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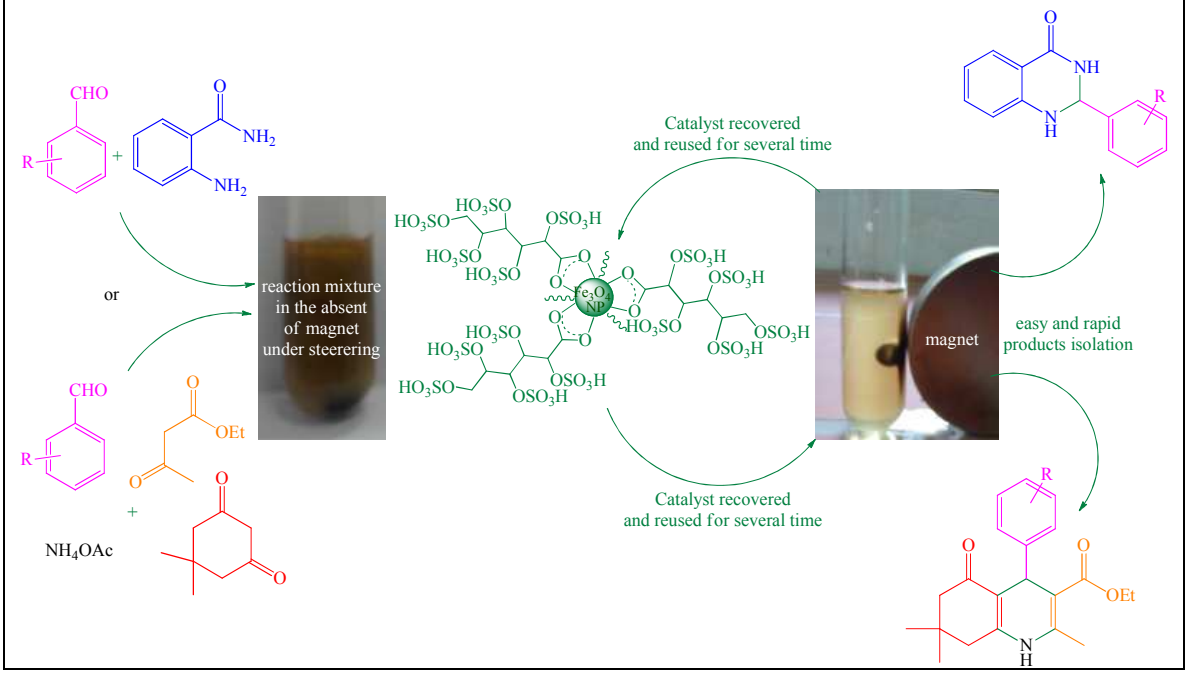
Graphical Abstract

Synthesis and characterization of Glucosulfonic acid supported on Fe_3O_4 nanoparticles as novel and magnetically recoverable nanocatalyst and its application in the synthesis of Polyhydroquinoline and 2,3-dihydroquinazolin-4(1H)-one Derivatives

Maryam Hajjami* and Bahman Tahmasbi



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ARTICLE

Synthesis and characterization of Glucosulfonic acid supported on Fe_3O_4 nanoparticles as novel and magnetically recoverable nanocatalyst and its application in the synthesis of polyhydroquinoline and 2,3-dihydroquinazolin-4(1H)-one derivatives

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Maryam Hajjami* and Bahman Tahmasbi

Glucosulfonic acid immobilized on Fe_3O_4 magnetic nanoparticles (GSA@MNPs) as an efficient and magnetically reusable nanocatalyst has been reported for the clean and one-pot synthesis of polyhydroquinoline and 2,3-dihydroquinazolin-4(1H)-one derivatives, with short reaction times in good to high yields in ethanol. After completing reactions the catalyst was easily separated using an external magnetic field from the reaction mixture and reused for several consecutive runs without significant loss of their catalytic efficiency. This new catalyst was characterized by FT-IR spectroscopy, TGA, XRD, VSM, TEM, EDS and SEM.

1. Introduction

The immobilization of homogeneous catalysts on various support materials such as organic polymers and inorganic silica and other metal oxides, to combine the advantages of both homogeneous and heterogeneous catalysis have been widely used as useful recoverable and reusable catalysts from organic synthesis [1]. Nanoparticulate supports can use as an efficiently bridge the gap between homogeneous and heterogeneous catalysis [2]. However, the nanocatalyst supported can be isolated from products by difficult, time consuming and expensive conventional techniques such as filtration or centrifugation [3]. This drawback can be overcome by using magnetic nanoparticles (MNPs), which can be easily and rapidly separated from the reaction mixture with the assistance of an external magnet [4]. Magnetic nanoparticles are a highly favourable materials for the attachment of homogeneous inorganic and organic containing catalysts [5]. More important, magnetic separation of the MNPs is more effective and easier than filtration or centrifugation, simple, economical, clean separation and promising for industrial applications [6-8]. One of the most promising MNPs supports for the development of high performance catalyst supports is superparamagnetic iron oxide [9]. The notable advantages of Fe_3O_4 NPs are simple synthesis, readily available, low cost, high surface area, low toxicity, operation simplicity and much easier and more effective separation than filtration or centrifugation [10]. Therefore, Fe_3O_4 NPs are considered as ideal supports for the heterogenization of homogeneous catalysts [11]. The outstanding potential of Fe_3O_4 nanoparticles has stimulated the extensive development of the synthetic technologies, which could be broadly classified. Among them, the chemical coprecipitation method for preparation of Fe_3O_4 is very simple and efficient [12]. While many supports such as mesoporous silicas or nano particles required high temperature for calcination and a lot of time and tedious condition to prepare [13-16].

High active surface of magnetic nanoparticles and their superparamagnetism properties which leads to the agglomeration of the bare nanoparticles of iron oxides. Therefore, coating the catalyst surface with an organic or an inorganic shell is an appropriate strategy to prevent agglomeration [17]. More importance, organic coat over iron nano-core imparts various desirable properties, such as thermal and chemical stability, high mechanical tolerance and ease of functionalization [18]. In the other hand, a terminal amine or hydroxyl group in extrinsically surface layers can be functionalized and convert a homogeneous catalyst into a heterogeneous catalytic system. In recent years Impressive efforts was made in the development of new catalytic systems which are immobilized onto Fe_3O_4 [19-25].

Polyhydroquinoline and 2,3-Dihydroquinazolinone derivatives are very well-known including six membered heterocyclic ring molecules that have been reported to possess a wide range of biological properties and pharmaceutical activities [9,10]. Polyhydroquinoline (PHQ) derivatives contain a large family of medicinally important compounds that have attracted much attention because of their diverse pharmacological and therapeutic properties, such as vasodilator, hepatoprotective, antiatherosclerotic, bronchodilator, antitumor, geroprotective,

antidiabetic activity and also their ability to modulate calcium channels [26,27]. Thus the synthesis of these heterocyclics has become an area of great interest. Also, 2,3-Dihydro-4(1H)-quinazolinones are important bicyclic heterocycles which have emerged as versatile biologically active compounds possessing applications as diuretic, vasodilating, tranquilizing, antitumor, antidefibrillatory, antibiotic, antihistaminic, anticonvulsant, anticancer, herbicidal activity, plant growth regulation ability and antihypertensive agents [4,10,28]. They are also reported to possess the ability to inhibit enzymes of biological importance [29]. In addition, these compounds can be easily oxidized to their quinazolin-4(3H)-one analogues [10], which also include important pharmacologically active compounds, Generally, 2,3-dihydroquinazolin-4(1H)-ones were prepared using the reductive cyclization of aldehydes or ketones with 2-aminobenzamide in the presence of acid catalysts [9,29].

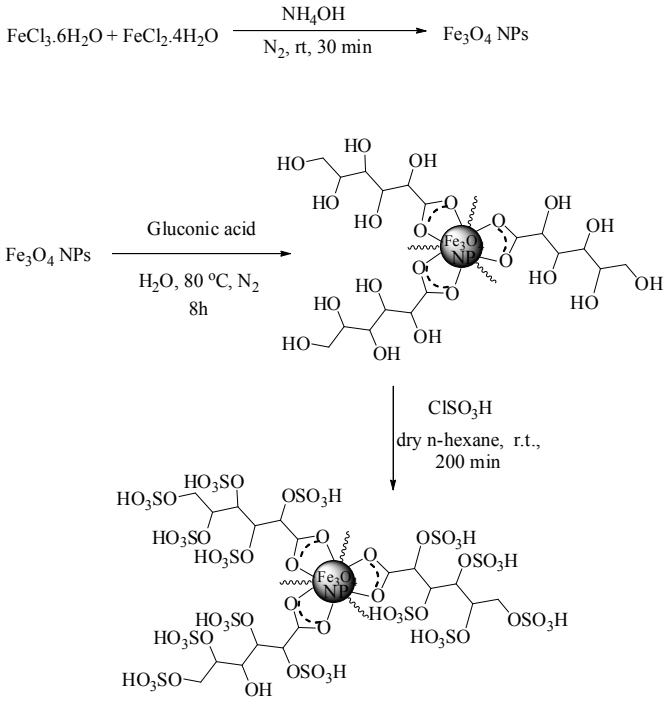
For these reasons, many methods have been developed including microwave and ultrasound irradiation techniques using various catalytic systems [26-29]. Although, most of these processes suffer from one or several drawbacks such as longer reaction time, tedious workup, harsh reaction conditions, unsatisfactory yields, use of large quantity of environmentally toxic and expensive catalysts. While magnetic glyconanoparticles toxicity investigated and revealed to be non-toxic at high concentration and this is a safe and positive point of view of the environment and green chemistry [30].

In addition, some of this catalyst cannot be recovered and reused again. Thus, there is a necessity to develop a simple and efficient method for the synthesis of polyhydroquinolines and 2,3-dihydroquinazolin-4(1H)-ones in high yields under mild reaction conditions.

2. Results and discussion

2.1. Catalyst preparation

In continuation of our studies [31] herein, we report a simple and efficient method for the synthesis of polyhydroquinolines and 2,3-dihydroquinazolin-4(1H)-ones in the presence of catalytic amounts of GSA@MNPs in ethanol and under reflux condition. The details of the supported catalyst preparation procedure are presented in Scheme 1. Initially, the magnetic core of Fe_3O_4 nanoparticles has been prepared by a chemical coprecipitation technique using $FeCl_3.6H_2O$ and $FeCl_2.6H_2O$ in basic solution at 80 °C [4,9]. Ultimately, after coating of Fe_3O_4 nanoparticles with Gluconic acid solution, the functionalization of facial hydroxyl groups with chlorosulfonic acid led to supported Glucosulfonic acid on Fe_3O_4 nanoparticles (GSA@MNPs).

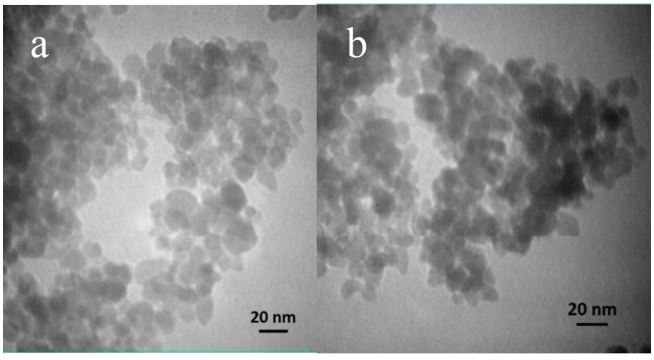


Scheme 1. Synthesis of GSA@MNPs.

2.2. Catalyst characterization

The catalyst has been characterized by Transmission electron microscopy (TEM), scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR) and Vibrating Sample Magnetometer (VSM).

The morphological and size of the catalyst was evaluated using scanning electron microscopy and Transmission electron microscopy. It can be seen that most of the particles are quasi-spherical with an average diameter about 10 nm. (Figure 1). To investigate the catalyst characterization state of the supported sulfonic acid species, the synthesized catalyst was analyzed using EDS. As shown in figure 2, EDX spectrum of catalyst showed the presence of S, O and C species in the catalyst (Figure 2).



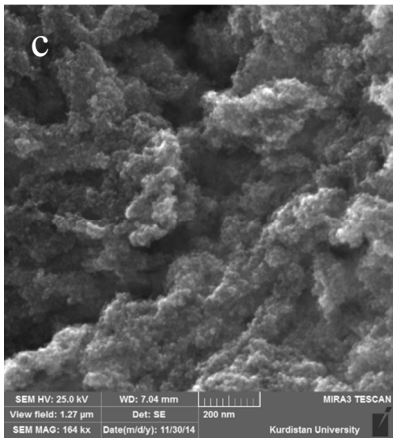


Figure 1. TEM (a and b) anf SEM (c) image of GSA@MNPs.

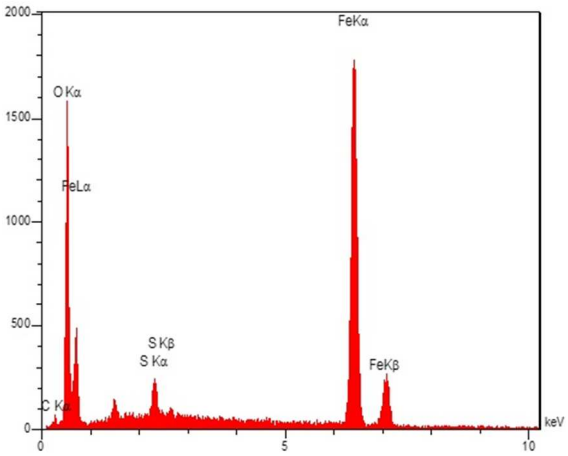


Figure 2. EDS spectrum of GSA@MNPs.

The formation of a magnetite crystal phase in a Glucosulfonic acid-coated Fe_3O_4 aggregate powder was identified from the X-ray diffraction pattern (Figure 3). As seen in Figure 3, the iron oxide phase was identified from the XRD patterns by the peak positions at 30.2 (2 2 0), 35.5 (3 1 1), 43.0 (4 0 0), 57.1 (5 1 1) and 62.9 (4 4 0), which were in agreement with magnetite standard data [32].

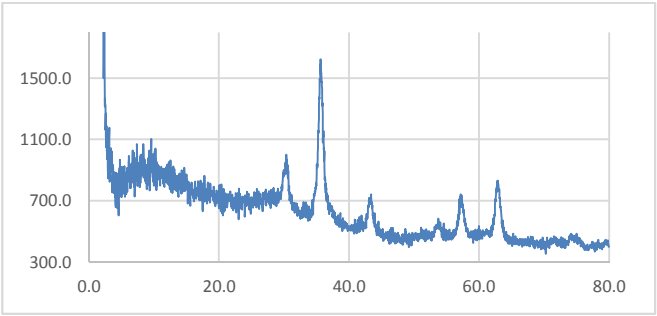


Figure 3. The XRD pattern of GSA@MNPs.

One indication of bond formation between the Fe_3O_4 and the catalyst can be inferred from thermogravimetric analysis (TGA). Figure 4 shows the TGA curves for bare Fe_3O_4 nanoparticles (blue curve), Gluconic acid coated nanoparticles (red curve) and the catalyst treated nanoparticles (green curve). The magnetite only curve reveals little in terms of mass loss. Strongly adsorbed water and dehydration of surface hydroxy groups are lost at approximately 250 °C. The weight loss at temperatures below 200 °C is due to the removal of physically adsorbed solvent and surface hydroxyl groups. The weight loss of about 2% between 260 and 350 °C may be associated to the thermal crystal phase transformation from Fe_3O_4 to γ-Fe_2O_3 [33] and decomposition of sulfunic acid and formation of sulfur dioxide [34]. Organic groups have been reported to desorb at temperatures above 260 °C. The Gluconic acid coated magnetite nanoparticles (GA@MNPs) are found to have a mass percentage loss about of 12%, while the catalyst loaded particles have the greatest mass loss, at 28%.

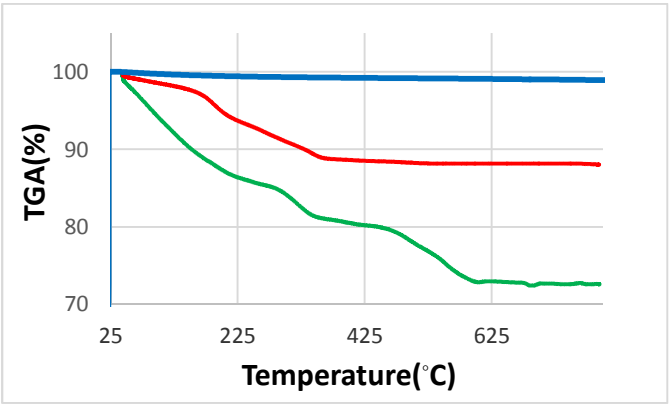


Figure 4. TGA diagram of (blue line) Fe_3O_4 NPs, (red line) GA@MNPs, (green line) GSA@MNPs.

Successful functionalization of the Fe_3O_4 NPs can be inferred from FT-IR technique. The FT-IR spectrum of GSA@MNPs shows several peaks that are characteristic of a functionalized Glucosulfonic acid, which clearly differs from that of the unfunctionalized Fe_3O_4 nanomagnets and GA@MNPs nanoparticles (Figure 5). The FT-IR spectrum for the Fe_3O_4 alone shows a stretching vibration at 3420 cm^{-1} which incorporates the contributions from both symmetrical and asymmetrical modes of the O-H bonds which are attached to the surface magnetic nanoparticles. The strong bands at low wavenumbers (≤700 cm^{-1}) come from vibrations of Fe-O bonds of iron oxide [4]. The presence of an adsorbed water layer is confirmed by a stretch for the vibrational mode of water found at 1631 cm^{-1}. In the FT-IR spectra of GA@MNPs, The presence of the anchored Glucosulfonic acid group is confirmed by C–H stretching vibrations that appear at 2970 and 2850 cm^{-1} and also O-H stretching vibration modes as a broad band that appear at 3400 cm^{-1}. Reaction of GA@MNPs with chlorosufonic acid produces GSA@MNPs in which the presence of SO_3H moiety is asserted with 998-1220 cm^{-1} bands in FT-IR spectra. Also, vibrations in the range of 2850-3500 cm^{-1} are attributed to the terminal acidic groups. In addition, in the spectrum of GSA@MNPs the peak at 3405 cm^{-1} was probably attributed to the SO_3-H groups, which is overlapped by the C-H stretching vibration [9]. All of those bands reveal that the surface of Fe_3O_4 nanoparticles is successfully modified with Glucosulfonic acid.

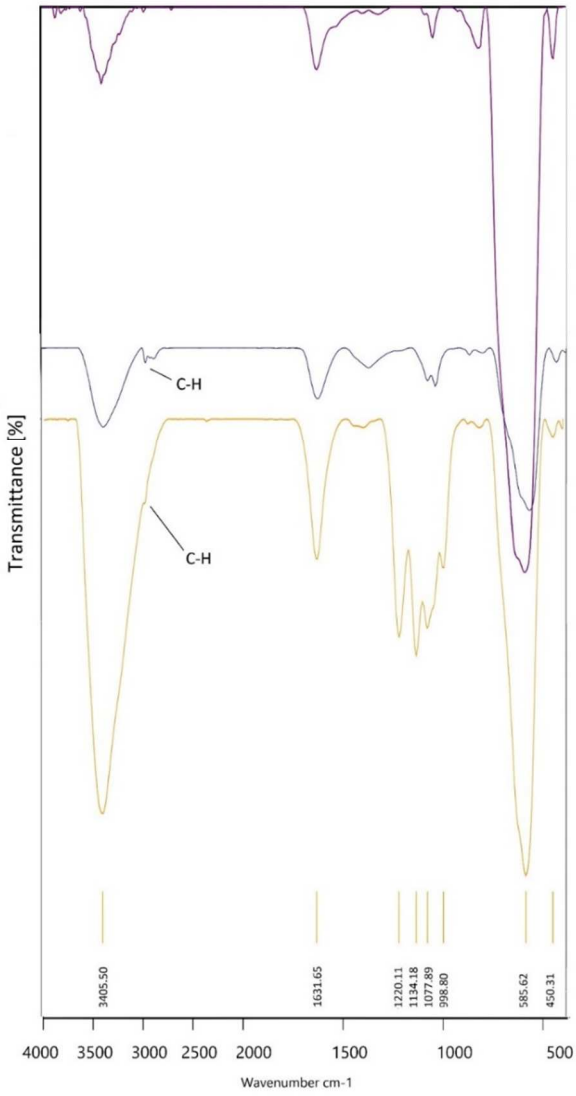


Figure 5. FT-IR spectra of (a) Fe_3O_4 NPs, (b) GA@MNPs, (c) GSA@MNPs.

Superparamagnetic particles are beneficial for magnetic separation, the magnetic property of MNPs and GSA@MNPs were characterrized by VSM. The room temperature magnetization curves of MNPs and GSA@MNPs are shown in Figure 6. The magnetic measurement shows that the GSA@MNPs have a saturated magnetization value of 49 emu g-1.

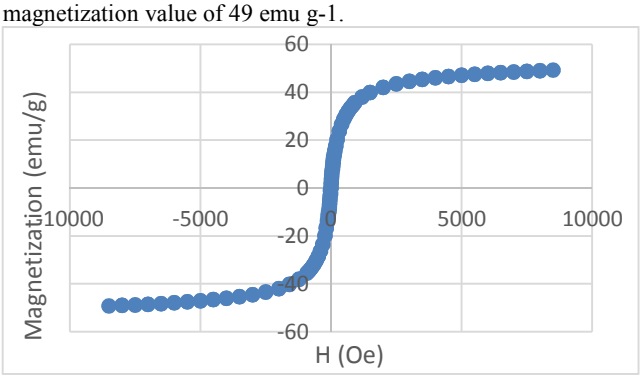
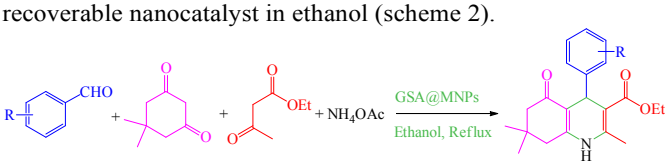


Fig 6. Magnetization curves for GSA@MNPs at room temperature.

2.3. Catalytic study

As a part of our ongoing program directed towards the development of new methods for the catalytic activity of GSA@MNPs in organic reactions, we were interested in finding a simple and efficient method for the one-pot synthesis of polyhydroquinoline derivatives using magnetic nanoparticles bonded Glucosulfonic acid (GSA@MNPs) as a magnetically recoverable nanocatalyst in ethanol (scheme 2).



Scheme 2. GSA@MNPs catalyzed the one-pot synthesis of polyhydroquinoline derivatives

The reaction conditions for one-pot synthesis of polyhydroquinoline derivatives was optimized from reaction of 4-chlorobenzaldehyde whit dimedone, ammonium acetate and ethylacetoacetate in the influence of different amounts of GSA@MNPs in ethanol as a model reaction (Table 1). It is noteworthy that only a 50% of the desired product was isolated using TLC plate in the absence of the catalyst after 200 min at 80 ºC (Table 1, entry 1). As shown in Table 1, 4-chlorobenzaldehyde (1 mmol), dimedon (1 mmol), ethylacetoacetate (1 mmol) and ammonium acetate (1.2 mmol) in the presence of catalytic amount of GSA@MNPs (0.05 g) in ethanol under reflux conditions was found to be ideal reaction conditions for the one-pot synthesis of polyhydroquinoline derivatives.

Table 1. Optimization of the synthesis polyhydroquinolines conditions for the condensation of 4-chlorobenzaldehyde, dimedon, ethylacetoacetate and ammonium acetate as a model compound in ethanol for 200 min.

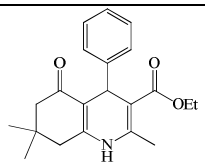
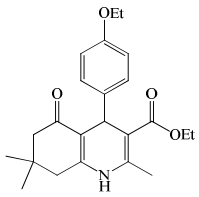
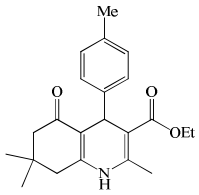
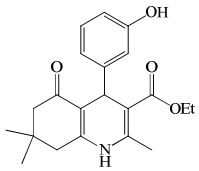
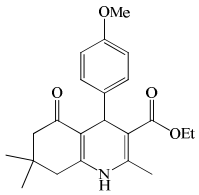
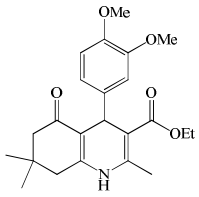
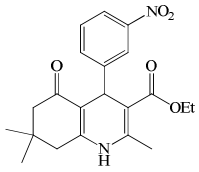
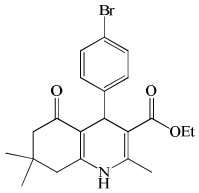
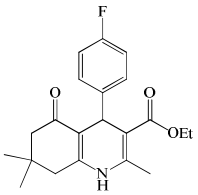
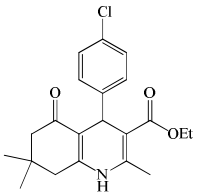
Entry	Catalyst (mg)	Temperature (ºC)	Yielde (%)[a]
1	-	80	41
2	0.02	80	54
3	0.03	80	61
4	0.04	80	77
5	0.05	80	94
6	0.05	60	67
7	0.05	-	Trace

[a] Isolated yield.

The reaction of the various benzaldehyde derivatives, including electron-donating and electron-withdrawing groups on aromatic ring with dimedon, ethylacetoacetate and ammonium acetate was then investigated to confirm the generality of the present method. The polyhydroquinoline derivatives were obtained in high yields. The results of this study are summarized in Table 2. The effect of substitution present on aromatic aldehyde on the reaction rate and the overall yield was also studied. As shown, a variety of benzaldehydes bearing electron-donating (Table 2, entries 2-6) and electron-withdrawing substituents (Table 2, entries 7-10) were successfully employed to prepare the corresponding polyhydroquinoline derivatives in excellent yields.

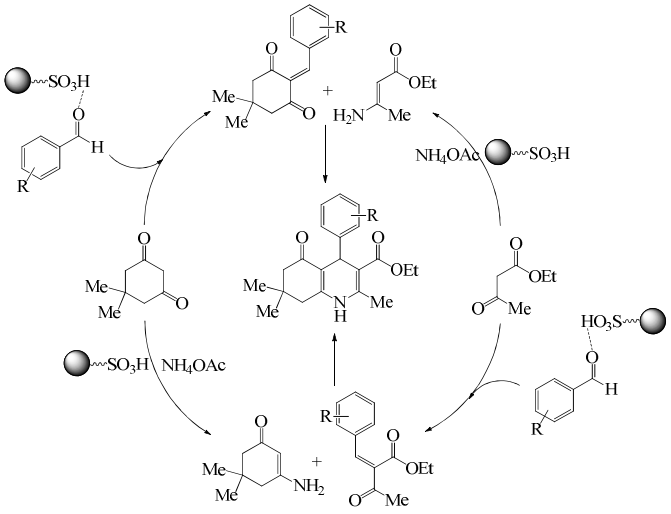
Table 2. Synthesis of polyhydroquinolines catalyzed by GSA@MNPs in ethanol and at 80 ºC.

Entry	Product	Time (min)	Yield (%)[a]	Melting point (ºC)	Ref.

1		240	90	218-220	[36]
2		250	92	176-179	[9]
3		260	89	252-254	[9]
4		200	88	230-232	[36]
5		250	94	249-250	[9]
6		200	88	204-205	[35]
7		300	80	176-178	[27]
8		280	91	251-252	[9]
9		210	93	184-186	[9]
10		200	94	238-239	[35]

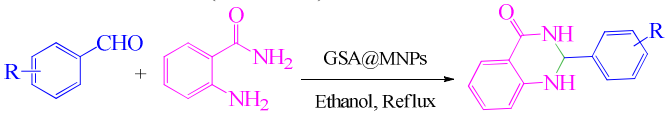
[a]Isolated yield.

The mechanism of this reaction was shown in Scheme 3 [37]. The role of catalyst comes in the Knoevenagel type coupling of aldehydes with active methylene compounds and in the Michael type addition of intermediates to give final product.



Scheme 3. The proposed mechanism of synthesis polyhydroquinoline derivatives in the presence of GSA@MNPs.

In the second of our study on the application of catalytic activity of GSA@MNPs in organic synthesis, we were interested in finding a simple and efficient method for the synthesis of 2,3-dihydroquinazolin-4(1H)-one derivatives in the influence of GSA@MNPs as reusable nanocatalyst with short reaction times in good to excellent yields in ethanol under reflux condition using cyclocondensation reaction of aldehydes and anthranilamide (Scheme 4).



Scheme 4. GSA@MNPs catalyzed the synthesis of 2,3-dihydroquinazolin-4(1H)-one derivatives.

The reaction condition for the synthesis of 2,3-dihydroquinazolin-4(1H)-one derivatives was optimized by

cyclocondensation reaction of anthranilamide (1 mmol) and 4-chlorobenzaldehyde (1 mmol) in ethanol in the presence of different amounts of GSA@MNPs as a model reaction at wide range of temperature (Table 3). As shown in Table 3, 4-chlorobenzaldehyde (1mmol) in the presence of catalytic amount of GSA@MNPs (0.01 g) in ethanol at 80 ºC was found to be ideal reaction conditions for the synthesis 2,3-dihydroquinazolin-4(1H)-ones. In order to show activity of GSA@MNPs, we subject the cyclocondensation of 4-chlorobenzaldehyde with anthranilamide in the absence of catalyst, in which the reaction did not occur even after prolonged reaction time (Table 3, entry 1).

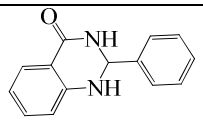
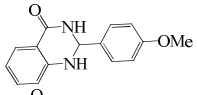
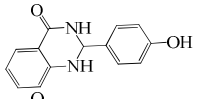
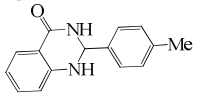
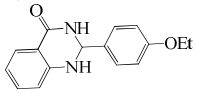
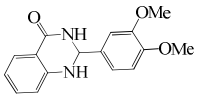
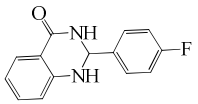
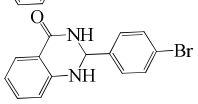
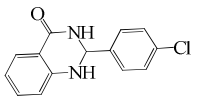
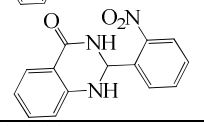
Table 3. Optimization of the synthesis 2,3-dihydroquinazolin-4(1H)-ones conditions for the condensation of 4-chlorobenzaldehyde whit anthranilamide as a model compound in ethanol for 50 min.

Entry	Catalyst (g)	Temperature (ºC)	Yielde (%)[a]
1	-	80	-[b]
2	0.005	80	45
3	0.007	80	67
4	0.01	80	99
5	0.01	60	72
6	0.01	-	trace

[a] Isolated yield, [b]no reaction.

After the obtimomization of the reaction condition, the various aldehyde including several of functional groups have been described in optimum condition and the corresponding 2,3-dihydroquinazolin-4(1H)-one compounds were obtained in good to excellent yields . The results of this studies are summarized in Table 4. As shown, a variety of benzaldehydes bearing electron-donating (Table 4, entries 2-6) and electron-withdrawing substituents (Table 4, entries 7-10) were successfully employed to prepare the corresponding 2,3-dihydroquinazolin-4(1H)-one derivatives in excellent yields. The experimental procedure is very simple and convenient, and has the ability to tolerate a variety of other functional groups such as hydroxyl group, halides, nitro, alkyl and alkoksy under the reaction conditions.

Table 4. Synthesis of 2,3-dihydroquinazolin-4(1H)-ones catalyzed by GSA@MNPs in ethanol and at 80 ºC.

Entry	Product	Time (min)	Yield (%)[a]	Melting point (ºC)	Ref.
1		55	90	221-223	[4]
2		75	94	190-192	[9]
3		25	96	275-278	[10]
4		70	92	228-230	[9]
5		75	93	167-169	[4]
6		25	98	211-213	[10]
7		35	99	197-199	[10]
8		65	96	197-199	[9]
9		50	99	202-204	[4]
10		80	91	190-192	[10]

[a]Isolated yield.

2.4. Comparison of the catalyst

To show the merit of Glucosulfonic acid@Fe_3O_4 in comparison with other reported catalysts, we summarize several results for the preparation of 2-(4-chlorophenyl)-2,3-dihydoquinazolin-4(1H)-one from 4-chlorobenzaldehyde and anthranilamide in table 5. It is obvious that showed good reaction time and higher yield than other catalysts used in literature. Also the new catalyst is comparable in terms of price, non-toxicity, stability and easy separation.

Table 5. Comparison results of Glucosulfonic acid@Fe_3O_4 with other catalysts for the reaction of anthranilamide and 4-chlorobenzaldehyde

Entry	Catalyst (mol %)	Time (min)	Yield (%)	Conditions [Ref.]
1	2-Morpholino ethanesulfonic acid (10)	180 12	91 93	Ethanol, Reflux MW,60 ºC, [38]
2	Propylphosphonic anhydride (0.5 mmol)	10	87	CH_3CN, sealed tub, [39]
3	[hnmp][HSO_4] (5) [NMP][HSO_4] (5) [NMP][H_2PO_4] (5)	28 22 38	83 84 79	Solvent-free,80ºC, [40]
4	[Bmim]PF_6 (2 mL)	40	90	Ionic liquid,75 ºC, [41]
5	Co-Carbon nanotubes (0.008 g)	12	91	Solvent-free, rt, [42]
6	$H_3PW_{12}O_{40}$ (0.1)	10	90	H_2O, rt, [43]
7	Poly(4-vinylpyridine) supported acidic ionic liquid (0.2 g)	8	90	Ethanol, rt, Ultrasonic irradiation, [44]
8	β-Cyclodextrin-SO_3H (0.1 mmol)	30	83	H_2O, rt, [45]
9	Citric acid (0.4 mmol), Acidic Al_2O_3 (0.5 g)	15	85	Solvent-free, rt, Grinding, [46]
10	Glucosulfonic acid@Fe_3O_4 (0.01 g)	50	99	Ethanol, Reflux, [This work]

2.5. Recyclability of the catalyst

The GSA@MNPs as magnetically reusable nanocatalyst, can be easily recycled for repeatedly synthesis of polyhydroquinoline. For practical purposes the ability to easily recycle the catalyst is highly desirable. To investigate this issue, the recyclability of the catalyst was examined for the reaction of 4-chlorobenzaldehyde with dimedon, ethylacetoacetate and ammonium acetate as a model reaction in ethanol using 0.05 gr

of catalyst. We found that this catalyst demonstrated remarkably excellent reusability; after the completion of the reaction, the catalyst was easily and rapidly recovered from the reaction mixture using an external magnet, the remaining magnetic nanocatalyst was washed with ethanol to remove residual product and decantation of the reaction mixture (Figure 7). Then, the reaction vessel was charged with fresh 4-chlorobenzaldehyde, dimedon, ethylacetoacetate and ammonium acetate and subjected to the next run. As shown in Figure 8, the catalyst was used over 6 runs without any significant loss of activity. The average isolated yield for 6 successive runs was 96%, which clearly demonstrates the practical recyclability of this catalyst. In addition, one of the attractive features of this novel catalyst system is the rapid (within 5s) and efficient separation of the catalyst (100%) using an appropriate external magnet, which minimizes the loss of catalyst during separation.

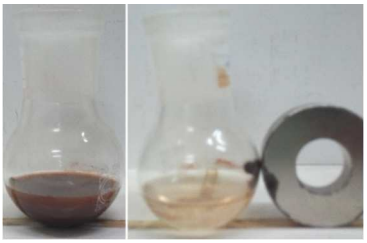


Fig 7. Image showing GSA@MNPs can be separated by applied magnetic field. A reaction mixture in the absence (left) or presence of a magnetic field (right).

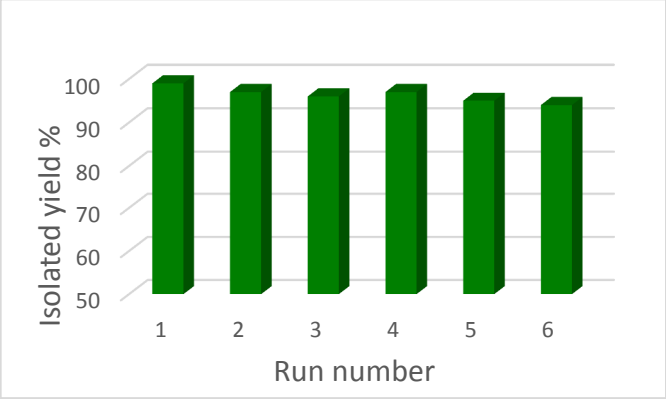


Fig 8. The recycling experiment of GSA@MNPs in condensation of 4-chlorobenzaldehyde, dimedon, ethylacetoacetate and ammonium acetate.

3. Conclusions

In summary, we have demonstrated that GSA@MNPs can be used as a green, efficient and reusable nanocatalyst for the synthesis of a wide range of polyhydroquinoline and 2,3-dihydroquinazolin-4(1H)-one derivatives in ethanol under reflux condition. The advantages of these protocol are the use of a commercially available, eco-friendly, cheap and chemically stabile materials, the operational simplicity, practicability and good to high yields. The product separation and catalyst recycling are easier and simpler with the assistance of an external magnet. The catalyst can be reused for 6 times with little loss of activity.

4. Experimental

4.1. Preparation of the Fe_3O_4 magnetic nanoparticles

The free Fe_3O_4 NPs using chemical precipitation of ions Fe^{3+} and Fe^{2+} were prepared with a molar ratio of 2:1. Typically, $FeCl_3.6H_2O$ (5.838 g, 0.0216 mol) and $FeCl_2.4H_2O$ (2.147 g, 0.0108 mol) were dissolved in 100 mL deionized water at 80 ºC under N_2 atmosphere and vigorous mechanical stirring conditions. Then, 10 mL of 25% NH_4OH was added to the reaction mixture. After 30 minutes, the mixture of reaction was cooled to room temperature. After completion of the reaction, Nanoparticles (Fe_3O_4) were washed two times with distilled water and 0.02 M solution of NaCl, and each time was decanted with external magnetf.

4.2. Preparation of magnetic nanoparticles bonded Gluconic acid (GA@MNPs)

The obtained Fe_3O_4 NPs (2 g) was dispersed in 15 mL water, and solution by sonication for 30 min, and then Gluconic acid solution (8 mL) was added to the reaction mixture. The reaction mixture was stirred under N_2 atmosphere at 80 ºC for 8 h. Then, the final product was separated by magnetic decantation and washed by ethanol to remove the unattached substrates. The nanoparticles product (GA@MNPs) was dried at room temperature.

4.3. Preparation of supported Glucosulfonic acid on Fe_3O_4 magnetic nanoparticles (GSA@MNPs)

The GA@MNPs (0.5 g) were dispersed in dry n-hexane (5 mL) by ultrasonic bath for 20 min. Subsequently, chlorosulfunic acid (1.2 mL) was added drop wise over a period of 30 min and the mixture was stirred for 4h at room temperature. Then, the final product was separated by magnetic decantation and washed twice by dry n-hexane, ethanol and n-hexane respectively to remove the unattached substrates. The product (GSA@MNPs) stored in a refrigerator to use.

4.4. General procedure for the synthesis of polyhydroquinoline derivatives

A mixture of aldehyde (1 mmol), dimedon (1 mmol), ethylacetoacetate (1 mmol), ammonium acetate (1.2 mmol) and GSA@MNPs (0.05 g) was stirred in ethanol under reflux conditions and the progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by an external magnet and washed with ethylacetate. Then, the solvent was evaporated and all products was recrystalized in ethanol, which the pure polyhydroquinoline derivatives were obtained in good to excellent yields.

4.5. General procedure for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones derivatives

A mixture of GSA@MNPs (0.01 g), anthranilamide (1 mmol) and aldehyde (1 mmol) was stirred at 80 ºC in ethanol (2 mL). The progress was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature. CH_2Cl_2 (2 ×5 mL) was added and the catalyst was separated using an external magnet. CH_2Cl_2 was evaporated under reduced pressure to afford the essentially pure products and all products was recrystalized in ethanol for further purification.

4.6. Characterization data of selected compounds

Ethyl-4-(4-ethoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 2, table 2):
Mp: 176-179 °C. IR (KBr) cm^{-1}: 3446, 3276, 3198, 1684, 1607, 1494. ^1H NMR (400 MHz, DMSO-d_6): δ_H= 7.28-7.19 (m, 2H), 6.74-6.72 (d, *J*=8, 2H), 5.80 (s, 1H), 4.99 (s, 1H), 4.07-4.05 (t, *J*=4, 2H), 3.97-3.96 (t, *J*=3.6 ,2H), 2.39-2.15 (m, 7H), 1.38-1.37 (m, 3H), 1.21-1.20 (m, 3H), 1.07 (s, 3H), 0.95 (s, 3H) ppm.
Ethyl-4-(4-methylphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 3, table 2):
Mp: 252-254 °C. IR (KBr) cm^{-1}: 3276, 3276, 3246, 3208, 1702, 1648, 1423. ^1H NMR (400 MHz, DMSO-d_6): δ_H= 9.04 (s, 1H), 7.05-7.03 (d, *J*=8, 2H), 7.00-6.98 (d, *J*=8, 2H), 4.82 (s, 1H), 4.00-3.95 (q, *J*=7.2, 2H), 2.45-2.41 (d, *J*=16, 1H), 2.31-2.27 (m, 4H), 2.21-2.15 (m, 4H), 2.10-1.96 (d, *J*=16, 1H), 1.17-1.13 (t, *J*=6.8, 3H), 1.02 (s, 3H), 0.86 (s, 3H) ppm.
Ethyl-4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 5, table 2):
Mp: 249-250 °C. IR (KBr) cm^{-1}: 3278, 3246, 3208, 1701, 1649, 1423. ^1H NMR (400 MHz, DMSO-d_6): δ_H= 9.04 (s, 1H), 7.08-7.06 (d, *J*=8.4, 2H), 6.77-6.75 (d, *J*=8.4, 2H), 4.80 (s, 1H), 4.02-3.96 (q, *J*=7.2, 2H), 3.69 (s, 3H), 2.52-2.45 (d, *J*=29.2, 1H), 2.31-2.29 (m, 4H), 2.20-2.16 (d, *J*=16, 1H), 2.01-1.97 (d, *J*=16.4, 1H), 1.17-1.14 (t, *J*=7.2, 3H), 1.02 (s, 3H), 0.87 (s, 3H) ppm.
Ethyl-4-(3,4-dimethoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 6, table 2):
Mp: 204-205 °C. IR (KBr) cm^{-1}: 3280, 3213, 1696, 1645, 1452. ^1H NMR (400 MHz, DMSO-d_6): δ_H= 9.05 (s, 1H), 6.79-6.76 (m, 2H), 6.65-6.63 (d, *J*=8, 1H), 4.80 (s, 1H), 4.04-3.99 (q, *J*=7.2, 2H), 3.69-3.68 (d, *J*=4.4, 5H), 2.47-2.42 (d, *J*=17.2, 2H), 2.35-2.27 (m, 4H), 2.22-2.18 (d, *J*=16, 1H), 2.03-1.99 (d, *J*=16, 1H), 1.20-1.16 (t, *J*=6.8, 3H), 1.03 (s, 3H), 0.90 (s, 3H) ppm.
Ethyl-4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 8, table 2):
Mp: 251-252 °C. IR (KBr) cm^{-1}: 3276, 3243, 3207, 1703, 1649, 1421. ^1H NMR (400 MHz, DMSO-d_6): δ_H= 9.14 (s, 1H), 7.41-7.39 (d, *J*=8.4, 2H), 7.13-7.11 (d, *J*=8, 2H), 4.84 (s, 1H), 4.01-3.96 (q, *J*=6.8, 2H), 2.52-2.46 (d, *J*=26.4 1H), 2.31-2.27 (m, 4H), 2.21-2.17 (d, *J*=16, 1H), 2.01-1.97 (d, *J*=16, 1H), 1.15-1.12 (t, *J*=7.2, 3H), 1.02 (s, 3H), 0.85 (s, 3H) ppm.
2-(4-methylphenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 4, table 4):
Mp: 228-230 °C. IR (KBr) cm^{-1}: 3313, 1658, 1611, 1439. ^1H NMR (400 MHz, DMSO-*d*6): δ_H = 8.21 (s, 1H), 7.62-7.59 (d, *J*=7.5, 1H), 7.38-7.35 (d, *J*=7.5, 2H), 7.26-7.14 (m, 3H), 7.03 (s, 1H), 6.75-6.64 (m, 2H), 5.71 (s, 1H), 2.49-2.42 (s, 3H) ppm.
2-(4-ethoxyphenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 5, table 4):
Mp: 167-169 °C. IR (KBr) cm^{-1}: 3301, 1650, 1613, 1443. ^1H NMR (400 MHz, DMSO-d_6): δ_H= 7.95-7.94 (b, 1H), 7.52-7.50 (m, 2H), 7.34 (s, 1H), 7.26 (s, 1H), 6.95-6.90 (m, 3H), 6.68-6.67 (m, 1H), 5.85 (s, 1H), 5.75 (s, 1H), 4.07-4.05 (q, *J*=4, 2H), 1.46-1.44 (s, 3H) ppm.
2-(3,4-dimethoxyphenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 6, table 4):
Mp: 211-213 °C. IR (KBr) cm^{-1}: 3335, 1671, 1610, 1436. ^1H NMR (400 MHz, DMSO-d_6): δ_H= 8.21 (s, 1H), 7.64-7.62 (d, *J*=7.6, 1H), 7.28-7.24 (t, *J*=0.8, 1H), 7.15 (d, *J*=1.6, 1H), 7.04-6.97 (m, 2H), 6.95 (s, 1H), 6.78-6.76 (d, *J*=8, 1H), 6.72-6.67 (t, *J*=1.2, 1H), 5.71 (s, 1H), 3.77 (s, 3H), 3.76 (s, 3H) ppm.
2-(4-bromophenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 8, table 4):
Mp: 197-199 °C. IR (KBr) cm^{-1}: 3310, 1656, 1608, 1433. ^1H NMR (400 MHz, DMSO-d_6): δ_H= 8.17-8.14 (m, 1H), 7.80-7.78 (m, 1H), 7.63-7.59 (m, 3H), 7.47-7.44 (m, 2H), 7.30-7.24 (m, 1H), 6.77-6.72 (d, *J*=19.2, 1H), 6.71-6.68 (m, 1H), 5.76 (s, 1H) ppm.
2-(4-chlorophenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 9, table 4):
Mp: 202-204 °C. IR (KBr) cm^{-1}: 3309, 1655, 1611, 1435. ^1H NMR (400 MHz, DMSO-d_6): δ_H= 8.29 (s, 1H), 7.61-7.43 (m, 5H), 7.26-7.20 (t, *J*=7.5, 1H), 7.12 (s, 1H), 6.75-6.63 (m, 2H), 5.75 (s, 1H) ppm.
2-(2-nitrophenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 10, table 4):
Mp: 190-192 °C. IR (KBr) cm^{-1}: 3372, 1667, 1613, 1517, 1453, 1342. ^1H NMR (400 MHz, DMSO-d_6): δ_H= 8.26 (s, 1H), 8.10-8.08 (d, *J*=8, 1H), 7.89-7.87 (d, *J*=8, 1H), 7.83-7.80 (t, *J*=0.8, 1H), 7.70-7.63 (m, 2H), 7.30-7.26 (m, 1H), 7.04 (s, 1H), 6.81 (d, *J*=1.2, 1H), 6.77-6.72 (m, 1H), 6.36 (m, 1H) ppm.

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Notes and references

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