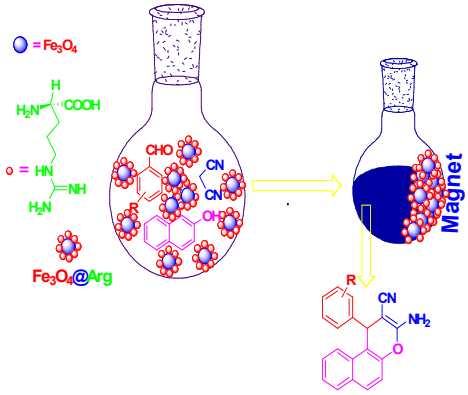


Fig. 6: Magnetization curve of nanoparticle Fe_3O_4@Arginine

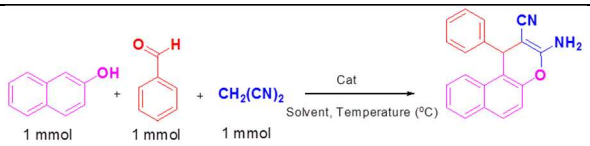
Catalytic Performances

We afforded to develop a multicomponent environmental method for the synthesis of chromenes. To optimize the conditions, the reaction was done by applying various solvents and also solvent free conditions, to obtain maximum of the yield. In the absence of catalyst, no product was found and when we used L-Arginine as catalyst led to formation of chromene in the satisfactory yield. By supporting Arginine on the magnetic surface not only improved the yield but also reused the catalyst. In the next step, the effect of temperature on the progressing of the reaction was examined in the presence of 20 mg Fe_3O_4@Arginine under solvent-free conditions (Scheme 1). 100 ^oC was chosen as the best temperature for the reaction. The amount of catalyst was also optimized. It was found that 40 mg of Fe_3O_4@ Arginine was enough to progress the reaction. An increasing of the amount of catalyst didn't change product yield. To optimize the reaction conditions, we also performed several experiments at r.t, 50, 80 ^oC under ultrasonic irradiation without solvent. It was found that the yield of a could reach 94% when ultrasonic irradiation was employed. As can be seen from Table 1, room temperature is the most suitable reaction temperature under ultrasonic irradiation. Also results suggested that Fe_3O_4@ Arginine played a key role in the transformation process. Thus the optimal reaction conditions were considered to include arylaldehyde (1mmol), malononitrile (1mmol) and β-naphthol (1 mmol) at room temperature for 1 h under ultrasonic irradiation without solvent. (Table 1, Entry 21).



Scheme 1: Synthesis of chromenes using Fe_3O_4@Arginine MNPs

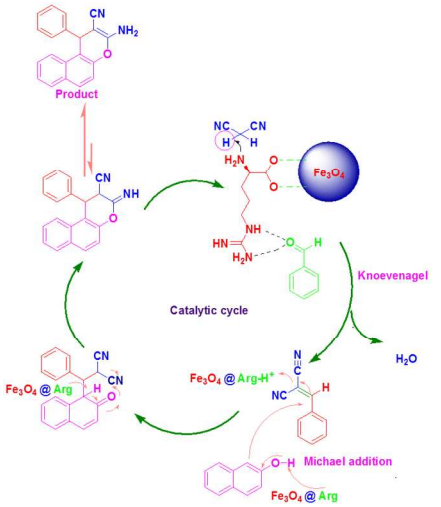
Table 1: Results of screening the conditions [a]



Entry	Catalyst	(mg)	Solvent	Time(h)	Temp (° C)	Yield (%)[b]
1	-	-	-	12	100	0
2	Arginine	10	-	12	100	40
3	Arginine	20	-	12	100	70
4	Arginine	20	EtOH	12	80	62
5	Arginine	20	H_2O	12	100	50
6	Arginine	20	MeOH	12	80	45
7	Fe_3O_4	20	-	12	100	50
8	Fe_3O_4	40	-	12	100	60
9	Fe_3O_4@Arginine	20	-	12	r.t	20
10	Fe_3O_4@Arginine	20	-	12	50	65
11	Fe_3O_4@Arginine	40	-	12	50	85
12	Fe_3O_4@Arginine	40	-	12	80	90
13	Fe_3O_4@Arginine	40	-	12	100	95
14	Arginine	20		3	r.t(ultrasound)	70
15	Arginine	40		3	r.t(ultrasound)	80
16	Fe_3O_4	20		3	r.t(ultrasound)	50
17	Fe_3O_4	40		3	r.t(ultrasound)	60
18	Fe_3O_4@Arginine	-	-	3	r.t(ultrasound)	45
19	Fe3O4@Arginine	10	-	3	r.t(ultrasound)	65
20	Fe3O4@Arginine	20	-	3	r.t(ultrasound)	73
21	**Fe_3O_4@Arginine**	**40**	**-**	**1**	**r.t(ultrasound)**	**94**
22	Fe_3O_4@Arginine	40	-	1	50(ultrasound)	95
23	Fe_3O_4@Arginine	40	-	1	80(ultrasound)	95

[a] Base on the reaction of benzaldehyde and malononitrile and β-naphthol
[b] Yields refer to isolated pure product

A plausible mechanism for the synthesis of chromene from the reaction between benzaldehyde, malonnitrile and β-naphthol has been suggested in Scheme 2. Benzaldehyde condenses with active malononitrile anion in the presence of base catalyst with elimination of water to afford benzylidine malononitrile. Also, Fe_3O_4@Arginine generates the naphtholate anion that reacts apace with the dicyanoolefin. Then cyclization and finally rearrangement affords corresponding chromene.



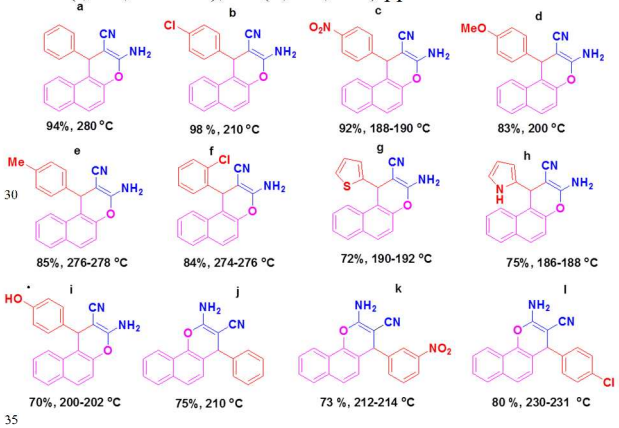
Scheme 2: Plausible reaction pathway for the condensation reaction in the presence of Fe_3O_4@ Arginine

All of the synthesized products are listed below and characterized by the collation of their spectroscopic and physical data with the genuine samples (Scheme 3). The spectral data for new products are given below:

3-Amino-1-(thiophen-2-yl)-1*H*-benzo[f]chromene-2-carbonitrile (g): IR (KBr, cm^{-1}): 3442, 3344, 2178, 1640, 1588, 1408; ^1H NMR (DMSO-d_6, 300 MHz): δ= 5.70(s, 1H, CH), 6.87(dd, 1H, *J*=4.8, 3.4 Hz , CH), 7.01(d, 1H, *J*= 3.3 Hz, CH), 7.10(S, 2H, NH_2), 7.24-7.31(m, 2H, CH), 7.42-7.53(m, 2H, CH), 7.93(d, 2H, *J*=8.7 Hz, CH), 8.03(d, 1H, *J*= 8.2 Hz, CH) ppm.

3-Amino-1-(1*H*-pyrrol-2-yl)-1*H*-benzo[f]chromene-2-carbonitrile (h): IR (KBr, cm^{-1}): 3476, 3334, 3297, 2186, 1645, 1582, 1406; ^1H NMR (DMSO-d_6, 300 MHz): δ= 5.29(s, 1H, CH), 5.78(d, 2H, *J*=21 Hz, CH), 6.48(d, 1H, *J*= 1.4 Hz, CH), 6.9(S, 2H, NH_2), 7.27(d, 1H, *J*= 8.9 Hz, CH), 7.38-7.48(m, 2H, CH)7.86-7.90(m, 2H, CH), 7.98(d, 1H, *J*= 8.9 Hz, CH), 10.57(S, 1H, NH) ppm.

3-Amino-1-(4-hydroxyphenyl)-1*H*-benzo[f]chromene-2-carbonitrile (i): IR (KBr, cm^{-1}): 3388, 2923, 2149, 1628, 1515; ^1H NMR (DMSO-d_6, 300 MHz): δ= 5.55(s, 1H, CH), 6.60(t, 1H, *J*=9 Hz, CH), 6.76-6.79(m, 2H, CH), 6.86(S, 2H, NH_2), 6.90-6.95(m, 1H, CH), 7.28(d, 1H, J= 9 Hz), 7.36-7.46(m, 2H, CH), 7.89(t, 3H, J= 9 Hz), 9.8(S, 1H, OH) ppm.



Scheme 3: Synthesis of chromene derivatives

In addition to a green method or catalyst, the recovery of catalyst is significant in green synthetic process. Reusability of the catalyst in the presence of an external magnet with the intrinsic stability of both the organic and nanoparticle catalyst components, allows the catalyst to be recycled over 4 times without any perceivable loss of its activity (Fig. 7).

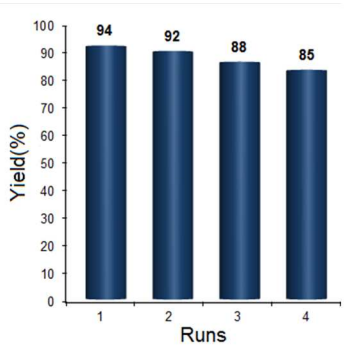


Fig 7: Activity lost as a function of the number of reused times of the Fe_3O_4@ ArginineMNPs for the synthesis of (**a**)

Studies to further explore the potential of this immobilization strategy for the preparation of other heterogeneous organocatalysts of high synthetic utility are initiated. To inconsistency any contribution of homogeneous catalysis, we tried to test the reaction leaching so after 30 min from the beginning of reaction by adding CH_2Cl_2 and ejection of catalyst by magnet we observed that the reaction did not complete even after 24 h. This clearly confirmed that active species were not floated above or on the surface. Also ICP analysis was done to determine leaching of metal in the solvent; therefore we sonicated and heated Fe_3O_4@Arginine MNPs suspension without reactants. After 4 h, we remove the catalyst by an external magnet. If ions are released to the solvent, ICP should be shown but ICP analysis didn't show any runway of ions in the solvent. The results obtained with benzaldehyde, malononitrile and β-naphthol under the optimized conditions were compared with the best ones published for this reaction using other catalysts, the data listed in Table 2. The advantages of this work are evident regarding the yields, conditions of the reactions, easy separation and reusability of the catalyst.

Table 2: Different catalytic system for the synthesis of **a**

Entry	Catalyst	Condition	Time	Yield [a] (%)
1	Expanded Perlite [32]	H_2O (Reflux)	4 h	92
2	Cu (SO_4). $5H_2O$ [33]	H_2O (Reflux)	1 h	95
3	[Bmim(OH)] [34]	H_2O (Reflux)	0.16 h	91
4	CTABr/ultrasound irradiation [35]	H_2O, r.t	150 min	92
5	[cmmim]Br [36]	110(Solvent free)	30 min	91
6	Fe_3O_4@Arginine /ultrasound irradiation(Present work)	r.t(Solvent free)	1 h	94

[a] Isolated yield

Experimental

FT-IR spectra were obtained over the region 400-4000 cm^{-1} with NICOLET IR100 FT-IR with spectroscopic grade KBr. Ultrasound assisted reactions were carried out using a BANDELIN:DT102H(Sonorex Digitec) ultrasound cleaner with a frequency of 35 kHz and a nominal power of 350 W. The powder X-ray spectrum was recorded at room temperature by

model: Pilips X, pert 1710 difractometer using Cu Kα (α =1.54056Å voltage: 40 Kv, current: 40 mA, and the data were collected from 10^o to 90^o (2θ) with a scan speed of 0.02°/s. The morphology of catalyst was studied with scanning electron microscopy using SEM (Philips XL 30 and S-4160) with gold coating equipped with energy dispersive X-ray spectroscopy. The magnetic property of Fe_3O_4@Arginine was measured with vibrating sample magnetometer/Alternating Gradient Force Magnetometer (VSM/AGFM, Meghnatis Daghigh Kavir Co, Iran). Transmission electron microscopy (TEM) measurements were carried out at 120 kV (Philips, model CM120). Thermogravimetric/Differential thermal analyses (TG/DTA) was done on a Thermal Analyzer with a heating rate of 20°C min^{-1} over a temperature range of 25–1100 °C under flowing compressed N_2.

Preparation of nanoparticle Fe_3O_4@ Arginine:

5 mmol $FeCl_3.6H_2O$ and 2.5 mmol $FeCl_2.4H_2O$ salts were dissolved in 100 mL deionized water under vigorous stirring then 2 mmol of Arginine and NH_4OH solution(25%, w/w, 30 mL) were added to the above mixture until the pH was raised to 11 at which a black suspension was formed. This suspension was then refluxed at100°C for 6 h, with vigorous stirring. Fe_3O_4@Arginine nanoparticles were separated from the aqueous solution by magnetic decantation, washed with water several times before being dried in an oven overnight.

General procedure for the direct synthesis of chromene derivatives using Fe_3O_4@Arginine nanoparticles under thermal conditions:

To a mixture of arylaldehyde (1mmol) and malononitrile (1mmol) and α- or β-naphthole (1 mmol) was added a catalytic amount of Fe_3O_4@Arginine (40 mg, containing 0.017 mmol Arginine) at 100 °C under solvent-free conditions. After completion of the reaction (after 12 h, monitored by TLC), the product was dissolved in CH_2Cl_2 to remove the catalyst by an external magnet. After drying the precipitate, it was re-crystallized in ethanol. The catalyst washed with CH_2Cl_2 and dried to reuse. The catalyst could be recycled 4 times without measurable loss of its activity.

General procedure for the direct synthesis of chromene derivatives using Fe_3O_4@Arginine nanoparticles under sonochemical conditions:

A mixture of arylaldehyde (1mmol) and malononitrile (1mmol) and α- or β-naphthole (1 mmol) in the presence of Fe_3O_4@Arginine (40 mg, containing 0.017 mmol Arginine) was sonicated at ambient conditions in an ultrasonic bath for 1 h. After completion of the reaction (after 1 h, monitored by TLC), the product was dissolved in CH_2Cl_2 to remove the catalyst by an external magnet. After drying the precipitate, it was re-crystallized in ethanol.

Conclusions

Finally, we have supported basic Arginine on the magnetic nanoparticles without using any supplemental linkers. An ultrasound assisted and efficient method has been developed for the synthesis chromenes in the presence of magnetically basic catalyst. The cooperation between ultrasound and supported magnetic nanoparticles has caused enhanced reaction rates, the synthesis of chromene derivatives. We also investigated the reaction times and yields for the Fe_3O_4@Arginine MNPs catalyzed synthesis of chromenes under thermal conditions, which were comparable. The use of Fe_3O_4@Arginine MNPs, which can be separated from the reaction mixture, short reaction times, and excellent isolated yields cause this methodology an improved practical alternative to synthesis chromene derivatives.

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