FULL PAPER



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Fe₃O₄@MCM-41@ZrCl₂: A novel magnetic mesoporous nanocomposite catalyst including zirconium nanoparticles for the synthesis of 1-(benzothiazolylamino)phenylmethyl-2-naphthols

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The present article reports the synthesis of a new magnetic mesoporous nanocomposite with core-shell structure, formulated as Fe₃O₄@MCM-41@ZrCl₂. The prepared reagent was successfully characterized using different types of methods. The combination of unique properties of MCM-41 as an inimitable mesoporous compound, satisfying magnetic nature of the Fe₃O₄ magnetic nanoparticles and substantial catalytical applications of zirconium, caused the favorable efficiency of the intended nanocomposite in the synthesis of 1-(benzothiazolylamino)phenylmethyl-2-naphthols via a multicomponent condensation reaction of 2-aminobenzothiazole, 2-naphthol, and aromatic aldehydes in absence of solvent in good to high yields (70-90%). Green conditions of the reactions, easy separation, practicability, product purity, reusability of the catalyst, affordability, and environmentally profits are the considerable advantages of this protocol.

KEYWORDS

1-(benzothiazolylamino)phenylmethyl-2-naphthols, Fe₃O₄@MCM-41@ZrCl₂, magnetic nanoparticles (MNPs), MCM-41, zirconium

INTRODUCTION 1

In spite of significant advances in the field of mesoporous materials and the growing expansion of new types of them,^[1-8] the first and foremost member of M41S called MCM-41 still has attracted growing research attention owing to its chemical versatility.^[9-13] Its capabilities, especially in the field of catalytic activity, all come from its unique properties, such as high surface area $(\sim 1000 \text{ m}^2 \text{ g}^{-1})$, narrow pore size distribution, uniform pore size, and the possibility of adjusting the diameter of the pores between 2 and 10 nm. These features result in high thermal stability and the possibility of using it in a wide range of applications such as catalization,^[13-15] sensors.[22-24] isolation,^[16-18] photocatalysis,^[19-21]

absorption,^[25-27] and so forth.^[28] Moreover, in order to make such compounds more applicable in terms of recyclability, use of magnetic nanoparticles (MNPs) for the preparation of nanocomposites is so helpful leading to their simple recovery by using an external magnetic field, which increases their performance in the next reuses.^[29-32] In this regard, iron oxides especially Fe₃O₄ are preferable because of their good magnetic properties compared with other MNPs, high resistance to degradation and lower toxicity.^[33,34]

In order to obtain interesting and remarkable catalytic capabilities from these magnetic mesoporous nanocomposites, modification of their surface by stabilization of metal nanoparticles on their structure is one of the best selections.^[14,32,35-39] This method is also a useful way

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of preventing the accumulation of metal nanoparticles. In this field, zirconium (IV)-based nanoparticles are one of the most useful cases because of their commercial availability, low price, and low toxicity.^[40] Also these compounds represent a good *Lewis* acid behavior and high catalytic activity characteristics,^[41–43] which come from a high coordinating ability due to the higher charge-to-size value of Zr^{4+} compared with most of the metal ions.^[44,45] Incorporation of Zr (IV) nanoparticles into the framework of mesoporous materials not only enhances their catalytic applicability but also increases their thermal and hydrothermal stability. On the other hand, this process makes them stable against moisture and corrosiveness and also be easy to handle.^[46–48]

The extensive and significant role of 2-aminobenzothiazole core, as a privileged scaffold, in pharmaceutical, biological, and industrial chemistry is undeniable.^[49-58] Among these types of compounds, 1-(benzothiazolylamino)phenylmethyl-2-naphthols have two biologically active components, 2-aminobenzothiazole and a Betti's base. Betti's base, a structure called 1-(α -aminoalkyl)-2-naphthols with two active amino and hydroxyl groups, plays a major role in synthetic chemistry due to the possibility of C-C bond formation under mild laboratory conditions.^[58] These benefits have navigated numerous efforts to synthesize 1-(benzothiazolyl amino)phenylmethyl-2- naphthols employing various catalysts such as sodium dodecyl sulfate (SDS),^[59] NaHSO₄.H₂O,^[60] heteropolyacid (HPA),^[61] maltose,^[62] 3-methyl-1-(4-sulfonic acid) propylimidazolium hydrogen sulfate [(CH₂)₃SO₃HMIM] [HSO₄],^[63] fumaric acid,^[64] oxalic acid,^[58] x-aminobutyric (GABA),^[65] phosphate fertilizers,^[66] acid and NH₃(CH₂)₅NH₃BiCl₅.^[67]

Although all reports have their own credits, some defects such as toxicity and expensiveness of the catalyst, environmental pollution, challenging synthesis, inaccessible reactions, long-term reaction times, and undesirable yields are still notable. Therefore, further research is needed to find greener and more economical methods. In continuation of our prior reports on the application of different acidic and basic catalysts, especially mesoporous, zirconium-based, and supported reagents in organic transformations,^[46,68-76] and in order to overcome the above mentioned restrictions, we intended to prepare a diverse range of 1-(benzothiazolylamino) phenylmethyl-2-naphthols through a three-component condensation reaction of 2-aminobenzothiazole, 2-naphthol, and a variety of aldehydes in the presence of a new magnetic mesoporous nanocomposite formulated as Fe₃O₄@MCM-41@ZrCl₂. This reagent is synthesized via a simple method and characterized using different types of techniques.

2 | EXPERIMENTAL

2.1 | Materials

All chemicals including $FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$, tetraethylorthosilicate (TEOS), cetyl trimethylammonium bromide (CTAB), NaOH, NaF, $ZrCl_4$, 2-aminobenzothiazole, 2-naphthol, and aldehydes were bought with high purity from Merck chemical company (Munich). All solvents were provided from Merck (Munich), and with the aim of the minimization of the absorption of the atmosphere moisture, besides getting distilled before being used, they were saved sealed in airtight containers as well.

2.2 | Characterization techniques

All products were characterized by comparing their physical constants, and also infrared (IR) and nuclear magnetic resonance (NMR) spectra with authentic samples and those reported in the literature. The pureness measurement of the substrate and reaction monitoring was appended by thin-layer chromatography (TLC) on a silica gel Polygram SILG/UV 254 plate. Melting points measuring were achieved using an electrothermal IA9100 melting point apparatus in capillary tubes. The pelletized samples of the synthesized nanocomposite were distinguished via Fourier transform infrared spectroscopy (FT-IR) measurements by Brucker Alpha series in the range of 400–4000 cm⁻¹. Investigation on crystal phases and crystallinity of the synthesized MNPs were fulfilled by X-PERT instrument with CuKa radiation of Sharif University of Technology (Iran) in the range of 0.7° -80° $(2\ominus)$. Transmission electron microscopy (TEM) images were prepared with a Zeiss-Sigma VP device from Oxford instruments company (England). The energy dispersive spectrometer (EDS) was performed on a TESCAN MIRA II (Czech) device to detect the presence of elements. Absorption-desorption nitrogen gas isoterms and surface area (S_{BET}) were determined using a BELSORP-mini II device at a temperature of 77°K. The samples were outgassed at 373°K and 1 mPa for 12 h before adsorption measurements.

2.3 | Preparation of the catalyst

2.3.1 | Preparation of Fe₃O₄-MNPs

The synthesis of Fe_3O_4 -MNPs was fulfilled according to our previous method with slight modification.^[77] Accordingly, 6.3-g FeCl₃·6H₂O, 4.0-g FeCl₂·4H₂O, and 1.7-mL HCl (12 mol L^{-1}) were mixed in 50 mL of deionized water in a beaker. Then, the solution was degassed with argon gas and heated to 80°C in a reactor. Concurrently, 250 mL of a 1.5 mol L^{-1} ammonia solution was gently added to the solution under argon gas protection and vigorous stirring (1000 rpm). After completion of the reaction, the resultant black solid of Fe₃O₄-MNPs was separated from the reaction medium using an external magnet followed by washing four times with 500-mL double distilled water. Eventually, the black powder of Fe₃O₄-MNPs was achieved.

2.3.2 | Preparation of Fe₃O₄@MCM-41 magnetic nanocomposites

To synthesize Fe_3O_4 @MCM-41, we followed the method described by Saadatioo et al.^[78] Typically, a mixture of 50 mL of deionized water, 5 mL of ammonia solution (2.5 M), and 1.5 g of the synthesized Fe₃O₄-MNPs was sonicated for 30 min. Then, 10 mL of tetraethyl orthosilicate (TEOS), 0.9 g of sodium hydroxide (NaOH), and 0.19 g of sodium fluoride (NaF) were added to it and stirred vigorously for 2 h. Afterwards, 3 g of cetyltrimethylammonium bromide (CTAB) was added to the mixture and stirred for 2 h again. After this time, the mixture was transferred to an autoclave with hydrothermally treating in an oven at 100°C for 48 h under static conditions. The acquired sediment was separated by an external magnet and washed several times with distilled water and dried at 100°C. Lastly, in order to eliminate the surfactant, the as-synthesized Fe₃O₄@MCM-41 was calcined at 300°C for 3 h. At this step, the nanocomposite was obtained in the form of an orange powder with a magnetic feature.

2.3.3 | Preparation of magnetic mesoporous nanocomposites including zirconium nanoparticles Fe₃O₄@MCM-41@ZrCl₂

For the synthesis of $Fe_3O_4@MCM-41@ZrCl_2$ magnetic nanocomposite, we followed the procedure reported by Kamali and Shirini^[46] with minor modification. Typically, to a mixture of 0.5 g of $ZrCl_4$ in 15 mL of chloroform, 0.5 g of the calcined $Fe_3O_4@MCM-41$ nanocomposite was added. The resulting slurry was continuously stirred at room temperature for 24 h. The gained sediment was separated using an external magnet and washed with chloroform for several times and then dried at 100°C. Thus, the desired mesoporous magnetic nanocomposite was achieved (Scheme 1).

2.4 | General procedure for the synthesis of 1-(benzothiazolylamino)phenylmethyl-2-naphthols (See supporting information)

A mixture of 2-aminobenzothiazole (1 mmol), 2-naphthol (1 mmol), aromatic aldehyde (1 mmol), and the prepared nanocatalyst (0.05 g) was heated in an oil bath at 100° C under neat conditions. The reaction progress was investigated by TLC using a mixture of *n*-hexane:ethyl acetate (2:1) solvents until the completion of the reaction. After completion of the reaction, ethanol (10 mL) was added to the reaction vessel, and the catalyst was separated from the mixture by an external magnet. The solvent was evaporated from the residue, and the product was purified by recrystallization from ethanol. The spectral data of some compounds are as follows:

Table 1, Entry 13: IR (neat) $\nu = 3315$, 3052, 1589, 1540, 1441, 1321, 1263 cm⁻¹; ¹H NMR (DMSO- d_6 , 400 MHz): $\delta = 7.02-7.95$ (m, 18H), 8.99 (s, 1H), 10.24 (s, 1H) ppm; ¹³C NMR (DMSO- d_6 , 100 MHz): $\delta = 118.6$, 119.0, 119.5, 121.5, 121.6, 122.9, 124.4, 125.5, 125.9, 126.02, 126.6, 126.78, 126.80, 127.9, 128.17, 128.22, 129.09, 129.14, 130.2, 131.2, 132.3, 132.7, 133.2, 140.7, 152.4, 153.8, 166.9 ppm.

Table 1, Entry 14: IR (neat) $\nu = 3356$, 3056, 1592, 1543, 1445, 1323, 1262 cm⁻¹; ¹H NMR (DMSO- d_6 , 400 MHz): $\delta = 7.24$ –7.77 (m, 26H), 8.81 (s, 2H), 10.14 (br, 2H) ppm; ¹³C NMR (DMSO- d_6 , 100 MHz): $\delta = 118.1$, 118.5, 118.8, 119.0, 121.3, 121.4, 122.8, 125.9, 125.9, 126.4, 127.2, 129.0, 129.9, 130.0, 131.2, 132.5, 140.8, 152.5, 153.6, 153.6, 166.7 ppm.

Table 1, Entry 15: IR (neat) $\nu = 3375$, 1581, 1540, 1443, 1329, 1261 cm⁻¹; ¹H NMR (DMSO- d_6 , 400 MHz): $\delta = 2.22$ (s, 3H, CH₃), 7.02–7.80 (m, 15H), 8.80 (s, 1H), 10.15 (br, 1H) ppm; ¹³C NMR (DMSO- d_6 , 100 MHz): $\delta = 21.7$, 119.3, 121.4, 121.4, 122.9, 123.7, 123.7, 125.9, 126.0, 126.8, 126.9, 127.1, 127.4, 127.5, 128.4, 128.5, 129.1, 130.0, 131.2, 132.6, 137.5, 143.0, 152.6, 153.6, 166.8 ppm.

Table 1, Entry 16: IR (neat) $\nu = 3310$, 1620, 1593, 1535, 1502, 1440 cm⁻¹; ¹H NMR (DMSO- d_6 , 400 MHz): $\delta = 3.81$ (d, J = 22.81 Hz, 1H), 3.88 (d, J = 22.81 Hz, 1H), 7.05–7.97 (m, 18H), 8.88 (s, 1H), 10.21 (s, 1H) ppm; ¹³C NMR (DMSO- d_6 , 100 MHz): $\delta = 53.8$, 118.6, 118.9, 119.0, 119.4, 120.1, 120.2, 121.4, 121.5, 122.9, 123.2, 125.3, 125.5, 125.9, 126.8, 127.0, 127.2, 127.6, 129.1, 129.1, 130.1, 131.3, 132.7, 139.9, 141.3, 142.0, 152.6, 153.7, 166.8 ppm.



SCHEME 1 Preparation of Fe₃O₄@MCM-41@ZrCl₂ nanocomposite

3 | RESULTS AND DISCUSSION

3.1 | Characterization of the catalyst

3.1.1 | FT-IR analysis

The FT-IR spectra of Fe_3O_4 (a), Fe_3O_4 @MCM-41 [before and after removal of the template (b,c)], $ZrCl_4$ (d) and Fe_3O_4 @MCM-41@ZrCl₂ (e) are indicated in Figure 1. Obviously, in comparison, the absorption band at 560 cm⁻¹ is attributed to the vibrations of the Fe–O bond in bare MNPs (spectrum a).^[79] As can be seen, in all spectra, the absorption bands related to the stretching and bending vibrations of the O–H bond appeared at 3446 and 1640 cm⁻¹, respectively. Strong bands at 2850 and 2920 cm⁻¹ in spectrum (b) are related to the symmetric and asymmetric vibrations of the CH₂ groups of the surfactant, respectively. The potential decrease of the intensity of such bands in the spectrum (b) verifies the prosperous removal of the surfactant. In both spectra (b and c), the appeared bands at 465, 890, and 1,080 cm⁻¹ are indexed as characteristic absorptions of MCM-41 structure resulted from the symmetric and asymmetric bending and stretching vibrations of Si–O–Si bonds.^[80] In addition, the attendance of 560 cm⁻¹ vibration band at all the magnetic synthesized materials confirms the presence of Fe₃O₄ nanoparticles. It is notable that because of overlapping of the vibration bands of Zr–O–Si with the asymmetric vibration bands of Si–O from sylanol groups at 960 cm⁻¹, this band is not observable.^[72]

3.1.2 | Powder XRD analysis

The X-ray diffraction (XRD) patterns of the Fe_3O_4 @ MCM-41 nanocomposite at low and wide angle region (Figure 2) show the peaks that can be assigned to the structure of Fe_3O_4 MNPs and the MCM-41 mesoporous

Entry	Amounts of the catalyst (g)	Solvent	Temperature (°C)	Time (min.)	Conversions
1	0.03	-	r.t.	90	Not completed
2	0.03	-	50	90	Trace
3	0.03	-	100	90	Trace
4	0.03	H ₂ O	50	90	Not completed
5	0.03	H ₂ O	100	90	Trace
6	0.03	EtOH	50	90	Not completed
7	0.03	EtOH	100	90	Trace
8	0.04	-	100	90	$100 (85)^{a}$
9	0.05	-	100	15	100 (90) ^a
10	0.06	-	100	15	$100(87)^{a}$
11 ^b	0.05	-	100	90	Trace
12 ^c	0.05	-	100	90	Not completed
13 ^d	0.05	-	100	90	Not completed
14 ^e	0.05	-	100	45	$100(70)^{a}$

TABLE 1	Optimization of the amounts of	the catalyst, tempera	ture, and solvent in th	he reaction of 2-a	aminobenzothiazol	e (1 mmol),
2-naphthol (1	mmol), and 4-chlorobenzaldehy	de (1.1 mmol) in the	presence of Fe ₃ O ₄ @M	ICM-41@ZrCl ₂ r	nanocomposite as t	he catalyst

^aIsolated yields. ^bFe₃O₄.

^cFe₃O₄@MCM-41.

^dMCM-41.

^eZrCl₂.



FIGURE 1 The Fourier transform infrared spectroscopy (FT-IR) spectra of (a) Fe_3O_4 , (b,c) Fe_3O_4 @MCM-41 before and after of the template removing, (d) $ZrCl_4$, and (e) Fe_3O_4 @MCM-41@ZrCl₂ nanocomposite

material. As clearly shown, in wide angle degree, the characteristic peaks of the Fe₃O₄ structure appeared at $2 \ominus = 30.43^{\circ}$, 35.61° , 43.47° , 53.7° , 57.22° , and 63.03° and established the presence of Fe₃O₄ in the structure of the synthesized nanocomposite. These data are corresponding with the XRD pattern of the standard Fe₃O₄ from Joint Committee on Powder Diffraction

Standards (JCPDS No. 19-692).^[81] By surveying the represented pattern of Figure 2a, manifestly, a sharp and welldefined diffraction peak is available at $2 \ominus = 2.63$, which corresponded to the peak (100), and the weaker peak at $2 \ominus = 4.65$ validates the peak (110), as the characteristics of mesoporous materials, and verifies the existence of hexagonal structure.^[82,83] After introducing of ZrCl₄, as can be seen in Figure 2b, the mentioned nanocomposite revealed a strong undeniable diffraction peak at $2 \oplus = 2.55^{\circ}$, representative of the Bragg plane reflection (100), and the weaker one at 4.65° , indexed as (110) reflection, indicating the preservation of the regular mesoporous structure of MCM-41 after incorporation of the zirconium nanoparticles on this mesoporous support. As a more accurately description, the stabilization of zirconium metal nanoparticles resulted in the reduction of the intensity of peaks, especially of (100) plane and their relative shift towards the lower angle region, while the overall diffraction patterns of the indexed appeared peaks originated from the mesoporous material structure in the desired nanocomposite have been completely preserved.

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3.1.3 | BET analysis

The nitrogen adsorption/desorption isotherms of the $Fe_3O_4@MCM-41@ZrCl_2$ mesoporous nanocomposite



before and after the stabilization of the zirconium nanoparticles are shown in Figure 3. By investigation in the obtained diagrams, it is deduced that both isotherms correlate with type IV (in the IUPAC classification), accompanied by the absorption-desorption hysteresis in the relative pressure region $(P/P_{\circ} = 0.3-1)$, which is expectable as the characteristic of the ordered mesoporous materials isotherm.^[84] The obtained Brunauer-Emmet-Teller (BET) surface areas, total pore volume, and Barret-Joyne-Halendu (BJH) mean pore diameter were estimated 694.32 m² g⁻¹, 0.699 cm³ g⁻¹, and 4.02 nm, respectively. After loading ZrCl₄, as it is shown in Figure 3b, the surface area and the residual total pore volume of the Fe₃O₄@MCM-41@ZrCl₂ mesoporous nanocomposite were determind to be 271.11 $m^2 g^{-1}$ and $0.278 \text{ cm}^3 \text{ g}^{-1}$, respectively. The relative diminution of the surface area and total pore volume is affected by the occupancy of the stabilized metal nanoparticles in the structure of the mesoporous material and as sufficient evidence confirms the prospering synthesis of the mentioned nanocomposite.^[85] Although after ZrCl₄ impregnation, the BET surface area and total pore volume were lessened, high surface areas and total pore volume were perceived in Fe₃O₄@MCM-41@ZrCl₂, and as a result, it could be deduced that well-organized Fe₃O₄@MCM-41@ZrCl₂ mesoporous nanocomposite with a high enough surface area could be achieved using this method.

3.1.4 | EDX analysis

The results of the energy dispersive X-ray (EDX) analysis derived from the magnetic mesoporous nanocomposite comprising zirconium nanoparticles ($Fe_3O_4@MCM-41@ZrCl_2$) are presented in Figure 4, indicating the presence of all the expected elements (Fe, Si, O, and Zr). This confirms the successful loading of zirconium-based nanoparticles on the mesoporous nanocomposite structure.

3.1.5 | TEM analysis

The TEM analysis of the catalyst is performed and illustrated in Figure 5. Accordingly, there are the spherical-like nanoparticles that are structured of dark MNPs cores surrounded by amorphous silica shells owning metals nanoparticles. The synthesized magnetic mesoporous nanocomposites are perceptibly agglomerated affected by the magnetic nature of the synthesized nanoparticles.

3.1.6 | VSM analysis

In order to clarify the magnetic behavior of the synthesized magnetic mesoporous nanocomposite, in



FIGURE 4 The energy dispersive X-ray (EDX) profiles of Fe₃O₄@MCM-41@ZrCl₂ nanocomposite



FIGURE 5 The transmission electron microscopy (TEM) image of Fe_3O_4 @MCM-41@ZrCl₂ nanocomposite

addition to the conventional distinguishing test of its magnetic feature by applying a magnetic stirrer bar, the vibrating-sample magnetometry (VSM) analysis was performed, too. In this line, the obtained magnetic hysteresis curves of MNPs are exhibited in Figure 6 stating about 38 and 7 emu g^{-1} as the estimated amount of saturation magnetization value (M_s) for Fe₃O₄@MCM-41 and Fe₃O₄@MCM-41@ZrCl₂ nanoparticles, respectively. Based on a reasonable justification, the observed decrease in Ms value is evidence of loading nonmagnetic metal nanoparticles on the magnetic mesoporous support while it should be pointed out that the obtained magnetization value of the final catalyst is sufficiently as high as it could be magnetically separated using a conventional magnet.



FIGURE 6 The magnetic hysteresis curves of (a) $Fe_3O_4@MCM-41$ and (b) $Fe_3O_4@MCM-41@ZrCl_2$ nanocomposites

3.2 | Catalytic activity

After identification of the prepared novel magnetic mesoporous nanocomposite, evaluation of its catalytic role was the subsequent step. In this line, preparation of a series of 1-(benzothiazolylamino)phenylmethyl-2-naphthols via a three-component condensation reaction of 2-aminobenzothiazole, 2-naphthol, and different types of aromatic aldehydes, in the presence of Fe₃O₄@MCM-41@ZrCl₂, was intended. At first and in order to determine the best reaction conditions, the effect of different parameters such as amounts of the catalyst, temperature, solvent, and also solvent-free conditions on the reaction of 2-aminobenzothiazole (1 mmol), 2-naphthol (1 mmol), 4-chlorobenzaldehyde (1 mmol), as the model reaction, was investigated. The related outcomes are given in Table 1, illustrating that the most suited conditions are as shown in Scheme 2 (Table 1, Entry 9). In addition to investigating the effect of diverse aforementioned parameters on the promotion of the model reaction, and in order to further establishing the capability of the introduced catalyst to catalyze this transformation, the reaction progress was studied in the presence of Fe₃O₄, Fe₃O₄@MCM-41, MCM-41, and ZrCl₂ separately. Based on the obtained data, Fe₃O₄ nanoparticles slightly proceeded with the reaction while MCM-41and Fe₃O₄@MCM-41 were more effective due to a large number of hydroxy groups on the high surface area of the mesostructured moiety relative to the magnetite nanoparticles. The use of zirconium nanoparticles caused the reaction to proceed completely, which is

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reasonably due to the acidic nature of the utilized metal nanoparticles that is the main factor in advancing the reaction (as shown in the proposed mechanism illustrated in Scheme 3). But in comparison with the introduced catalyst, the much higher density of zirconium nanoparticles stabilized on the surface of the mesostructured support increases the acidic strength of the entire catalyst, leading to boosted yields of the target product and enhanced reaction rate.

different Accordingly, derivatives of 1-(benzothiazolylamino)phenylmethyl-2-naphthols using a variety of aromatic aldehydes were prepared. The results of this survey, along with the time, yield, and melting point of each sample, are exhibited in Table 2. Based on the information given in this table, it is ascertained that, under the selected conditions, the target compounds are obtained at short reaction times with satisfactory yields. After completion of the reaction, a scanty amount of the products lost during the work-up process, and isolated yields got less than conversion yields while the utilized magnetic nanocomposite can be almost completely isolated from the reaction media. This fact is manifested in Figure 7, so that in the proximity of an external magnet, Fe₃O₄@MCM-41@ZrCl₂ nanocomposite was easily separated from its aqueous suspension in a few seconds.

In order to a more comprehensive and more accurate evaluation of the catalytic capability of the novel introduced catalyst in the 1-(benzothiazolylamino) phenylmethyl-2-naphthols beget, a comparison with the performance of other reported catalysts in the synthesis of 1-((benzo[*d*]thiazol-2-ylamino)(4-chlorophenyl)methyl) naphthalen-2-ol (Entry 2, Table 2) was performed in Table 3. This comparison reveals that the introduced catalyst in this project has an adequate ability to generate the desired product at an acceptable time with a very good yield. Accordingly, Fe₃O₄@MCM-41@ZrCl₂ can be stated as a beneficial catalyst in terms of great activity, low consumption of organic solvents, adaptability with the environment, easy separation via an external magnetic field, satisfactory yields of the products, and acceptable reaction times compared with the other reported systems.

To comprehend the reaction proceeding in the presence of the catalyst discussed, a credible mechanism is outlined in Scheme 3. According to the proposed mechanism, the reaction proceeds via activating the carbonyl group of the aldehyde by the Lewis acidic catalyst Fe₃O₄@MCM-41@ZrCl₂ followed by nucleophilic attack of 2-naphthol on the activated carbonyl of the aldehyde leading to the formation of the intermediate (I). In the next step, the addition of 2-aminobenzothiazole to this intermediate results in the production of the intermediate (II) and ultimately the main product.



SCHEME 3 A plausible mechanism for the preparation of 1-(benzothiazolylamino) phenylmethyl-2-naphthols derivatives catalyzed by Fe₃O₄@MCM-41@ZrCl₂ nanocomposite

				[28]	[64]		[64]
		Ref.	Shaabani et al. ^[86]	Maghsoodlou et al.	Maghsoodlou et al.	Seddighi et al. ^[87]	Maghsoodlou et al.
te as the catalyst		Reported	204-205	208-210	187–189	211-213	188-190
Cl₂ nanocomposit	m.p (°C)	Observed	205-206	207-209	187–188	210-213	190-192
04@MCM-41@Zr0		Yield (%) ^[a]	28	8	88	88	85
vatives by using Fe ₃		Time (min.)	40	15	25	13	32
nino)phenylmethyl-2-naphthol der			S HO	S N HO	S N HO N HO	S N HO	HU HU HU
(benzothiazolylan		Product		Ŭ			
Preparation of 1-		Aldehyde	H N		B	H H H H H H H H H H H H H H H H H H H	NO2
TABLE 2		Entry	-	7	с	4	Ś

(Continues)



					m.p (°C)		
Entry	Aldehyde	Product	Time (min.)	Yield (%) ^[a]	Observed	Reported	Ref.
٥	H NO NO		28	8	197-199	198–199	Shaabani et al. ^[86]
м			20	75	218-219	218-220	Seddighi et al. ^[87]
×	OCH3	H,coot	25	8	176–178	175-176	Shaabani et al. ^[86]
σ	OCH3	OCH3 H N N N N N N N N	50	82	227-229	225-228	Shaterian and Hosseinian ^[63]
10	H O 	Ho Ho	20	68	186–188	186–187	Kamali and Shirini ^[46]

TABLE 2	(Continued)				m.p (°C)			
Entry	Aldehyde	Product	Time (min.)	Yield (%) ^[a]	Observed	Reported	Ref.	
=	CH ₃	H ₁ C	25	70	183-185	182-183	Shaabani et al. ^[86]	
12	CH ^O	HD HO N HO HO HO HO HO HO HO HO HO HO HO HO HO	30	72	190-192	191-193	Kamali and Shirini ^[46]	
51	≖-¢	S Z HO	35	8	198-199	197-199	Seddighi et al. ^[87]	
14	H H H H H H H H H H H H H H H H H H H		30	8	216-217	215-217	Seddighi et al. ^[87]	
							(Continues)	



^aIsolated yields.

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3.3 | Reusability of the catalyst

In order to show the recyclability of the catalyst the preparation of 1-((benzo[d]thiazol-2-ylamino))(4-chlorophenyl)methyl)naphthalen-2-ol was investigated again. After completion of the reaction, ethanol was added to the mixture, and the catalyst was separated



FIGURE 7 Photographs of an aqueous suspension of $Fe_3O_4@MCM-41@ZrCl_2$ magnetic nanocomposite before (a) and after (b) magnetic capture

magnetically, washed with ethanol, dried at 50° C in air, and finally tested for its activity in the next run. As shown in Figure 8, this process was repeated at least for 4 times with the scant change in the reaction times and yields. Moreover, after comparing the spectra of the as-synthesized catalyst with the recovered one in the laboratory, showing no significant differences, we came to this conclusion that the stability of the structure of the prepared catalyst is good enough.





 $\label{eq:comparison} TABLE 3 \quad \mbox{Comparison of the efficiency of $Fe_3O_4@MCM-41@ZrCl_2$ nanocomposite with other reported catalysts in the reaction of 2-aminobenzothiazole, 2-naphthol, and 4-chlorobenzaldehyde$

Entry	Catalyst	Amount	Conditions	Time (min.)	Yield (%)	Ref.
1	HPA	0.12 g	H ₂ O/ultrasonic/40°C	110	90	Javanshir et al. ^[61]
2	LiCl	0.5 g/0.071 mol	$H_2O/90^\circ C$	360	92	Shaabani and Rahmati ^[86]
3	ZnCl ₂	0.1 mol	Solvent-free/70 $^{\circ}$ C	120	39	Hosseinian et al. ^[60]
	[(CH ₂) ₃ SO ₃ HMIM] [HSO ₄]	0.1 mol	Solvent-free/100°C	30	55	Shaterian and Hosseinian ^[63]
4	Zn(OAc) ₂ .2H ₂ O	0.1 mol	Solvent-free/70°C	35	62	Hosseinian and Shaterian ^[60]
5	ZrO ₂	0.1 mol	Solvent-free/70°C	60	65	Hosseinian and Shaterian ^[60]
6	YbCl ₃	0.2 mol	$H_2O/100^\circ C$	360	40	Kumar et al. ^[59]
7	Fe ₂ O ₃	0.1 mol	Solvent-free/70°C	60	43	Hosseinian and Shaterian ^[60]
8	$MgCl_2$	0.1 mol	Solvent-free/70°C	19	71	Hosseinian and Shaterian ^[60]
9	Sc(OTf) ₃	0.2 mol	$H_2O/100^\circ C$	60	55	Kumar et al. ^[59]
10	$Al(H_2PO_4)_3$	0.1 mol	Solvent-free/70°C	53	62	Hosseinian and Shaterian ^[60]
11	DABCO	0.1 mol	Solvent-free/70°C	120	40	Hosseinian and Shaterian ^[60]
12	Fe ₃ O ₄ @MCM-41@ZrCl ₂	0.05 g	Solvent-free/100 $^{\circ}$ C	15	90	This work

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4 | CONCLUSION

In the present study, the synthesis and identification of a novel nanocomposite consists of MNPs and masoporous materials containing zirconium element were intended. In fact, the increased catalytic efficiency was achieved via the use of Fe₃O₄ magnetic nanoparticles for the possibility of easy separation, MCM-41 as a masoporous silica compound with the aim of providing a greater surface area and zirconium derivatives as the effective metal nanoparticles to gain more catalytic activity. In this regard, Fe₃O₄@MCM-41@ZrCl₂ as a new magnetic mesoporous nanocomposite was successfully identified according to different analyses and exhibited satisfactory catalytic activity in begetting diverse range of 1-(benzothiazolylamino)phenylmethyl-2-naphthols derivatives. The green conditions, great yields, practicability, operational ease, product purity, stability, affordability, recyclability, and environmentally profits are the considerable advantages of this protocol.

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AUTHOR CONTRIBUTIONS

Reyhaneh Pourhasan Kisomi: Formal analysis; investigation; validation; visualization. **Mostafa Golshekan:** Conceptualization; validation.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available in the supplementary material of this article.

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REFERENCES

- N. Noroozi Pesyan, G. Rezanejade Bardajee, E. Kashani, M. Mohammadi, H. Batmani, *Res. Chem. Intermed.* 2020, 46, 347.
- [2] H. Sepehrmansouri, M. Zarei, M. A. Zolfigol, A. R. Moosavi-Zare, S. Rostamnia, S. Moradi, *Mol. Catal.* **2020**, *481*, 110303.
- [3] M. Nikoorazm, M. Khanmoradi, M. Mohammadi, Appl. Organomet. Chem. 2020, 34, e5504.
- [4] J. C. Mansano Willig, G. Granetto, D. Reginato, F. R. Dutra, É. F. Poruczinski, I. M. de Oliveira, H. A. Stefani, S. D. de Campos, É. A. de Campos, F. Manarin, G. V. Botteselle, *RSC Adv.* **2020**, *10*, 3407.
- [5] H. Alinezhad, M. Cheraghian, S. Ghasemi, J. Organomet. Chem. 2020, 907, 121069.
- [6] W.-J. Sun, E.-Q. Gao, Appl. Catal., A 2019, 569, 110.

- [8] K. Madasamy, S. Kumaraguru, V. Sankar, S. Mannathan, M. Kathiresan, New J. Chem. 2019, 43, 3793.
- [9] J. A. S. Costa, R. A. de Jesus, D. O. Santos, J. F. Mano, L. P. C. Romão, C. M. Paranhos, *Microporous Mesoporous Mater.* 2020, 291, 109698.
- [10] D. R. Do Carmo, P. F. P. Barbosa, L. R. Cumba, *Silicon* 2020, 12, 1111.
- [11] M. Golshekan, F. Shirini, Silicon 2020, 12, 747.
- [12] W. Kaewprachum, S. Wongsakulphasatch, W. Kiatkittipong, A. Striolo, C. K. Cheng, S. Assabumrungrat, J. Environ. Chem. Eng. 2020, 8, 102920.
- [13] A. Na Rungsi, A. Luengnaruemitchai, N. Chollacoop, S.-Y. Chen, T. Mochizuki, H. Takagi, Y. Yoshimura, *Appl. Catal.*, A 2020, 590, 117351.
- [14] H. Filian, A. Kohzadian, M. Mohammadi, A. Ghorbani-Choghamarani, A. Karami, *Appl. Organomet. Chem.* 2020, 34, e5579.
- [15] M. Nikoorazm, M. Mohammadi, M. Khanmoradi, Appl. Organomet. Chem. 2020, n/a, e5704.
- [16] K. Kawahara, S. Kohiki, T. Yoshitomi, S. Nishi, H. Shimooka, M. Mitome, Y. Bando, T. Shishido, M. Oku, *Mater. Lett.* 2008, 62, 3682.
- [17] X. Chu, Y.-Y. Le, Q. Zhu, K. Fan, W.-L. Dai, *Appl. Surf. Sci.* 2011, 257, 8605.
- [18] M. A. Florea, B. Purcareanu, A. Bicu, V. Drumea, C. E. Gird, M. Grigoroscuta, D. E. Mihaiescu, G. Vasilievici, L. Olariu, *IOP Conference Series: Materials Science and Engineering* **2019**, 572, 012008.
- [19] W. Jia, T. Liu, Q. Li, J. Yang, Catal. Today 2019, 335, 221.
- [20] S. Esmaeili, M. A. Zanjanchi, H. Golmojdeh, S. Shariati, *Microporous Mesoporous Mater.* 2020, 292, 109714.
- [21] L. Luo, J. Ma, H. Zhu, J. Tang, Nanoscale 2020, 12, 7339.
- [22] S. Kunchakara, M. Dutt, A. Ratan, J. Shah, V. Singh, R. K. Kotnala, J. Porous, *Mater.* **2019**, *26*, 389.
- [23] S. Kunchakara, A. Ratan, J. Shah, R. K. Kotnala, V. Singh, J. Mater. Sci.: Mater. Electron. 2019, 30, 15646.
- [24] M. Dutt, A. Kaushik, M. Tomar, V. Gupta, V. Singh, J. Porous, *Mater.* 2020, 27, 285.
- [25] V. Rizzi, E. A. Prasetyanto, P. Chen, J. Gubitosa, P. Fini, A. Agostiano, L. De Cola, P. Cosma, J. Mol. Liq. 2019, 273, 435.
- [26] S.-Y. Cheng, Y.-Z. Liu, G.-S. Qi, J. Nanomater. 2020, 2020, 6187656.
- [27] P. Shao, H. Chen, Q. Ying, S. Zhang, Energ. Fuel. 2020, 34, 2089.
- [28] G. Q. Lu, X. S. Zhao, Nanoporous Materials: Science and Engineering, Imperial College Press, London 2004.
- [29] J. P. Dhal, T. Dash, G. Hota, J. Porous, Mater. 2020, 27, 205.
- [30] Y. Deng, X. Xu, R. Wang, Y. Zhao, Waste Biomass Valoriz. 2020, 11, 1491.
- [31] W. Li, F. Fu, *Microporous Mesoporous Mater.* **2020**, *298*, 110060.
- [32] S. Abaeezadeh, D. Elhamifar, M. Norouzi, M. Shaker, Appl. Organomet. Chem. 2019, 33, e4862.
- [33] Y. Kobayashi, M. Horie, M. Konno, B. Rodríguez-González, L. M. Liz-Marzán, J. Phys. Chem. B 2003, 107, 7420.
- [34] K. Ojaghi Aghbash, N. Noroozi Pesyan, H. Batmani, Appl. Organomet. Chem. 2019, 33, e5227.

- [35] R. Hajian, A. Ehsanikhah, Chem. Phys. Lett. 2018, 691, 146.
- [36] Z. Roosta, A. Izadbakhsh, A. M. Sanati, S. Osfouri, J. Porous, *Mater.* 2018, 25, 1135.
- [37] E. Karakhanov, A. Maximov, A. Zolotukhina, V. Vinokurov, E. Ivanov, A. Glotov, *Catalysts* **2020**, 10.
- [38] T. Sun, M. Gong, Y. Cai, S. Xiao, L. Zhang, Y. Zhang, Z. Xu, D. Zhang, Y. Liu, C. Zhou, *Res. Chem. Intermed.* **2020**, *46*, 459.
- [39] W.-H. Zhang, J.-L. Shi, L.-Z. Wang, D.-S. Yan, Mater. Lett. 2000, 46, 35.
- [40] A. Yamaguchi, M. Yokoyama, A. Suzuki, Y. Iwasawa, H. Sakai, M. Yuasa, M. Abe, *Phys. Scr.* 2005, 834.
- [41] Q. Guo, S. Rao, J. Xu, S. Ren, Chemistry Bulletin/Huaxue Tongbao 2014, 77, 353.
- [42] L. Sadighnia, B. Zeynizadeh, S. Karami, M. Abdollahi, J. Chin. Chem. Soc. 2019, 66, 535.
- [43] S. Kumar, A. Singh, P. K. Singh, H. Miyaoka, V. Kain, Y. Kojima, Int. J. Hydrogen Energy 2020, 45, 14413.
- [44] A. K. Chakraborti, R. Gulhane, Synlett 2004, 2004, 627.
- [45] Z.-H. Zhang, T.-S. Li, Curr. 2009, 13, 1.
- [46] F. Kamali, F. Shirini, Appl. Organomet. Chem. 2018, 32, 3972.
- [47] X. X. Wang, F. Lefebvre, J. Patarin, J.-M. Basset, *Microporous Mesoporous Mater.* 2001, 42, 269.
- [48] X. Yang, L. Zhou, C. Chen, J. Xu, Mater. Chem. Phys. 2010, 120, 42.
- [49] Y. Oba, N. Yoshida, S. Kanie, M. Ojika, S. Inouye, *PLoS One* 2014, 8, 84023.
- [50] M. C. Van Zandt, M. L. Jones, D. E. Gunn, L. S. Geraci, J. H. Jones, D. R. Sawicki, J. Sredy, J. L. Jacot, A. T. DiCioccio, T. Petrova, A. Mitschler, A. D. Podjarny, *J. Med. Chem.* 2005, 48, 3141.
- [51] E. R. Atkinson, F. E. Granchelli, J. Pharm. Sci. 1976, 65, 618.
- [52] S. N. Manjula, N. Malleshappa Noolvi, K. Vipan Parihar, S. A. Manohara Reddy, V. Ramani, A. K. Gadad, G. Singh, N. Gopalan Kutty, C. Mallikarjuna Rao, *Eur. J. Med. Chem.* 2009, 44, 2923.
- [53] C. G. Mortimer, G. Wells, J.-P. Crochard, E. L. Stone, T. D. Bradshaw, M. F. G. Stevens, A. D. Westwell, *J. Med. Chem.* 2006, 49, 179.
- [54] C. Rodríguez-Rodríguez, N. Sánchez de Groot, A. Rimola, Á. Álvarez-Larena, V. Lloveras, J. Vidal-Gancedo, S. Ventura, J. Vendrell, M. Sodupe, P. González-Duarte, *J. Am. Chem. Soc.* 2009, 131, 1436.
- [55] C. Desai, K. Desai, Orient. J. Chem. 2000, 16, 311.
- [56] M. Yamaguchi, D. Pratt, M. Aimi, Y. Ishiwata, *Hair Dye Composition*, Google Patents, 2009.
- [57] D. Fajkusova, M. Pesko, S. Keltosova, J. Guo, Z. Oktabec, M. Vejsova, P. Kollar, A. Coffey, J. Csollei, K. Kralova, J. Jampilek, *Bioorg. Med. Chem.* 2012, 20, 7059.
- [58] M. T. Maghsoodlou, M. Karima, M. Lashkari, B. Adrom, J. Aboonajmi, J. Iran. Chem. Soc. 2017, 14, 329.
- [59] A. Kumar, M. S. Rao, V. K. Rao, Aust. J. Chem. 2010, 63, 1538.
- [60] A. Hosseinian, H. R. Shaterian, Phosphorus, Sulfur Silicon Relat. Elem. 2012, 187, 1056.
- [61] S. Javanshir, A. Ohanian, M. M. Heravi, M. R. Naimi-Jamal, F. F. Bamoharram, J. Saudi, *Chem. Soc.* 2014, 18, 502.
- [62] B. Adrom, M. T. Maghsoodlou, N. Hazeri, M. Lashkari, Res. Chem. Intermed. 2015, 41, 7553.
- [63] H. R. Shaterian, A. Hosseinian, *Res. Chem. Intermed.* 2015, 41, 793.

- [64] M. Maghsoodlou, M. Karima, M. Lashkari, B. Adrom, N. Hazeri, Bulg. Chem. Commun. 2016, 48, 369.
- [65] M. Fardpour, A. Safari, S. Javanshir, Green Chem. Lett. Rev. 2018, 11, 429.
- [66] O. Zimou, B. Malek, A. Elhallaoui, T. Ghailane, R. Ghailane, S. Boukhris, N. Habbadi, A. Hassikou, A. Souizi, *Bulletin of Chemical Reaction Engineering & Catalysis* 2019, 14, 238.
- [67] Z. Benzekri, S. Sibous, H. Serrar, A. Ouasri, S. Boukhris, R. Ghailane, A. Rhandour, A. Souizi, J. Mol. Struct. 2020, 1202, 127308.
- [68] F. Shirini, M. A. Zolfigol, A. Pourhabib, Russ. J. Org. Chem. 2003, 39, 1191.
- [69] F. Shirini, M. Ali Zolfigol, E. Mollarazi, Synth. Commun. 2005, 35, 1541.
- [70] F. Shirini, M. Ali Zolfigol, E. Mollarazi, Synth. Commun. 2006, 36, 2307.
- [71] F. Shirini, M. A. Zolfigol, A. Safari, J. Chem. Res. 2006, 2006, 154.
- [72] F. Kamali, F. Shirini, New J. Chem. 2017, 41, 11778.
- [73] R. Pourhasan-Kisomi, F. Shirini, M. Golshekan, Appl. Organomet. Chem. 2018, 32, 4371.
- [74] R. Pourhasan-Kisomi, F. Shirini, M. Golshekan, J. Nanosci. Nanotechnol. 2019, 19, 3859.
- [75] M. Haghighat, F. Shirini, M. Golshekan, J. Mol. Struct. 2018, 1171, 168.
- [76] M. Haghighat, F. Shirini, M. Golshekan, J. Nanosci. Nanotechnol. 2019, 19, 3447.
- [77] M. Golshekan, S. Shariati, N. Saadatjoo, RSC Adv. 2014, 4, 16589.
- [78] N. Saadatjoo, M. Golshekan, S. Shariati, H. Kefayati, P. Azizi, J. Mol. Catal. A: Chem. 2013, 377, 173.
- [79] S. Ghafoor, S. Ata, J. Chil. Chem. Soc. 2017, 62, 3588.
- [80] W. Xie, X. Zang, Food Chem. 2016, 194, 1283.
- [81] M. Aliahmad, N. N. Moghaddam, Mater. Sci-Poland 2013, 31, 264.
- [82] T. F. Parangi, R. M. Patel, U. V. Chudasama, Bull. Mater. Sci. 2014, 37, 609.
- [83] M. Nikoorazm, F. Ghorbani, A. Ghorbani-Choghamarani, Z. Erfani, *Phosphorus, Sulfur Silicon Relat. Elem.* 2018, 193, 552.
- [84] T. Chen, X. Peng, H. Dai, J. Porous, Mater. 2016, 23, 987.
- [85] S. Luo, G. Fan, M. Luo, J. Li, G. Song, J. CO2 Util. 2016, 14, 23.
- [86] A. Shaabani, A. Rahmati, E. Farhangi, *Tetrahedron Lett.* 2007, 48, 7291.
- [87] M. Seddighi, F. Shirini, M. Mamaghani, C. R. Chim. 2015, 18, 573.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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