Heterocyclic Letters
Vol. 7| No.4|1035-1043|Aug-Oct|2017
ISSN : (print) 2231–3087 / (online) 2230-9632
CODEN: HLEEAI
http://heteroletters.org

NANO MAGNETIC ZIRCONIA PHOSPHORIC ACID AS AN EFFICIENT AND RECYCLABLE CATALYST FOR THE CLEAN SYNTHESIS OF BISCOUMARINS

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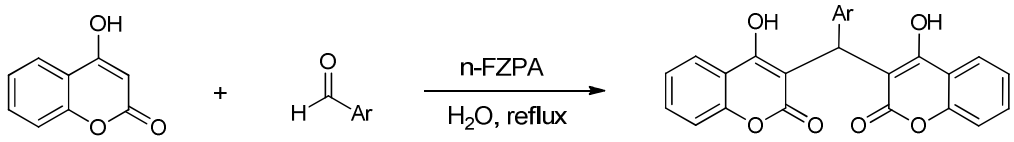
ABSTRACT
Core–shell zirconia-coated magnetite nanoparticle bearing phosphoric acid groups (nano-Fe_3O_4@ZrO_2-H_3PO_4) have been prepared and used as an efficient acid catalyst in the synthesis of biscoumarin derivatives by the reaction of 4-hydroxycoumarin and aromatic aldehydes. The results showed that Fe_3O_4@ZrO_2-H_3PO_4 nanoparticles exhibited high catalytic activity towards the synthesis of biscoumarin derivatives. Furthermore, this new catalytic method for the synthesis of biscoumarins provides rapid access to the desired compounds in high yields in presence of water as the solvent at reflux condition following a simple work-up procedure. This method therefore represents a significant improvement over the methods currently available for the synthesis of biscoumarin derivatives.

KEYWORDS: nano-Fe_3O_4@ZrO_2-H_3PO_4, heterogeneous catalyst, reusability, clean synthesis, biscoumarines,

INTRODUCTION
Coumarins are a large group of heterocycles with diverse and interesting biological activities. These compounds are reported to possess significant anticoagulant, insecticidal, antihelminthic, hypnotic, antifungal, and HIV protease inhibition activities[i]. Biscoumarins, the bridge substituted dimers of 4-hydroxycoumarin, have enormous potential as anticoagulants[ii]. A number of biscoumarins have also been found to be urease inhibitors[iii]. The synthesis of biscoumarins is succeeded *via* a domino Knoevenagel−Michael reaction between 4-hydroxycoumarin and aromatic aldehydes, and various procedures involving different solvents and catalysts such as some Brønsted-acidic ionic liquids[iv-vi], TiO_2-SO_3H[vii], $[TBA]_2[W_6O_{19}]$[viii], $RuCl_3.nH_2O$[ix], I_2[x], RHA-SO_3H[xi], Alum [$KAl(SO_4)_2.12H_2O$}[xii], Nano isopolyoxomolybdate[xiii]. Most of these methodologies suffer from disadvantages such as unsatisfactory yields, toxic organic solvents, harsh reaction conditions, long reaction times, and the use of relatively expensive reagents. These findings prompted us to perform investigations to find new method for the synthesis of biscoumarin derivatives[ix-xiii].

The current research work is the development of our earlier studies of reusable catalysts for the synthesis of organic compounds[xiii-xxviii]. We report here nano-Fe_3O_4@ZrO_2-H_3PO_4 (n-FZPA) as a green catalyst for the synthesis of biscoumarins **3a–m** by one-pot reaction between 4-hydroxycoumarin **1** and various aromatic aldehydes **2a–m**, in water under reflux condition (Scheme 1).



1 **2a-m** **3a-m**

Ar = Ph (**a**), 4-$MeOC_6H_4$ (**b**), 4-MeC_6H_4 (**c**), 4-$O_2NC_6H_4$ (**d**), 3-$O_2NC_6H_4$ (**e**), 4-ClC_6H_4 (**f**), 2-ClC_6H_4 (**g**), 2,4-$Cl_2C_6H_3$ (**h**), 4-BrC_6H_4 (**i**), 3-BrC_6H_4 (**j**), 4-FC_6H_4 (**k**), 4-NCC_6H_4 (**l**), 4-HOC_6H_4 (**m**)

Scheme 1. n-FZPA catalyzed synthesis of biscoumarins.

EXPERIMENTAL

All chemicals employed in this work were purchased from Fluka (Buchs, Switzerland) or Merck Companies and were utilized without further purification. The n-FZPA catalyst were characterized by X-ray diffraction (XRD) (Bruker D8 Advance) using Cu-Kα radiation (λ=1.5406 Å). The FT-IR spectra of the products were obtained with KBr disks, using a Tensor 27 Bruker spectrophotometer. The ^{1}H NMR spectra were recorded using Bruker 400 spectrometers in $CDCl_3$.

General experimental procedure

A mixture of 4-hydroxycoumarin (2 mmol), aromatic aldehyde, and n-FZPA (0.05 g) was placed in a round bottomed flask. The materials were mixed and refluxed in water (5 ml) for appropriate time. The progress of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, the catalyst was separated using an external magnet and washed with hot ethanol (10 mL). The solvent of the reaction mixture was concentrated by half and allowed to stand at room temperature. The precipitated solid was collected by filtration, and recrystallized from ethanol 96% to give desired compounds in high yields.

^{1}H NMR and FT-IR data:

3,3'-(phenylmethylene)bis(4-hydroxy-2*H*-chromen-2-one) (3a)[xxxvi] IR spectrum, ν, cm^{-1}: 3437, 3023, 1659, 1601, 1557, 1488, 1359, 1258, 1093, 764. ^{1}H NMR spectrum, δ, ppm: 6.15 s (1H, CH), 7.24 d (2H, *J* = 7.4 Hz, H_{arom}), 7.31 t (1H, *J* = 5.3 Hz, H_{arom}), 7.35 t (2H, *J* = 7.2 Hz, H_{arom}), 7.35–7.47 m (4H, H_{arom}), 7.64 t (2H, *J* = 7.2 Hz, H_{arom}), 8.05– 8.20 m (2H, H_{arom}), 11.31 s (1H, OH), 11.53 s (1H, OH).

3,3'-((4-methoxyphenyl)methylene)bis(4-hydroxy-2*H*-chromen-2-one) (3b)[xxxvi] IR spectrum, ν, cm^{-1}: 3431, 3074, 1666, 1600, 1562, 1518, 1358, 1262, 1088, 779. ^{1}H NMR spectrum, δ, ppm: 3.85 s (3H, OCH_3), 6.12 s (1H, CH), 6.84 d (2H, *J* = 8.4 Hz, H_{arom}), 7.13 d (2H, *J* = 8.4 Hz, H_{arom}), 7.33–7.52 m (4H, H_{arom}), 7.64 t (2H, *J* = 7.5 Hz, H_{arom}), 8.00–8.15 m (2H, H_{arom}), 11.35 s (1H, OH), 11.56 s (1H, OH).

3,3′-((4-methylphenyl)methylene)bis(4-hydroxy-2*H*-chromen-2-one) (3c)[xxxvii] IR spectrum, ν, cm^{-1}: 3427, 3043, 2991, 1669, 1603, 1571, 1483, 1356, 1311, 1075, 772. ^{1}H NMR spectrum, δ, ppm: 2.33 s (3H, CH_3), 6.12 s (, 1H, CH), 7.12 q (4H, *J* = 8.2 Hz, H_{arom}), 7.35–7.43 m (4H, H_{arom}), 7.61 td (2H, *J* = 8.4, 1.4 Hz, H_{arom}), 8.08 d (1H, *J* = 7.4 Hz, H_{arom}), 8.13 d (1H, *J* = 7.4 Hz, H_{arom}), 11.35 s (1H, OH), 11.55 s (1H, OH).

3,3′-((4-nitrophenyl)methylene)bis(4-hydroxy-2*H*-chromen-2-one) (3d)[xxxvi] IR spectrum, ν, cm^{-1}: 3422, 3057, 1653, 1601, 1566, 1497, 1456, 1354, 1278, 1100, 788. ^{1}H NMR spectrum, δ, ppm: 6.16 s (1H, CH), 7.43–7.50 m (6H, H_{arom}), 7.68 t (2H, *J* = 7.4 Hz, H_{arom}),

8.09 d (1H, *J* = 7.4 Hz, H_{arom}), 8.17 d (1H, *J* = 8.2 Hz, H_{arom}), 8.25 d (2H, *J* = 8.5 Hz, H_{arom}), 11.42 s (1H, OH), 11.63 s (1H, OH).

3,3'-((3-nitrophenyl)methylene)bis(4-hydroxy-2*H*-chromen-2-one) (3e)[xxxvi] IR spectrum, ν, cm^{-1}: 3423, 3051, 1646, 1619, 1569, 1493, 1451, 1352, 1314, 1126, 779. ^{1}H NMR spectrum, δ, ppm: 6.14 s (1H, CH), 7.39–7.45 m (4H, H_{arom}), 7.55 t (1H, *J* = 7.6 Hz, H_{arom}), 7.63 d (1H, J = 7.4 Hz, H_{arom}), 7.72 t (2H, *J* = 7.6 Hz, H_{arom}), 8.08 d (1H, *J* = 8.1 Hz, H_{arom}), 8.12–8.15 m (2H, H_{arom}), 8.18 d (1H, *J* = 8.1 Hz, H_{arom}), 11.39 s (1H, OH), 11.59 s (1H, OH).

3,3′-((4-chlorophenyl)methylene)bis(4-hydroxy-2*H*-chromen-2-one) (3f)[xxxvi] IR spectrum, ν, cm^{-1}: 3432, 3076, 1672, 1621, 1565, 1493, 1456, 1348, 1315, 1089, 762. ^{1}H NMR spectrum, δ, ppm: 6.11 s (1H, CH), 7.15 dd (2H, *J* = 8.5, 0.8 Hz, H_{arom}), 7.34 d (2H, *J* = 8.5 Hz, H_{arom}), 7.36–7.47 m (4H, H_{arom}), 7.61–7.66 m (2H, H_{arom}), 7.95 d (1H, *J* = 7.2 Hz, H_{arom}), 8.13 d (1H, *J* = 7.2 Hz, H_{arom}), 11.39 s (1H, OH), 11.58 s (1H, OH).

3,3′-((2-chlorophenyl)methylene)bis(4-hydroxy-2*H*-chromen-2-one) (3g)[xxxvi] IR spectrum, ν, cm^{-1}: 3433, 3081, 1650, 1559, 1491, 1477, 1341, 1299, 1272, 1103, 777. ^{1}H NMR spectrum, δ, ppm: 6.13 s (1H, CH), 7.25–7.45 m (7H, H_{arom}), 7.45 d (1H, *J* = 7.3 Hz, H_{arom}), 7.63 td (2H, *J* = 7.5, 1.2 Hz, H_{arom}), 8.05–8.20 m (2H, H_{arom}), 11.31 s (1H, OH), 11.63 s (1H, OH).

3,3'-((2,4-dichlorophenyl)methylene)bis(4-hydroxy-2*H*-chromen-2-one) (3h)[xxxvi] IR spectrum, ν, cm^{-1}: 3429, 3078, 1646, 1562, 1503, 1473, 1342, 1300, 1273, 1098, 776. ^{1}H NMR spectrum, δ, ppm: 6.13 (1H, s, CH), 7.25 td (2H, *J* = 8.4, 1.7 Hz, H_{arom}), 7.41 td (2H, *J* = 6.3, 1.7 Hz, H_{arom}), 7.43 d (2H, *J* = 8.2 Hz, H_{arom}), 7.45 s (1H, H_{arom}), 7.63 td (2H, *J* = 8.4, 1.5 Hz, H_{arom}), 8.10 d (2H, *J* = 6.2 Hz, H_{arom}), 11.39 s (1H, OH), 11.58 s (1H, OH).

3,3'-((4-bromophenyl)methylene)bis(4-hydroxy-2*H*-chromen-2-one) (3i)[xiii] IR spectrum, ν, cm^{-1}: 3433, 3081, 1642, 1567, 1511, 1471, 1340, 1310, 1267, 1099, 779. ^{1}H NMR spectrum, δ, ppm: 6.04 s (1H, CH), 7.12 d (2H, *J* = 8.4 Hz, H_{arom}), 7.39–7.47 m (6H, H_{arom}), 7.65–7.69 m (2H, H_{arom}), 8.01–8.10 m (2H, H_{arom}), 11.35 s (1H, OH), 11.56 s (1H, OH).

3,3′-((3-bromophenyl)methylene)bis(4-hydroxy-2*H*-chromen-2-one) (3j)[xiii] IR spectrum, ν, cm^{-1}: 3433, 3071, 1663, 1616, 1555, 1492, 1473, 1353, 1319, 1090, 773. ^{1}H NMR spectrum, δ, ppm: 6.11 s (1H, CH), 7.17–7.47 m (9H, H_{arom}), 7.65– 7.75 m (2H, H_{arom}), 8.07 d (1H, *J* = 8.4 Hz, H_{arom}), 8.13 d (1H, *J* = 8.4 Hz, H_{arom}), 11.35 s (1H, OH), 11.65 s (1H, OH).

3,3′-((4-fluorophenyl)methylene)bis(4-hydroxy-2*H*-chromen-2-one) (3k)[xxxvi] IR spectrum, ν, cm^{-1}: 3456, 3062, 1678, 1558, 1512, 1451, 1358, 1311, 1101, 769. ^{1}H NMR spectrum, δ, ppm: 6.09 (s, 1H, CH), 7.08 t (2H, *J* = 8.2 Hz, H_{arom}), 7.18–7.24 m (2H, H_{arom}), 7.40–7.50 m (4H, H_{arom}), 7.64 td (2H, *J* = 8.1, 1.2 Hz, H_{arom}), 8.05 d (1H, *J* = 7.4 Hz, H_{arom}), 8.13 d (1H, *J* = 7.4 Hz, H_{arom}), 11.34 s (1H, OH), 11.56 s (1H, OH).

4-(bis(4-hydroxy-2-oxo-2*H*-chromen-3-yl)methyl)benzonitrile (3l)[ix] IR spectrum, ν, cm^{-1}: 3425, 3066, 1652, 1623, 1548, 1489, 1462, 1343, 1321, 1111, 782. ^{1}H NMR spectrum, δ, ppm: 6.12 s (1H, CH), 7.37–7.47 m (6H, H_{arom}), 7.64–7.71 m (4H, H_{arom}), 8.02 d (1H, *J* = 7.4 Hz, H_{arom}), 8.11 d (1H, *J* = 8.1 Hz, H_{arom}), 11.38 s (1H, OH), 11.57 s (1H, OH).

3,3'-((4-hydroxyphenyl)methylene)bis(4-hydroxy-2*H*-chromen-2-one) (3m)[xxxvi] IR spectrum, ν, cm^{-1}: 3427, 3098, 1662, 1629, 1551, 1491, 1460, 1341, 1331, 1101, 788. ^{1}H NMR spectrum, δ, ppm: 5.61 s (1H, OH), 6.05 s (1H, CH), 6.80 d (2H, *J* = 8.2 Hz, H_{arom}), 7.11 d (2H, *J* = 8.2 Hz, H_{arom}), 7.40–7.45 m (4H, H_{arom}), 7.63 t (2H, *J* = 8.2 Hz, H_{arom}), 8.00–8.05 m (2H, H_{arom}), 11.31 s (1H, OH), 11.48 s (1H, OH).

RESULTS AND DISCUSSION

To begin our study, the n-FZPA catalyst was prepared according to the literature procedure[xxix]. The n-FZPA was characterized by FT-IR, X-ray diffraction (XRD), thermal gravimetric (TG), and pH analysis.

The FT-IR spectrums of nano-ZrO_2, nano-Fe_3O_4, nano-Fe_3O_4@ZrO_2, and nano-Fe_3O_4@ZrO_2-H_3PO_4 are shown in Figure 1. In Figure 1(a), the characteristic vibrational bands of the Zr–O bond related to the ZrO_2 appears at 576 and 758 cm^{-1}, as well band belonging to the Zr–OH group at 1622 cm^{-1}[xxx]. The characteristic absorption band of Fe_3O_4 appears at 585 cm^{-1} in Figure 1(b). The spectrum of the Fe_3O_4@ZrO_2 nanoparticles (Figure 1(c)) shows a new absorption peak related to the characteristic absorption of zirconia at 629 cm^{-1} which confirmed the successful formation of Fe_3O_4@ZrO_2 nanoparticles[xxxi]. The FT-IR spectrum of the n-FZPA catalyst prepared in the current study revealed new bonds at 900–1400, 1627, and 3000–3600 cm^{-1} corresponding to the characteristic absorption of the P–O, P=O, and P–O–H stretching vibration of the phosphoric acid, respectively[xxxii].

The XRD patterns of the prepared nano-Fe_3O_4, nano-Fe_3O_4@ZrO_2, and nano-Fe_3O_4@ZrO_2-H_3PO_4 are presented in Figure 2. In Figure 2(a), the signals at the values of 2θ equal to 30.13° (220), 35.21° (311), 43.32° (400), 53.49° (422), 55.79° (511) and 62.91° (440) corresponds to cubic structure of Fe_3O_4 and has good agreement with (JCPDS file PDF no. 65-3107)[xxxiii]. The XRD pattern of the nano-Fe_3O_4@ZrO_2 sample shows peaks at 31.32° and 36.22° belong to Fe_3O_4 which have shifted from 30.13° and 35.21°, respectively. Besides the peaks for Fe_3O_4, two small nonmagnetic related peaks located in 50.88° and 61.02° are found which can be indexed to the diffraction of (112) and (211) planes of the standard data for ZrO_2 (JCPDS file no. 88-1007)[xxxiv]. The peaks position of n-FZPA unchanged during modification by H_3PO_4 shows that the crystalline structure of the core-shell nanomagnetic is maintained after functionalization.

The TG curves of nano-Fe_3O_4@ZrO_2, and nano-Fe_3O_4@ZrO_2-H_3PO_4 are shown in Figure 3. In the TG curve of nano-Fe_3O_4@ZrO_2 (Figure 3(a)) Two-stage decomposition is seen corresponding to different mass lose ranges. In the first region, a mass loss approximately 6% weight occurred below 120 °C is attributable to the loss of trapped water, organic solvents, and surface hydroxyl groups. A mass loss of approximately 1% weight occurred lower than 750 °C possibly related to the slow mass loss of dehydroxylation of ZrO_2. The TG curve of n-FZPA (Figure 3(b)) was divided into several regions relating to different mass lose ranges. The first region, which occurred below 110 °C, shown a mass loss 7% weight that is attributable to the evaporation of the H_2O, and organic solvents molecules adsorbed onto the surface and the release of the structural water resulted from the bonded hydroxyl groups. The mass loss of approximately 16% weight occurred between 110 and 160 °C is related to the slow mass loss of PO_3H_2 groups. Finally, the mass loss of approximately 7 % weight occurred between 160 and 280 °C is related to the sudden loss of PO_3H_2 groups[xxxv]. From the TG, it can be concluded that the prepared catalyst could be safety used in organic reactions in the range of 80-180 °C.

The density of the PO_3H_2 groups was measured using NaOH (0.08 N) as titrant by acid-base potentiometric titration. The amount of PO_3H_2 in the catalyst was 2.7 mmol/g.

Evaluation of catalytic activity of n-FZPA in the synthesis of biscoumarins.

Different reaction parameters were optimized for the synthesis of compound **3e** by the one-pot two-component reaction of 4-hydroxycoumarin **1** (2 mmol), and 4-chlorobenzaldehyde **2e** (1 mmol), as a model reaction in the absence and presence of n-FZPA as catalyst. The results are summarized in Table 1. Only trace amounts of the product 3e was formed in the absence of the catalyst in refluxing H_2O or EtOH and also under solvent-free conditions (Entries 1–3) indicating that the catalyst is necessary for the reaction. Several reactions were scrutinized using various solvents, such as H_2O, EtOH, MeOH, CH_3CN, CH_2Cl_2, and also under solvent-free conditions in the presence of n-FZPA as catalyst. As can be seen in Table 1, presence of solvent is necessary for the reaction and also polar solvents are better than other non-polars. Therefore, the best yield of this reaction (97%) obtained in the presence of 0.05 g of n-FZPA

and 5 mml of H_2O as solvent under reflux conditions to afford the desired product 3e in 14 min (entry 6). All subsequent reactions were carried out in these optimized conditions.

Table 1. Optimization of reaction conditions for the synthesis of compound **3e** catalyzed by n-FZPA*.

Entry	Catalyst (g)	Solvent	T/°C	Time/min	Isolated Yield/%
1	None	EtOH	Reflux	60	29
2	None	H_2O	Reflux	60	42
3	None	Solvent-free	110	150	23
4	0.05	Solvent-free	110	100	31
5	0.03	H_2O	Reflux	30	92
6	**0.05**	**H_2O**	**Reflux**	**14**	**97**
7	0.07	H_2O	Reflux	20	95
8	0.05	H_2O	80	40	90
9	0.05	H_2O	r.t.	40	82
10	0.03	EtOH	Reflux	35	86
11	0.05	EtOH	Reflux	30	92
13	0.05	MeOH	Reflux	30	84
15	0.05	CH_3CN	Reflux	30	78
16	0.05	CH_2Cl_2	Reflux	30	47

* Reaction conditions: 4-hydroxycoumarin **1** (2 mmol), and 4-chlorobenzaldehyde **2e** (1 mmol).

According to these results, and in order to generalize this model reaction, we developed the reaction of 4-hydroxycoumarin, and various aromatic aldehydes under the optimized reaction conditions (Table 2). The n-FZPA efficiently catalyzed the reactions, giving the products 3a-3m in high yields over relatively short reaction times. Easy separation of obtained products from the catalyst makes this method useful for the synthesis of biscomarin derivatives. Purity and structure of all known products checks with TLC, melting points, and ^{1}H NMR spectroscopic data reveal that only one product is formed in all cases and no undesirable side-products are observed.

Table 2. n-FZPA catalyzed synthesis of biscoumarin derivatives[a].

Entry	**Ar**	**Product[b]**	**Time/min**	**Isolated Yield/%**	**m.p. (°C)**	
					Found	**Reported**
1	Ph	**3a**	14	91	230-232	229-231[xxxvi]
2	4-$MeOC_6H_4$	**3b**	13	92	251-253	250-253[xxxvi]
3	4-MeC_6H_4	**3c**	15	96	270-272	269-270[xxxvii]
4	4-$O_2NC_6H_4$	**3d**	16	95	231-233	233-235[xxxvi]
5	3-$O_2NC_6H_4$	**3e**	14	96	213-215	215-217[xxxvi]
6	4-ClC_6H_4	**3f**	12	97	260-262	262-264[xxxvi]
7	2-ClC_6H_4	**3g**	16	89	200-202	202-204[xxxvi]
8	2,4-$Cl_2C_6H_3$	**3h**	13	93	197-199	198-200[xxxvi]
9	4-BrC_6H_4	**3i**	15	93	265-267	266-268[xxxvi]
10	3-BrC_6H_4	**3j**	11	89	287-289	286-288[xiii]
11	4-FC_6H_4	**3k**	13	94	210-212	211-213[xxxvi]
12	4-NCC_6H_4	**3l**	15	95	242-244	240-242[ix]
13	4-HOC_6H_4	**3m**	16	88	195-197	194-196[xxxvi]

[a]Reaction conditions: 4-hydroxycoumarin **1** (2 mmol), aldehyde **2a–m** (1 mmol), n-FZPA (0.05 g), water (5 mL), reflux.

[b]All the products were characterized by their FT-IR and ^{1}H NMR spectral data and by comparison of their melting points with those of authentic samples.

We also used the model reaction under optimized reaction conditions to evaluate the reusability of the n-FZPA catalyst. After completion of the reaction, the catalyst was recovered as described in the experimental section. The separated catalyst was dried at 50 ºC under vacuum for 1 h before being reused in a similar reaction. The catalyst could be used at least four times without significant reduction in its activity (97, 95, 94, 94 % yields in first to fourth use, respectively) which clearly demonstrates the practical reusability of this catalyst. Furthermore, the FT-IR spectra of the fourth run recovered catalysts (Figure 1(e)) were almost identical to the spectrum of the fresh catalyst (Figure 1(d)), indicating that the structure of the catalyst was unchanged by the reaction.

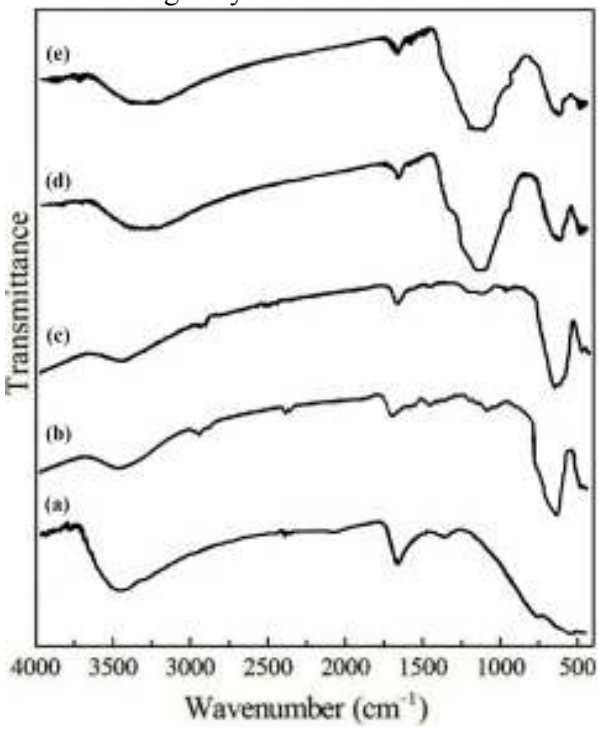


Figure 1. FT-IR spectra of nano-ZrO_2 (a) nano-Fe_3O_4 (b) nano-Fe_3O_4@ZrO_2 (c) nano-Fe_3O_4@ZrO_2-H_3PO_4 (first run (d)) nano-Fe_3O_4@ZrO_2-H_3PO_4 (fourth run (e))

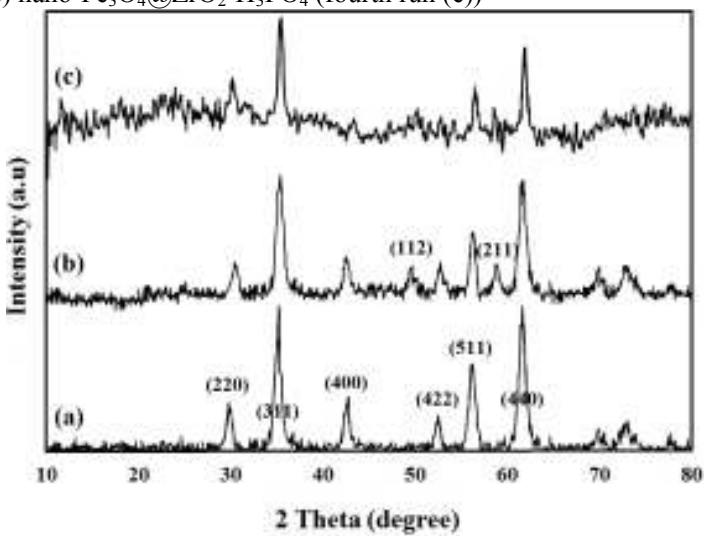


Figure 2. XRD patterns of nano-Fe_3O_4 (a) nano-Fe_3O_4@ZrO_2 (b) and nano-Fe_3O_4@ZrO_2-H_3PO_4 (c)

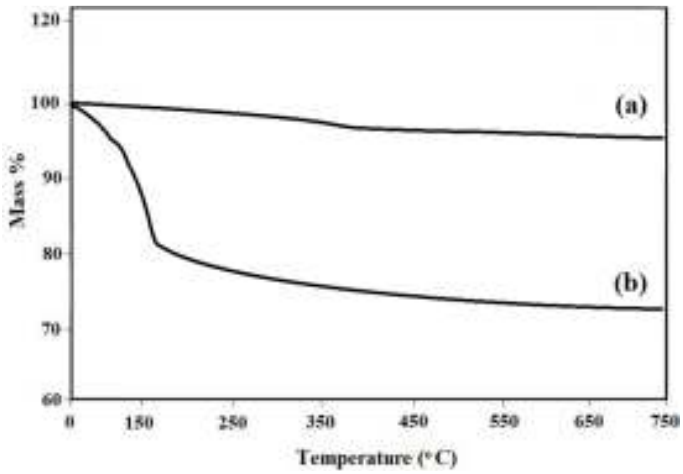
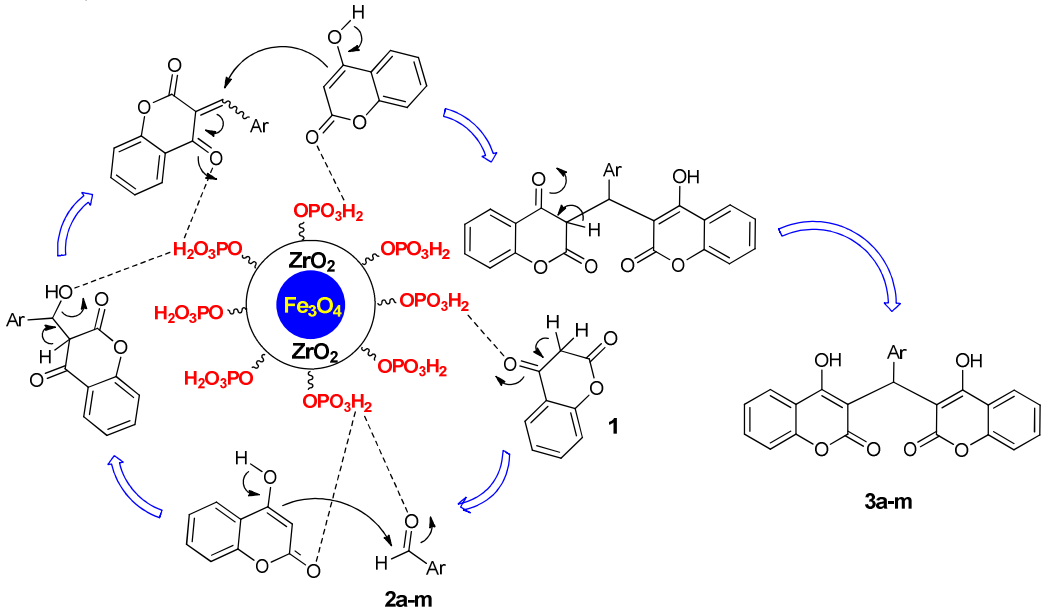


Figure 3. Thermal gravimetric (TG) analysis of nano-Fe_3O_4@ZrO_2 (a), and nano-Fe_3O_4@ZrO_2–H_3PO_4 (b)

Mechanistically, it is possible that the catalyst could acts as Brönsted acid related to the –PO_4H_2 groups and therefore promote the necessary reactions. The catalyst would play a significant role in increasing the electrophilic character of the electrophiles in the reaction (Scheme 2).



Scheme 2. Plausible mechanism for the n-FZPA catalyzed formation of biscoumarin derivatives

CONCLUSION

In summary, we showed that n-FZPA, efficiently catalyzed the synthesis of biscoumarin derivatives by the two-component reaction of 4-hydroxycoumarin, and aromatic aldehydes in water as green solvent under reflux condition. The method was relatively fast and high yielding, and the work-up was easy. The catalyst can be recycled after simple handling, and used at least fourth times without any substantial reduction in its catalytic activity. The procedure is also advantageous in the sense that it is a fast reaction in refluxing water and

therefore operates under environmentally friendly conditions. Also, easy magnetic separation makes this catalyst attractive in view of green chemistry and catalysis science.

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Received on September 5, 2017.