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Synthesis of benzodiazepines catalyzed by $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-PrNH}_2$ nanoparticles as a reusable catalyst

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Abstract: $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-PrNH}_2$ nanoparticles have been used as an efficient catalyst for the preparation of benzodiazepines by multi-component reactions of 1,2-phenylenediamine, dimedone, different aldehydes or Meldrum's acid and isocyanides. This method provides several advantages including mild reaction conditions, the applicability to a wide range of substrates, the reusability of the catalyst and low catalyst loading.

Keywords: benzodiazepines; CoFe_2O_4 nanoparticles; heterogeneous catalyst; one-pot reaction.

1 Introduction

Benzodiazepines have emerged as a group of important heterocycles in organic and medicinal chemistry due to their potency and wide spectrum of biological activities including antimicrobial [1], anticancer [2], anti-anxiety [3], inhibitors of HIV protease [4] and antipsychotics [5]. These activities make benzodiazepines attractive targets in organic synthesis. The synthesis of benzodiazepines has been reported in the presence of diverse catalysts such as $\text{Hg}(\text{OTf})_2$ [6], organic acid [7], $\text{Yb}(\text{OTf})_3$ [8], ceric ammonium nitrate [9], $\text{Sc}(\text{OTf})_3$ [10], nano- $\text{Fe}_3\text{O}_4/\text{SiO}_2$ [11], $\text{Fe}_3\text{O}_4@\text{cellulose}$ composite [12], nano- $\text{Fe}_3\text{O}_4@\text{chitosan}$ [13] and nano- Fe_3O_4 [14]. Despite the use of these ways, there remains adequate purpose to offer a new way for an efficient, high yielding and mild approach to achieve such systems. The eco-compatibility and utilization of multicomponent reactions (MCRs) are enhanced when the multicomponent strategy is applied in conjugation

with a heterogeneous catalyst [15, 16]. The surface of magnetic nanoparticles (MNPs) can be functionalized simply through suitable surface modifications to provide the attachment of a variety of favorable functionalities. The expansion of surface modification of MNPs as significant candidates in the search for supporting catalysts is presently a subject of increasing interest [17, 18].

Herein, we report the use of $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-PrNH}_2$ NPs as an efficient catalyst for the preparation of benzodiazepines by multi-component reactions of 1,2-phenylenediamine, dimedone, different aldehydes or Meldrum's acid and isocyanides (Scheme 1).

2 Results and discussion

The particle size and morphology of $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-PrNH}_2$ NPs was determined by scanning electronic microscopy (SEM). The statistic of results from SEM images clearly demonstrates that the average size of $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-PrNH}_2$ is about 15–20 nm (Fig. S1, see Supplementary Information).

Figure S2 (see Supplementary Information) shows the powder X-ray diffraction (XRD) pattern. The pattern agrees well with the reported pattern for CoFe_2O_4 (JCPDS No. 22-1086). The crystallite size of $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-PrNH}_2$ NPs calculated by the Debye–Scherer equation is about 20 nm, which is in good agreement with the result obtained by SEM.

Figure S3 (see Supplementary Information) shows Fourier transform infrared (FT-IR) spectra of $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-PrNH}_2$ NPs. The bands at 464, 1079, 1628 and 3418 cm^{-1} are the characteristic absorptions of SiO_2 , which shows evidence for the formation of a silica shell. The presence of Co–O and Fe–O bonds in magnetic particles is confirmed by the characteristic peak appeared at 592 cm^{-1} . The intense and broad peaks near 1079 and 3400 cm^{-1} are characteristic absorption bands of the vibration of OH moieties, which overlap with the NH_2 vibrations. The enhancement of the bands at 1628 cm^{-1} provides direct evidence to verify the existence of the N–H deformation vibration [19].

Initially, we had explored and optimized different reaction parameters for the synthesis of benzodiazepines

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Scheme 1: Synthesis of benzodiazepines catalyzed by $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-PrNH}_2$ nanoparticles.

by the MCR of 1,2-phenylenediamine, dimedone and 4-chlorobenzaldehyde as a model reaction. Meanwhile, we carried out the MCR among 1,2-phenylenediamine, Meldrum's acid and *tert*-butyl isocyanide at room temperature as a model reaction in the presence of different catalysts (Table 1). These reactions were carried out in the presence of various catalysts, such as SiO_2 , CH_3COOH , $\text{CH}_3\text{SO}_3\text{H}$, CF_3COOH , triethylamine, MgO NPs, CuO NPs, *p*-toluene sulfonic acid (*p*-TSA), nano- CoFe_2O_4 , $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ and nano- $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-PrNH}_2$. The best results were obtained in the presence of nano- $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-PrNH}_2$. In order to optimize the reaction conditions, we performed the reaction using varied quantities of the catalyst. There was no difference in yield and reaction time when catalyst loading was enhanced to 30 mg.

To investigate the scope and limitation of this catalytic process, different aldehydes and isocyanides were chosen

as substrates (Table 2). The above results obviously show that the present catalytic procedure is extendable to a wide variety of substrates to construct a diversity-oriented library of benzodiazepines.

Reusability of the catalysts is one of the significant properties of every catalyst used in large-scale production. Therefore, the reusability of the heterogeneous catalyst was explored using the model reaction system under the optimized conditions. After completion of the reaction, the magnetic nanocatalyst is easily and efficiently separated from the product by an external magnetic field. The nano- $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-PrNH}_2$ was washed three to four times with ethanol and dried at room temperature for 5 h. The reusability of the nano-catalyst was examined for the synthesis of **4a**, and it was found that product yields decreased to a small extent on each reuse (run 1: 95%; run 2: 95%; run 3: 94%; run 4: 94%; run 5: 93%, run 6: 91%).

The proposed mechanism for the reaction is shown in Scheme 2. Initially, intermolecular imine formation from 1,2-phenylenediamine and dimedone promoted by the $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-PrNH}_2$ nanocatalyst occurs. The amino groups distributed on the surface of $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ activate the $\text{C}=\text{O}$ groups of dimedone through hydrogen bonding, and the amino group of 1,2-phenylenediamine attack the carbonyl group of dimedone with elimination of H_2O leading to imine intermediate **I**. A 1,3-hydrogen shift then results in isomeric form (tautomerized) to give enamine **II**. After this step, the other amino group of the 1,2-phenylenediamine part of enamine **II** attacks the carbonyl group of aldehyde, which is itself activated by the catalyst through hydrogen bonding to form intermediate **III**. Finally, the seven-membered ring products **4a-e** are afforded via intramolecular cyclization of **III** [13].

A possible mechanism for the formation of products **4'a-e** is shown in Scheme 3. It is conceivable that the initial event is the formation of intermediate **II** from a condensation reaction between *o*-phenylenediamine and Meldrum's acid. The amino groups distributed on

Table 1: Optimization of reactions conditions using different catalysts.

Entry	Catalyst	Time (min)	Yield (%)
		4a/4'a	4a/4'a
1	–	400/300	10/trace
2	SiO_2 NPs (5 mol%)	200/300	45/60
3	MgO NPs (3 mol%)	250/300	38/52
4	Triethylamine (20 mol%)	250/300	20/28
5	CuO NPs (3 mol%)	200/240	50/69
6	<i>p</i> -TSA (7 mol%)	200/300	55/45
7	$\text{CH}_3\text{SO}_3\text{H}$ (5 mol%)	80/300	65/52
8	CF_3COOH (3 mol%)	80/300	60/55
9	CoFe_2O_4 NPs (30 mg)	60/200	70/65
10	$\text{CoFe}_2\text{O}_4@\text{SiO}_2$ (30 mg)	60/200	75/71
11	$\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-PrNH}_2$ NPs (10 mg)	50/100	87/84
12	$\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-PrNH}_2$ NPs (20 mg)	50/100	95/92
13	$\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-PrNH}_2$ NPs (30 mg)	50/100	95 ^a /92 ^b

^aIsolated yield (reaction conditions: 1,2-phenylenediamine, dimedone and 4-chlorobenzaldehyde at room temperature in EtOH).

^bIsolated yield (reaction conditions: 1,2-phenylenediamine, Meldrum's acid and *tert*-butyl isocyanide at room temperature in CH_2Cl_2).

Table 2: Synthesis of benzodiazepines catalyzed by $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-PrNH}_2$ nanoparticles.

Entry	Product	Time (min)	Yield (%) ^a	M.p. (°C)	M.p. (°C) [ref.]
1	4a	50	95	234–236	237–238 [13]
2	4b	60	87	225–227	229–231 [20]
3	4c	55	90	240–242	246–248 [20]
4	4d	50	95	235–237	241–242 [20]
5	4e	53	92	230–232	232–233 [13]
6	4'a	100	92	>300	>300 [21]
7	4'b	120	86	286–288	286–288 [14]

Table 2 (continued)

Entry	Product	Time (min)	Yield (%) ^a	M.p. (°C)	M.p. (°C) [ref.]
8	4'c	110	88	304–306	306–308 [14]
9	4'd	110	92	>300	>300 [21]
10	4'e	110	90	280–282	–

^aIsolated yield. Scheme 2: Proposed reaction pathway for the synthesis of **4a–e**.

the surface of $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ activate the $\text{C}=\text{O}$ groups of Meldrum's acid and intermediate **I** through hydrogen bonding. Then, intermediate **II** under a Knoevenagel condensation reaction with *in situ* liberated acetone produces intermediate **III**. Then, isocyanides reacts with α,β -unsaturated carbonyl compound (intermediate **III**) to form intermediate **IV** (Michael-type addition reaction), followed by nucleophilic attack of a H_2O molecule on the nitrilium moiety to form the product [21]. In this mechanism, $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-PrNH}_2$ acts as a highly efficient and green catalyst activating the $\text{C}=\text{O}$, $\text{C}\equiv\text{N}^+$ groups for better

reaction with nucleophiles through hydrogen bonding [22, 23].

3 Conclusions

In conclusion, we have developed a straightforward and efficient method for the synthesis of benzodiazepines by multi-component reactions of 1,2-phenylenediamine, dimedone, different aldehydes or Meldrum's acid and

Scheme 3: Proposed reaction pathway for the synthesis of **4'a-e**.

isocyanides. The method offers several advantages including cleaner reaction profiles, easy availability, high yields, shorter reaction times, reusability of the catalyst and low catalyst loading.

4 Experimental section

All organic materials were purchased commercially from the Sigma-Aldrich and Merck and were used without further purification. All melting points are uncorrected and were determined in a capillary tube on a Boetius melting point microscope. FT-IR spectra were recorded with KBr pellets using a Magna-IR spectrometer 550 (Nicolet). NMR spectra were recorded on a Bruker 400 MHz spectrometer with dimethyl sulfoxide (DMSO) as solvent and tetramethylsilane (TMS) as an internal standard. Powder XRD was carried out on a Philips diffractometer of X'pert Company. Microscopic morphology of products was visualized by SEM (MIRA3 TESCAN).

4.1 Preparation of $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-PrNH}_2$ NPs

$\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-PrNH}_2$ NPs were prepared according to the method reported in the literature with some modifications [19]. CoFe_2O_4 NPs were prepared by a chemical

co-precipitation method using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ as precursors. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5.4 g) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (2.38 g) were dissolved in 100 mL distilled water. Then, the mixture solution was transferred into a three-necked flask equipped with a mechanical stirrer. Fifty milliliters of 3 mol/L NaOH solution was added into the flask under vigorous stirring. The mixture was heated to reflux for 1 h to yield a black dispersion. When the reaction had finished, the black product was washed with doubly distilled water for several times until the pH value of the solution became neutral. The black precipitate was separated by a permanent magnet, followed by washing three times with ethanol and drying at 100°C in a vacuum for 24 h.

Coating of a layer of silica on the surface of the CoFe_2O_4 NPs was achieved by pre-mixing (ultrasonic) a dispersion of the purified CoFe_2O_4 NPs (1 g) obtained previously with distilled water (80 mL) for 1 h at 40°C. A concentrated ammonia solution (1.5 mL) was added and the resulting mixture stirred at 40°C for 30 min. Subsequently, tetraethyl orthosilicate (1.0 mL) was charged to the reaction vessel and the mixture continuously stirred at 40°C for 24 h. The silica-coated NPs were collected using a permanent magnet, followed by washing three times with ethanol, diethyl ether and drying at 100°C in a vacuum for 24 h.

$\text{CoFe}_2\text{O}_4@\text{SiO}_2$ (1 g) was added to the solution of 3-aminopropyltriethoxysilane (2 mmol, 0.44 g) in dry toluene (20 mL) and refluxed for 24 h. After the reaction had finished, the aminated $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ were separated by a permanent magnet, washed with doubly distilled water and anhydrous ethanol, and dried at 80°C for 8 h to give the surface-bound amino group $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-PrNH}_2$.

4.2 General procedure for the preparation of benzodiazepines (**4a-e**)

A mixture of 1,2-phenylenediamine (1 mmol), dimedone (1 mmol), aldehyde (1 mmol) and $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-PrNH}_2$ nanocatalyst (20 mg) was stirred in EtOH (10 mL) at room temperature. After completion, as indicated by thin-layer chromatography (TLC) (EtOAc:n-hexane , 3:1), the catalyst was separated from the mixture using an external magnet, and the residue was washed with EtOH to give pure benzodiazepines **4a-e**.

4.3 General procedure for the preparation of benzodiazepines (**4'a-e**)

$\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-PrNH}_2$ NPs (20 mg) were added to a mixture of 1,2-phenylenediamines (1 mmol), Meldrum's acid (1 mmol)

and isocyanide (1 mmol) in 5 mL dichloromethane. The progress of the reaction was continuously monitored by TLC. After completion of the reaction the residue was dissolved in methanol and the nanocatalyst was separated by the use of an external magnet. The solvent was evaporated under vacuum and the solid obtained was washed several times with acetone to afford pure benzodiazepine.

4.4 Physical and spectroscopic data

4.4.1 3,3-Dimethyl-2,3,4,5,10,11-hexahydro-11-[(4-chloro)-phenyl]-1H-dibenzo[b,e][1,4]diazepin-1-one (4a)

Pale green solid, yield: 95%; m.p. 234–236°C. – IR (KBr): $\nu = 3302, 3237, 3055, 2957, 1587, 1382, 1534, 1328, 1425, 1276 \text{ cm}^{-1}$. – ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$): δ (ppm) = 1.02 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 2.12 (A.Bq, 2H, $J = 16.0 \text{ Hz}$, CH_2), 2.54 (s, 2H, CH_2CO), 4.96 (s, 1H, NH), 6.07 (s, 1H, CH), 6.46 (d, 1H, $J = 8.2 \text{ Hz}$, Ar), 6.54 (m, 3H, Ar), 6.85 (d, 1H, $J = 8.2 \text{ Hz}$, Ar), 6.97 (d, 2H, $J = 8.4 \text{ Hz}$, Ar), 7.01 (d, 1H, $J = 8.4 \text{ Hz}$, Ar), 8.61 (s, 1H, NH). – ^{13}C NMR (100 MHz, $[\text{D}_6]\text{DMSO}$): δ (ppm) = 28.16, 28.69, 32.25, 44.85, 49.90, 56.43, 109.38, 120.62, 120.73, 121.05, 123.11, 123.29, 128.36, 131.45, 138.07, 146.08, 150.02, 152.06, 192.82. – Analysis for $\text{C}_{21}\text{H}_{21}\text{ClN}_2\text{O}$: Calcd. C 71.48, H 6.00, N 7.94; found C 71.54, H 6.09, N 7.95.

4.4.2 3,3-Dimethyl-2,3,4,5,10,11-hexahydro-11-[(2-chloro)-phenyl]-1H-dibenzo[b,e][1,4]diazepin-1-one (4e)

White solid; yield: 92%; m.p. 230–232°C. – IR (KBr): $\nu = 3293, 3236, 3064, 2958, 1586, 1383, 1517, 1317, 1424, 1279 \text{ cm}^{-1}$. – ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$): δ (ppm) = 1.02 (s, 3H, CH_3), 1.06 (s, 3H, CH_3), 2.08 (A.Bq, 2H, $J = 16.0 \text{ Hz}$, CH_2), 2.52 (s, 2H, CH_2CO), 5.72 (s, 1H, NH), 5.75 (s, 1H, CH), 6.35 (d, 1H, $J = 7.2 \text{ Hz}$, Ar), 6.45–6.65 (m, 2H, Ar), 6.72 (d, 1H, $J = 7.6 \text{ Hz}$, Ar), 6.83 (d, 1H, $J = 7.6 \text{ Hz}$, Ar), 6.86–7.02 (m, 2H, Ar), 7.20 (d, $J = 7.6 \text{ Hz}$, 1H, Ar), 8.53 (s, 1H, NH). – ^{13}C NMR (100 MHz, $[\text{D}_6]\text{DMSO}$): δ (ppm) = 28.15, 28.73, 32.25, 44.85, 49.87, 56.43, 109.33, 120.61, 120.65, 121.14, 123.14, 123.43, 126.11, 128.53, 128.62, 131.42, 138.05, 146.07, 149.59, 151.08, 192.83. – Analysis for $\text{C}_{21}\text{H}_{21}\text{ClN}_2\text{O}$: Calcd. C 71.48, H 6.00, N 7.94; found C 71.51, H 6.10, N 7.90.

4.4.3 N-tert-butyl-2-(2,3,4,5-tetrahydro-2,4-dioxo-1H-benzo[b][1,4]diazepin-3-yl)-2-methylpropanamide (4'a)

White powder, yield: 92%; m.p. >300°C. – IR (KBr): $\nu = 3387, 2967, 2902, 1691, 1646, 1601, 1528 \text{ cm}^{-1}$. – ^1H NMR

(400 MHz, $[\text{D}_6]\text{DMSO}$): δ (ppm) = 1.21 (9H, s, $\text{C}(\text{CH}_3)_3$), 1.37 (6H, s, 2CH_3), 3.18 (1H, s, CH), 6.15–7.15 (5H, bs, 4H-Ar and –NH), 10.38 (2H, bs, 2NH). – ^{13}C NMR (100 MHz, $[\text{D}_6]\text{DMSO}$): δ (ppm) = 23.12 (2CH_3), 28.92 ($\text{C}(\text{CH}_3)_3$), 43.63 (CH), 50.42 (C), 55.10 (C), 122.42, 125.41, 130.32, 167.12, 177.30 (2 CO). – Analysis for $\text{C}_{17}\text{H}_{23}\text{N}_3\text{O}_3$: C 64.33, H 7.30, N 13.24; found: C 63.90, H 7.26, N, 13.09.

4.4.4 2-(2,3,4,5-Tetrahydro-2,4-dioxo-1H-benzo[b][1,4]diazepin-3-yl)-N-(4-methoxy-3-methyl phenyl)-2-methylpropanamide (4'e)

White powder, yield: 90%; m.p. 280–282°C. – IR (KBr): $\nu = 3448, 1705, 1662, 1518, 1246 \text{ cm}^{-1}$. – ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$): δ (ppm) = 1.51 (s, 6H, 2CH_3), 2.29 (s, 3H, CH_3), 3.44 (s, 1H, CH), 3.89 (s, 3H, OCH_3), 6.99–7.55 (m, 7H, ArH), 8.18 (bs, 1H, NH), 10.37 (bs, 2H, 2NH). – ^{13}C NMR (100 MHz, $[\text{D}_6]\text{DMSO}$): δ (ppm) = 19.92, 42.70, 43.62, 55.22, 56.84, 122.73, 123.75, 125.56, 128.58, 130.84, 131.52, 135.32, 136.63, 138.45, 142.25, 167.77, 169.84.

5 Supplementary information

Some characteristics of the $\text{CoFe}_2\text{O}_4@\text{SiO}_2\text{-PrNH}_2$ nanoparticles and copies of the ^1H NMR spectra of the products are given in the Supplementary Information available online (DOI: 10.1515/znb-2017-0023).

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