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1. Introduction

In the last few years, different types of homogeneous base catalysts have been utilized on a large scale to catalyze different kinds of organic reactions.¹ Many reports on homogeneous base catalysts have been published, where different types of homogeneous catalysts such as piperidine,² chitosan,³ ionic liquids,⁴ pyrrolidine,⁵ and $K_2HPO_4^6$ have been utilized as base catalysts. Homogeneous catalysis is known for its marvellous catalytic activity and selectivity, but the problem associated with homogeneous catalysis is that, it suffers from difficulties in the separation of the catalyst from the reaction mixture resulting in poisoning of the final product.⁷ To overcome this difficulty, the scientific community has utilized various solid support materials for the immobilization of basic catalytic active moieties either covalently or non-covalently. Different types of

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solid support materials such as, Al₂O₃,⁸ MCM-41,⁹ MCM-48,¹⁰ SBA-15,¹¹ hollow mesoporous carbon,¹² graphene oxide,¹³ and MWCNTs¹⁴ have been utilized to heterogenize the homogeneous catalysts. It has been observed that silica-based materials possesses great potential for surface modifications because of their larger surface area, nanometre size, large number of silanol groups, high mechanical and thermal stability.^{15–17} But there are some disadvantages associated with the silica-based materials, such as the tedious method of its separation from the reaction mixture such as filtration and centrifugation. Mesoporous silica materials, such as MCM-41, and SBA-15 have tubular pores, which lead to the blocking of pores on covalent immobilization of organosilane derivatives.¹⁸ This ultimately reduces the accessibility of active sites for the reactant molecules and consequently leads to the decrease in the catalytic efficiency of the nanocatalyst.¹⁹⁻²² To overcome this complexity, different types of silica-based fibrous materials were reported such as KCC-1,²³ dendritic SiO2,24 and cSiO2@DFNS.25 These materials have fibrous morphology with high surface area, large pore size and pore volume and due to this the chances of pore-blocking significantly reduces. A drawback associated with fibrous silica

as an efficient and recyclable base catalyst‡

Magnetic core-shell dendritic mesoporous

silica nanospheres anchored with diamine

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In the present study, diamine-functionalized magnetic core-shell dendritic mesoporous silica nanospheres have been successfully synthesized by an oil-water biphasic stratification-coating strategy. The shape, size and morphology of the synthesized magnetic nanocatalyst could be characterized by various physicochemical techniques such as, field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The characteristic information about the successful immobilization of various functionalities on the nanospheres could be obtained with the help of X-ray powder diffraction (XRD) patterns, Fourier transform-infrared spectroscopy (FT-IR), energy dispersive X-ray spectroscopy (EDX) and thermo-gravimetric analysis (TGA). The details about the magnetic behaviour and surface area of the nanocatalyst could be acquired by vibrating sample magnetometry (VSM) and BET surface analysis, respectively. The synthesized diamine-functionalized magnetic nanoparticles were then explored as a highly efficient catalyst for the Knoevenagel condensation and one-pot synthesis of polyhydroquinolines using aromatic/heteroaromatic aldehydes and aliphatic aldehydes with active methylene compounds under very mild conditions. The synthesized magnetic core-shell dendritic mesoporous silica nanospheres had large surface areas. This large surface area and pore volume could facilitate a proper interaction and penetration of the reactant molecules with the basic amine groups present on the dendritic mesoporous silica nanospheres. The supported nanocatalyst revealed no sign of leaching of the amine groups present inside the dendrimers and therefore, could be reused up to nine times without any noteworthy loss in catalytic activity.



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Fig. 1 Structures of few bioactive polyhydroquinolines.

is the difficulty in separating it from the reaction mixture. The difficulty in the separation of dendritic silica could be solved by supporting it on a material that could be easily recovered without the tedious method of filtration and centrifugation. Fe₃O₄ magnetic nanoparticles gained more attention due to their large surface area, easy availability, low toxicity and their ability to be easily recycled using an external magnetic field.²⁶ Therefore, Fe₃O₄ magnetic nanoparticles could be extensively used as solid support materials in designing heterogeneous catalysts. Many reports have been published where magnetic nanoparticles were utilized as solid support materials such as Fe₃O₄@MCM-41-SO₃H,²⁷ SBA-15@Fe₃O₄@Isa,²⁸ Fe₃O₄@mSiO₂-NH₂,²⁹ nano-FGT, ³⁰ Fe₃O₄@D-NH-(CH₂)₄-SO₃H, ³¹ Fe₃O₄@SiO₂^{32,33} Fe₃O₄@ SiO₂-OSO₃H,³⁴ and Fe₃O₄(a)SiO₂-IL.³⁵ These nanocatalysts were utilized for various organic transformations such as Knoevenagel condensation, Michael addition, Hantzsch condensation and N-formylation of amines. In order to overcome the above said limitations, the development of highly efficient nanocatalysts having high surface area, large pore volume and easy recoverability is still currently in demand.

Knoevenagel condensation is an important reaction for the generation of C–C bonds.³⁶ This is a nucleophilic addition reaction between aromatic aldehydes and active methylene compounds, which results in the production of various pharmaceutical compounds.³⁷ There are several reports that have been published for the synthesis of Knoevenagel condensation products including Fe₃O₄@SiO₂@PAMAM-G2.³⁸ The products obtained from Knoevenagel condensation are used as intermediates for the synthesis of many heterocyclic compounds of medicinal importance.

On the other hand, multicomponent reactions (MCRs) play a vital role in the formation of many C–C and C–N bonds.^{39,40} The first synthesis of biologically active 1,4-dihydropyridines (DHPQs) was reported by Arthur Hantzsch in 1881 by four component reactions between aromatic aldehydes, active methylene compounds, ammonium acetate and ethylacetoacetate.⁴¹

Different studies have been published for the one-pot synthesis of polyhydroquinolines such as $Fe_3O_4(@SiO_2/ZnCl_2,^{42} DBH$ or DCH,⁴³ and MMWCNTS-D-(CH₂)₄-SO₃H.⁴⁴ DHPQs are a special class of heterocyclic system owing their remarkable pharmacological properties; they are also known as calcium channel blockers. The DHPQ derivatives are used as antidiabetic,⁴⁵ antitumor,⁴⁶ antitherosclerotic,⁴⁷ bronchodilator,⁴⁸ and geroprotective agents.⁴⁹ The structures of few biologically active polyhydroquinolines are given in Fig. 1.

In continuation of attempts to synthesize nanostructured materials for numerous organic transformations,^{50,51} the present study reports the synthesis of diamine-functionalized magnetic core–shell dendritic mesoporous silica nanospheres (Fe₃O₄@SiO₂@DSiO₂–NH₂). The prepared nanocatalyst turned out to be a highly efficient, stable, eco-friendly, magnetically recoverable, low cost and heterogeneous catalyst for the Knoevenagel and Hantzsch condensations. The synthesized nanocatalyst showed excellent catalytic activity towards both the reactions and was efficiently utilized for a number of catalytic cycles without any noticeable loss in catalytic activity.

2. Experimental

2.1 Materials

 $Fe_2(SO_4)_3$ and $FeSO_4 \cdot 7H_2O$ were purchased from Sigma-Aldrich. Tetraethyl orthosilicate (TEOS), cetyltrimethylammonium chloride (CTAC) and cyclohexane were purchased from Sigma-Aldrich, whereas 3-(2-aminoethylamino) propyltrimethoxysilane was purchased from Alfa Aesar. All the other chemicals were purchased from Thomas Baker, Spectrochem and Merck. All the reagents were used without any further purification.

2.2 Synthesis of magnetic nanoferrites

The Fe₃O₄ nanoparticles were synthesized by a previously reported co-precipitation method.⁵² In a typical procedure, Fe₂(SO₄)₃ (3.0 g) and FeSO₄·7H₂O (2.1 g) were dissolved in distilled water (160 mL) and the resulting mixture was vigorously stirred for an hour until the solution became orange in colour. Furthermore, the pH of the reaction mixture was maintained at 10 by dropwise addition of NH₄OH (25%). On addition of ammonium hydroxide, the colour changes instantaneously from orange to black. The reaction mixture was stirred continuously for two hours at 60 °C. The black coloured precipitates of magnetic nanoparticles were separated by using an external magnet. The obtained black precipitate was washed several times with distilled water and ethanol until the pH of the reaction mixture became neutral. The obtained Fe₃O₄ nanoparticles were dried at 60 °C in vacuum for 6 h.

2.3 Synthesis of silica-coated magnetic nanoferrites

Silica-coated magnetic nanoferrites were synthesized by using the sol–gel method. In a typical procedure, Fe_3O_4 nanoparticles (1.0 g) were dispersed in ethanol (250 mL) followed by dropwise addition of NH₄OH 25% (6.0 mL) and TEOS (2.0 mL). The brownish precipitates were collected after constant stirring for 24 h. The precipitates were then washed with distilled water and ethanol multiple times and dried at 60 $^{\circ}$ C in a vacuum for 6 h.

2.4 Synthesis of magnetic core-shell dendritic mesoporous silica

The dendritic mesoporous silica was synthesized on the surface of silica-coated magnetic nanoferrites by using an oil-water biphasic stratification method. In this typical procedure, 0.2 g of silica-coated magnetic nanoferrites was dispersed in a mixture containing CTAC (24 mL) and H₂O (36 mL), followed by the addition of TEA (0.18 g), and then the resulting mixture was ultrasonicated for about an hour. Afterwards, the reaction mixture was maintained at 60 °C for about another hour. Subsequently, a mixture of cyclohexane (20 mL) and TEOS (4 mL) was added dropwise to the reaction mixture, while stirring at 60 °C. The reaction mixture was stirred continuously under reflux conditions at 60 °C in an oil bath for 12 h. The product was extracted using an external magnet. The product was washed several times with ethanol and distilled water. Then, the collected solid residue was dried under vacuum at 60 °C for approximately 6 h. Later on, calcination was done at 600 °C to remove the template i.e. CTAC surfactant and the hydrophobic organic phase. Finally, the magnetic core-shell dendritic mesoporous silica nanospheres were obtained.

2.5 Synthesis of diamine-functionalized magnetic-core shell dendritic mesoporous silica (Fe₃O₄@SiO₂@DSiO₂-NH₂)

For the synthesis of diamine-functionalized magneticcore shell dendritic mesoporous silica, magnetic core shell dendritic mesoporous silica (500 mg) was stirred with excess of *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (762 μ L) in toluene (250 mL) at 80 °C for 6 h. The solution was filtered and the residue was thoroughly washed with toluene (3 \times 20 mL), and then with ethanol (3 \times 20 mL) and ultimately the solid product was air-dried.

2.6 Synthesis of the Knoevenagel condensation product

In a typical procedure for Knoevenagel condensation, aldehyde (1 mmol) and active methylene compound (1 mmol) were added to a round bottom flask containing distilled water (2 mL) followed by addition of $Fe_3O_4(@SiO_2@DSiO_2-NH_2$ nanocatalyst (5 mg). The mixture was magnetically stirred at room temperature for an appropriate time. The progress of the reaction was monitored by thin layer chromatography (TLC). Following the completion of the reaction, the nanocatalyst was recovered by using an external magnet and washed with ethanol and dried for further use. The product of the reaction was extracted with DCM. The filtrate was removed by a rotary evaporator to obtain the solid product. The pure product was obtained after recrystallizing in absolute ethanol.

2.7 One-pot synthesis of polyhydroquinolines

In a typical synthesis of polyhydroquinolines, aldehyde (1 mmol), dimedone (140.18 mg), ethyl acetoacetate (128 μ L), ammonium acetate (77.8 mg) and the catalyst (10 mg) were



added in water (2 mL). The reaction mixture was ultrasonicated for 10 minutes and after that the reaction mixture was stirred at 35 °C. The progress of the reaction was monitored by TLC. The solid product was extracted with ethyl acetate. The catalyst was recovered by using an external magnet. The pure products were obtained after recrystallization using hot ethanol.

3. Characterization techniques

The FT-IR spectra of the stepwise synthesized nanocatalyst *i.e.* Fe₃O₄@SiO₂@DSiO₂-NH₂ were recorded using a PerkinElmer Spectrum RXI-Mid Infra-red spectrometer in the range of 4000–400 cm⁻¹ through the KBr pellet method. Powdered X-ray diffraction (XRD) was recorded at a scanning rate of 4° min⁻¹ using 3 kW radiation on a Bruker D8 Discover diffractometer in the range of 5° to 80°. The TG Analysis was done at a temperature range of 50 °C-850 °C by using a Pyris Diamond TGA-DTA instrument. Through this method, the changes in the chemical and physical properties of the synthesized nanomaterial were analyzed at a constant heating rate throughout the process. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) provided the information about morphology, shape, size and structure of the nanocatalyst by using the TALOS model. An energy dispersive X-ray (EDX) spectroscopic technique was utilized to determine the elemental composition of the synthesized nanomaterials. BET surface analysis was done with a Quantachrome Instrument, ASI-CI-11 model. The ¹H and ¹³C NMR spectra of the Knoevenagel and Hantzsch condensation products were obtained using 400 MHz and 100 MHz Jeol JNM-EXCP 400 instruments, respectively.



Fig. 2 FT-IR spectra of (a) Fe_3O_4 , (b) Fe_3O_4 @SiO₂, (c) Fe_3O_4 @SiO₂@DSiO₂ and (d) Fe_3O_4 @SiO₂@DSiO₂-NH₂.

4. Results and discussion

The diamine-functionalized magnetic core shell dendritic mesoporous silica nanospheres were synthesized in a stepwise manner as described in Scheme 1. The Fe_3O_4 nanoparticles could be synthesized by the previously reported coprecipitation method in an aqueous medium.⁵² Following that, silica-coated magnetic nanoparticles could be easily prepared by the previously reported sol–gel method.⁵³ Furthermore, silica-coated magnetic nanoparticles could be modified with dendritic mesoporous silica by an oil–water biphasic coating strategy.⁵⁴ Subsequent to successful synthesis of magnetic core–shell dendritic mesoporous silica, the surface of this material could be further modified by functionalization with a base through covalent bond formation between surface hydroxyl groups and organosilane derivatives as shown in Scheme 1.

The FT-IR spectra of the synthesized nanocatalysts are shown in Fig. 2. Firstly, the spectrum represented in Fig. 2(a) is for the magnetic nanoferrite particles, where the absorption band at 582 cm⁻¹ could be due to the Fe-O vibration and the broad peak at 3404 cm⁻¹ could be due to the surface hydroxyl groups present on the nanoparticles. The spectrum represented by Fig. 2(b) is for silica-coated magnetic nanoferrite particles where the three additional bands at 1081 cm^{-1} , 962 cm^{-1} and 801 cm⁻¹ could probably correspond to Si-O-Si antisymmetric stretching, Si-O symmetric and Si-O-Si symmetric modes, respectively. This confirms the successful coating of the silica layer on the surface of magnetic nanoparticles. The spectrum represented by Fig. 2(c) is for dendritic mesoporous silicacoated magnetic nanoparticles in which the characteristic bands peaking at 466 cm⁻¹, 799 cm⁻¹ and 1085 cm⁻¹ could be attributed to the Si-O-Si plane bending, Si-O symmetric vibrations and Si-O asymmetric vibrations; respectively. The intense peak at 3386 cm⁻¹ could be due to the large number of



Fig. 3 Magnetization curves (a) Fe_3O_4 , (b) Fe_3O_4 @SiO₂, (c) Fe_3O_4 @SiO₂@DSiO₂ and (d) Fe_3O_4 @SiO₂@DSiO₂-NH₂.

Si–OH groups, which could be further used for the functional modification of diamine groups over it. The spectrum shown by Fig. 2(d) is for diamine-functionalized dendritic mesoporous silica nanospheres. The absorption band at 1017 cm⁻¹ could correspond to Si–O stretching and the peak at 2924 cm⁻¹ could be due to $-CH_2$ stretching. The new absorption band at 1589 cm⁻¹ could be due to the characteristic peak of the N–H bending mode and the peak at 3442 cm⁻¹ could be attributed to the broad peak of N–H stretching. These observations could confirm the successful modification of diamine derivatives on the surface of magnetic core shell dendritic mesoporous silica.

The magnetization curves of the synthesized nanocatalysts are shown in Fig. 3. Based on the results, it could be clearly observed that the synthesized nanocatalyst was magnetic in nature. The saturation magnetization value of Fe₃O₄ nanoparticles was found to be approximately 51.0 emu g^{-1} as represented in Fig. 3(a). Following the silanation of the ferrite nanoparticles, a decrease in the saturation magnetization of silica-coated nanoparticles could be observed and this could be due to the successful coating of a silica layer on the surface of Fe₃O₄ nanoparticles. The value of saturation magnetization also decreased up to 34.36 emu g^{-1} as shown in Fig. 3(b). Followed by the introduction of the dendritic mesoporous silica over the surface of silica-coated Fe3O4 particles (Fe3O4@ SiO₂(a)DSiO₂), there was a slight decrease in the magnetization of dendritic mesoporous silica nanospheres and then saturation magnetization value obtained was 33.46 emu g^{-1} as represented in Fig. 3(c). In the final step of the synthesis protocol, *i.e.* after the successful immobilization of the diamine derivative on the surface of dendritic mesoporous silica, there was a rapid decrease in the saturation magnetization value and it was found to be 17.20 emu g^{-1} as shown in Fig. 3(d).

The energy dispersive spectroscopic analysis could be utilized to determine the chemical composition of the prepared Fe_3O_4 @SiO_2@DSiO_-NH₂ nanocatalyst. The EDX spectrum shows that it contains various elements such as, carbon, nitrogen, iron,



silicon and oxygen and their corresponding peaks are shown in Fig. 4. The percentage composition of the corresponding elements present in Fe₃O₄@SiO₂@DSiO₂-NH₂ could be determined from the CHN analysis. Based on the CHN analysis, it

was found that the synthesized nanomaterial contained around 17.84% carbon, 4.35% hydrogen and 7.04% nitrogen.

The morphology and the structural features of the synthesized magnetic-core shell dendritic mesoporous silica nanospheres



Fig. 5 FE-SEM images of (a) $Fe_3O_4@SiO_2@DSiO_2$, (b) $Fe_3O_4@SiO_2@DSiO_2-NH_2$, (c) TEM images of $Fe_3O_4@SiO_2@DSiO_2$ at 200 nm and (d) at 50 nm magnification.



Fig. 6 (a) TG analysis of $Fe_3O_4@SiO_2@DSiO_2$ and $Fe_3O_4@SiO_2@DSiO_2-NH_2$. (b) X-ray diffraction pattern of $Fe_3O_4@SiO_2@DSiO_2$ and $Fe_3O_4@SiO_2@DSiO_2-NH_2$, (c-d) N₂ adsorption-desorption curves of $Fe_3O_4@SiO_2@DSiO_2$ and $Fe_3O_4@SiO_2@DSiO_2-NH_2$, respectively, and pore size distributions (insets).

could be analysed from the TEM images (Fig. 5(c and d)). Based on the TEM images it could be observed that the synthesized nanomaterial had a magnetic core surrounded by non-porous silica, with mesoporous dendritic silica on the outermost surface. Moreover, the surface of the silica layer was uniform and monodispersed in nature. FE-SEM images of $Fe_3O_4@SiO_2@$ $DSiO_2-NH_2$ revealed that the nanoparticles had spherical morphology as shown in Fig. 5(a and b).

In the TG analysis, a small amount of weight loss could be observed in both curves below 140 °C, which could be due to the evaporation of physically adsorbed water molecules on the surface of the nanocatalysts. Fig. 6(a) shows that in the case of Fe₃O₄@SiO₂@DSiO₂ nanospheres, no further weight loss could be observed below 600 °C. This could demonstrate that the magnetic core shell dendritic mesoporous silica does not break below 600 °C and remains undamaged. Furthermore, as evident from the spectrum of Fe₃O₄@SiO₂@DSiO₂-NH₂ a weight loss of 17.0% could be seen between 140 °C and 600 °C and this could

be due to the destruction of the organic structure on the surface of the dendritic mesoporous silica. No weight loss could be observed after 600 °C (Fig. 6(a) red line curve). On comparing the above results, it could be concluded that more organosilane derivatives have been successfully grafted due to the large pore size and dendritic structure, as shown by the red line curve. Hence, it could be inferred that the thermal stability of the prepared nanocatalyst was excellent.

The powdered X-ray diffraction pattern of Fe₃O₄@SiO₂@ DSiO₂ and Fe₃O₄@SiO₂@DSiO₂-NH₂ are shown in Fig. 6(b). Both the XRD pattern contains broad peaks in the 2θ range of 10° to 27° could indicate the presence of an amorphous silica layer throughout the magnetic nanoparticles. Furthermore, it could be clearly seen in the diffraction patterns of both the samples that they possess the characteristic diffraction peaks at 2θ values of 30.1°, 35.5°, 42.3°, 53.4°, 58.7° and 62.1°. These peaks are attributed to corresponding planes *i.e.* (220), (311), (400), (422), (511) and (440), respectively, shown by the green line. 1

2

 $DSiO_2 - NH_2(5)$

Table 1 Optimization study for the Knoevenagel condensation



3	Fe ₃ O ₄ @SiO ₂ @	DCM	50	40	78
	$DSiO_2-NH_2(5)$				
4	Fe ₃ O ₄ @SiO ₂ @	THF	80	40	45
	$DSiO_2 - NH_2(5)$				
5	Fe ₃ O ₄ @SiO ₂ @	H_2O	25	20	75
	$DSiO_2 - NH_2(3)$				
6	Fe ₃ O ₄ @SiO ₂ @	H_2O	25	7	99
	$DSiO_2 - NH_2(5)$				
7	Fe ₃ O ₄ @SiO ₂ @	H_2O	25	20	99
	$DSiO_2 - NH_2(10)$				
8	Fe ₃ O ₄ @SiO ₂ @	Neat	50	40	Trace
	$DSiO_2 - NH_2(5)$				
9	Fe_3O_4 (a) $SiO_2 - NH_2(5)$	H_2O	40	40	85
10	Fe ₃ O ₄ @SiO ₂ @	H_2O	40	40	30
	$DSiO_2(5)$				
11	Blank	H_2O	40	40	10

Reaction conditions: 4-nitrobenzaldehyde (1 mmol), malononitrile (1 mmol) and solvent (2 mL).

These values are in good agreement with the data of the standard Fe₃O₄ structure [JCPDS entry 19-0629]. Following the successful immobilization of basic moieties on the surface of Fe₃O₄@SiO₂@DSiO₂, no change in the crystalline structure of magnetic nanoparticles could be observed as evident from Fig. 6(b) (pink line). From these observations, it could be inferred that the developed nanomaterial have a face centred cubic structure (FCC) and inverse spinel structure. It remained the same (*i.e.* inverse spinel structure) even after incorporation of the base on the surface of dendritic mesoporous silica.

The N_2 adsorption-desorption isotherms of Fe₃O₄(a) SiO₂@DSiO₂ are shown in Fig. 6(c). These investigations were conducted to determine the surface area and pore size of the prepared nanocatalyst. The BET curve, clearly shows that Fe₃O₄@SiO₂@DSiO₂ possesses the dendritic mesoporous silica channels with uniform nanoscopic space between dendrimers. The BET surface area and pore volumes of the magnetic core shell dendritic mesoporous silica nanospheres was found to be 571.30 m² g⁻¹ and 0.954 cm³ g⁻¹; respectively. The pore size was found to be about 8.52 nm, this could be proved by the pore size distribution plot (inset Fig. 6(c)). This could be attributed to the highly porous structure of dendritic mesoporous silica. Based on these results, it could be said that the availability of space between the dendrimers was more and this could help further in the functionalization with the amine groups. On immobilization of diamine functionalities over the dendritic mesoporous silica nanospheres, the surface area decreases from 571.0 to 197.0 m² g⁻¹; the pore diameter decreases slightly from 8.52 to 6.58 nm and pore volume from 0.954 to 0.658 cm³ g⁻¹ as shown in Fig. 6(d). This could authenticate the successful incorporation of basic moieties over the dendrimers. This confirmed that the synthesized nanomaterial was highly porous and the reactant molecules could easily access the active diamine moieties deep inside the dendrimers.

Following complete characterization of the synthesized nanomaterial, its catalytic activity for the Knoevenagel and Hantzsch condensations was studied in detail. In the Knoevenagel condensation, benzaldehyde and malononitrile were selected as substrates for a model test reaction. In order to

Table 2 Optimization study for the one-pot synthesis of 1,4-polyhydroquinolines



Reaction conditions: 4-nitrobenzaldehyde (1 mmol), dimedone (1 mmol), ammonium acetate (1 mmol), ethyl acetoacetate (1 mmol) and solvent (2 mL).

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Entry	Aldehyde	Active methylene compound	Product	Time (min)	Isolated yield (%)	TON (TOF)
1	CHO	NC	CN CN	15	98	64 (256)
2	O ₂ N CHO	NC	O ₂ N CN	5	99	65 (778)
3	СІСНО	NC		7	99	65 (554)
4	СНО	NC		20	80	52 (157)
5	MeO	NC	H ₃ CO	10	96	63 (376)
6	OH CHO	NC COOEt	COOEt CN	20	94	61 (184)
7	CHO	NC COOEt	COOEt	20	92	60 (180)
8	CHO N	NC COOEt	COOEt	20	89	58 (174)
9	МеО СНО	NC COOEt	MeO CN CN	10	94	61 (368)
10	Н3С	NC	H ₃ C	12	97	63 (317)
11	но	NC	HO	15	98	64 (256)
12	CHO NO ₂	NC		20	93	61 (182)



Reaction conditions: aldehyde (1 mmol), active methylene compounds (1 mmol), water (2 mL), and catalyst (5 mg).

optimize the reaction conditions, the effect of various parameters such as temperature, solvent and amount of loading of the catalyst were studied (Table 1). It was found that the yield of the product decreased when DCM, ethanol, CH₃CN and THF were used as solvents (Table 1, entries 2, 3 and -4). However, excellent results could be obtained when water was used as a solvent and the reaction was carried out at 25 °C. Furthermore, the yield of the product was found to be maximum when 5 mg catalyst was used and on decreasing the amount of catalyst to 3 mg, the yield of the product reduced to 75%. In the absence of the catalyst it could be said that only 10% transformation occurred even at 40 °C in 40 minutes (Table 1, entry 11). There was no further increase in the yield of the product on increasing the amount of the catalyst (Table 1, entry 7). Hence, it could be concluded that the maximum conversion could be obtained when the reaction was carried out with 5 mg of the catalyst and using water as a solvent at 25 °C (Table 1, entry 6).

Similarly, in the case of the Hantzsch condensation, 4-nitrobenzaldehyde, dimedone, ammonium acetate and ethyl acetoacetate were taken as substrate molecules for the model reaction and the optimization was done in a manner similar to that in the case of the Knoevenagel condensation. It was found that the yield of the product was maximum when the reaction was carried out with 10 mg of the catalyst in water at 35 $^{\circ}$ C (Table 2, entry 7).

Using the optimized conditions, the catalytic efficiency of the $Fe_3O_4@SiO_2@DSiO_2-NH_2$ nanocatalyst was investigated for the Knoevenagel condensation (Table 3) as well as the one-pot synthesis of 1,4-polyhydroquinolines (Table 4). Firstly, in the Knoevenagel condensation it was found that aromatic aldehydes having electron withdrawing groups resulted in excellent yield of the product in lesser reaction time as compared to the aldehydes having electron donating groups (which took more time for the reaction to complete). In the case of hydroxybenzaldehydes, the 4-substituted isomer was found to be more reactive as compared to the 2-substituted isomer due to steric hindrance in the case of the latter one (Table 3, entries 6 and 11). Heteroaromatic aldehydes were found to be less reactive towards the nucleophilic addition reaction (Table 3, entry 4). Aliphatic aldehydes were also investigated but they are less reactive as compared to aromatic and heteroaromatic aldehydes (Table 3, entries 14, 15, and 16). In the case of the aldehyde derivatives of pyridine, 2-substitued aldehyde derivatives of pyridine were found to be more reactive than 4-substituted aldehyde derivative and this could be due to the more pronounced inductive effect of the nitrogen atom at the ortho-position than at the para-position (Table 3, entries 7, and 8).

Similarly, in the case of the Hantzsch condensation, aldehydes with electron withdrawing groups (Table 4, entries 2,5 and 9) as well as those with electron donating groups resulted in the excellent yields of the polyhydroquinolines (Table 4, entries 3, 4 and 8). In the case of heteroaromatic aldehydes, like pyridine-2-aldehyde and thiophen-2-aldehyde, the desired products could be obtained in good yields (90–94%). Furthermore, as reported in the literature, it could be observed that in multicomponent reactions, aliphatic aldehydes were less reactive as compared to aromatic aldehydes. Hence, the yield of the product formed is lesser (Table 4, entries 12, and 13). The 1 H and 13 C NMR spectra of the synthesized products are provided in the ESI.† Based on these observations, it could be concluded

	R-CHO +	$\int_{0}^{0} + \int_{0}^{0} \int_{0}^{+} NH_{4}OA$	c		
Entry	Aldehyde	Product	Time (min)	Isolated yield (%)	TON (TOF)
1	CHO	COOEt	20	97	32 (95)
2	CHO		25	96	31 (75)
3	CH ₃ CHO	COOEt	15	98	32 (128)
4	OCH ₃ CHO	COOE OCH3	12	99	32 (162)
5			10	98	32 (192)
6	CI		22	96	31 (85)

	R-CHO +	0 + 0 0 $^{+}$ NH ₄ OA	water, 35°C		
Entry	Aldehyde	Product	Time (min)	Isolated yield (%)	TON (TOF)
7	OH CHO	H COOEt O OH	25	92	30 (72)
8	H ₃ C CHO	COOEt O CH3	22	95	31 (85)
9	Br		20	97	32 (95)
10	СНО		20	94	31 (92)
11	O ₂ N CHO		22	98	32 (87)
12			25	90	29 (70)
13			22	91	30 (82)

Reaction conditions: aldehyde (1 mmol), dimedone (1 mmol), ethyl acetoacetate (1 mmol), ammonium acetate (1 mmol), solvent (2 mL) and catalyst (10 mg).



Fig. 7 (a) Recyclability test for Fe₃O₄@SiO₂@DSiO₂-NH₂ in Knoevenagel and Hantzsch condensations. (b) TEM image of the recycled nanocatalyst after nine runs. (c) FT-IR spectra of the recycled (after nine runs) and fresh nanocatalysts. (d) Magnetization curve of the recycled nanocatalyst after nine runs.

that the $\rm Fe_3O_4@SiO_2@DSiO_2-NH_2$ nanocatalyst showed excellent catalytic activity towards both Knoevenagel as well as Hantzsch condensation.

Following completion of the reaction, the magnetic nanocatalyst could be easily recovered from the reaction mixture by using an external magnet followed by washing with ethanol. Since easy recyclability is stated to be a very important aspect for a sustainable process, the magnetically recoverable nanocatalyst could be further used for nine consecutive cycles without any significant loss in the catalytic activity (Fig. 7(a)). Slight changes in the morphology of the recycled nanocatalyst due to harsh reaction conditions in the nine consecutive cycles were observed, as shown in Fig. 7(b). The FT-IR spectrum of the recycled nanocatalyst after nine consecutive runs for synthesis of polyhydroquinolines is depicted in Fig. 7(c). It is observed that the peak at 2929 cm⁻¹ corresponds to $-CH_2$ stretching frequency of organosilane derivatives. Other peaks at 3342 cm^{-1} 1056 cm⁻¹ and 453 cm⁻¹ correspond to hydroxyl groups, Si-O-Si asymmetric stretching and Fe-O vibrations, respectively. This confirms that the diamine moieties remain attached to the solid support material. No sign of destruction of organic moieties was observed after the recycling procedure. The magnetization curve of the recycled nanocatalyst after nine consecutive runs is depicted in Fig. 7(d). From this curve it could be observed that the saturation magnetization of the recycled nanocatalyst decreases slightly *i.e.* from 17.20 emu g^{-1} to 16.25 emu g^{-1} . This confirms that the magnetization of the recycled nanocatalyst was maintained after catalyzing the reactions for nine consecutive cycles. These consequences reveal that the synthesized nanocatalyst was well constructed and could tolerate the reaction conditions. Hantzsch condensation requires harsh reaction conditions as compared to Knoevenagel condensation. Therefore, complete

Table 5Comparative study of $Fe_3O_4@SiO_2@DSiO_2-NH_2$ with previously reported catalysts for Knoevenagel condensation using 4-nitrobenzaldehydeand active methylene compounds

Entry	Catalyst	Catalyst amount	Time	Temperature (°C)	Solvent	Isolated yield (%)	Ref.
1	PMO-IL-NH ₂	0.5 mol %	90 min	RT	Solvent free	97	55
2	Fe ₃ O ₄ @SiO ₂ -PVAm	0.05 g	10 min	RT	Ethanol	98	56
3	Fe ₃ O ₄ @SiO ₂ -3N	5 mg	10 min	75 °C	Water	94	57
4	MSiO ₂ -NH ₂	20 mg	5 h	RT	Ethanol	95	58
5	Chitosan	25 mg	6 h	40 °C	Ethanol	90	59
6	WSiO ₂ -NH ₂	20 mg	100 min	RT	Ethanol	93	60
7	Fe ₃ O ₄ @SiO ₂ @DSiO ₂ -NH ₂	5 mg	5 min	25 °C	Water	99	This work

Table 6 Comparative study of Fe₃O₄@SiO₂@DSiO₂-NH₂ with previously reported catalysts using 4-nitro benzaldehyde, active methylene compounds and NH₄OAc

Entry	Catalyst	Catalyst amount	Time	Temp (°C)	Solvent	Isolated yield (%)	Ref.
1	La ₂ O ₃	10 mol%	85 min	RT	TFE	87	61
2	L-Proline	10 mol%	6 h	RT	Ethanol (reflux)	91	62
3	Ni(NO ₃) ₂ -imine/thiophene-Fe ₃ O ₄ @SiO ₂	20 mg	60 min	100 °C	Solvent-free	86	63
4	Pd(0) NPs	0.04 Equiv.	4 h	_	THF, reflux, Na ₂ CO ₃ , TBAB	92	64
5	Fe ₃ O ₄ @chitosan	0.03 g	40 min	RT	Ethanol	93	65
6	MCM-41	1 mol%	25 min	90 °C	Solvent-free	84	66
7	γ-Fe ₂ O ₃ /Cu@cellulose	3 mg	35 min	RT	Solvent-free	80	67
8	Fe ₃ O ₄ @SiO ₂ @PPh ₃ @Cr ₂ O ₇ ²⁻	0.003 g	25 min	RT	Solvent-free	80	68
9	Fe ₃ O ₄ @SiO ₂ @PPh ₃ @[CrO ₃ Br]	0.01 g	60 min	RT	Ethanol	93	69
10	Fe ₃ O ₄ @PEO-SO ₃ H	0.010 g	15 min	RT	Ethanol	94	70
11	Fe ₃ O ₄ @SiO ₂ @DSiO ₂ -NH ₂	10 mg	10 min	35 °C	H_2O	98	This work

recycle-characterization was done for the Hantzsch condensation to prove the stability of the synthesized nanocatalyst.

In order to investigate the efficacy of this catalyst, the results obtained in Knoevenagel and Hantzsch condensations were compared with those of the previously reported catalysts (Tables 5 and 6). It was found that as compared to the previously reported systems the catalytic efficiency of Fe₃O₄@SiO₂@DSiO₂-NH₂ was superior in terms of shorter reaction time, recyclability, temperature and excellent yield in green solvents. Hence, it could be said that the diamine-functionalized magnetic core-shell dendritic mesoporous silica (Fe₃O₄@SiO₂@DSiO₂-NH₂) could be used as a highly efficient and cost-effective catalyst for both Knoevenagel and Hantzsch condensations.

It was also found that $Fe_3O_4(@SiO_2(@DSiO_2-NH_2)$ was superior in comparison to other previously reported catalysts for the onepot synthesis of polyhydroquinolines. In the case of some of the catalysts there were certain limitations encountered during the extraction of product from the reaction mixture, while in the case of some other catalysts, there was difficulty faced in the separation of the catalysts (Table 6, entries 2, and 6) or they required longer reaction times, high amount of catalyst loading and higher reaction temperatures (Table 6, entries 3, 7, and 8) and often resulted in lower yields of products or required the use of organic solvents (Table 6 entries 1, 4 and 5).

Finally, in order to explore the leaching of the catalyst in the reaction mixture during the progress of Knoevenagel condensation,



Fig. 8 Proposed reaction mechanism for (a) Knoevenagel condensation and (b) Hantzsch condensation.

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a hot filtration test was carried out with 4-nitrobenzaldehyde and malononitrile as substrates for the model reaction. When half of the reaction was completed, the catalyst was magnetically separated from the reaction mixture and the reaction was allowed to continue for a considerable amount of time without the catalyst. It was found that, no further progress could be observed in the reaction. Similarly, for Hantzsch condensation 4-nitrobenzaldehyde, dimedone, ethyl acetoacetate and ammonium acetate are chosen as model substrates and the same procedure was repeated as before for the Knoevenagel condensation. From these observations, it was confirmed that there was no leaching of diamine groups from the nanocatalyst *i.e.* Fe_3O_4 @SiO₂@DSiO₂-NH₂ during the progress of the reaction.

5. Plausible mechanism

5.1. Knoevenagel condensation

A mechanism can be proposed for the synthesis of the Knoevenagel product through the nucleophile addition reaction using Fe₃O₄(a) SiO₂(a)DSiO₂–NH₂ as a heterogeneous base catalyst (Fig. 8(a)). In the first step, the –NH₂ group could abstract the proton from the active methylene compound. This could lead to the generation of negative charge over the active methylene compound, which could act as a nucleophile. Subsequently, the nucleophilic attack of this nucleophile on carbonyl carbon could lead to the formation of a β -hydroxyl compound (the Knoevenagel adduct) and finally the catalyst could be regenerated. This Knoevenagel adduct could ultimately lead to the formation of the product by the elimination of a molecule of water.

5.2. Hantzsch condensation

The multicomponent synthesis of biologically active 1,4polyhydroquinolines proceeds through different mechanistic pathways to the conventional ones. The synthesized nanocatalyst possesses magnetic core-shell dendritic mesoporous silica nanospheres with high surface area *i.e.* 571.30 m² g⁻¹. Therefore, more space is available deep inside dendrimers for successful incorporation of basic moieties over the magnetic core-shell dendritic mesoporous silica owing to more and more base immobilization. Due to the highly basic environment of the nanocatalyst the reaction proceeds very efficiently in just a few minutes. Also, there is more space available between the dendrimers for effective interaction of the reactant molecules on the surface of the catalyst. The synthesis of polyhydroquinolines occurs very efficiently by employing this high surface area nanocatalyst. A plausible mechanism for the Hantzsch reaction catalysed by Fe₃O₄@SiO₂@DSiO₂-NH₂ is depicted in Fig. 8(b). First of all, activated aldehyde could be attacked by the enol form of the dimedone, which could results in the formation of adduct-I. This is assumed to be facilitated through the synergistic interaction between diamine moieties and the surface silanol groups of the supported nanocatalyst. In another step, the active methylene compound (β -keto ester) could result in the formation of enamine (II) after reaction with ammonium acetate in the presence of the above said catalyst.

Ultimately, adduct (1) and intermediate (II) could generate intermediate (III) *via* a Michael addition reaction to form intermediate (III), which could result in the formation of the desired product through intramolecular cyclization and dehydration.

6. Conclusion

In conclusion, the present work describes the successful synthesis of Fe_3O_4 @SiO₂@DSiO₂-NH₂ nanospheres (with assured core-shell nanostructures and accessible dendritic mesoporous channels) by combining the co-precipitation, sol-gel approach and an oil-water biphasic stratification-coating strategy. The as-synthesized Fe_3O_4 @SiO₂@DSiO₂-NH₂ nanocatalyst displayed excellent catalytic activity for both Knoevenagel condensation and the one-pot synthesis of polyhydroquinolines. This could be due to the easy accessibility of active diamine sites and super paramagnetic nature of the prepared nanocatalyst. The prepared catalyst could be utilized for multiple catalytic cycles without any notable loss in the activity.

Conflicts of interest

There are no conflicts to declare.

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